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High-Power Infrared-Laser Windows

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13. ABSTRACT The successful development of powerful infrared (IR) lasers, notably various types of CO ₂ lasers and certain chemical lasers, during the past five years has opened up many applications for IR-laser beams. Requirements exist for the creation and transmission of high-power diffraction-limited-infrared beams. Most efforts have so far been directed toward the construction of IR lasers for the generation of high-power radiation. No comparable effort was devoted to the special materials problems which arise in the case of high-power transmission. The report of the Committee reviews in detail the state of the art and problems presented by each of the seven subject areas into which the field could be divided. These are: Propagation of IR Radiation in Window Materials; Fundamental Absorption Mechanisms; Experimental Aspects in the Characterization of High-Power IR-Window Materials; Single Crystal II-VI, III-V, and IV IR-Window Materials; Chalcogenide Glass IR-Window Materials; and Polycrystalline IR-Window Materials. The Committee draws several conclusions in each of these areas and recommends in the report various research and development programs for influencing the choice and criteria for window materials and for advancing materials science in this field.			

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HIGH-POWER INFRARED-LASER WINDOWS

**Report of
The Ad Hoc Committee on
High-Power Infrared-Laser Windows**

**National Materials Advisory Board
Division of Engineering - National Research Council**

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NOTICE

The study reported herein was undertaken under the aegis of the National Research Council with the express approval of the Governing Board of the NRC. Such approval indicated that the Board considered that the problem is of national significance; that elucidation or solution of the problem required scientific or technical competence and that the resources of NRC were particularly suitable to the conduct of the project. The institutional responsibilities of the NRC were then discharged in the following manner:

The members of the study committee were selected for their individual scholarly competence and judgment with due consideration for the balance and breadth of disciplines. Responsibility for all aspects of this report rests with the study committee, to whom sincere appreciation is expressed.

Although the reports of our study committees are not submitted for approval to the Academy membership or to the Council, each report is reviewed by a second group of appropriately qualified individuals according to procedures established and monitored by the Academy's Report Review Committee. Such reviews are intended to determine, inter alia, whether the major questions and relevant points of view have been addressed and whether the reported findings, conclusions, and recommendations arose from the available data and information. Distribution of the report is approved, by the President, only after satisfactory completion of this review process.

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We express here our indebtedness to all these people for their invaluable services to the Committee on High-Power Infrared-Laser Windows.

Nicolaas Bloembergen, Chairman
National Materials Advisory Board
Ad Hoc Committee on High-Power
Infrared-Laser Windows

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I. INTRODUCTION AND CHARGE TO THE COMMITTEE

The successful development of powerful infrared (IR) lasers, notably various types of CO₂ lasers and certain chemical lasers, during the past five years has opened up many applications for IR-laser beams. Requirements exist for the creation and transmission of high-power diffraction-limited IR beams. Most efforts have so far been directed toward the construction of IR lasers for the generation of high-power radiation. No comparable effort has been made to solve the special materials problems that arise in conjunction with high-power transmission. Components that are capable of transmitting low-power IR beams without optical degradation present serious limitations at high-power levels. The handling of high-power beams requires nearly lossless reflection from mirrors and nearly reflectionless and lossless transmission through windows. Materials damage by laser beams with high-flux density is well known, but optical distortion of the beam during passage through a window usually becomes unacceptable well before the window fails mechanically. The main cause of this distortion has been identified as heating by a small residual absorptivity of the transparent material exposed to the high-power beam.

Consequently, several research programs were undertaken during the past few years to develop high-power-IR windows. Since the development of new materials is a costly process and since no known and available material could meet the simultaneous requirements of size (diameters

in excess of 10 cm) and of good mechanical and optical properties at high-power levels, it appeared that a systematic review of various materials-research efforts to develop high-power IR windows would be advisable. Such a study could also identify the most promising materials and, possibly, make recommendations for the materials-research and-development program for the next few years.

With this background, the Advanced Research Projects Agency (ARPA) requested that the National Materials Advisory Board (NMAB) of the National Academy of Sciences-National Research Council initiate an appropriate ad hoc committee study to explore the various IR window materials problems for high-power lasers, such as CO₂, CO, and chemical lasers, and to recommend programs directed to their solution. More specifically, the task of this study for the Department of Defense was to assess the importance of factors deleterious to the transmission of high-power diffraction-limited laser beams with wavelengths between 2 and 6 micrometers (μm) and near 10.6 μm through solid windows, to assess the importance of various possible absorption mechanisms, and to make recommendations for the most suitable composition and form of materials for these windows.

The National Materials Advisory Board accepted the charge and an ad hoc Committee on High-Power Infrared-Laser Windows was established in June 1971. The full committee, consisting of seven members plus eight liaison representatives from the Army, Navy, Air Force, and ARPA, held five formal two-day meetings during the period from

September 1971 through April 1972. In addition, there were several smaller sessions involving various groups of committee members. At the full committee meetings, presentations were made by leading research experts in government, university, and industrial laboratories. This report contains the results of the deliberations of the committee members, liaison representatives, and invited speakers.

The major findings of this study are summarized in the next chapter. The remaining chapters review, in detail, the state of the art and the problems presented by each of seven subject areas into which the field could be divided. These are:

- Propagation of Infrared Radiation in Window Materials
- Fundamental Absorption Mechanisms
- Experimental Aspects in the Characterization of
 - High-Power Infrared-Laser-Window Materials
- Single Crystal Alkali-Halide Infrared-Window-Materials
- Single Crystal II-VI, III-V, and IV Infrared-Window Materials
- Chalcogenide Glass Infrared-Window Materials
- Polycrystalline Infrared-Window Materials

There are numerous other engineering problems in the window design besides the development of suitable window materials. Mechanical details of mounting, the manner of cooling the window surfaces and rims, the protection of the optical windows during periods when no laser beam is transmitted, the question of segmenting the

window area by using a honeycomb frame with smaller and thinner window panes, aerodynamic loading, the maintenance of a controlled-temperature profile, the single pulse, pulse train, of the quasi-continuous mode of power transmission: these are all important aspects of the high-power IR-laser-window problem. The scope of the present report, however, is limited to window materials. Over-all system design and engineering considerations are not included, although it will be pointed out that certain materials may be better suited for or have special advantages in certain modes of window design and operation. Conversely, results of engineering studies will influence the choice and criteria for window materials.

II. SUMMARY OF COMMITTEE
CONCLUSIONS AND RECOMMENDATIONS

In this chapter the main conclusions and recommendations of the report are summarized. This summary is based on the detailed discussions in Chapters III through IX, which should be consulted for both supporting evidence and the general context in which these conclusions and recommendations should be viewed.

Conclusion 1

The basic theories for propagation of high-power IR-laser beams through window materials are well understood. The effects of thermal lensing distort the optical quality of the beam and this effect usually occurs before material damage of the window sets in. In either case the basic criteria for the selection of suitable window materials are, therefore, well established. An optical figure of merit has been defined which is best for materials with the lowest absorptivity and lower thermal coefficient of the index of refraction. Unfortunately, the classes of materials with the best optical figure of merit often have less desirable mechanical, chemical, and thermal properties so that trade-offs must be made.

Conclusion 2

No material available in its present form is suitable for the fabrication of a high-power IR-laser window, but the prospects that such a material may be

developed within two years are encouraging. Since material development is expensive, funds will be saved if large-scale-crystal growth, processing, and fabrication is avoided until the required optical figure of merit and acceptable mechanical and chemical properties have been demonstrated on small test samples.

Conclusion 3

High-power IR-laser-window materials will need anti-reflection (AR) coatings. In addition, several of the more promising materials will need protective coatings against the deleterious effects of the atmosphere, especially of water vapor. Very little work has been done on such coatings in the IR regions of interest, near $10.6\mu\text{m}$ and between $2\text{-}6\mu\text{m}$. The feasibility of such coatings should first be established on small-scale samples. The absorption in coatings and surface layers must also be measured before scale-up in fabrication is attempted.

Conclusion 4

Many optical, mechanical, chemical, and thermal properties of a material must be monitored during the stages of the development process. Most of these are routine but the measurement of low absorptivity requires a specially constructed calorimeter arrangement, and the determination of small- and large-angle scattering and optical distortion requires special optical bench arrangements. Preliminary testing may be done conveniently with

visible light if the materials are also transparent in that region. Access to infrared optical-test facilities is essential for development of IR-laser-window materials.

Conclusion 5

Materials with the lowest demonstrated optical absorptivity and the highest demonstrated optical figure of merit at $10.6\mu\text{m}$ may be found among the alkali halides, notably KBr. The pure crystal is, however, mechanically weak but can be strengthened by about an order of magnitude by the addition of Sr^{2+} ions with an unknown effect on the absorptivity. The crystal needs a protective coating against the atmosphere but successful preliminary tests with coatings of As_2S_3 glass have been reported. It has been demonstrated that alkali-halide crystals can be grown in large sizes.

Conclusion 6

The $\text{Tl}(\text{Br}, \text{I})$ materials are not hygroscopic and do not need a protective coating. They should have a low-intrinsic absorptivity but the lowest value reported is $\beta = 5 \times 10^{-3} \text{ cm}^{-1}$. To date, however, no special effort has been made to purify the material. In its polycrystalline sintered form, the material has attractive mechanical properties. The temperature coefficient of the index is large and the figure of merit is lower than for the alkali halides, but it may still be acceptable in well-cooled window configurations.

Conclusion 7

In the spectral region between 2-6 μ m, the fluorides BaF₂ and SrF₂ are serious candidates for window materials. They are not hygroscopic, have a high optical figure of merit, and have better mechanical properties than the alkali halides. Anti-reflection coatings must be developed. Sapphire, MgO, and certain semiconductors should also be considered in this wavelength region.

Conclusion 8

The most promising semiconductor materials for windows at 10.6 μ m are Ge, GaAs, ZnSe, and CdTe. To avoid excessive absorption by free carriers, germanium must be in an ultrapure form for which the free-carrier contribution to the absorption coefficient is expected to be about 10⁻³ cm⁻¹. The values of β so far obtained for ZnSe, GaAs, and CdTe are not low enough for an acceptable window material. The intrinsic value of β could well be lower and may be attainable by further purification. The questions of growing samples in large sizes and preparing anti-reflection coatings are unsolved.

Conclusion 9

Chalcogenide glasses have excellent mechanical properties, are resistant to the atmosphere, and are obtainable in large pieces. However, their optical figure of merit demonstrated to date is inadequate for bulk window material. The absorptivity is fairly high due to

oxygen impurities and possibly multiphonon absorption. Compositional changes and control of oxygen content may improve the situation. These glasses have shown promise for protective and anti-reflective coatings.

Conclusion 10

The outlook for developing polycrystalline materials of required optical quality and figure of merit is not bright by particulate consolidation method, but chemical vapor deposition and casting processes have shown promise. Recrystallization by press forging and extrusion can substantially improve mechanical properties. There is some indication that this can be accomplished without unacceptable degradation of the optical properties.

Conclusion 11

Present knowledge of bulk absorptivities in pure substances is sufficient to provide guidelines for the present selection of candidates for window materials. For long-range progress it is, however, important to refine our understanding of the theory of fundamental bulk and surface absorption and of the role of free-carrier absorption, grain boundaries, and impurities. Further experimental data on fundamental absorption edges are required for many materials, and experimental data on surface absorption and the influence of radiation damage are needed.

Conclusion 12

In the case of extremely high-power-flux densities, exceeding $10 \text{ megawatts/cm}^2$, a variety of nonlinear effects, such as laser-induced self-focusing breakdown and stimulated Brillouin scattering, may play a role. Such power densities can occur in extremely short pulses and are of interest for thermonuclear power generation. The nonlinear effects in the infrared are not sufficiently understood.

Recommendations

Based on these conclusions, the following recommendations, listed in their approximate order of priority, are made. For a sustained effort, all should be implemented. (Short-range effort means a 1- to 2-year period, while long-range efforts are 2-5 years. Where a short-range effort of 4 man-years is specified, this means 2 men for 2 years or 4 men for 1 year. A man-year corresponds roughly to an expenditure of \$50,000.)

Recommendation 1

A strong effort should be made to evaluate the alkali-halide crystals as suitable window materials. The system KBr:Sr or related systems are recommended for intensive study. The following successive steps in a short-term program are identified as needing immediate attention:

- 1) Purify KBr and SrBr_2 and remove as far as possible OH^- , F^- , Cl^- , CN^- , etc.
- 2) Grow small size single crystals of KBr:Sr and obtain the required mechanical strength and optical properties.
- 3) Develop a protective (chalcogenide glass) and anti-reflective coatings.
- 4) Fabricate and test small size coated windows cut from crystals oriented in a $\langle 111 \rangle$ direction.

An effort of 6 man-years over the next 2 years at an estimated cost of \$300,000 is recommended.

Recommendation 2

The assessment of semiconductor material for window applications should be continued. Primary attention should be given to a continuation of chemical vapor deposition of ZnSe. Further work on germanium and high-resistivity GaAs and further purification of ZnSe and CdTe is also recommended. In addition, the fundamental absorption edges and background absorptivities of many other substances should be measured to assess their potential for window application before embarking on a materials-development program for those materials. The following program elements are recommended:

- 1) Continuation of the improvement of absorptivity of ZnSe and CdTe, both in single crystal form and by chemical vapor deposition techniques. A total effort of 6 man-years over the next 2 years is recommended at an estimated cost of \$300,000.
- 2) Evaluation of the potential of ultrapure Ge.
- 3) A survey of general spectral absorption measurements and determination of other physical properties on a variety of available crystals, especially GaAs, which may have sufficient transparency in the infrared. An effort of 4 man-years over the next 2 years is recommended at an estimated cost of \$200,000.
- 4) Development of anti-reflective coatings for semiconductors.

Recommendation 3

It is recommended that a basic research program be maintained in parallel with the window development programs and research programs on specific materials mentioned in the other recommendations. The following parts of a basic program should be carried out concurrently:

- 1) Basic theoretical and experimental studies of fundamental absorption processes in pure bulk crystals, at surfaces, and by imperfections and conduction electrons. An effort of 3 man-years over the next 2 years at an estimated cost of \$150,000 is recommended.

- 2) Basic experimental studies of infrared nonlinear effects occurring at very high-flux densities. An effort of 3 man-years over the next 2 years at a cost of \$150,000 is recommended.

It should be kept in mind that the basic programs have a long-range character and it is probably advisable to extend them beyond the two-year period at a comparable annual level of funding.

Recommendation 4

Since the 2-6 μ m wavelength region is of considerable future interest, a program should be initiated now to develop suitable windows for this spectral region. It is recommended that the initial program concentrate on the materials SrF₂ and BaF₂ in the following steps:

- 1) Purify SrF₂ and BaF₂.
- 2) Grow small size single crystals and determine mechanical and optical properties.
- 3) Develop anti-reflective (AR) coating.
- 4) Fabricate and test a small size coated window.

An effort of 5 man-years over the next 5 years at an estimated cost of \$250,000 is recommended.

Recommendation 5

The absorption by surface layers and coatings and the resistance of such layers to temperature rise and mechanical deformation when exposed to high-power-IR fluxes should receive more attention. The influence of ultraviolet and nuclear radiation on the optical and mechanical properties of coatings and bulk materials must also be investigated. The cost of these investigations is partly absorbed in the cost estimates for the other recommendations. In addition, an independent coating research program is recommended at the rate of 1 man-year for 2 years at an estimated cost of \$100,000.

Recommendation 6

An effort should also be initiated immediately to assess the suitability of $Tl(Br, I)$ as a window material. The following steps in a short-term program are recommended:

- 1) Purify $TlBr$, TlI , and $BaBr_2$.
- 2) Grow small size single crystals of $Tl(Br, I):Ba$ and determine their mechanical and optical properties.
- 3) Develop AR coating.
- 4) Fabricate a small size coated window and test in a high-power beam at $10.6\mu m$.

An effort of 3 man-years over the next 2 years at an estimated cost of \$150,000 is recommended.

Recommendation 7

The method of recrystallization, for example by press forging and extrusion, to improve mechanical properties of window materials with tolerable optical degradation, should be further applied to single crystals of alkali halides of low absorptivity. A 2 man-year effort over the next 2 years is recommended at an estimated cost of \$100,000.

Recommendation 8

The assessment and improvement of chalcogenide glasses as coatings and as bulk window materials should be continued. Emphasis should be given to a reduction of absorption due to oxygen impurity and other sources. Anti-reflective coating for the glasses should also be developed. An effort of 4 man-years over the next 2 years at an estimated cost of \$200,000 is recommended.

Recommendation 9

It is recommended that experimental facilities to measure all pertinent optical, thermal, mechanical, and chemical properties be closely integrated with each of the development projects recommended above. Arrangements for exchange of data and samples as well as access to testing facilities and computational programs of other groups should be improved.

Recommendation 10

If any of the development programs in the previous recommendations have led to small size test windows with acceptable characteristics, scale-up programs should be started immediately on that particular window material. The scale-up should not only involve the growing of large crystals but also the cutting and polishing of large windows and the application of coatings to large surfaces. The scale-up operations will be expensive and no estimates of cost, time, and manpower are given. It is strongly recommended, however, that no premature scale-up be attempted beyond the size needed to assess the required properties.

III. PROPAGATION OF INFRARED RADIATION IN LASER WINDOWS

A. Introduction

There is steady progress in the development and use of high-power lasers. As CW power and energy per pulse increase, a class of problems is encountered which is not found with low optical powers. Optically induced changes in the propagation characteristics can take place. These self-induced effects can occur in a variety of places, for example: inside the optical gain medium, at mirrors and windows, and in the medium intervening between the laser source and the point where the radiation is to be received (e.g., the atmosphere). Solid high-power-laser windows are necessary to isolate different regions through which the laser beam must propagate. Section B of this chapter deals with what is believed to be the most important propagation problem in nearly transparent high-power-laser windows. Other problems will be considered briefly at the end of the chapter.

B. Self-Induced Effects Due to Absorption

When electromagnetic radiation passes through matter some portion is absorbed. The absorbed energy can cause changes in the physical characteristics of the material including its optical properties. If the radiation flux is large enough, the material may undergo catastrophic changes such as melting or fracture. Due to the energy deposited, the absorption constant can increase or

decrease and changes can occur in optical phase through thermal expansion and changes in index of refraction. It is the dependence of optical phase on the optical flux that limits the amount of optical energy which may be transmitted through a window, assuming that negligible distortion in the optical wavefront is desired. Equivalently, one can describe the optical phase changes as the introduction of an aberrated lens into the beam. (1-3) This self-induced thermal lens effect can spread the far-field beam pattern.

The conditions can be determined under which phase-front distortions are severe enough to limit an optical systems ability to send collimated beams of light over large distances or to focus the radiation to high-flux densities. A reasonable criterion for negligible phase distortion is:

$$\left| \delta\varphi_i^{n.c.} - \delta\varphi_j^{n.c.} \right|_{\max} < \pi/4, \quad (\text{III-1})$$

where $\delta\varphi_i^{n.c.}$ and $\delta\varphi_j$ are the noncorrectable (n.c.) phase distortions at two arbitrary points in the beam profile. That this criterion is not overly severe is evident from the normal optical design criteria of 1/10 to 1/20 wave. The phase change due to the presence of the window for a cylindrically symmetric beam can be written -

$$\varphi(r) = k_o \int_0^{l(r)} dz \{n(r,z) - 1\}, \quad (\text{III-2})$$

where $k_0 = 2\pi/\lambda$, λ is the wavelength, z is the coordinate in the direction of propagation, r is the radial coordinate, l is the thickness of the window, and n is the index of refraction. The nonlinear phase change is expected to be small compared to the normal linear optical change in phase, so that

$$\delta\phi(r) = k_0 \left\{ (n_0 - 1) \delta l(r) + l \delta n(r) \right\}, \quad (\text{III-3})$$

where n_0 is the normal index of refraction of the window, l is the thickness, $\delta l(r)$ is the induced change in thickness, and $\delta n(r)$ is the induced change in index of refraction averaged along the direction of propagation. Using (III-1), (III-2), and (III-3), an approximate criterion for aberrationless propagation through the window can be taken to be

$$\left| \left\{ \frac{\Delta l}{l} + \frac{\Delta n}{(n_0 - 1)} \right\} \right| < \frac{\lambda}{8(n_0 - 1)l}, \quad (\text{III-4})$$

where $\Delta l = \delta l(r_1) - \delta l(r_2)$ and $\Delta n = \delta n(r_1) - \delta n(r_2)$, r_1 and r_2 being a suitably chosen pair of radial coordinates (e.g., the beam center and the $1/e$ point in a Gaussian beam). For simplicity the superscripts n.c. are suppressed. It is useful to consider what occurs when the above criterion is strongly violated. The deflection of a ray after passing through the window is given by

$$\theta(r) = \left| \frac{\partial}{\partial r} \int_0^l [n(r, z) - 1] dz \right|. \quad (\text{III-5})$$

As an example, a sketch of the phase profile and deflection is given in Figure 1 for a highly aberrated case. The ray deflection in this case has a maximum at finite radius. For this to occur, phase variations depending on powers of the radial coordinate higher than quadratic must contribute appreciably. In this case rays from different parts of the beam (as it leaves the window) can reach the same point in the far field and interfere either constructively or destructively. This leads to a series of aberration rings and the far field intensity is degraded from the aberrationless case. Figure 2 shows the aberration rings produced in the conductive steady state for an argon laser beam passing through lead glass.

The induced changes in phase arise from the absorption of energy. Generally, this energy is rapidly thermalized and can be considered to be heat. Therefore, the effect of the deposition of heat on the optical properties is considered. A linear dependence of δn and δl on temperature change and strain is assumed. There are several time regimes of interest. The shortest time regime occurs when the optical pulses are so short that the system is far from stress-strain steady-state and the index change is entirely a local phenomenon. An intermediate regime occurs when the stress-strain steady-state is reached but the thermal steady-state is not. Finally, for sufficiently long times thermal conduction becomes important in determining the temperature profile and hence the index profile.

20 (a)

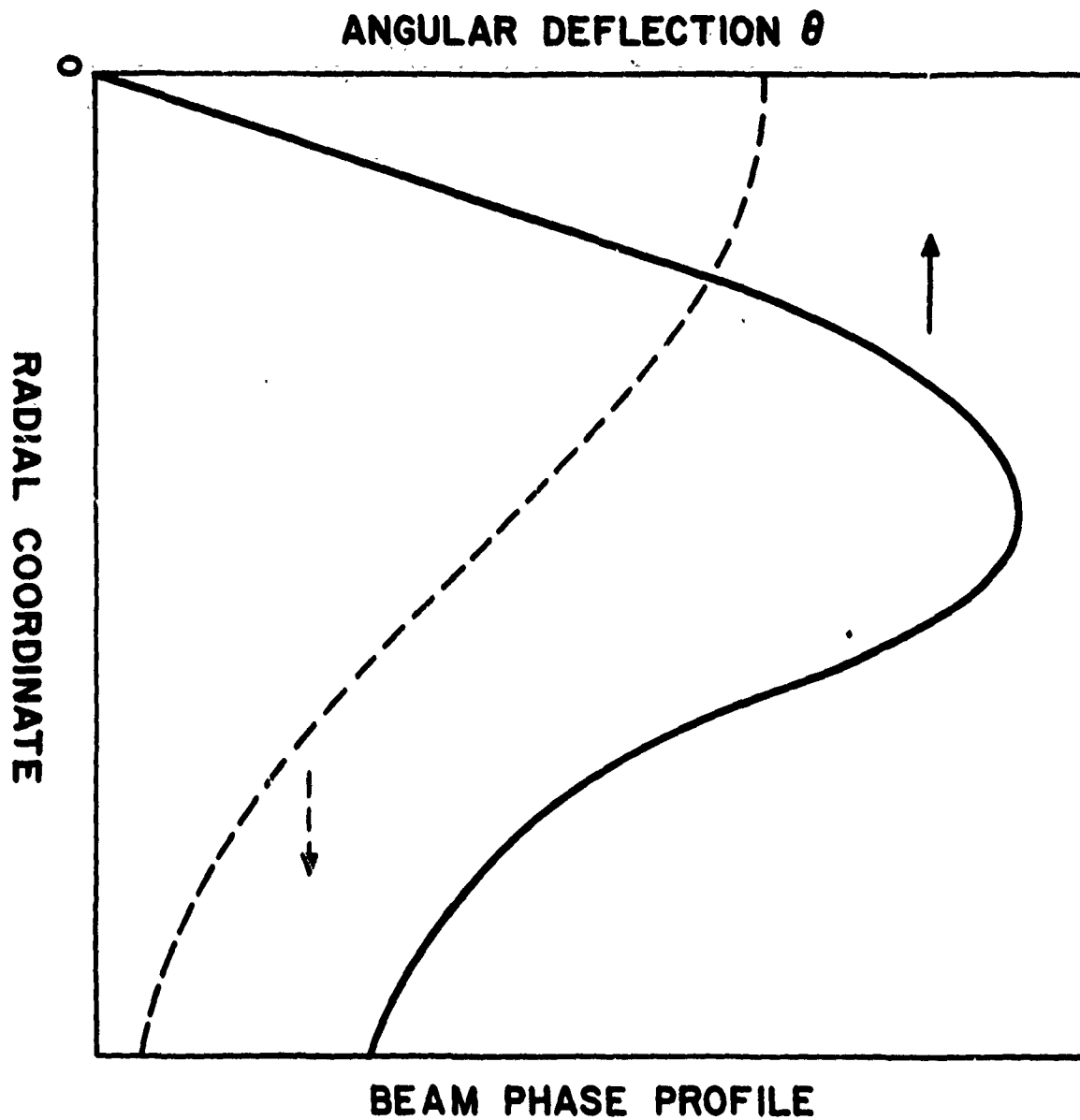


Figure 1. Solid curve - representation of angular deflection vs radial coordinate.
Dashed curve - beam phase profile.

20 (b)

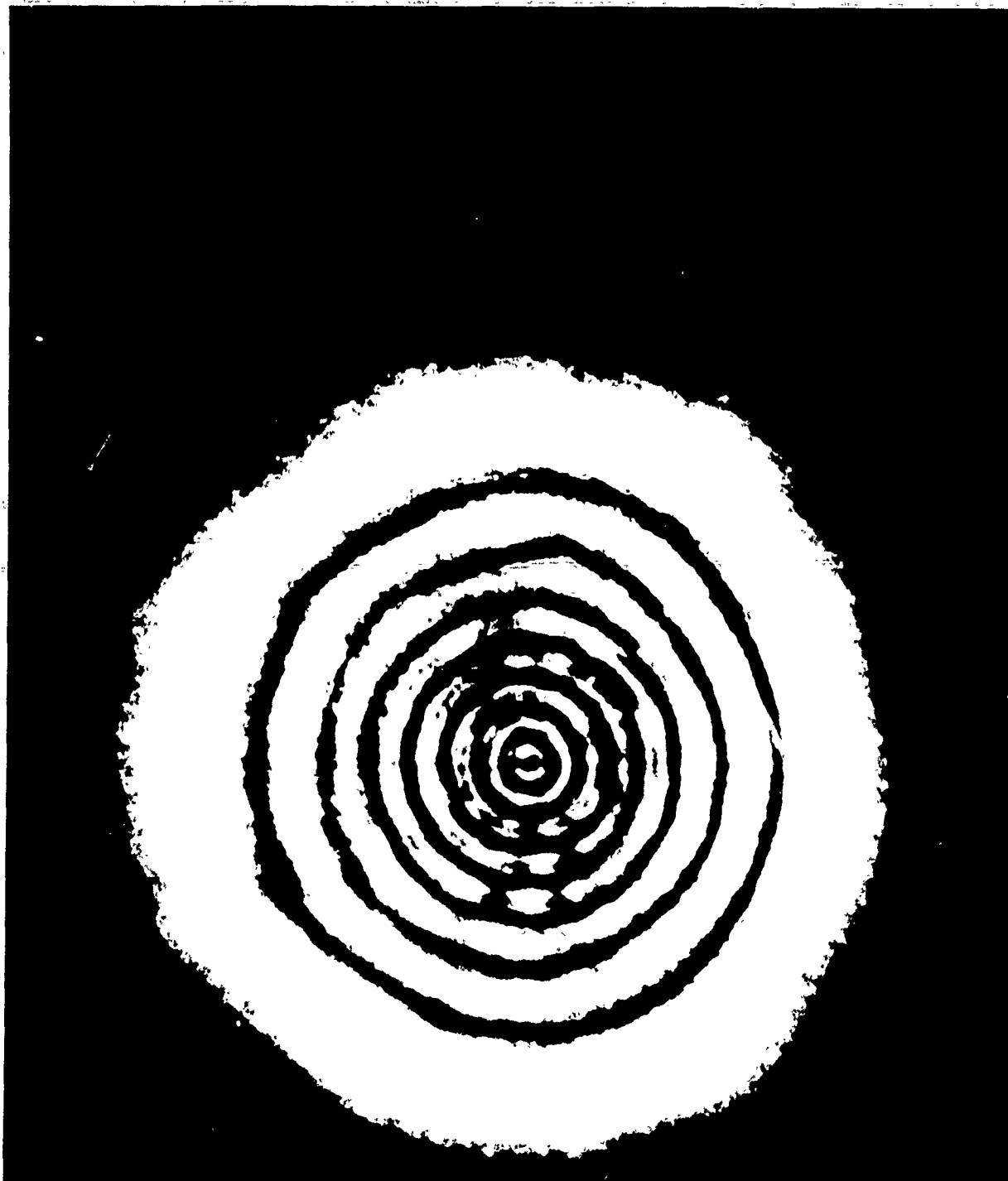


Figure 2. Far-field pattern of 1 watt Argon laser beam ($\lambda=0.488\mu\text{m}$, initial $1/e^2$ radius = 0.1 mm, initial beam slightly divergent) after passing through 1.2 cm of lead glass ($\beta=0.20\text{ cm}^{-1}$). The conductive steady state has been reached. From F. W. Dabby, et al, Appl. Phys. Letters 16, 362 (1970).

In the short-time regime, when $l/v_s \gg t$, where v_s is the velocity of sound, and therefore thermal expansion cannot occur, the criterion (III-4) becomes

$$\left| \frac{\partial n}{\partial T} \right|_{\rho} \Delta T < \frac{\lambda}{8l}, \quad (\text{III-6})$$

where $\partial n / \partial T \big|_{\rho}$ is the index change with temperature at constant density, and $\Delta T = \delta T(r_1) - \delta T(r_2)$.

In stress-strain steady-state a cylindrical beam passing through a cylindrical window exhibits birefringence between the azimuthal and radial directions. For this case, the change in optical phase with temperature has been estimated by Sparks⁽²⁾ for a cylindrical slab window such $d \gg l$ (d is the window diameter) using an approximate stress distribution with the assumption of ~~un~~strained edges. For simplicity, average strain values in the two directions of polarization are used here so that the effect of birefringence is eliminated. This does not mean, however, that birefringence effects are unimportant, but rather that to include these effects correctly is a problem too detailed in scope for the present report. Furthermore, satisfying the criteria developed here should, as can be seen from more detailed analyses, also eliminate the birefringence effects. With the above considerations in mind, the criterion (III-4) becomes

$$\left| \delta_{nlT} \Delta T \right| < \frac{\lambda}{8l}, \quad (\text{III-7})$$

where

$$\delta_{nlT} = \left[\frac{\partial n}{\partial T} \Big|_{\rho} - \frac{(1+\nu)}{4} n_o^3 (\rho_{11} + 3\rho_{12}) \alpha \right] + (n_o - 1) \alpha (1+\nu), \quad (\text{III-8})$$

where ν is Poisson's ratio, ρ_{11} and ρ_{12} are strain-optic coefficients, and α is the linear coefficient of thermal expansion. The term in square brackets represents the change in refractive index, while the last term is the change in length. For some materials the temperature dependence of the index of refraction is known under stress-free conditions but ρ_{11} and ρ_{12} are unknown, in which case it is necessary to replace δ_{nlT} by an approximate value δ'_{nlT} , where

$$\delta'_{nlT} = \frac{\partial n}{\partial T} \Big|_{\sigma=0} + (n-1) \alpha (1+\nu), \quad (\text{III-9})$$

where $\partial n / \partial T \Big|_{\sigma=0}$ is the temperature derivative of refractive index found experimentally under stress-free conditions. $\partial n / \partial T \Big|_{\sigma=0}$ can be expressed as

$$\frac{\partial n}{\partial T} \Big|_{\sigma=0} = \frac{\partial n}{\partial T} \Big|_{\rho} - \frac{n_o^3}{2} (\rho_{11} + 2\rho_{12}) \alpha. \quad (\text{III-10})$$

In some materials δ_{nlT} and δ'_{nlT} are both available. In halogen compounds δ'_{nlT} may be as much as a factor of two larger than δ_{nlT} , while for covalent materials the values δ_{nlT} and δ'_{nlT} are very close.

Note that by replacing the inequality in (III-6) and (III-7) by an equality and solving for ΔT we can obtain an estimate of the temperature difference between two radial points in the beam profile at which thermal-beam distortion

becomes appreciable. In addition to heating by the beam itself, this temperature difference can occur because of the environment in which the window is used.

In the majority of cases of interest, the time constant for radial conduction is much longer than the time duration of the laser radiation, so that radial conduction may be neglected. The radial temperature profile therefore follows the beam profile. If the beam profile is a Gaussian truncated at the $1/e^2$ radius, the $1/e$ radius is a reasonable point at which to determine the temperature rise with respect to the beam center. Also, the quadratic phase term is assumed to be compensated for by refocusing. (It is somewhat questionable whether any compensation is possible in many practical situations; however, the results which are obtained would be changed by numerical factors of the order of 2 to 4 by the inclusion of the quadratic term or conversely by the incorporation in the system of a focus correction which minimizes the over-all effect of window phase distortion. These numerical factors will be indicated below.) With the above considerations in mind, the temperature difference is found to be given by

$$\Delta T = \frac{1}{e} \Delta T_0, \quad (\text{III-11})$$

where ΔT_0 is the temperature rise at the center of the beam. For the materials considered in this report, $\partial n / \partial T|_p$ and $\delta_{n\lambda T}$ are in the range $2 \times 10^{-6} - 2 \times 10^{-4} / K$,

so that from (III-6), (III-7), and (III-11) it is seen that

$$l\Delta T_o < 2-200 \text{ cm-K}, \quad (\text{III-12})$$

at $10\mu\text{m}$, for distortionless propagation.

The temperature rise on the beam axis is given by

$$\Delta T_o = \frac{\beta I_o t_1}{C}, \quad (\text{III-13})$$

where β is the absorption constant, I_o is the central intensity, C the heat capacity per unit volume, and t_1 is a characteristic time. Surface absorption is included in the distributed absorption as follows:

$$\beta = \beta_o + \frac{b_1 + b_2}{l}, \quad (\text{III-14})$$

where β_o is the actual volume absorption, and b_1 and b_2 are the fractional absorptions at the surfaces. This is, of course, only an approximation; to obtain a more accurate result, one must solve a difficult problem in thermal stress and heat-transfer analysis. There can also be serious breakdowns in the approximation if the surface heating is large enough to cause deviations in the assumed dependence of material properties on temperature change and strain. If optical intensities are high enough, surface damage can occur due to surface absorption.

For times short compared to the time for heat transfer by conduction to the surface and subsequent

removal from the surface,

$$t_1 = t, \quad (\text{III-15})$$

where t is the time elapsed from the onset of irradiation of the window. For times long compared to the heat transfer time,

$$t_1 \approx t_c + t_s, \quad (\text{III-16})$$

where

$$t_c \approx \frac{Cl^2}{3k}, \quad (\text{III-17})$$

$$t_s \approx \frac{Cl}{h}, \quad (\text{III-18})$$

k is the thermal conductivity of the window, and h is the surface heat-transfer coefficient.

Combining the above results, the following set of criteria is obtained which, if satisfied, will allow radiation to propagate undistorted through the window.

Region 1. ($t < l/v_s$),

$$\left| \frac{\partial n}{\partial T} \right|_{\rho=0} \beta I_o t / C < e\lambda / 8l. \quad (\text{III-19})$$

Region 2. $(t_c + t_s > t > l/v_s, d/v_s),$

$$|\delta_{nlT}| \beta I_o t / C < e\lambda / 8l. \quad (\text{III-20})$$

Region 3. $(t > t_c + t_s),$

$$|\delta_{nlT}| \beta I_o (t_c + t_s) / C < e\lambda / 8l, \quad (\text{III-21})$$

where δ_{nlT} is given by (III-8) or (III-9) and t_c and t_s are given by (III-17) and (III-18). Replacing the inequality by an equality in (III-19) through (III-21) and solving for $I_o t$ (the energy per unit area) in (III-19) and (III-20) and I_o (the intensity) in (III-21), we obtain values of energy per unit area and intensity at which the thermal lens effect becomes appreciable. These criteria would be more stringent by about a factor of two if the quadratic term is uncompensated. Using Spark's analysis, it is estimated that the criteria could perhaps be a factor of four less stringent if the over-all window phase distortions are compensated for by focusing.

The thickness of the window, l , is usually determined by the pressure differential which the window must withstand (in the case of equalization of the average pressure, pressure fluctuations or buffeting determine how much pressure differential the window must withstand). The criterion for the window not to undergo inelastic change under a pressure difference Δp is

$$l > 0.56 \left(\frac{\Delta p f_{SF}}{\sigma_Y} \right)^{1/2} d, \quad (\text{III-22})$$

where σ_y is the yield or rupture stress (whichever is lower), d is the window diameter, and f_{SF} is an engineering safety factor. The above condition can be combined with (III-19) through (III-21) to obtain criteria, which depend only on window diameter and material parameters, for the capability of windows to transmit energy or power without phase-front distortion. In this case for regions 1 and 2 there is a linear dependence of the energy transmitted on window diameter.

The above calculations are for a single pulse. It is relatively easy to use these results to analyze any of the many situations which may be encountered in practice. For example, for a single pulse it may be found that $t < t_s + t_c$, but the average time between pulses ($\bar{t}_b$) in a series of pulses may be such that $\bar{t}_b > t_s + t_c$. In this case the average power-handling capability could be tested by (III-21), taking I_0 as the average power.

Several other detrimental effects induced by the absorption of radiation from the beam have been considered. (4) Thermal runaway, melting, and dissociation generally occur at much higher temperatures than those which produce the thermal lens effect. The criterion for thermally induced inelastic changes not to occur is given by

$$\Delta T_0 < 2\sigma_y / \alpha E, \quad (\text{III-23})$$

where ΔT_0 is the temperature rise in the center of the

window with respect to the edge, α is the linear coefficient of thermal expansion, and E is Young's modulus. The criterion (III-23) can also be re-expressed in terms of pulse energy or intensity using (III-12) and (III-14) or (III-15). The inequality (III-23) can also be compared with the inequalities which result in combining (III-6) or (III-7) with (III-11). For pure alkali-halide single crystals, thermally induced inelastic change occurs for very small temperature rises and these materials must be strengthened as discussed in a subsequent section.

Absorptively induced damage at inclusions and dielectric breakdown were discussed in the National Materials Advisory Board Glass Laser Damage Report⁽⁵⁾ and they are reconsidered briefly here. They can be considered to be high-peak-power effects. The significance of inclusion damage is strongly dependent on material preparation and it is, therefore, difficult to make a priori predictions. Generally, one would like to avoid these damage causing inclusions by careful material processing. A theory of inclusion induced damage has been given.⁽⁶⁾ Dielectric breakdown in alkali halides for 10^{-8} sec pulses at $10.6\mu\text{m}$ occurs⁽⁷⁾ at power densities in the vicinity of 10^9 watts/cm². At shorter wavelengths, the power densities for breakdown should be equal or higher.

C. Other Nonlinear Effects

Other detrimental nonlinear effects can occur at high-optical intensities ($> 10^6$ watts/cm²) such as

nonabsorptively induced refractive index changes leading to self-focusing⁽⁵⁾ and stimulated light scattering. Index nonlinearities due to electrostriction and the electronic Kerr effect are too small to cause significant phase distortion through a high-power-laser window at flux densities of less than 10^{11} watts/cm².

Stimulated light scattering is also a possible loss or damage mechanism in laser windows. Light scattering would produce light traveling in the plane of the window since the gain would be greatest for scattering into the longest dimension. Brillouin scattering at 90° would have a steady-state ($t_{\text{pulse}} > 10^{-5}$ sec) gain constant in single crystal KCl on the order of 0.05 cm/Mw at 10.6μm and a value perhaps two orders of magnitude smaller in polycrystalline materials on account of the large amount of acoustic scattering. The gain in the transient regime should be the same as the largest steady-state gain occurring for a fixed pulse energy. Nearly the same results would hold at short wavelengths except that the steady-state gain would hold for shorter pulse times. In semiconductor materials the Brillouin gains can be very high, for example, in Ge at 10.6μm the steady-state gain is 0.5 cm/Mw for 90° scattering. Backward Brillouin scattering has been observed in this material at 10.6μm.⁽⁸⁾ Again the use of polycrystalline material would greatly increase the threshold power.

First-order stimulated-Raman scattering is forbidden in the alkali halides because of symmetry restrictions, and second-order-Raman scattering would be expected to have a very high threshold. In other materials the steady-state Raman gain generally does not exceed the steady-state Brillouin gain at visible wavelengths. This is even more the case in the infrared since the Raman gain is inversely proportional to the Stokes wavelength. If the Brillouin scattering becomes a transient process, the Raman gain might exceed the Brillouin gain. This could occur for a pulse whose duration is much shorter than a nanosecond. Finally, absorptively induced stimulated-light scattering should be negligible on account of the low-absorption constant required for the window.

D. Summary

The self-induced thermal lens effect represents a serious difficulty which must be overcome for many practical applications of high-power-laser windows. In examining the criteria for a negligible thermal lens effect, it should be noted that the laser power, beam diameter, and pulse length are determined by the use which is to be made of the laser system. The time for removal of heat from the window surface (t_g) can be made reasonably short by the design of proper cooling systems. For a given window material, the remaining parameters which might be decreased to satisfy the criteria are the window thickness (ℓ) and the absorption constant (β). The thickness is dependent on the yield strength of the material

and the environment of the window. In a subsequent section various absorption processes will be discussed. For the present it is only necessary to recognize that the absorption of materials usually has an intrinsic component and a component which can be reduced and which arises from internal impurities, defects, etc., as well as from surface impurities. The central problems of high-power-laser windows involve the reduction of extrinsic absorption, producing high-yield strength and hardness without increasing absorption, the protection of surfaces from undesired impurities and the fabrication of windows of proper physical dimensions which retain the desired optical characteristics.

E. Recommendation

The following recommendation is made:

The high-intensity-nonlinear effects such as stimulated-light scattering would certainly bear more careful experimental and theoretical scrutiny than they have received at infrared-laser wavelengths. It is felt that with low energy but high-peak-power lasers [modest energy transverse electrical atmospheric (TEA) or electron beam preionization lasers] that experimental investigations of these effects could be undertaken. This could bear strongly on the development of laser technology for controlled thermonuclear reactions. These basic long-range experimental and theoretical investigations of nonlinear effects using infrared lasers of high-peak power should receive greater support. A rate of 3 man-years over the the next two years is recommended.

Subsequent chapters make recommendations concerning the study of linear propagation effects.

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IV. FUNDAMENTAL ABSORPTION MECHANISMS

A. Introduction

This chapter contains a review of what is known about physical mechanisms that are responsible for the small residual bulk absorption in the "transparent" wavelength regions of prospective high-power IR-window materials. An attempt is made to identify those areas in which better physical understanding would aid in the fabrication of materials of lower IR absorption.

It is convenient to separate the mechanisms that give rise to this small absorption into two classes, extrinsic and intrinsic. Extrinsic mechanisms are those associated with unwanted impurity atoms and molecules, deviations from stoichiometry, and lattice imperfections (dislocations, twinning, grain boundaries, etc.) that constitute deviations from a thermal equilibrium state of a glass or crystal. The intrinsic absorption mechanisms are those that give rise to the electronic and vibrational absorptions, which would exist in an ideal crystal or glass of some specified composition and possessing the structure and vacancy system appropriate to its ambient temperature. Generally speaking, extrinsic absorption mechanisms appear to be the more troublesome in the best contemporary materials; there seems to be no clear-cut case at this writing in which the absorption of a candidate material for a high-power IR window is intrinsic.

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All the important examples of extrinsic and intrinsic absorption, in bulk or on surface, are of three general kinds: 1) absorption by vibrational excitations without electronic change of state, 2) free-carrier absorption, and 3) absorption by excitation of bound electrons. Usually, the relevant absorption by each mechanism is the "linear" absorption whose coefficient, β in cm^{-1} , is not dependent on the laser or ambient radiation intensity. However, some nonlinear free-carrier-absorption mechanisms also may be important.

In the next section, B, of this chapter we review what is known of the dependence of the infrared absorption (at 10.6 and 2-5 μm) on extrinsic mechanisms. Then, in section C, the as yet imperfect methods of estimating the intrinsic absorption well below the band gap and above the intrinsic vibrational resonance frequencies are discussed. Section D includes comments on what is known of the corresponding mechanisms underlying the possibly troublesome absorption at surfaces, and also at thin anti-reflection or protective coatings. Finally, a summary of the most important unsolved problems and an estimate of the support that would be required to solve them is given in section E.

B. Extrinsic Absorption Mechanisms

In crystals and glasses of near ideal structure for a given composition, the small residual absorption due to impurities, dislocations, etc., can be considered as

simply a superposition of the absorption from each such imperfection. That is, the absorption per cm $\beta(\omega)$ is well-approximated at frequency ω by

$$\beta(\omega) = \sum_i N_i \sigma_i(\omega) , \quad (\text{IV-1})$$

where the sum is over the various types, i , of imperfections whose number densities are N_i and absorption cross sections are σ_i . The processes that give rise to the $\sigma_i(\omega)$ may be divided into three types which we discuss below: 1) excitation of polar bond vibrations or local modes, without electronic excitation, 2) absorption by free carriers donated by impurities, and 3) excitation of bound-electron impurity states.

1. Excitation of Polar Vibrations

There has been a great deal of experimental and theoretical work on the infrared absorption lines caused by the addition of various impurities to various crystals in various amounts. (See, for example, the review articles of Newman⁽¹⁾ and of Spitzer.⁽²⁾) The impurities may enter the lattice singly or multiply in a number of different types of configurations. Unfortunately, the impurity atoms or molecules, which appear to produce troublesome absorptions near 10.6 and 2-5 μm , have not yet been studied adequately in the candidate materials for high-power windows. These impurities are primarily oxygen and hydroxyl radicals covalently bonded in various configurations to produce absorption lines in the vicinity of

3, 9, and $13\mu\text{m}$.^(3,4) The cross sections σ_i , at $10.6\mu\text{m}$ for metal-oxygen-bond absorptions generally lie in the region of 10^{-18} to 10^{-20} cm^2 . The absorption cross section of an O-H bond around $3\mu\text{m}$ is likely to be of the same order of magnitude.

In any given material and at any specific frequency ω , the cross sections of relevant vibrations of these and other impurity atoms, ions, molecules, vacancies, boundaries, precipitates, striations, etc., must be determined by experiment. (An excellent review of current work on this is given in reference [5].) Theory can do little more than provide the phenomenological framework of Equation (IV-1) and suggest guidelines, such as that various covalent bond frequencies of a given atom or complex do not change much from one host to another.

There is another possible effect of impurities in the low-absorption region of crystals, whose importance has not yet been assessed. This is the change in the coupling constants of the electromagnetic field to the intrinsic phonons and also of the intrinsic phonons to each other, due to the disruption of the lattice periodicity. Since the intrinsic absorption in the "tail" of a fundamental reststrahl band at 10.6 and $2-5\mu\text{m}$ commonly involves the creation of 5 to 50 optical phonons with the annihilation of one photon, these coupling alterations might well enhance this absorption. Most importantly, heavy-ion impurities could contribute to this effect as much as the lighter impurities. When an accurate theory of the

intrinsic tail absorption becomes available, this type of impurity effect will be easier to assess.

2. Free-Carrier Absorption

Free carriers donated by impurities contribute a term, β_e , to the optical absorption; this absorption can be correlated roughly with the dc conductivity. Except in very pure nonpolar crystals, the free-carrier collision time, τ , is on the order of an infrared period (i.e., $\omega\tau \leq 1$) in which case the infrared conductivity is not orders of magnitude different from the dc conductivity and can be approximated by the Drude formula

$$\beta_e(\omega) = \left(\frac{30}{\rho n(\omega)} \right) / (1 + \omega^2 \tau^2) \text{ cm}^{-1}, \quad (\text{IV-2})$$

where ρ is the resistivity in ohm-cm and $n(\omega)$ is the real part of the refractive index. Therefore, high-power window materials with a resistivity less than, or on the order of, 10^3 ohm-cm usually have not been considered. An important exception is germanium whose τ is so large that the best commercially available material (whose impurity concentration is around 10^{14} cm^{-3} and dc resistivity is around 20 ohm-cm) has an absorption of only 0.025 cm^{-1} at $10.6\mu\text{m}$.⁽⁶⁾ This absorption appears to be partly from extrinsic free carriers, but mainly from extrinsic vibrational absorption (probably of oxygen).

3. Excitation of Bound-Electronic-Impurity States

Heavy impurities generally have their vibration frequencies so low that the wing of their vibrational absorptions contributes negligibly at $10.6\mu\text{m}$. This would typically be the case if $\sigma_v \leq 10^{-23} \text{ cm}^2$ for the vibrational cross section as the impurity density can be kept below 10^{19} cm^{-3} and we can tolerate $\beta \sim 10^{-4} \text{ cm}^{-1}$. However, heavy impurities might still absorb in the infrared via an electronic absorption tail. The electronic absorption cross section σ_e in the wing of a Lorentzian line of half width at half maximum $\Delta\omega$ is given by

$$\sigma_e(\omega) = \pi f r_o c \Delta\omega [(\omega - \omega_o)^{-2} - (\omega + \omega_o)^{-2}] \text{ cm}^2, \quad (\text{IV-3})$$

where r_o is the classical electron radius $2.8 \times 10^{-13} \text{ cm}$, c is the velocity of light, and $f \sim 1$ is the f-number of the transition. In the infrared, $\omega \ll \omega_o$, and

$$\sigma_e \rightarrow 2f r_o \lambda_o \omega / (\omega_o Q) \quad (\text{IV-4})$$

where $\lambda_o = 2\pi c / \omega_o$ and $Q = \omega_o / \Delta\omega$ is the "Q" of the transition. It is well known that heavy-ion-electronic excitations can have a small Q (~ 10 to 100 , as do the Cr^{3+} "pump" transitions in pink ruby which have $\lambda_o \sim 4,000$ and $5,500 \text{ \AA}$). Therefore, an electronic "tail" absorption cross-section σ_e might reasonably be of order 10^{-18} cm^2 if the line is Lorentzian in its low-frequency tail. If so, the tail of the electronic absorptions of heavy-ion impurities might well be an important factor in the absorption. This would

depend largely on whether or not the absorption falls off much more rapidly than a Lorentzian line in the low-frequency tail - a question which has not been studied sufficiently in solids.

How the extrinsic absorption of a typical material might dominate the transparent wavelength region of a crystal (and particularly the IR wavelengths of interest) is shown schematically in the plot of β vs. ω in Figure 3. Whether or not there are actually bumps in the extrinsic portion of β vs. ω , as indicated, is not yet known; the absorption below 10^{-2} cm^{-1} is too low to have been scanned by conventional techniques.

C. Intrinsic Absorption Mechanisms

At present, very little is known of the fundamental lower limit on the absorption of crystals at wavelengths where they are the most transparent to radiation, i.e., between their electronic-absorption edge and their lattice-vibration-absorption bands. Similarly, as for extrinsic absorption, the mechanisms that may be important in setting the intrinsic absorption limit may be divided into three categories: 1) absorption by lattice vibrations, where the electrons follow adiabatically and in which there is no electronic transition involved; 2) free-electron or free-carrier absorption; and 3) bound-electron absorption. We shall review what is known of each of these mechanisms separately below for both ideal crystals and glasses.

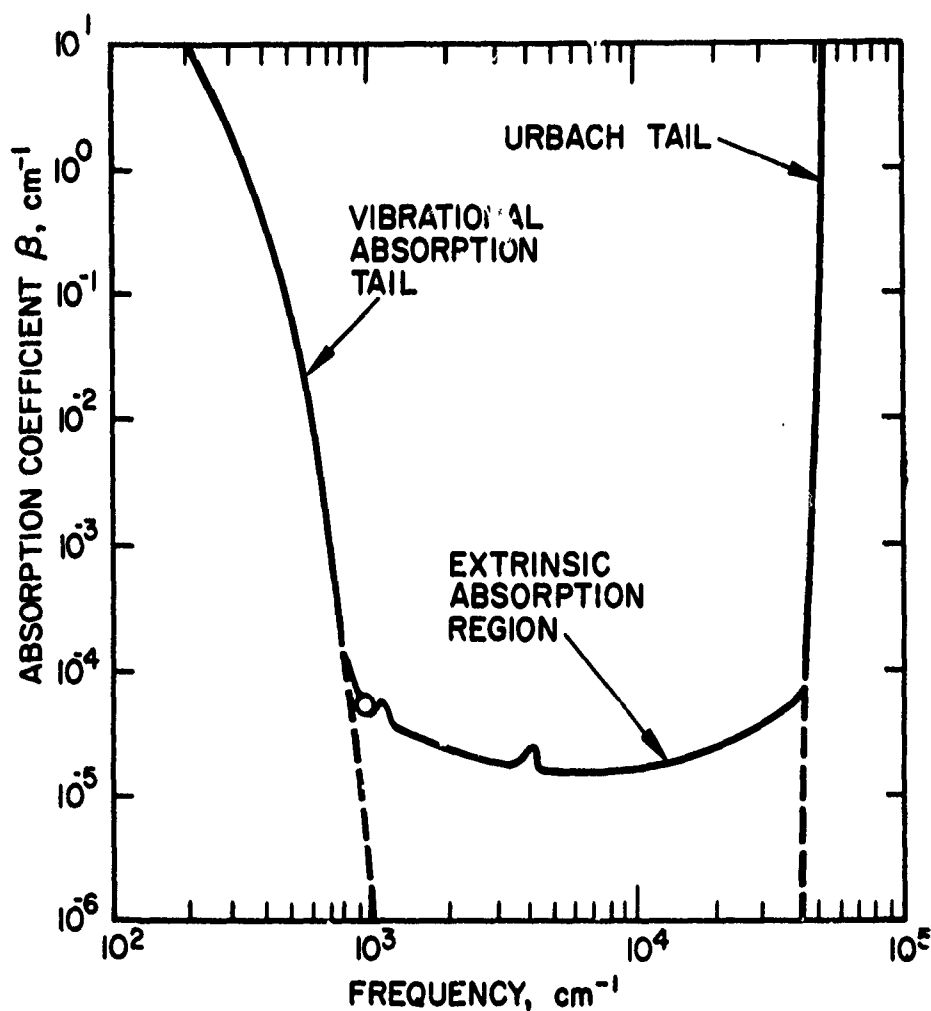


Figure 3. Schematic plot of the optical absorption coefficient vs. optical frequency, in the low-absorption region, of a typical candidate material for high-power IR windows. The $10.6 \mu\text{m}$ absorption, indicated by the circle, is shown in the extrinsic region, but near the intrinsic tail, as is the case for most candidate materials. As is discussed in the text, the exponential forms of the vibrational absorption tail and the electronic absorption (Urbach) tail appear to be universal. However, the extrinsic absorption region has never been scanned and is drawn here from imagination.

1. Lattice Vibration Absorption

There have been a number of recent studies of how the infrared absorption drops off as the frequency becomes much greater than the fundamental lattice absorption frequencies, and the prominent overtone or combination-absorption frequencies.⁽⁶⁻⁸⁾ These studies have been mainly on the alkali halides and MF_2 crystals. In the more highly purified samples, it appears that the absorption coefficient, $\beta(\omega)$, universally exhibits an exponential fall-off over the lowest two-to-four decades of β that are measurable. That is, for $\omega \gg \omega_{\text{TO}}$,

$$\beta(\omega) \propto e^{-\omega/\omega_0}, \quad (\text{IV-5})$$

where ω_0 is never far from the reststrahl frequency ω_{TO} ⁽⁹⁾ and varies little with temperature at room temperature. (For example, $\omega \sim \frac{1}{2} \omega_{\text{TO}}$ for KBr.)

In some crystals (e.g., Al_2O_3 , SrF_2 , BaF_2 , LiF , and CaF_2) the observed absorption at $10.6\mu\text{m}$ is clearly part of this tail and, therefore, probably intrinsic. However, in these cases the absorption at $10.6\mu\text{m}$ is so high that the crystals are not good window material candidates. It is probable, though not certain, that the observed low absorption at $10.6\mu\text{m}$ and $2\text{-}5\mu\text{m}$ in many of the more interesting candidate materials (KBr, $\text{Tl}(\text{Br}, \text{I})$, KCl , ZnSe , CdTe , GaAs , and Ge crystals and chalcogenide glasses) lies

above this intrinsic absorption tail roughly as illustrated in Figure 3. This is certainly the case in the 2-5 μ m region.

Whether this exponential absorption tail is characteristic of all other classes of materials, including glasses and nonpolar crystals, is not yet known.

2. Free-Carrier Absorption

The theory of B-2 above and the approximate Equation (IV-2) may also be applied to intrinsic free-carrier absorption. The only interesting material for which this absorption may be an important limiting factor at 10.6 μ m is "ultrapure" germanium, inch-size crystals which have recently become available.⁽¹⁰⁾ This case will be discussed in detail in Chapter VII.

It has been suggested that even though free-carrier absorption is negligible, free carriers may contribute significantly to absorption below the band gap by interband transitions in semiconductors.⁽¹¹⁾ The cross sections for such processes deserve further investigation. High intensities at infrared and/or visible and ultraviolet frequencies may increase the free-carrier concentration by photo-excitation. The resulting intensity-dependent (nonlinear) absorption has not yet been analyzed.

3. Bound-Electron Excitation

Only those materials that have a band gap (i.e., minimum nominal energy to excite bound electrons to a conduction band) much larger than the infrared frequencies of interest need to be considered. It is, therefore, only the low-frequency tail of the fundamental gap absorption that might be of importance in the low-absorption window under consideration. This tail, $\beta_t(\omega)$, to the fundamental electronic absorption has been observed to be of the form

$$\beta_t(\omega) \propto e^{\zeta \hbar \omega / k_B T} \quad (\text{IV-6})$$

in a wide variety of ionic, covalent, and amorphous materials. (Here, ζ is a constant of the order unity, k_B is Boltzmann's constant, and T the absolute temperature.) This dependence was first noticed by Urbach in alkali halides and has been found to be so widespread that it is called Urbach's rule.⁽¹²⁾ The most recent and promising of many attempts to construct a theoretical basis for this general behavior is that of Dow and Redfield.⁽¹³⁾

In any event, it would seem that we may estimate with some confidence the contribution β_t to the intrinsic absorption from electronic transitions by extrapolating measurements made just below the band gap.⁽¹⁴⁾ The Urbach tail for a typical material is indicated in the β vs ω plot of Figure 3. The Urbach tail is so steep that it could produce significant absorption only for those materials

whose band gap is not much above the infrared frequency one wishes to transmit, that is, only for small-band-gap semiconductors.

D. Surface and Coating Absorption

Surface and coating absorption can affect high-power-window performance in several ways. The surface heating can cause thermal distortions of the optical phase front. If fragile surfaces, such as of the alkali halides, are subjected to high-power beams, the surface cracks and imperfections may propagate or enlarge, or become hygroscopic. When anti-reflection or passivating coatings are used, surface absorption may tend to dislodge or even evaporate the coatings. The theory of surface and coating absorption may be thought of in terms of the same six categories that we have used in discussing bulk absorption: by vibrational, bound-electronic, or absorption free-electronic excitations of either extrinsic or intrinsic types. Problems of surface and thin-film coatings are commented on separately below.

1. Surface Absorption

There is some evidence that surface absorption by oxygen bonds has been observed near $2.7\mu\text{m}$ in various crystals.⁽⁶⁾ In this case, as in B-1, an absorption cross section, σ_i , is assigned to the i^{th} impurity bond type and the fraction of the beam, F_s , absorbed at the surface is written as

$$F_S(\omega) = \sum_i M_i \sigma_i(\omega) , \quad (IV-7)$$

where M_i is the number per unit surface area of this type of imperfection. For example, to estimate the surface absorption at $10.6\mu\text{m}$ due to a monolayer of oxygen, suppose that the cross section, σ_i , is on the order of the bulk absorption cross section ($\sim 10^{-18} \text{ cm}^2$), and the number per unit area, M_i , is the two-thirds power of the atomic density of the crystal ($\sim 10^{15}$). In this case F_S is estimated to be of order 10^{-3} . Although this is a significant fractional absorption in high-power applications, it is very difficult to measure with existing techniques. Perhaps if the σ_i could be determined for the important impurities, the more easily measured surface density, M_i , would give a useful estimate for the surface absorption, F_S , of a given sample.

Both linear and nonlinear absorption by surface free carriers and surface bound-electron states may well be important but have received little attention to date.

2. Thin-Film Coatings

In addition to introducing extra surfaces and their associated absorptions, thin-film coatings have a "bulk" absorption that may often be allowed to be significant in order to obtain other characteristics required of a useful coating. Unfortunately, it has become evident that the absorption coefficient, β , in films is generally much larger than the β for the same nominal material in bulk. (5)

The real part of the refractive index measured in a film is also different from that measured in bulk. These discrepancies have been observed to be a function of film preparation and the mechanisms responsible are not yet understood.⁽¹⁵⁾ Nonlinear absorption processes are more likely to be important in films than in bulk but estimates of these have not been made.

E. Conclusions and Recommendations

It is probable that the low, but deleterious, infrared absorption that has been measured in the best candidate materials for high-power-laser windows is extrinsic in origin. Therefore, the possibility exists that more careful preparation and purification of these materials will lower their absorption. Unfortunately, the materials with the best thermal and mechanical properties tend to need the most improvement in absorption. From our review in this chapter of the gaps in theoretical knowledge of mechanisms of absorption, we conclude that a better theoretical grasp of the following facets of the absorption problem would aid the choice and fabrication of a satisfactory high-power infrared-laser window. The list is arranged roughly as we see the relative priorities of the theoretical problems to window fabrication.

1. The limit to the improvement in absorption is set in most materials by the level of intrinsic vibrational absorption at frequencies well above the intrinsic absorption resonances. This absorption tail has been

traced experimentally so far mostly in polar crystals, where it has been found to be exponential over the lowest decades of absorption measured. This behavior should be given a theoretical basis from which to predict a) whether the exponential trend persists to lower absorptions, b) how the absorption tail behaves with changing temperature and composition, and c) if this tail is to be expected in other classes of materials, especially glasses and nonpolar crystals.

2. It is clear how various species of ionic impurities can vibrate to cause "local mode" or bond absorption resonances above the reststrahl bands. However, these impurities may cause a much less obvious raising of the background absorption by virtue of the anharmonicity, disruption of periodicity, and general change in phonon couplings which they cause. A simple model of this effect ought to be devised by which an estimate of the changed background vibrational absorption could be made.

3. At the high levels of both the infrared-beam intensity and the ambient visible and ultraviolet intensities that high-power infrared-laser windows may have to withstand, photoconductive free carriers may introduce troublesome added (nonlinear) absorption. From existing data on the wavelength dependence of photoconductivity, theoretical estimates should be made of this effect in candidate materials. These effects of photo-excitation seem to deserve special attention at surfaces and in surface coatings.

4. Free carriers, whether extrinsic, intrinsic, or photo-excited, may absorb by interband transitions. Such absorption might well peak at frequencies above the laser frequency and exceed normal (intraband) free-carrier absorption at wavelengths of interest. Some straightforward band theory ought to provide a prediction as to when such an effect might be important.

5. The absorption by electrons localized on impurities usually peaks at much shorter than infrared wavelengths. Such absorption commonly has been observed to be so strong at its peak that it may well contribute a small but significant absorption at the longer laser wavelengths of interest here. The theory of the shape of these electronic absorption tails on their low-frequency side should be developed in analogy with the existing theory of the Urbach tail.

6. Although many of the discrepancies observed between values of absorption and refractive index in bulk and in thin film can be attributed to "dirt" effects, there may be some intrinsic change occasioned by the forced lattice distortions and proximity of surface states in the films. It would be helpful to the development of window coatings if some rules-of-thumb could be developed to predict the nature of these absorption and index discrepancies.

To this list many other special topics might be added. Studying subjects such as the formation of color centers, radiation damage, and light scattering from

impurities might well expose some important contribution to the eventual amount of heat that will be deposited from a laser in the window material. The Committee can only hope to have uncovered some of the more obvious problems and assessed them cursorily in a study so brief as this.

Considering the nature and degree of complexity of the problems identified above, the Committee feels that about \$100,000 per year spent over the next two years is required to yield a body of answers that would provide satisfactory guides to window design.

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V. EXPERIMENTAL ASPECTS IN THE CHARACTERIZATION
OF HIGH-POWER INFRARED-WINDOW MATERIALS

The significance of a large number of mechanical and optical properties for high-power-infrared windows has been discussed extensively by Sparks⁽¹⁾ and others.⁽²⁾ The properties are listed below for the sake of completeness and may give the appearance of a formidable list, but it should be emphasized at the outset that only a few of the many characteristics will require special attention and that no major new survey of possible material candidates is required. For a complete characterization of a high-power infrared-window material, the following data must be obtained:

1. Optical absorption spectrum, including the determination of the band gap and optical phonon energies.
2. Index of refraction n and its temperature coefficient dn/dT , both in the wavelength region around $10.6\mu\text{m}$ and in the $2\text{-}6\mu\text{m}$ region.
3. Residual optical absorption coefficient β in transparent regions.
4. Light scattering characteristics and large-scale optical homogeneity.
5. Density, specific heat, and melting point.
6. Thermal conductivity and thermal expansion.
7. Hardness, and resistance to abrasion and moisture.

8. Yield and fracture strengths.
9. Elastic moduli and photo-elastic constants.
10. Electrical dc conductivity.
11. Resistance to radiation-induced optical damage.

Many of these properties have been tabulated for important classes of materials, and these tabulations may serve as a guideline in selecting candidates for infrared window materials. These general properties will be discussed separately for different classes of materials in the subsequent sections on ionic crystals, covalent semiconductors, glasses, and polycrystalline materials.

Whenever a new material or a new processing or fabrication technique is developed, all of the above-mentioned characteristics should be determined. Most of these quantities may be measured by standard experimental techniques. Several quantities are insensitive to details of the fabrication procedure and to the nature of additives and impurities, e.g., the band gap, optical phonon energies, specific heat, Poisson's ratio, etc.

The mechanical properties of hardness and tensile strength, and to a lesser degree thermal conductivity, are, of course, very sensitive to heat treatment, recrystallization procedures, alloying impurity content, and fabrication techniques including, for example, hot or cold pressing and sintering. However, once the material has been prepared, measurement of these properties poses no special problems.

The numerical values of these properties lie in a rather conventional range.

By contrast, the measurement of low-optical absorption-coefficients presents a more specialized problem. It is obviously desirable, as follows from the theoretical discussion in the preceding section, to minimize the optical absorption. Acceptable window materials usually have a bulk-absorption coefficient of $\beta < 10^{-3} \text{ cm}^{-1}$, and values of β near 10^{-4} cm^{-1} are often preferred. Such low values cannot be measured accurately by total attenuation of the beam in transmission. In this case one measures both losses due to scattering and absorption, and the former may well be dominant. Furthermore, the measurement of the absorption coefficient would be imprecise because the ratio of the incident and transmitted-light intensity is very close to unity.

The most reliable way to measure the (small) absorption coefficient is to measure the heating of the sample, when exposed to a well-defined laser beam of known power. The sample is mounted to provide sufficient thermal isolation and thermocouples are applied to sense the temperature at several points on its surface. The cooling rate may be varied by controlling the ambient-gas pressure. One measures the rate of heating and/or the final steady-state temperature in the presence of the laser beam, as well as the cooling rate when the laser beam is shut off. It is possible with this method to measure absorption coefficients as low as 10^{-5} cm^{-1} (4.3 db/km) with an

accuracy of ten percent. Such data were reported by Pinnow⁽³⁾ on fused silica with a Nd-Yag laser beam. Since cw CO₂ and CO laser beams, etc., in a well-defined geometry with power levels exceeding 10 watts are readily available, the same technique is clearly adequate to establish the absorption of infrared-window materials at the respective wavelengths. The rise in temperature could also be determined by optical interferometry. Another method of determining low-bulk absorptivity consists of measuring the thermal emissivity of the material over a range of temperature and wavelengths.

Scattering losses may be determined by directly observing the scattered light. Even in a perfectly homogeneous material there will be Rayleigh and Brillouin scattering due to entropy and pressure fluctuations. These intrinsic scattering losses have an order of magnitude of about 10^{-6} cm^{-1} in glasses. Since they can be calculated theoretically with good precision, the Brillouin components may be used to calibrate⁽³⁾ the scattering losses due to inhomogeneities, etc. This method has been applied to optical glasses at $1.06\mu\text{m}$ and in the visible range. The intrinsic scattering losses would be many orders of magnitude smaller at $10.6\mu\text{m}$ and would be very difficult to observe. Fortunately, the scattering in the infrared window is only of interest insofar as it substantially degrades the transmitted beam. Even if as much as one percent of the infrared light were scattered out of the incident mode, this would not impair the window operationally. It is necessary, however, to determine the spatial

characteristics and mode structure of the transmitted beam. One may expect significant small-angle scattering, especially in sintered, microcrystalline materials. This scattering could be determined experimentally by moving a pinhole across the beam profile a suitable distance away from the window sample.

The presence of a large amount of scattered light may influence the absorption measurements in a significant way, as was pointed out by Winsor.⁽⁴⁾ A substantial fraction of the scattered light may be repeatedly reflected totally, especially in window materials with a high index of refraction. In this manner the light will travel a very long path in the crystal and eventually be absorbed, leading to an apparent enhancement of the absorption coefficient. Although an erroneous value for β would be obtained, it must be pointed out that the calorimetric measurement in an actual window geometry measures precisely what is needed from an operational point of view. It measures the temperature rise due to all causes of absorption, including trapped scattered radiation. Apparently very little work has been done on the scattering of infrared radiation in window materials. Accurate measurements of the scattering in well-defined geometries, especially in the near forward directions, are needed.

There are obviously some experimental advantages, if the infrared-window materials are also transparent in the visible or near ultraviolet. Such is the case, for example, in the alkali halides. In this situation the

scattering characteristics may readily be observed in the visible range, and the infrared scattering properties deduced by appropriate scaling with wavelength. Since the low level residual absorption with $\beta \sim 10^{-3} \text{ cm}^{-1}$ can sometimes be attributed to impurities, which also have characteristic ultraviolet absorption spectra, the concentration of such impurities may more conveniently be monitored, with higher precision, at the shorter wavelengths. Over-all optical quality control of the window and its distortion due to thermal effects may in this case also be monitored by utilizing interferometric techniques in the visible range. This would again significantly simplify testing procedures.

Since high-power-infrared windows probably will need anti-reflection coatings in all cases, and the alkali halides, and perhaps some other materials, will need protective coatings to withstand attack by moisture from the atmosphere, ⁽⁵⁾ the optical absorption and scattering in surface coatings must also be determined. Unfortunately, low-index anti-reflection materials all have a high coefficient of absorption at $10.6\mu\text{m}$. The net absorption in a layer a few micrometers thick may equal the bulk absorption in a window several centimeters thick.

Molecular layers, especially those containing oxygen adsorbed on the surface, may absorb as much as one hundredth or even one tenth of one percent of the incident intensity. In addition, surfaces also may have an intrinsic absorption due to electronic surface states and surface

vibrational modes. The heat contact between coatings and the bulk window may be substantially lower than that calculated from bulk conductivities. Very few experimental data are available on the absorption of high-power-infrared radiation at surfaces. This important question needs immediate attention. If the heat is conducted into the bulk, calorimetric measurements will include the surface and coating absorption.

The scattering from coatings and surface layers is similarly included in the pinhole probing and interferometric techniques described above. If it is desired to measure the properties of coatings in situ, but separately from the bulk, this can be accomplished by a totally reflected beam technique.⁽²⁾ The laser beam is shone into the bulk window material from the side at such an angle that repeated total reflections at the surface layer occur. Absorption in the layer and scattering by the layer can thus be determined.

Conclusion

While most material characteristics of infrared windows may be determined by standard measurement techniques with commercially available instrumentation, the measurement of low absorptivities, small- and large-angle scattering, and optical distortion requires especially constructed calorimetric and optical-bench arrangements.

Recommendations

1. It is recommended that experimental facilities to measure all pertinent optical, thermal, and mechanical properties be closely integrated with each development project for infrared-window materials. Arrangements for exchange of data and samples, and access to testing facilities of other groups should be improved.
2. It is recommended that measurement of the absorptivity of surface layers and coatings and of the temperature rise and resistance to mechanical deformation of such layers, when exposed to high-power infrared-flux densities receive a high priority. Some attention also should be given to the changes in optical and mechanical properties of coating and window materials induced by exposure to ultraviolet and nuclear radiation and to thermal cycling.

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VI. SINGLE CRYSTAL ALKALI-HALIDE INFRARED-WINDOW MATERIALS

A. Introduction

In this chapter ionic crystals that are transparent for radiation at $10.6\mu\text{m}$ and $2\text{-}6\mu\text{m}$ wavelength are evaluated with respect to their potential as high-power infrared-window materials. The most promising substances in this class appear to be halides of certain monovalent and divalent metals.

The main advantages of materials in this class are their low-intrinsic absorption and their availability in sufficiently pure form and large sizes. Low-bulk absorptivities acceptable for window applications have been demonstrated. The optical figure of merit is high.

The main disadvantages of the pure ionic single-crystal materials lie in their mechanical properties; however means exist for improving these without sacrificing the optical quality. In addition, some material candidates at $10.6\mu\text{m}$ are hygroscopic and need a protective coating against atmospheric attack. The weak and strong points of ionic crystals are summarized in Table 1 and compared with the corresponding properties of semiconductors and glasses.

B. Optical Properties and Figure of Merit

The conditions for distortion-free transmission have been given in Chapter III and for this discussion Equations (III-20) and (III-21) shall be used. At

TABLE I
Advantages and Disadvantages of Materials for Use at 10.6μm

	Low Expected Absorption Coefficient	Low Measured Absorption Coefficient	Low Optical Distortion	Great Mechanical Strength	Low Water Absorption	Large J _{T0}	Thermal Conductivity	Available in Large Sizes	Small Required Thickness	High- Power Coating Available
Ge	Fair	Poor	Fair	Good	Good	Poor	Good	Fair	Good	Poor
GaAs	Fair	Fair	Fair	Good	Good	Poor	Good	Poor	Good	Poor
ZnSe	Good	Fair	Fair	No Data	Good	Fair	Fair	Poor	Good	Poor
CdTe	Good	Fair	Fair	Fair	Good	Poor	Poor	Poor	Fair	Poor
KBr	Good	Good	Good	Fair*	Poor	Good	Poor	Good	Fair*	Poor
KCl	Good	Good	Good	Fair*	Poor	Good	Poor	Good	Fair*	Poor
Tl (Br, I)	Unknown	Fair	Fair	Fair	Good	Fair	Poor	Good	Fair*	Poor
Ge ₂₈ Sb ₁₂ Se ₆₀ glass	Fair	Poor	Fair	Good	Good	Poor	Poor	Good	Good	Poor
As ₂ Se ₃ glass	Fair	Poor	Fair	Good	Good	Poor	Poor	Expect Good	Good	Poor

*Doped Materials

-66 (a)

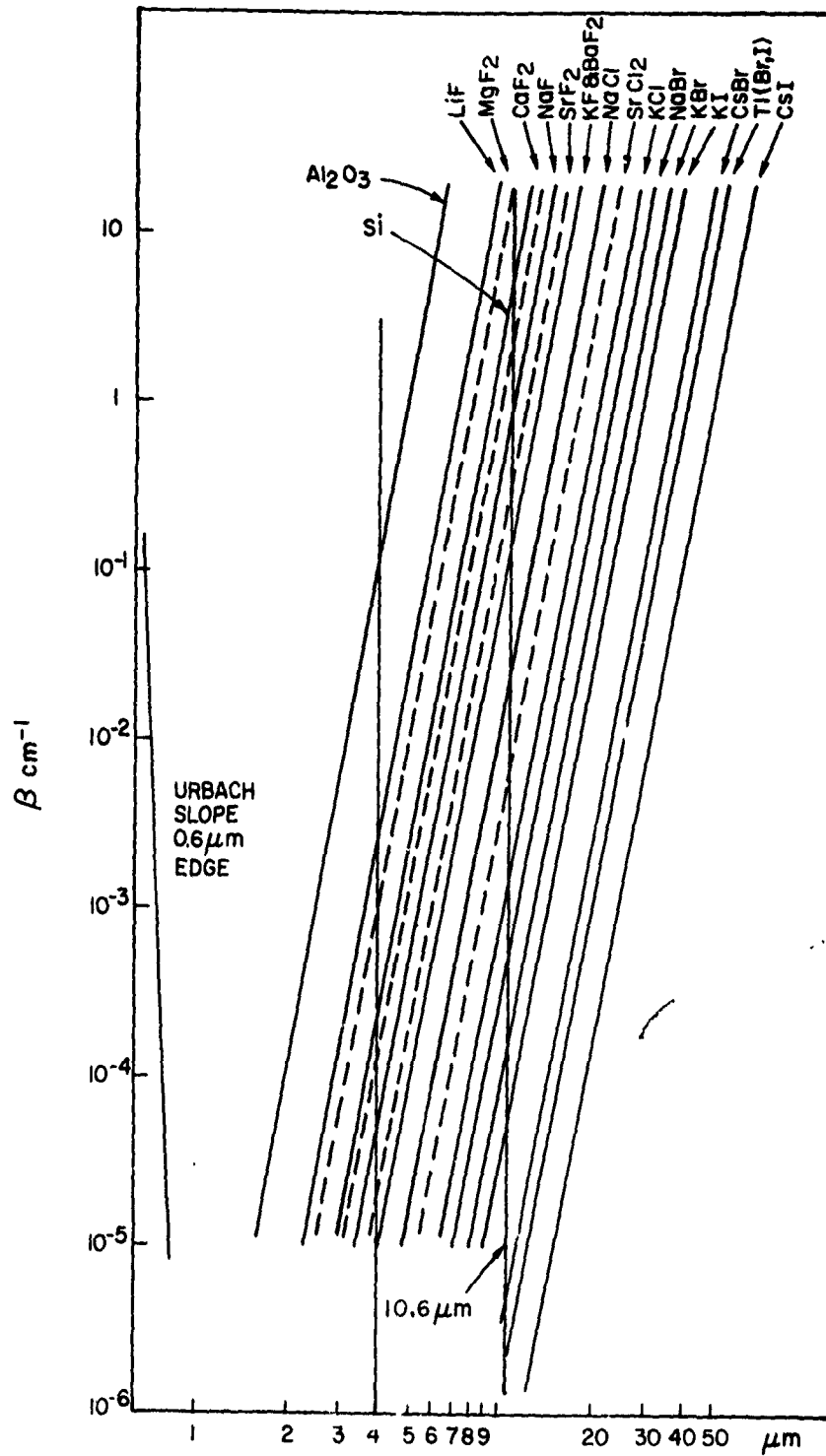


Figure 4. Approximate β vs wavelength for various materials

appears to have been made to lower the bulk absorptivity.⁽¹⁰⁾

Empirically, it is found that for the alkali halides the reststrahl edge is displaced toward longer wavelengths as the bond length from cation to anion increases. To the left of KCl in Figure 4, β tends to be too large to make the material of interest at $10.6\mu\text{m}$. To the right of KBr, poor thermal conductivity, low volume heat capacity, and larger values of δ_{nlT} tend to cancel any advantage due to a lower β . Furthermore, the difficulty in increasing yield strength or the greater hygroscopic character also adds complications for these compounds. However, the comparable Tl compounds are not hygroscopic and consequently do not require protection from moisture. Their tendency to develop a poorly defined (or mosaic) crystal structure is a source of considerable scatter at $0.68\mu\text{m}$ ⁽¹¹⁾ but is probably not serious at $10.6\mu\text{m}$. Physical properties and performance characteristics for various halides are listed in Table 2. CdTe, Si, and As_2Se_3 are added for purposes of comparison.

KBr appears to be one of the better choices for a low-loss window at $10.6\mu\text{m}$. As for other alkali halides this material requires protection from moisture. Young has shown that NaCl, tightly sealed with a vitreous coat of As_2S_3 , $\sim 2\mu\text{m}$ to $\lambda/2$ thick, can be remarkably stable.⁽⁷⁾ This is a convenient match for small windows as the thermal-expansion coefficient for As_2S_3 ($25 \times 10^{-6}/^\circ\text{C}$) is just a little less than that for NaCl ($31 \times 10^{-6}/^\circ\text{C}$). The difference is in the right direction to allow for the greater heating

TABLE 2
Properties and Limits for Distortion-Free Transmission

Material	β cm ⁻¹ 10.6 μ m	C (J/cm ³ / °C)	k (W/cm °C)	dn/dt (10 ⁻⁵ / °C)	$\delta n/T$ (10 ⁻⁵ / °C) 10.6 μ m	Reg. (2) ⁺ Limit I _t J/cm ²	Axial* Temp. Rise Limit ΔT_o °C	Req. (3) [§] Limit I _o 1/cm ²
KBr	5x10 ⁻⁵	1.2	0.048	-4.0	-1.09	8x10 ⁵	33	6000
Tl (Br, I)	est. 10 ⁻⁴	1	0.006	-23	-13.2	3x10 ⁴	3	170
KCl	5x10 ⁻⁴	1.35	0.065	-3.2	-1.11	9x10 ⁴	33	590
NaCl	5x10 ⁻³	1.84	0.065	-3.3	-0.92	1.4x10 ⁴	40	75
BaF ₂	0.15	2.0	0.12	-0.9	+0.06	4x10 ³	300	37
CdTe	1.5x10 ⁻³	1.22	0.07	+10.7	+12.0	2.4x10 ³	3	18
As ₂ Se ₃	10 ⁻²	0.35	0.0035	~ 8	~ 8	155	5	2
Figure 1 β , est. for 4 μ m								
$\delta n/T$ (10 ⁻⁵ / °C) for 4 μ m								
KBr	est. 10 ⁻⁵	1.2	0.048	-4.0	-0.35	4x10 ⁶	67	4x10 ⁴
NaCl	10 ⁻⁵	1.84	0.065	-3.3	-0.06	4x10 ⁷	230	2x10 ⁵
CaF ₂	2x10 ⁻⁴	2.71	0.092	-0.77	+0.35	5x10 ⁵	40	1800
SrF ₂	5x10 ⁻⁵	2.37	0.1	-1.2	-0.10	6x10 ⁶	135	3x10 ⁴
BaF ₂	2x10 ⁻⁵	1.96	0.12	-1.7	-0.18	8x10 ⁶	75	4x10 ⁴
Si	2x10 ⁻⁴	1.63	1.48	+13.0	+14.0	8x10 ³	1	49

+ $l = 1$ cm * $\Delta T_o = \beta I_o t/C$ ζ face-cooled, $h = 10^{-2}$ W/cm² - °C

All calculated values are based on $l = 1$

+* $I_o t$ and ΔT_o increase when l decreases

$I_o t$ varies as l^{-1} ; and I , for cw, varies as l^{-2} to l^{-3}

of the film due to higher absorption; vitreous films are required for these coatings as moisture will penetrate polycrystalline films by migrating along grain boundaries. (7) Selenide glasses are much less lossy than sulfide glasses at $10.6\mu\text{m}$. This suggests that As_2Se_3 would be a better coating for KBr windows at this wavelength. However, as the thermal expansion coefficient of As_2Se_3 is $\sim 21 \times 10^{-6} / ^\circ\text{C}$ as compared to $43 \times 10^{-6} / ^\circ\text{C}$ for KBr, expansion differences could be serious for large windows. This problem may be alleviated by using chalcogenide glasses with low elastic moduli. These include glasses with high Se or Br content. These vitreous coatings also serve as a protection against color center formation by ultraviolet radiation and may serve as the high index component of an anti-reflection coating (BaF_2 is commonly used as the lower index component).

The thallium halides, $\text{Tl}(\text{Br}, \text{I})$, have the advantage that they do not need protective coatings. They should also be capable of sufficient purification so that β values lower than 10^{-4} may be expected. They have, however, a large $\delta_{n\lambda T}$ value because the temperature coefficient of the index of refraction is high. Consequently, this material would need very good thermal control as the maximum permitted temperature differential ΔT across the window, according to Equations (III-7) and (III-11), is small $\Delta T_0 < e \lambda / (8\ell \left| \delta_{n\lambda T} \right|)$. This would appear to make these materials less desirable than some alkali halides, notably KBr, but their window potential should be more carefully evaluated. They could be most useful in geometries with very efficient and well-controlled cooling.

Although the β value for BaF_2 is large at $10.6\mu\text{m}$, the material may be of some interest at this wavelength due to a very small value of δ'_{nlT} by near cancellation of $(\partial n/\partial T)_c$ and thermal expansion. Such windows can tolerate a high-temperature gradient without excessive distortion. For thin BaF_2 windows, an axis to rim temperature difference of $\Delta T_0 > 100^\circ\text{C}$ is permissible. Low values of δ'_{nlT} seem to be characteristic of low- n materials such as the fluorides. Consequently, they may be used to great advantage in the $2\text{-}5\mu\text{m}$ region where their absorption is low.

Since the various terms that compose δ_{nlT} and δ'_{nlT} are functions of the optical index n , it is instructive to show an empirical trend. In Figure 5, δ_{nlT} values for $10.6\mu\text{m}$ and δ'_{nlT} values for $4\mu\text{m}$ are plotted versus n for the MF_2 fluorides. The comparable values for alkali halides are represented in Figure 6. It is of particular interest that, for the MF_2 compounds, both δ_{nlT} and δ'_{nlT} approach a zero value near $n \approx 1.43$. It should be kept in mind that the cancellation cannot be exact over a wide range of temperature and that anisotropic stress effects will also prevent a true zero. Nevertheless, BaF_2 and SrF_2 should have a good optical figure of merit for a wide range of wavelengths. They should be very desirable candidates in the $2\text{-}6\mu\text{m}$ region. The absorption is, however, excessive at $10.6\mu\text{m}$ under ordinary conditions ($\beta \sim 0.15 \text{ cm}^{-1}$ for BaF_2).⁽³⁾ This absorption in the tail of the infrared-phonon bands may be reduced and the yield stress increased⁽¹²⁾ by refrigeration, and the use of BaF_2 at $10.6\mu\text{m}$ in the form of very thin, segmented, refrigerated windows

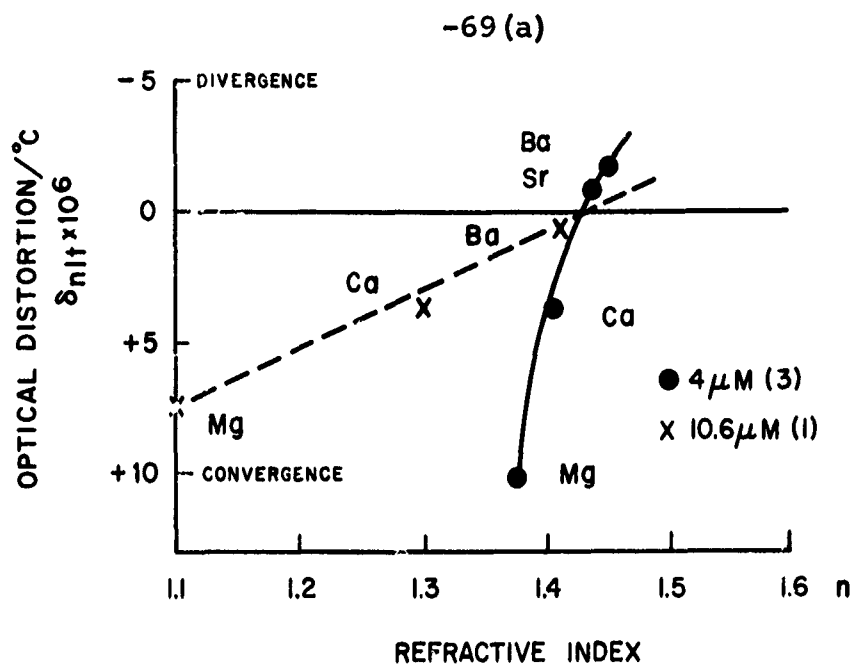


Figure 5. $A_{2,3}$ values for alkaline earth fluorides

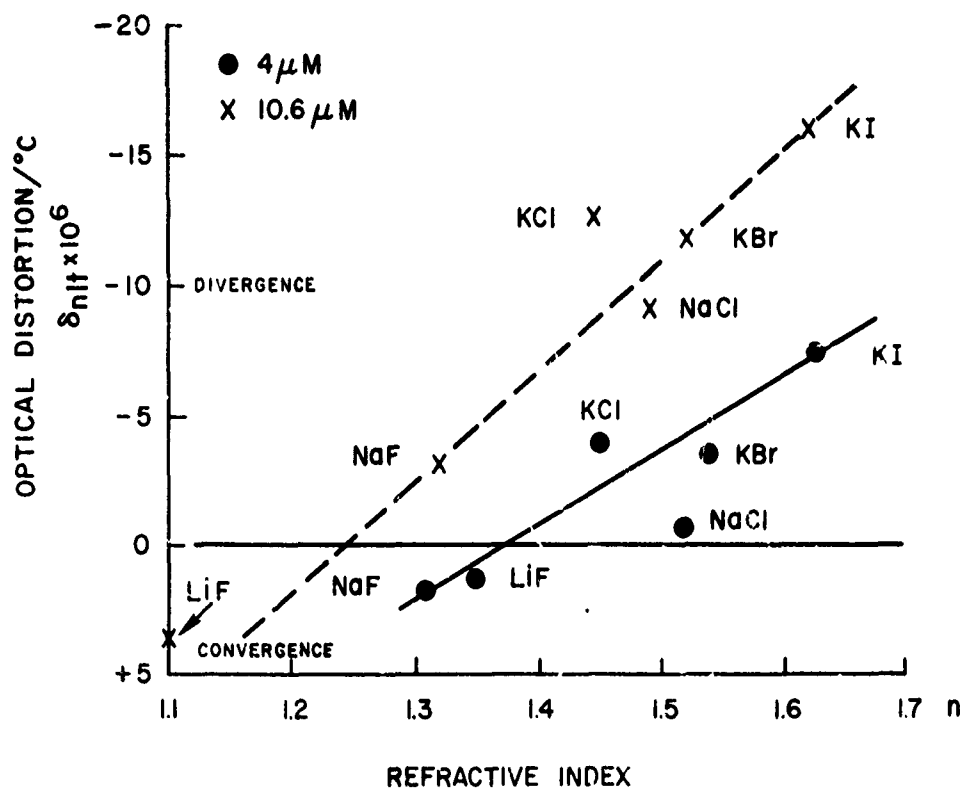


Figure 6. $A_{2,3}$ values for alkali metal halides

cannot be entirely excluded.

Anti-reflection coatings for BaF_2 should have an index of $n \approx 1.2$ at $10.6\mu\text{m}$. Such low values are difficult to obtain without taking advantage of dispersion and suffering the accompanying absorption effects. NaF may be used for this purpose.

C. Mechanical Properties of Ionic-Window Materials

The advantage of the excellent properties of some selected ionic crystals is unfortunately offset by less desirable mechanical properties of these crystals in their pure form. There are, however, ways to improve their mechanical strength. One method consists of using a mixture of cations or anions in single crystals. Another method which will be discussed in detail in Chapter IX consists of press forging single crystals so that some recrystallization takes place. It will be important to assess whether the desirable optical properties can be maintained when these methods are used.

The yield stress σ_y or the elastic limit must be as large as possible in a direction normal to the window. For the halides with the NaCl -type structure, the slip direction is $\langle 110 \rangle$ and the slip plane is $\{110\}$. Hence, if one aligns the window so that the axis is $\langle 111 \rangle$, either the slip direction or the slip plane normal is perpendicular to the pressure direction across the window. Therefore, the resolved shear stress is zero and slip or rupture is suppressed. For compounds with CsCl and

CaF₂-type structures (e.g., Tl(Br,I) and BaF₂), the comparable pressure resistant axial alignment is <100>. In practical cases the yield stress may be increased by proper orientation by a factor $f_x \approx 3$. The ratio of thickness l to window diameter d is inversely proportional to the σ_y value in the weakest direction and to f_x . If the maximum pressure differential ΔP is expressed in pounds per square inch and the safety factor, f_{SF} , is introduced, a uniformly loaded circular window needs the following thickness to diameter ratio:

$$\frac{l}{d} = 0.56 \left(\frac{\Delta P f_{SF}}{\sigma_y f_x} \right)^{\frac{1}{2}}.$$

For hardened KBr, with $f_{SF} = 10$, $f_x = 3$, and $\Delta P = 7.5$ psi, one obtains $l/d = 0.04$.

There will be some elastic distortion of the window due to ΔP . To a first approximation, the bending of a uniformly loaded window will not cause optical distortion, but a more precise analysis shows that effects exist proportional to $E^{2/5}$, where E is the Young's modulus in the normal direction.

There will be a self-imposed pressure differential due to the weight of the material alone. Comparison of the optical distortion induced by elastic deformations with those caused by thermal-expansion coefficient α at the maximum permissible temperature differential ΔT , shows that the ratio $\Delta P/E\alpha\Delta T$ is small compared to unity, except for extremely thick Tl halide windows.

The yield stress, (σ_Y), for the pure alkali halides may be as low as 100 psi; however, by mixing anions or incorporating divalent cations, $\sigma_{Y<100>}$ can be raised to > 5000 psi. The relation between Knoop's hardness H_K Young's modulus $E_{<111>}$ and $E_{<100>}$ and $\sigma_{Y<100>}$ for various materials is discussed in connection with Figures 7-9.

Figure 7 depicts relations between $E_{<111>}$ and $E_{<100>}$ and $H_{K<100>}$ for halides of monovalent cations. Comparable values for MF_2 compounds are given in Table 2. (3)

The values for Young's modulus were calculated from sound velocity measurements. (13) The values of H_K for the pure halides are from References 6 and 14.

The points plotted in Figure 7 are for $E_{<111>}$ while the arrows originating from these points extend to the values for $E_{<100>}$. In general, $H_{K<100>}$ for the simple K, Na, and Tl halides of Cl, Br, and I equals

$$H_{K<100>} \approx E_{<111>} \quad (VI-1)$$

when E is in units of 10^{11} dyne/cm². Deviations for CsBr, Tl (Br, I) and Tl (Br, Cl) are attributed to the presence of a mosaic structure and/or anion mixing.

Although Young's modulus is little affected by cation impurities, anion mixing, or mosaic structure, H_K and σ_Y may be increased by factors of two to three and two orders of magnitude respectively. Further, for the NaCl structure

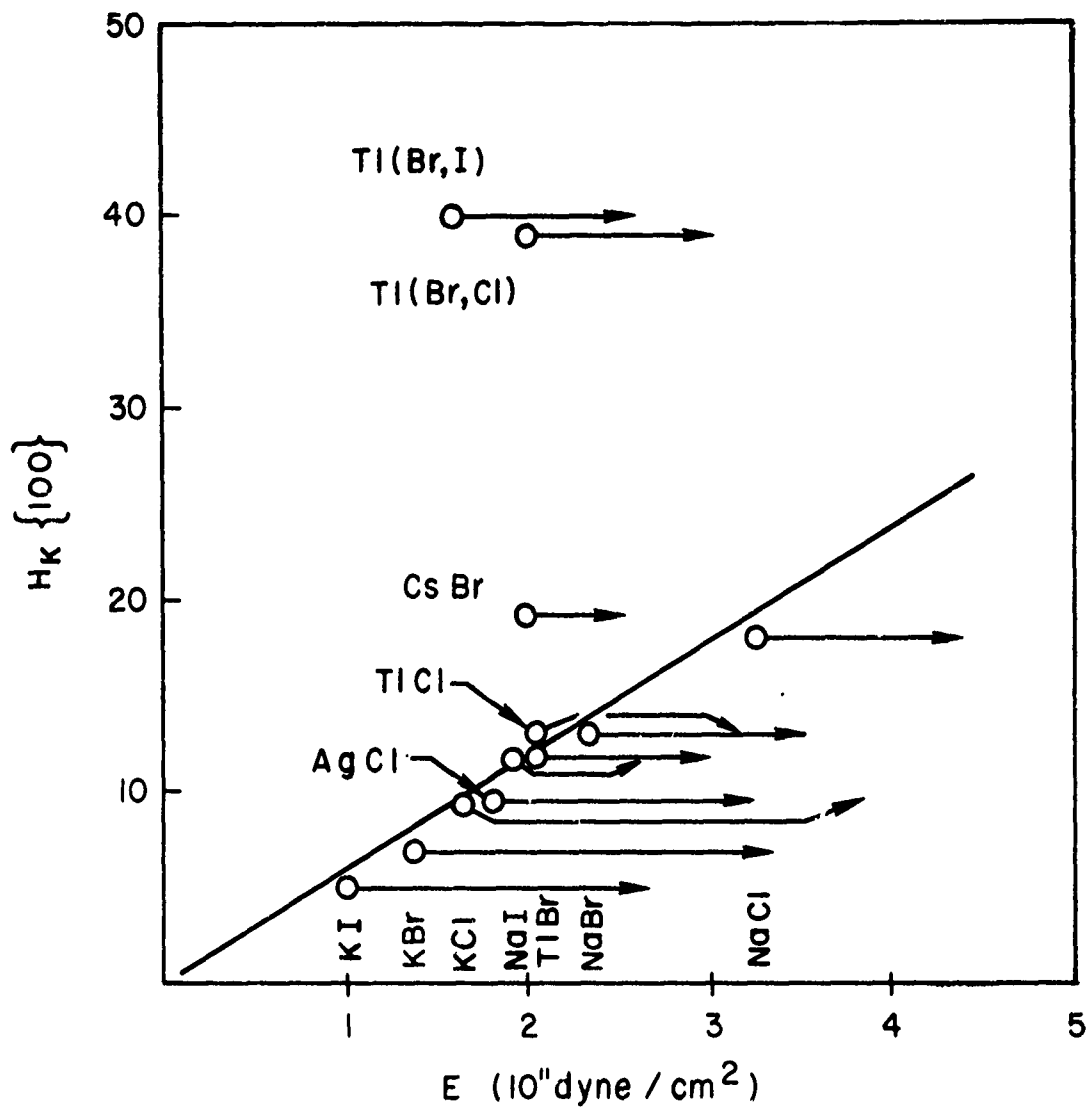


Figure 7. Knoop's hardness vs Young's modulus.

Deviations from linearity for the $\langle 111 \rangle$ data are attributed to mosaic structure. ⁽¹⁷⁾

TABLE 3

	$E_{\langle 111 \rangle}$	$E_{\langle 100 \rangle}$	$H_K \langle 100 \rangle$	Flexural Elastic Limit
	$(10^{11} \text{ dynes/cm}^2)$			
CaF_2	9.05	14.2	120	4500 psi
SrF_2	8.16	10.0	130	6000
PbF_2	6.97	5.6	200	1300
BaF_2	6.57	6.5	65	3000

$$\sigma_{Y<111>} \geq 2 \sigma_{Y<100>} ,$$

and for the CaF_2 structure

$$\sigma_{Y<100>} > \sigma_{Y<111>} .$$

The yield strengths discussed in the preceding paragraph refer to directions of easy yield as determined by preferred directions of cleavage or by a flexural method of testing. For properly oriented windows the applicable σ_Y value will be increased by the factor f_x , which may be as large as 3 to 5.

The relation between $H_{K<100>}$ and $\sigma_{Y<100>}$ for several series of alkali halides that have been doped with divalent cations (M^{2+}) are depicted in Figure 8. The composition of the melt from which the crystal was grown or the formula fraction of M^{2+} present is indicated. Values for samples annealed near 700°C for one-half hour in air are indicated by a bar above the M^{2+} symbol (e.g., $\overline{\text{Sr}}$). The data fall along parallel lines, one for each alkali-halide host. The slope is

$$\Delta\sigma_Y / \Delta H_K = 300, \quad (\text{VI-2})$$

when σ_Y is in units of psi, and the extrapolated intercept on the H_K axis is near the value for the pure halide. Therefore, one may write for the alkali halides

$$H_K = H_O + H_X , \quad (\text{VI-3})$$

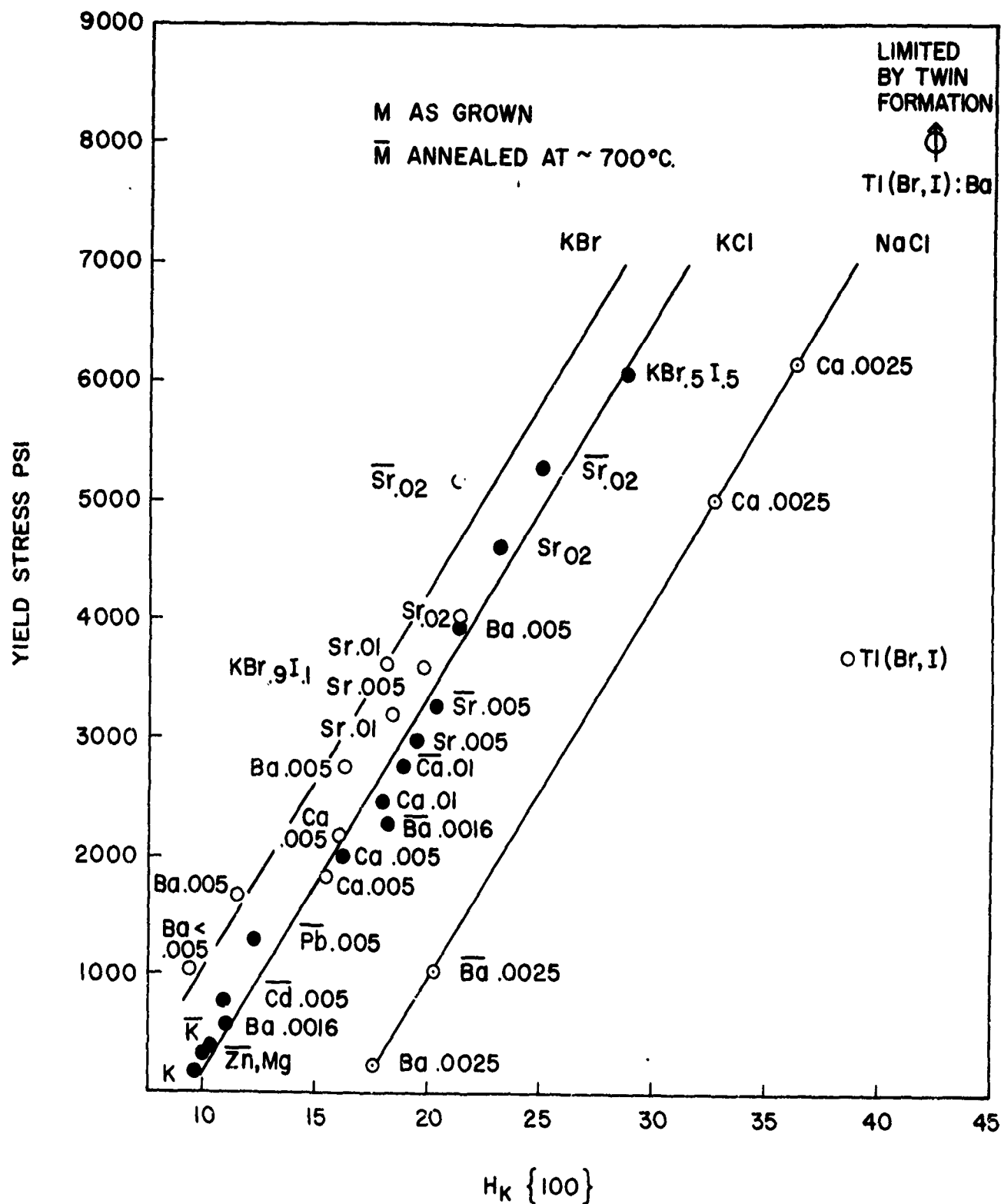


Figure 8. Yield strength vs Knoop's hardness for various halides. (17)

where H_0 is the Knoop's hardness of the pure ordered material and H_x is the additional hardening due to anion mixing, doping, or mosaic structure. Combining Equations (VI-1 through VI-3) one may estimate H_K , E , or σ_Y from

$$H_{K<100>} = 6 E_{<111>} + \sigma_{Y<100>} / 300, \quad (VI-4)$$

when employing the designated units.

It is apparent from Figure 8 that anion mixing and M^{2+} doping are effective in hardening KCl and KBr . However, the addition of Sr to a melt of KI and of Ca to a melt of NaI both failed to produce hardening.

The nominal M^{2+} contents are somewhat misleading as the distribution coefficient for M^{2+} between crystal and melt varies with the cation. For KCl and KBr they are ~ 0.03 , 0.10 and 0.15 for Ca , Sr , and Ba respectively. Additions of Li , Mg , Cd , Pb , and Zn to the melt were not as effective in producing hardening as those of Ca , Sr , and Ba . Since the distribution coefficient for Ca is low and only about 0.1 mole percent of Ba is held in solution in the crystal, Sr appears to be the most suitable additive for potassium halides. In general, M^{2+} ions of about the same size as the host cation are most useful. Also, the optical quality and hardness of the doped crystals are both improved by annealing and furnace cooling in a uniform temperature gradient to eliminate the presence of precipitates.

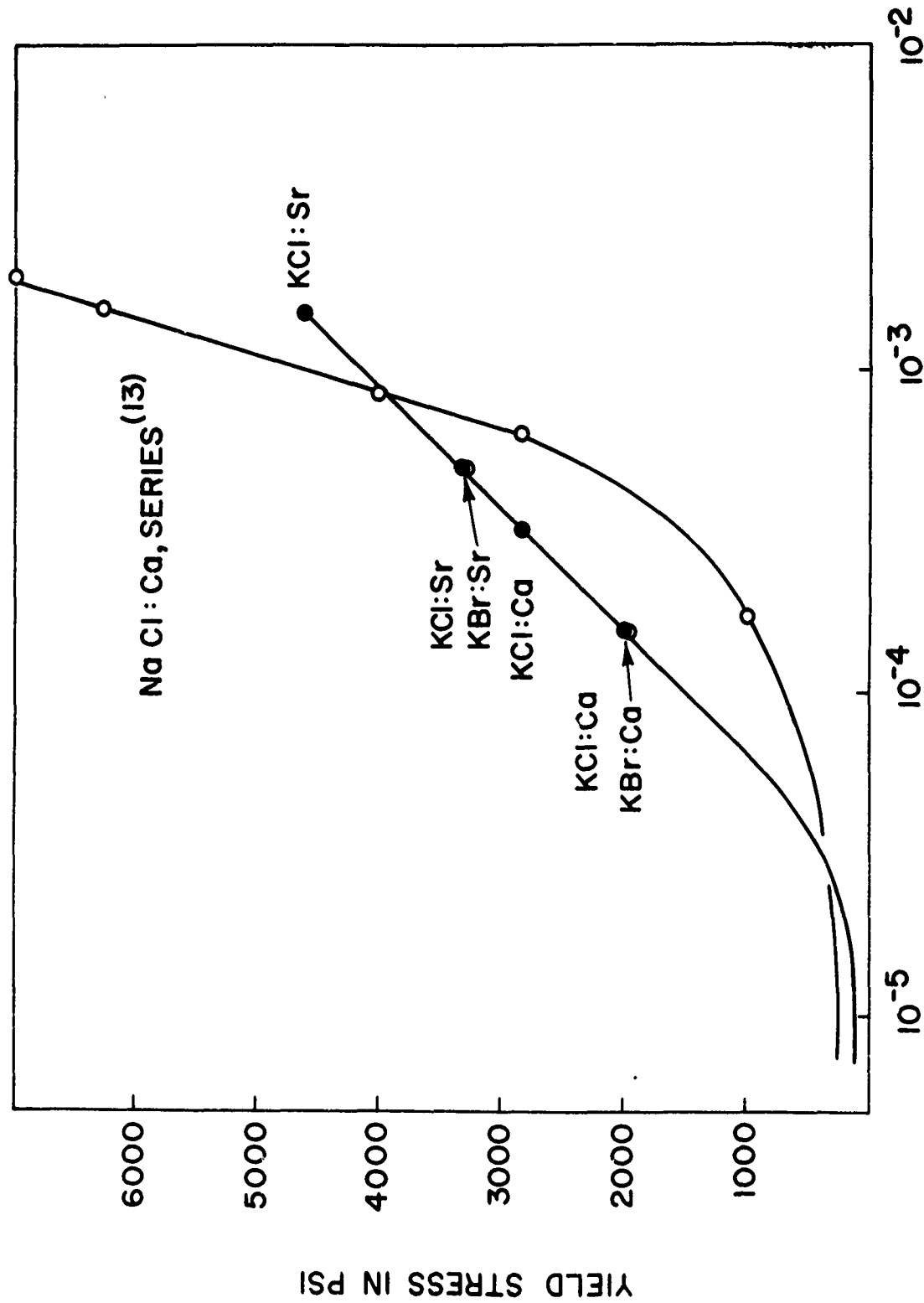
The ability of small amounts of M^{2+} to harden NaCl is discussed in the light of previous work by Harrison et al.⁽¹⁵⁾ The view that M^{2+} in a M^+ site is paired with cation vacancy to produce dipoles that strengthen the material through interaction with dislocations is supported by bulk-density studies on Ba doped NaCl.⁽¹⁶⁾

In Figure 9, $\sigma_{Y<100>}$ is plotted versus the analyzed formula fraction of M^{2+} in NaCl or KCl and KBr.^(15,17) It is apparent that small amounts of M^{2+} have a greater strengthening effect on the intrinsically weaker potassium compounds than on NaCl. This is of interest as the presence of excessive M^{2+} in the melt deters sound crystal growth.

Increased values of σ_Y were also obtained by adding Ba to Tl (Br,I). The addition of 0.57 percent to the melt had little effect on hardness, raising it from $H_K = 40$ to 43, but $\sigma_{Y<100>}$ increased from 3900 to ~ 8000 psi. Static tests at 2000 psi showed that even undoped Tl (Br,I) does not cold-flow below the elastic limit.

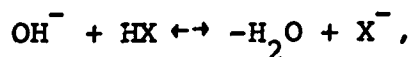
D. Preparation of Halides

Halides are commercially available in a wide variety of purities. Highly pure powders⁽¹⁸⁾ still must be processed to eliminate oxygen. Some cation impurities can be eliminated by zone refining.⁽¹⁹⁾ Others can be removed by chemical treatment and slow growth from solution.⁽²⁰⁾ Since OH^- can substitute for halogen ion (X^-), the interaction



MOLE FRACTION M^{2+} IN CRYSTAL

Figure 9. Yield strength vs divalent ion content for analyzed compositions. (17)



should be forced to the right. Therefore, growth or polishing in the presence of HX is favored.

Drawbacks of melt growth are that the crystals have defect counts that are several orders of magnitude greater than solution-grown crystals. Further, the likelihood of trapping impurities is greater because the rates of growth are greater. The cations with high-electron affinities are most likely to hold on to oxygen, tending to keep this source of infrared loss in the system. Nonetheless, melt-growth methods offer the most practical means of obtaining really large crystals suitable for infrared windows. Therefore, one should use zone refining⁽¹⁹⁾ or solution methods⁽²⁰⁾ to remove cation impurities, if necessary, and pass dry HX or X₂ through the molten material for several hours to eliminate oxygen as a step in the melt-growth process.⁽²¹⁾ Polishing processed parts using HX solutions and annealing in X₂ atmospheres should suffice to eliminate surface oxygen.^(21,22)

There are three physically different categories of halides to consider:

1. Ultrapure materials tend to have low-defect counts, low-impurity contents, and are less subject to attack by moisture. The main deficiency of the pure MX halides is low-yield strength. However, σ_y may be adequate in pure MX₂ compounds.

2. Halides containing small amounts of M^{2+} can be expected to have greater defect counts, are more susceptible to moisture, and are difficult to make oxygen free. However, σ_y and other properties can be enhanced.
3. Halides that are hardened by mixing anions are often strained and susceptible to mosaic distortions. However, σ_y can be large and oxygen removal is less of a problem than for M^{2+} doped melts.

Processing is usually simpler for categories 1 and 3. These materials are commonly grown by the Bridgeman-Stockbarger technique in rather large sizes. Where hardened materials are required and materials with mixed anions are not suitable, consideration should be given to category 2. In general, pulling from the melt is favored for this category as excess MX_2 must be freely rejected during crystal growth. Pulling may also be advantageous for categories 1 and 3 if self-nucleation on the crucible walls is a problem. In conclusion, it appears that the problems of purification and crystal growth are less formidable for the halides than for the semiconductor or glassy materials.

E. Conclusions and Recommendations

The most promising material for a window at $10.6\mu\text{m}$ appears to be a single crystal, KBr, strengthened with Sr^{2+} additions, oriented in a $\langle 111 \rangle$ direction normal to the window face and coated with a completed tight $N^{1/2}$ film of glassy As_2Se_3 . Possible alternatives are the systems $\text{KCl}:\text{Sr}$ and $\text{NaCl}:\text{Ca}$, similarly oriented and coated. A high-priority item to be verified is that the absorptivity of these doped halides remains acceptably low.

The $\text{Tl}(\text{Br}, \text{I})$ compounds are not hygroscopic and have not yet been obtained with the same low-absorption-coefficient β , although there is no reason to believe that this could not be achieved. They have, however, a large-temperature coefficient of the refractive index $\partial n / \partial T$. This restricts their use to configurations with very good and well-controlled cooling.

BaF_2 and SrF_2 have low-absorption coefficients and very small δ_{nlT} or $\partial n / \partial T$ values in the $2\text{-}6\mu\text{m}$ region. So does NaCl , but it is more hygroscopic and mechanically less strong than the fluorides. Although SrF_2 may have a somewhat higher loss than BaF_2 at $4\mu\text{m}$, it appears easier to grow in large sections.

The following program is therefore recommended:

Initial Stage

- (1) An evaluation of $\text{KBr}:\text{Sr}:(\text{As}, \text{Se}, \text{S}, \text{Br})$ will establish the adaptability of the (somewhat hygroscopic) alkali halides in general.

- (a) purify KBr and SrBr_2 to remove OH^- , F^- , Cl^- , CN^- , etc.,
 - (b) growth of single crystals of KBr:Sr and measure absorption coefficient,
 - (c) cut and polish $\langle 111 \rangle$ axis windows,
 - (d) develop a pliable chalcogenide glass (As, S, Br can be used temporarily),
 - (e) develop anti-reflective (AR) coatings.
- (2) The Tl (Br, I) compounds are not hygroscopic and when pure should have very low β values. Evaluate Tl (Br, I):Ba.
- (a) purify TlBr and TlI,
 - (b) grow single crystals of Tl (Br, I) and measure absorptivity,
 - (c) cut and polish $\langle 100 \rangle$ axis windows,
 - (d) AR coating.
- (3) NaCl, BaF_2 , and SrF_2 have very small $\delta_{n\lambda T}$ values at $4\mu\text{m}$. The last two are not hygroscopic. Although SrF_2 may be a little more lossy than BaF_2 at $4\mu\text{m}$, it appears to be easier to grow in large sections. Therefore, initial studies for a window that is little affected by the ambient temperature -
- (a) purify SrF_2 ,
 - (b) growth of crystals,
 - (c) cut and polish,
 - (d) AR coating.

The recommended program elements and estimated costs are as follows:

- (1) Purify KBr and SrBr_2 and grow single crystals of KBr:Sr, \$150,000.
- (2) Develop pliable chalcogenide coating, \$100,000.
- (3) String saw and polish $\langle 111 \rangle$ axis windows and coat in a protective environment, \$100,000.
- (4) Purify TlBr, TlI, and BaBr_2 , \$100,000.
- (5) Grow single crystals of Tl (Br,I):Ba, \$100,000.
- (6) Cut and polish $\langle 100 \rangle$ axis Tl (Br,I):Ba windows, \$50,000.
- (7) Purify SrF_2 and grow single crystals, \$100,000.
- (8) Cut and polish $\langle 100 \rangle$ axis SrF_2 windows, \$50,000.
- (9) Develop AR coatings for each window, \$100,000.
- (10) Testing, \$100,000.

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VII. SINGLE CRYSTAL II-VI, III-V, and IV
INFRARED-WINDOW MATERIALS

A. Introduction

In order to select candidate materials for high-power-infrared windows, the guidelines and selection criteria of Sparks⁽¹⁾ will be used. It should be noted that these guidelines are based on intrinsic absorption, and it may be difficult to obtain crystals of the quality required to reach the intrinsic limit.

Very briefly, these guidelines are as follows: In order to keep the lattice absorption as small as possible, the masses of all ions in the crystal should be large in order to keep the fundamental lattice frequency ω_f as far from the optical frequency ω as possible. For crystals such as ZnSe and GaAs containing two atoms in the basis, $\omega \propto \mu^{-1/2}$, where μ is the reduced mass. It is assumed that $\omega_f < \omega$; thus, increasing the values of μ increases the value of $|\omega_f - \omega|$, as stated.

For materials in the same row in the periodic table such as KBr, ZnSe, GaAs, and Ge, those near the center of the table, with their tighter covalent bonding, have higher resonant frequencies. Thus, the value of $|\omega_f - \omega|$ tends to increase, which implies a tendency for the lattice absorption to decrease in series such as Ge, GaAs, ZnSe, KBr. (Ge may be an exception to this tendency, since it is not a polar crystal.)

In order to keep the free-carrier absorption low at room temperature, the value of the energy gap E_g should be large. Very roughly, E_g should be greater than 0.7eV. For example, Ge, with $E_g = 0.7\text{eV}$, appears to be a borderline material. Since the value of E_g tends to increase as the masses of the elements in the crystal decrease and as the amount of ionic bonding increases, ionic crystals with light masses tend to have less free-carrier absorption. Free-carrier absorption usually is easy to identify experimentally since $\beta \sim \lambda^\eta$, where λ is the wavelength and $\eta \approx 2$.

The mechanical and chemical properties of materials (strength, hardness, hygroscopicity, etc.) tend to be better for crystals containing light masses and for those with small amounts of ionic bonding.

In summary, the masses of the elements in the crystal must not be too light or the lattice absorption will be too large, and they must not be too heavy or the free-carrier absorption will be too large and they will have poor physical and thermal properties. Highly ionic crystals tend to have low-lattice and free-carrier absorption, but their physical properties tend to be poorer than those of the crystals with a higher degree of covalent bonding.

By using these guidelines, which are summarized in Table 4, the most promising semiconductor materials for near-term high-power-infrared windows are

CdTe, ZnSe, GaAs, and Ge.

TABLE 4

Summary of Trends of Material Properties

Materials Containing Light Masses

High-lattice absorption

Low-free-carrier absorption

Good mechanical, chemical, and thermal properties

Ionically Bonded Materials

Low-lattice absorption

Low-free-carrier absorption

Poor mechanical, chemical, and thermal properties

(A summary of advantages and disadvantages of these materials, to be discussed below, was given in Table 4.)

Other candidates, considered to be less likely for the near term than the above, are:

GaSb, ZnTe, CdSe, (Ca,Sr,Ba) (Se,Te).

The symbol (Ca,Sr,Ba) (Se,Te) means the set of materials CaSe, CaTe, SrSe, SrTe, BaSe, and BaTe.

B. Absorption at 10.6 μ m of Ge, GaAs, ZnSe, and CdTe

Materials containing heavy elements generally will not be acceptable for use at room temperature because the size of the electronic band gap E_g decreases with increasing mass and a small value of E_g gives rise to free-carrier absorption, as discussed in Chapter IV. On the other hand, the masses should be heavy in order to keep the lattice absorption small. The four heaviest IIB-VI materials with $E_g > 0.7\text{eV}$ are (Zn,Cd) (Se,Te). Of these four materials, ZnSe and CdTe are chosen as the most promising for the near term since their properties are better known.

The lowest value of the absorption coefficient measured at 10.6 μ m to date for ZnSe (chemical vapor deposited) is⁽²⁾

$$B = 0.005 \text{ cm}^{-1}.$$

With this value of β , a 1-cm-thick sample of ZnSe can transmit 10^3 J/cm^2 in the pulse mode of operation.

The lowest value of β reported to date for CdTe is⁽³⁾

$$\beta = 1.5 \times 10^{-3} \text{ cm}^{-1},$$

which is believed to be larger than the intrinsic value. With this value of β , a 1-cm-thick sample of CdTe can transmit 860 J/cm^2 in the pulse mode of operation.

The two heaviest III-V materials with $E_g \gtrsim 0.7 \text{ eV}$ are GaAs and GaSb. The former is chosen as the most promising of the two for the near-term since more information is available on GaAs. With the smallest reported value of β for GaAs⁽⁴⁾

$$\beta = 5 \times 10^{-3} \text{ cm}^{-1},$$

a 1-cm-thick window of this material can transmit 190 J/cm^2 in the pulse mode of operation.

Ge previously was considered unsatisfactory because of thermal runaway^(2,4,5) ($E_g = 0.7 \text{ eV}$), which occurred at a temperature somewhat above room temperature. However, the allowed temperature rise in the window is severely limited by the thermally induced optical distortion; the allowable center-to-rim temperature defined in Equation (III-7) is $\Delta T_o = 0.5^\circ \text{ C}$.⁽⁶⁾ Furthermore, the thermal runaway problem could be avoided by operating the window below room temperature. Thus, it appears that thermal runaway will not prevent the use of Ge as a high-power-window material in some applications.

The minimum value of β for Ge reported to date is⁽⁵⁾

$$\beta_{\rho=\infty} + \beta_{fc} = 2 \times 10^{-2} + 5 \times 10^{-3} \text{ cm}^{-1} = 2.5 \times 10^{-2} \text{ cm}^{-1},$$

where β_{fc} and $\beta_{\rho=\infty}$ are the contribution from carriers and other sources, respectively. This Raytheon result was for a 20 ohm-cm n-type sample, which showed the smallest value of β_{fc} ($= 0.005 \text{ cm}^{-1}$) as a function of resistivity. Intrinsic samples showed a larger value of $\beta_{fc} = 0.01 \text{ cm}^{-1}$. The Raytheon results suggest that it may not be possible to reduce the room temperature value of β_{fc} below $5 \times 10^{-3} \text{ cm}^{-1}$, but that a substantial reduction in the value of β_{fc} can be obtained with a modest reduction in temperature, say to 270°K . The fact that the values of $\beta_{\rho=\infty}$ for the Raytheon samples varied considerably with the impurity level suggests that the intrinsic value of β may be smaller than the lowest Raytheon value of $\beta_{\rho=\infty} \approx 2 \times 10^{-2} \text{ cm}^{-1}$.

Ultrapure inch-size ingots of germanium with intrinsic room-temperature properties recently have become available on a limited basis.⁽⁷⁾ If these samples have small values of $\beta_{\rho=\infty}$, germanium will be a good candidate material, as discussed further in Section J. If a value of $\beta = 5 \times 10^{-3} \text{ cm}^{-1}$ is obtained, a 1-cm-thick sample of germanium can transmit 150 J/cm^2 in the pulse mode of operation.

C. Discussion of Other Semiconductor Materials

The material GaSb ($E_g = 0.7 \text{ eV}$) was considered unsatisfactory because of the potential thermal-runaway problem.⁽⁵⁾ Since large temperature rises are not allowed, as discussed above for Ge, GaSb could be considered further in a long-term program.

The properties of the IIA-VI compounds (Ca, Sr, Ba) (Se, Te) are not as well known as those of the IIB-VI compounds above, although the properties of the two types of materials probably are not too different.⁽⁸⁾ The IIA-VI materials have the NaCl structure and have larger electronegativity differences than the corresponding IIB-IV materials, which indicates that they have a higher degree of ionic bonding than do the IIB-VI materials. BaSe is known to be hygroscopic.⁽⁹⁾ The value of E_g for BaTe probably will not be too small since BaTe has the NaCl structure.

Finally, consider the reasons for eliminating many well-known semiconductor materials. The small values of E_g for Sn, Pb, (In, Tl) (As, Sb, Bi), and HgTe are expected to make these materials unacceptable for room temperature use. Some of these materials could be useful at lower temperatures. The light effective masses of (B, Al) (N, P, As, Sb, Bi), (Ga, In, Tl) (N, P), (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg) (O, S), and (Be, Mg) (Se, Te) make these materials unlikely candidates for use at $10.6\mu\text{m}$.

D. Scattering

Scattering in low- β single crystals should be checked experimentally.

E. Mechanical Strength

Values of the tensile strength of single crystals of Ge, GaAs, ZnSe, and CdTe are listed in Table 5. The

TABLE 5

Input Values in the Calculation of Quantities

Listed in Tables 6 and 7. Values of Other

Parameters Used are: $h=10^{-2}$ W/cm² K, $P=7.3$ psi,

$f_{SF}=10$, and $\nu=0.3$ for All Materials

	β (cm ⁻¹)	$\frac{dn}{dT}$ 10^{-4} °K ⁻¹ $\lambda=4\mu\text{m}$	n $\lambda=10.6\mu\text{m}$	C (J/cm ³ °K)	k (W/cm ² K)	σ_y (10 ⁴ psi)	E (10 ⁷ psi)
	$\lambda=10.6\mu\text{m}$	$\lambda=4\mu\text{m}$					
Ge	2.5×10^{-2}	3×10^{-3}	4	1.65	0.59	1.35	1.49
GaAs	5×10^{-3}	9×10^{-3}	3.3	1.42	0.37	2	1.23
ZnSe	5×10^{-3}	unknown	2.43	2.62	0.13	0.61*	1.03*
CdTe	1.5×10^{-3}	2×10^{-3}	2.67	1.23	0.09	0.3	0.53
Si	-	2×10^{-3}	3.43	1.58	1.2	0.9	1.9
MgO	-	1.3×10^{-3}	1.66	3.13	0.25	2**	3.61
Al ₂ O ₃	-	2×10^{-2}	1.78	3	0.25	6.5	5

* Irtran-4 Polycrystalline Values

** In Bending

Committee is not aware of any studies to improve the strength of single crystal semiconductor materials. Values of the window thickness-to-diameter ratio (l/D) required in order for a clamped window to withstand a given pressure differential without fracturing are listed in Table 6.

F. Preparation and Production of Large Samples

One of the greatest disadvantages of most II-VI, III-V, and IV materials is that they are not available as large single crystals. Hughes Research Laboratories has grown 1.8-inch diameter, 2-inch long single crystals of CdTe with reproducible values of $\beta = 3 \times 10^{-3} \text{ cm}^{-1}$ (which is a factor of two greater than the smallest value reported to date). Gould Laboratories has grown 1-inch diameter single crystals of ZnSe but the β values are not yet known. Bell and Howell Laboratories has grown 2-inch diameter GaAs crystals. Eight-inch diameter single crystals of Ge have been grown by Texas Instruments, and the ultrapure General Electric samples (see section B) have been grown in 1-inch sizes. Six-inch single crystals of Si and Al_2O_3 are available for use at 2-6 μm . The possibility of obtaining large polycrystalline samples of semiconductor materials is discussed in Chapter IX.

TABLE 6

Calculated Values of Figures of Merit, Temperature
Difference between Center and Rim of Window,
and Critical Thickness at $\lambda=10.6\mu\text{m}$

	EI_o Pulse Mode $(\frac{J}{2}) (\frac{1}{l})$ cm	I_o cw $(\frac{W}{2}) (\frac{1}{l})$ cm	ΔT_o (°K)	δ_{nlT} (10^{-4}K^{-1})	l/D (Dimension- less)
Ge	80	0.5	0.5	3	0.032
GaAs	500	4	0.7	2.0	0.026
ZnSe	5,000	20	2	0.6	0.047
CdTe	2,000	20	1.0	1.3	0.068

G. Surface Coatings

The Committee knows of no previous experimental investigations of anti-reflection or protective surface coatings for II-VI, III-V, or IV materials for high-power infrared use. A theoretical study of the heating of windows by absorption in a surface coating has been made. (10) Anti-reflection coatings are especially important for semiconductor materials since their large values of the index of refraction give rise to large reflection losses. Moisture protective coatings should not be required.

H. Figures of Merit

Values of the figures of merit for the semiconductor materials of interest are listed in Table 6 for $10.6\mu\text{m}$ operation and in Table 7 for $4\mu\text{m}$ operation, and a brief general discussion of figures of merit was given in Chapter III. The small values of I_0 in the cw case indicate that for high-power applications the semiconductor materials will be most useful in the pulse mode of operation.

I. Outlook at $2-6\mu\text{m}$

The problem of finding suitable materials for high-power-infrared windows in the $2-6\mu\text{m}$ range is considerably simpler than for the $10.6\mu\text{m}$ range, since lighter element materials with their generally superior mechanical and thermal properties can be used in the $2-6\mu\text{m}$ range and still have small values of β . In addition to the materials discussed for use at $10.6\mu\text{m}$, the II-VI, III-V, and IV

TABLE 7

Calculated Values of Figures of Merit, Temperature
Difference between Center and Rim of Window,
and Critical Thickness at $\lambda=4\mu\text{m}$

	EI_o Pulse Mode $(\frac{J}{2}) (\frac{1}{l})$ $\frac{\text{cm}}{\text{cm}}$	I_o cw $(\frac{W}{2}) (\frac{1}{l})$ $\frac{\text{cm}}{\text{cm}}$	ΔT_o (°K)	δ_{nlT} (10^{-4}K^{-1})	l/D (Dimensionless)
Ge	200	1.4	0.2	3.2	0.032
GaAs	130	1.0	0.3	1.6	0.026
CdTe	700	6	0.4	1.2	0.068
Si	800	5	0.4	1.4	0.039
MgO	1.2×10^4	40	1.9	0.26	0.026
Al_2O_3	1,300	4	3	0.16	0.014

materials commonly considered for use at 2-6 μ m are Si and MgO. Sapphire (Al_2O_3) also is considered as a good candidate. Figures of merit for these seven materials are listed in Table 7. There are many other materials such as other oxides, sulfides, phosphides, and compounds of Al and Mg that should be investigated systematically, as discussed in Section J.

It should be mentioned that the near- λ^2 dependence of the free-carrier absorption should make the free-carrier absorption in Ge much less of a problem at 2-6 μ m than at 10.6 μ m. However, it is conceivable that interband scattering in germanium and other semiconductors could limit their usefulness in the 2-6 μ m range. If this turns out to be the case, the common belief that a material that is good at 10.6 μ m will be even better for 2-6 μ m operation is not correct in general for semiconductor materials.

J. Optical-Absorption-Coefficient Study

It is believed that most, perhaps all, of the 10.6 μ m values of the optical-absorption coefficient, β , of the candidate materials discussed in the present report are larger than the intrinsic values. In order to evaluate the potential of candidate materials, it is important to know or at least to have estimates of the intrinsic value of β . This is especially important since expensive imperfection-identification and sample-purification programs should be undertaken only if there is a good chance of reducing the value of β .

The value of the multiphonon contribution to β as a function of ω in semiconductor materials shows systematic trends in going from the two-phonon to the three-phonon region and to higher-phonon regions. At sufficiently large values of ω , it is expected that the imperfection contribution to β will appear as a deviation from this trend. The temperature dependence of β might assist in identifying the onset of the imperfection process and should be studied further.

Assuming that the relatively smooth exponential or power-law behavior of β as a function of ω for the ionically bonded alkali halides and MF_2 crystals discussed in Chapter IV are characteristic of the intrinsic absorption, the onset of the imperfection process should be even easier to identify in these crystals than in the semiconductors. In order to identify and reduce the imperfection contribution to β , both ultrapurification and intentional-doping programs of carefully selected materials should be useful.

K. Recommendations

CdTe, ZnSe, GaAs, and Ge Programs. The value of β of the ultrahigh purity General Electric samples of germanium should be measured. This could be done at no cost in an existing program. Scale-up studies should not be started until an acceptable value of β is demonstrated.

The present effort to lower the absorption of small-size ZnSe and CdTe crystals, both in single-crystal

form and by chemical vapor deposition techniques, should be continued. A total effort of 4 man-years over the next 2 years is recommended at an estimated cost of \$300,000.

Gallium arsenide should be studied in the program discussed in Section J before further purification or scale-up programs are undertaken.

Anti-reflection coatings are especially important for these high-index materials and should be studied. (See Recommendation 5 in Chapter II.)

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VIII. CHALCOGENIDE GLASS
INFRARED-WINDOW MATERIALS

A. Homogeneous Chalcogenide Glasses

1. Introduction

In one sense homogeneous chalcogenide glasses based on the heavier members of the oxygen family may be considered homologues of oxide network glasses in which the lighter elements [B(III); Si(IV); O(II)] are replaced by the corresponding heavier elements [As(III) or Sb(III); Ge(IV); S(II), Se(II), or Te(II)]. The analogy is borne out in the structures of a number of the stoichiometric compositions, GeS_2 having a tetrahedrally coordinated three-dimensional-network structure similar to that of SiO_2 , and As_2S_3 and As_2Se_3 having two-dimensional-layer structures analogous to (but not identical to) that of B_2O_3 . Plumat⁽¹⁾ has noted that GeS_2 alkali sulfide and GeSe_2 alkali-selenide melts appear to form phase-separated glasses, in much the same fashion as SiO_2 alkali-oxide melts.

On the other hand, there exists also a reasonable analogy between chalcogenide glasses and organic polymers, the individual atoms of the chalcogenide glass fulfilling the role of monomeric units. For instance, elemental S or Se glasses are similar to organic chain polymers, As_2S_3 and As_2Se_3 to two-dimensionally cross-linked sheet polymers, and GeS_2 to a three-dimensionally cross-linked-network polymer. As is expected from this analogy, the glass transition temperatures of chalcogenide

glasses increase with the "degree of cross-linking" ^(2,3) as shown in the series polymeric S ($T_g = 27^\circ\text{C}$), As_2S_3 ($T_g = 185^\circ\text{C}$), and GeS_2 ($T_g = 490^\circ\text{C}$). Because of the small differences in electronegativity between the constituent elements, chalcogenide glasses do not follow the sort of stoichiometric rules that tend to keep the B:O or Si:O ratios fixed in oxide glasses. Rather the number of components in the chalcogenide glass must be taken to be the number of different elements, in line with the polymer analogy using the atoms as monomeric units. Thus arsenic and selenium combine to give glass-forming melts over the large composition range Se to $\text{As}_{61}\text{Se}_{39}$ ⁽⁴⁾ (subscripts refer to atomic percent), although glasses between Se and $\text{As}_{40}\text{Se}_{60}$ are suspected of being phase-separated. ⁽⁵⁾ Two good examples of studies of structural variations of chalcogenide glasses over composition ranges of this sort may be found in the papers of Tsuchihashi and Kawamoto on the As-S ⁽⁶⁾ and the Ge-S ⁽⁷⁾ systems.

Oxide-network glasses are most frequently ionic conductors, the electrical conductivity of even the pure "network formers" such as SiO_2 or B_2O_3 being due to impurity alkali ions or protons. Plumat ⁽¹⁾ has presented some evidence for ionic conduction in GeS_2 alkali-sulfide glasses, but other chalcogenide glasses are almost inevitably electronic semiconductors, including such glasses as those formed from $\text{Tl}_2\text{Se}-\text{As}_2\text{Se}_3$, which bear a formal resemblance to thallium-borate glasses.

In the following sections those properties of homogeneous chalcogenide glasses important for use as infrared windows, particularly at the CO_2 laser wavelength of $10.6\mu\text{m}$ are reviewed. (Hilton⁽⁸⁾ has published a recent review on this subject; the somewhat older review of Savage and Nielsen⁽⁹⁾ is also of considerable utility.) For reference in the sections to follow, we list in Table 8 important properties of three IR-transmitting homogeneous-chalcogenide glasses: As_2Se_3 , probably the most widely studied chalcogenide glass, and $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ and $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$, two high-softening-temperature glasses developed by Texas Instruments Corporation for possible commercial use.

2. Infrared Absorption

Barring for the moment impurity bands (water in oxide glasses, trace oxides in non-oxide glasses), the boundaries to the infrared window in network glasses are generally determined on the high-frequency side by the electronic charge transfer absorption edge and on the low-frequency side by overtones of the nearest neighbor vibrational band (the reststrahl band). The IR window spans roughly the wavelength range $0.2 - 3\mu\text{m}$ for oxide glasses, $0.6 - 11\mu\text{m}$ for sulfide glasses, $1 - 15\mu\text{m}$ for selenide glasses, and $2 - 20\mu\text{m}$ for telluride glasses. The shifts of both of the IR-window edges to longer wavelengths with increasing atomic mass are in accord with simple predictions based on the effects of increasing atomic mass

-99(a)-

TABLE 8

PHYSICAL PROPERTIES OF HOMOGENEOUS
CHALCOGENIDE IR-TRANSMITTING GLASSES

Property*	Glass		
	As ₂ Se ₃	Ge ₂₈ Sb ₁₂ Se ₆₀ (TI-1173)	Ge ₃₃ As ₁₂ Se ₅₅ (TI-20)
Transmission Range (μm)	1-15 ^a	1-16 ^a	1-15 ^a
Refractive Index, n @ 5 μm	2.79 ^b	2.62 ^a	2.49 ^a
Temperature coefficient of index of refraction, $\Delta n/\Delta T (^{\circ}\text{K}^{-1})$	-	80×10^{-6} a	-
Absorption coefficient, β (cm ⁻¹) @ 10.6 μm**	0.01 ^c	0.03 ^d	0.02 ^e
Density ρ (g/cm ³)	4.54-4.68 ^{f-i}	4.61 ^d	4.40 ^e
Linear coefficient of thermal expansion, $\alpha (^{\circ}\text{K}^{-1})$	21×10^{-6} j	15×10^{-6} a	13×10^{-6} e
Softening point ($^{\circ}\text{C}$)***	236 ^k	326 ^a	474 ^a
Glass Transition temperature, T _g ($^{\circ}\text{C}$)****	175 ^l	271 ^m	353 ^m
Specific heat, C _p (cal/g $^{\circ}\text{K}$)	0.075 ^{i, l}	0.065 ^m	0.071 ^m
Thermal conductivity, K (W/cm $^{\circ}\text{K}$)	$\left\{ \begin{array}{l} 7.7 \times 10^{-3} \text{ f} \\ 2.9 \times 10^{-3} \text{ o} \end{array} \right\}$	2.6×10^{-3} d	-
Hardness, Knoop Scale	114 ^a	150 ^a	171 ^a
Young's modulus (psi)	2.6×10^6 h	4.2×10^6 a	4.5×10^6 a
Shear modulus (psi)	1.0×10^6 h	-	-
Poisson's ratio	0.30 ^h	-	-
Rupture modulus (psi) (annealed)	-	-	2500 ^a
(thermally tempered)	-	-	7000-10,000 ^a
Resistivity (ohm cm)	10^{12} n	-	-

* Properties are those in the vicinity of 25°C.

** Lowest measured β known to author at time of writing.

*** At softening point viscosity is approximately 7.6 poise.

**** Measured by DTA at heating rate of 20°K/min.

Table 8 (continued) :

Sources of Data

- a) Reference 8
- b) Reference 9
- c) Reference 10
- d) Reference 11
- e) Reference 12
- f) Reference 13
- g) Reference 14
- h) Reference 15
- i) Reference 16
- j) Reference 17
- k) Reference 18
- l) Reference 19
- m) Reference 20
- n) Reference 21
- o) Reference 29

on ionization energies (decreasing ionization energy decreases charge transfer band frequency) and on nearest neighbor vibrational frequencies ($\nu_{\text{vib}} \propto \mu^{-1/2}$, where μ is the appropriate reduced mass). Hence chalcogenide glasses owe their excellent IR-transmission characteristics primarily to their high average atomic weights. The best of the IR-transmitting-chalcogenide glasses to date have been based on selenium, since, on the one hand, the selenide glasses transmit substantially further into the IR than do the sulfide glasses, while, on the other hand, selenide melts are considerably better glass-formers than the more metallic telluride melts.

Shown in Figure 10 are IR-transmission spectra of As_2Se_3 glass and a high-softening temperature Ge-As-Se glass taken from the paper of Savage and Nielsen.⁽⁹⁾ The two impure glasses each contain about 500 ppm of oxygen contaminant. As is evident from the figure, a small amount of oxygen impurity causes a drastic deterioration in the IR-transmission characteristics of selenide glasses at wavelengths longer than $8\mu\text{m}$. The principal absorption at the CO_2 laser wavelength of $10.6\mu\text{m}$ is seen to arise from the tail of an oxide impurity band centered in both glasses around $13\mu\text{m}$. (The smaller impurity bands at around 9.5 and $8\mu\text{m}$ for the two respective glasses are probably combination bands of the reststrahl band and the $13\mu\text{m}$ oxygen band.) Rough estimates of the absorption coefficients, β , at $10.6\mu\text{m}$ due to the oxide impurities for the two glasses of Figure 10 yield:

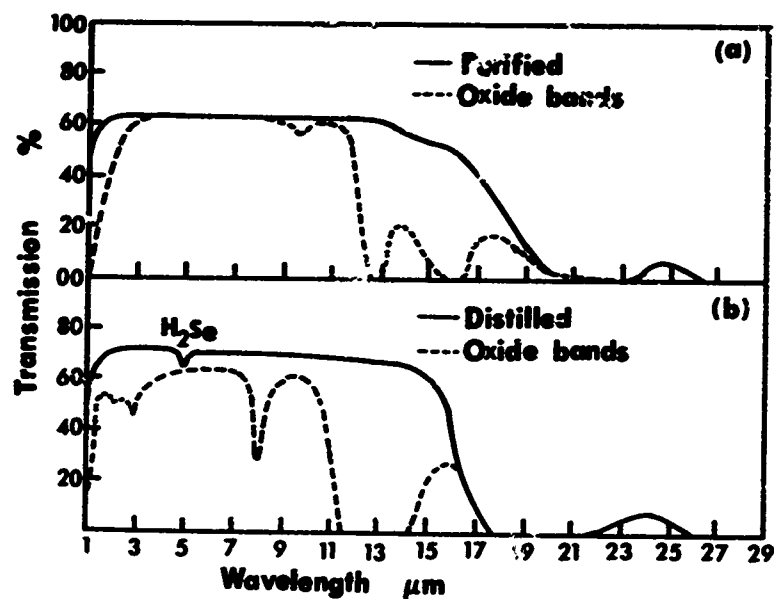


Figure 10. The infrared transmissions of purified selenide glasses. The dashed curves show the impurity bands.

- (a) $\text{As}_{40}\text{Se}_{60}$ specimen thickness 0.175 cm.
- (b) $\text{Ge}_{34}\text{As}_9\text{Se}_{58}$ specimen thickness 0.180 cm.

$$\text{As}_2\text{Se}_3 \quad \beta / \text{ppmO} \sim 5 \times 10^{-4} \text{ cm}^{-1} \text{ ppmO}^{-1},$$

$$\text{Ge}_{34}\text{As}_8\text{Se}_{58} \text{ glass} \quad \beta / \text{ppmO} \sim 5 \times 10^{-3} \text{ cm}^{-1} \text{ ppmO}^{-1}.$$

Similar estimates can be obtained from the data of Vasko, Leval, and Srb.⁽²²⁾ It appears that the presence of Ge leads to a ten-fold increase in β/ppmO in selenium-based glasses at $10.6\mu\text{m}$. This is most likely due to the fact that Ge forms the most stable bonds with oxygen of the three elements, Ge, As, Se, so that the oxygen present in the glass bonds preferentially to Ge atoms.⁽²³⁾ At the same time, the higher Ge-O-bond energy leads to a larger force constant for the Ge-O vibration, which, in turn, enhances the absorption at shorter wavelengths. This is, of course, rather unfortunate, since, as will be detailed below, Ge is a highly desirable component of chalcogenide glasses in terms of improving their mechanical and thermal properties. On the basis of the above figures, the maximum oxygen content allowable if β is to be kept below 10^{-3} cm^{-1} is around 2 ppm for As-Se glasses and around 0.2 ppm for Ge-As-Se glasses.

Hilton and Jones⁽²³⁾ and Savage and Nielsen⁽²⁴⁾ have published studies of the sources of oxygen contamination and their remedies in chalcogenide glasses. Chalcogenide melts for glass production are commonly synthesized from the elements under vacuum in sealed Pyrex, Vycor, or fused silica containers at temperatures ranging from 350 to 1000°C . The most likely sources of oxygen in the glass are:

- a) oxygen or water impurities in the elemental starting materials,
- b) oxygen or water adsorbed on the surface of the containment vessel,
- c) reaction with the oxide glass containment vessel.

At the present no really firm criteria are available for assessing the minimum oxygen content attainable in a reasonable synthesis of chalcogenide melts.

Past efforts to minimize oxygen contents have included:

- a) handling and heating of materials under inert gas or vacuum,
- b) prepurification, including reduction in a hydrogen atmosphere, of the elemental starting materials,
- c) baking out of silica containment vessels under vacuum to remove adsorbed water prior to the synthesis, ⁽²⁴⁾
- d) distillation of the melt, ⁽²⁴⁾
- e) reduction of synthesis temperature to reduce the extent of the (probably endothermic) reaction of the melt with the oxide glass containment vessel, ⁽²⁵⁾
- f) chemical scavenging of the melt by treatment with or addition of reducing agents such as hydrogen, carbon, magnesium, beryllium, and aluminum. ^(12,24,26)

Most of these procedures were aimed primarily at reducing the infrared absorption due to oxide impurities to a level well below the reflection losses (around 30-40

percent) at the sample surface, but not necessarily to a level well below the inherent absorptivity of the oxygen-free materials. A substantial amount of research is needed in this area, since until oxygen-free glasses are obtained, the contributions to the IR absorption of chalcogenide glasses from other sources (free-carrier absorption or multiphonon processes) cannot be assessed. As an example, the purified As_2Se_3 glass spectrum of Figure 10 exhibits a noticeable shoulder (which has been observed at a number of laboratories) at around $15\mu\text{m}$, the tail of which appears to be the main source of IR absorption at $10.6\mu\text{m}$. This $15\mu\text{m}$ shoulder may arise from residual oxide impurities in the As_2Se_3 glass. On the other hand, values of the reststrahlen frequency for the As-Se vibration in As_2Se_3 reported from three independent laboratories are 228 cm^{-1} , $(25) 217\text{ cm}^{-1}$, (27) and 237 cm^{-1} . (28) The first overtone of the reststrahl band ($1/2\nu_r \approx 22\mu\text{m}$) is prominent in Figure 10, and the second overtone ($1/3\nu_r \approx 15\mu\text{m}$) may well account for the $15\mu\text{m}$ shoulder in the purified As_2Se_3 glass.

As shown in Table 8, the lowest $10.6\mu\text{m}$ absorption coefficient obtained for chalcogenide glasses is on the order of 10^{-2} cm^{-1} . Whether this value can be lowered by more stringent oxygen removal techniques or whether it is set by multiphonon processes inherent to the bulk glass remains to be determined. In the event that absorption at $10.6\mu\text{m}$ in the glasses so far studied is due to multiphonon processes (overtone of the reststrahl band), it also remains to be determined whether the absorption coefficient can be reduced by changes in the glass composition.

3. Scattering

Scattering is not expected to be a problem with homogeneous chalcogenide glasses.

4. Mechanical and Thermal Properties

As noted in Section 1, the most highly cross-linked homogeneous chalcogenide glasses, (i.e., those containing substantial proportions of quadrivalent elements such as Si or Ge) are also those which exhibit the highest glass-transition temperatures and softening points. As may be seen by comparison of the properties of As_2Se_3 with those of the germanium-containing glasses of Table 8, and as detailed in the review article of Hilton, Jones, and Brau,⁽³⁰⁾ increases in the Si or Ge content of homogeneous chalcogenide glasses also correlate strongly with increases in the mechanical and rupture moduli and Knoop hardness and decreases in the thermal expansion coefficient.

Given in Table 9 are some typical mechanical and thermal properties for oxide-network glasses. Comparison with Table 8 shows that the best homogeneous chalcogenide glasses developed to date ($\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ and $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$) are markedly inferior to typical oxide glasses in strength and upper use temperature (which is set roughly by the glass transition temperature, T_g).

Thermal conductivities near room temperature of selenide glasses determined by two laboratories^(11,29) seem to fall fairly regularly in the range $K \sim 0.002 - 0.003 \text{ W/cm}^{\circ}\text{K}$, with no significant changes in K perceptible

TABLE 9

MECHANICAL AND THERMAL PROPERTIES
OF TYPICAL OXIDE GLASSES

Linear coefficient of thermal expansion, ($^{\circ}\text{K}^{-1}$)	$8-9 \times 10^{-6}$
Glass transition temperature, T_g ($^{\circ}\text{C}$)	500
Hardness, Knoop scale	300 - 600
Young's modulus (psi)	$7-10 \times 10^6$
Rupture modulus (psi)	
(annealed)	5000
(thermally tempered)	15,000 - 20,000
(chemically strengthened)	100,000

due to changes in the degree of cross-linking of the glass. Russian investigators,⁽¹³⁾ however, have measured K values for the same types of glasses which are 2 to 3 times larger than those reported above.

Specific heats of chalcogenide glasses in the temperature range -100°C up to the glass transition temperature are closely approximated by the Debye heat capacity function.^(19,20) For selenide glasses, for instance, the specific heat may be estimated to within a few percent by the formula

$$C_p (\text{cal/g}^\circ \text{K}) = \frac{C(T/\theta_d)}{M}, \quad (\text{VIII-1})$$

where $C(T/\theta_d)$ is the Debye heat capacity per gram-atom for reduced temperature T/θ_d ,⁽³¹⁾ M is the average atomic weight, and θ_d is the Debye characteristic temperature, which may be taken as around 375°K for selenide glasses.^(19,20)

5. Production of Large Samples

Scale-up for production of large pieces of melt-cast glass is generally not a major problem, although chalcogenide glasses present some difficulties in that the melting, casting, and annealing processes must be carried out in an oxygen-free environment to avoid contamination of the glass. Because they are easy to produce in large pieces, chalcogenide glasses possess a major advantage over melt-grown single crystals or hot-pressed polycrystalline materials. Texas Instruments Corporation is now capable of

supplying their $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glass in 12-inch by 24-inch plates.

6. Surface Coatings

Because of their high indices of refraction ($n \sim 2.5 - 3.5$), chalcogenide glasses exhibit high surface-reflection losses (30-40 percent) at IR wavelengths. Consequently, their use as IR windows will require the use of anti-reflection coatings. On the other hand, chalcogenide glasses are generally unreactive with water and resistant to atmospheric oxidation at temperatures near and below 25°C , so that no surface protection from water or atmospheric attack is required for them.

7. Radiation Damage

To this Committee's knowledge, no studies have been made of the effect of ultraviolet, x-ray, or nuclear radiation damage in/on IR-transmission-chalcogenide glasses. Chemical bonds in chalcogenide glasses are weak and it is to be expected that energetic radiation would give rise to extensive disruption of the glass network bonds, followed probably by rearrangement of the local structure. Such rearrangement would undoubtedly result in localized changes in the density and in inhomogeneities in the refractive index of the glass, particularly at the surface where most of the hard radiation would be absorbed. Whether these refractive-index inhomogeneities would be of sufficient amplitude and dimension to adversely affect the IR transmission in the $10\mu\text{m}$ range remains to be determined experimentally.

8. IR Transmission at 2-6 μ m

The 2-6 μ m region is the optimum transmission region for chalcogenide glasses, being well removed from absorption bands both of the bulk glass and of oxide impurities (see Figure 10). The only known absorption bands in this region that have been detected in chalcogenide glasses are thought to arise from H₂S or H₂Se impurities introduced during treatment of the melt with hydrogen to remove oxide impurities. (23,24)

B. Chalcogenide Glass-Ceramics

1. Introduction

In addition to the absorption at 10.6 μ m due to oxide impurities, homogeneous chalcogenide glasses possess a number of inherent drawbacks to their use as high-energy IR-laser-exit windows, namely, low strengths, low thermal conductivities, and high coefficients of thermal expansion. In this section the feasibility of producing a new variety of material suitable for use as a laser-exit window will be discussed. This chalcogenide ceram offers the possibility of combining the superior thermal and mechanical properties of polycrystalline metallic chalcogenides with the ease of fabrication (melt-casting of large window blanks) of glasses.

2. Structure of Glass-Ceramics

Glass-ceramic or ceram is the generic name for a material that is melted and formed as a glass and then almost completely crystallized during a subsequent heat treatment.⁽³²⁻³⁴⁾ The most characteristic feature of the ceram is that the crystals are minute and of uniform size. This is achieved by selecting a base glass which exhibits liquid-liquid immiscibility above the glass transition. If the base glass is chosen near the center of the immiscibility dome, the two immiscible phases will have roughly equal volume fractions, and the glass microstructure will be of small dimension and exhibit a high degree of interconnectivity. Provided that the glass viscosity remains sufficiently high, no appreciable growth of the size of the phase-separated microregions will occur during the subsequent heat treatment leading to nucleation and crystallization of one of the phases. The inter-connected structure will block growth of the crystals beyond the boundaries of the region undergoing crystallization, so that a fine dispersion of small crystals of uniform size will result from crystallization of the first phase. A follow-up heat treatment can then result in partial crystallization of the second phase, so that the final product, i.e., the glass ceram, consists of 80-90 percent crystalline material imbedded in a glass matrix.

3. Properties of Glass-Ceramics

Oxide glass-ceramics have been formed which are transparent in the visible region.^(35,36) For glass-ceramics in which the crystal volume is a large fraction of the total volume, we do not have a closed-form expression for the attenuation coefficient, β . However, the predictions of Rayleigh scattering from spheres⁽³⁸⁾ can give us the qualitative dependence of β on the size, refractive index, and number per unit volume of crystals for the glass-ceramic. For the oxide glass-ceramics transparent in the visible,^(35,36) the average crystal size was around $0.1\mu\text{m}$ so that transparency to light of wavelength $0.5\text{--}0.8\mu\text{m}$ was a result of both small crystal size and a close match between the indices of refraction of the crystals and the glass matrix. The attenuation coefficient goes inversely as λ^4 , so for light of wavelength $10\mu\text{m}$, which must be transmitted by the chalcogenide glass-ceramic, the index of refraction match will not be as critical, provided that the crystal size can still be kept at or below $0.1\mu\text{m}$, and infrared transmission losses by scattering from crystals in the material should be tolerably small.

The chalcogenide ceramic would share the advantage of the homogeneous chalcogenide glasses in that up-scaling the production process to produce large samples is a relatively minor problem. The glass-ceramic is initially cast from the melt in one piece as a phase-separated glass and is crystallized subsequently by heat treatment of the entire blank.

The ceram possesses several material advantages over comparable single-phase homogeneous glasses. The upper use temperature for homogeneous glasses is the glass transition temperature. For 80-90 percent crystalline glass-ceramics, barring other effects such as reaction with the atmosphere, the upper use temperature may approach the melting point of the crystals ($\sim 1350^{\circ}\text{C}$ for CdSe, a possible major component of ceram compositions presently under consideration). The strength (abraded modulus of rupture) of glass-ceramics is typically considerably larger than the strength of comparable single-phase glasses. In oxide materials the abraded rupture modulus is increased from 1 kpsi for annealed glass to 10-20 kpsi for the glass-ceramic. The small crystals of the ceram act as crack terminators preventing build-up of large internal stresses which lead to failure. Further surface treatments can enhance the modulus of rupture values of both the glass and the ceram, but for similar treatments the ceram generally continues to enjoy its rupture modulus advantage over the single-phase glass. For oxide cerams, modulus of rupture values as large as 155 kpsi have been attained. In addition, creep coefficients of cerams are exceedingly small. The system is not rheologically simple in that the ordinary processes of creep in crystals (grain boundary diffusion in polycrystals, dislocation growth, and motion in single crystals) are suppressed. Further, delayed elastic effects, which can be a problem in glasses, are severely restricted in cerams by the interconnected crystal structure.

The improved mechanical strength of a chalcogenide ceram would lead indirectly to an improvement in optical properties with respect to single-phase chalcogenide glasses, since thinner windows could be used with the ceram, which would lead to a corresponding reduction in light absorption. In addition, the casting and heat treatment of large samples becomes easier the smaller the thickness.

When a composite material is 80-90 percent crystalline, one obtains values for such properties as the thermal expansion coefficient α , temperature coefficient of refractive index dn/dT , and thermal conductivity K that closely approach those in the pure crystal. Chalcogenide cerams are presently under development⁽³⁷⁾ in which the crystalline phase would be principally a metallic chalcogenide semiconductor such as PbSe or CdSe. This represents a considerable potential improvement over presently existing single-phase chalcogenide glasses, since one wishes to maximize K and minimize α in the laser window material. Some typical comparison figures are given below:

Chalcogenide semiconductor	$\alpha \sim 5 \times 10^{-6} \text{ deg}^{-1}$ $K \sim 0.1 \text{ watt/cm deg.}$
TI 1173 glass ($\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$)	$\alpha \sim 16 \times 10^{-6} \text{ deg}^{-1}$ $K \sim 0.003 \text{ watt/cm deg.}$

These improvements in α and K can probably be realized without any sacrifice in dn/dT , since the dn/dT values are essentially the same for ZnSe or CdTe crystals as for the TI 1173 glass.

C. Suggested Areas of Research and Priorities

Because of the ease of fabrication of large pieces and the lack of reactivity with water, chalcogenide glasses and glass-ceramics should remain candidates for both bulk material and coatings for the high-power CO_2 laser window. Research should be continued on the assessment and improvement of these materials, with emphasis on the reduction of absorption due to impurities and other sources. Anti-reflection coatings for the glasses should also be developed. An effort of 4 man-years over the next 2 years at an estimated cost of \$200,000 is recommended.

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IX. POLYCRYSTALLINE INFRARED-WINDOW MATERIALS

A. Introduction

The potential of polycrystalline materials as laser windows at $10.6\mu\text{m}$ and $2-6\mu\text{m}$ wavelengths is evaluated in terms of absorption, scattering, mechanical properties, preparation and scale-up production, surface coatings, radiation damage, and program recommendations. Primary emphasis is given to the $10.6\mu\text{m}$ wavelength range and in this connection consideration is given to the II-VI, III-V, and I-VII compounds, e.g., ZnSe, CdTe; GaAs; and KBr, KCl, etc., respectively.

B. Polycrystalline Materials

1. Absorption

Chapters VI and VII of this report have already discussed absorption in Group II-VI, III-V, and I-VII compounds primarily treated as single crystals. The current discussion is concerned with a treatment of these compounds in polycrystalline form.

In general, other things being equal, one might expect absorption to be always greater for a given compound in polycrystalline form as compared to single-crystal form for reasons given below:

a) Free-Carrier Problem at Grain Boundaries

The increased dislocation density associated with grain boundaries could conceivably increase the concentration of free carriers in compounds of the II-VI and III-V category. Some experimental work is required to confirm this, which involves measuring absorption in both single crystal and polycrystalline samples with the latter prepared by the recrystallization of single crystals. In this way, complicating extrinsic effects may be minimized.

For the I-VII compounds, however, free carriers are not a problem.

b) Increased Impurity Concentration

This factor is likely to be greater in polycrystalline material prepared by normal particulate processing methods; however, chemical vapor transport and single crystal recrystallization processes offer alternative approaches to reduce the significance of this problem. Selective distillation and melt-refining do make it possible to further purify starting materials.

The presence of second-phase^{*} impurities and/or solid solution^{**} additives can lead to increased absorption at site locations, and unless methods are developed for

* A crystalline or amorphous material distinct from the primary or host material.

** An impurity material that enters the lattice of the primary or host material, interstitially or substitutionally.

preparing and handling raw materials with minimum contamination, polycrystalline fabrication approaches are not likely to be very successful.

2. Scattering

Bulk scattering of incident radiation in the II-VI cubic polycrystalline materials is likely to be much more dependent on residual porosity than on the presence of grain boundaries. The presence of second-phase impurities would also present scattering sites, although these impurities could be more significant in absorption.

In a recent effort on a Yttralox^{*} polycrystalline-ceramic laser,⁽¹⁾ the influence of residual porosity on laser threshold was well demonstrated. Levels of porosity of the order 3×10^{-5} percent to 10^{-3} percent increased laser threshold values from 30 joules to 50 joules with the best attenuation of the order of 10^{-2} cm^{-1} .

These represent about the lowest porosity values reported for the case of a sintered polycrystalline ceramic, yet there was still sufficient remanent porosity to significantly reduce radiant transmission.

Scattering is likely also to be a problem with II-VI and III-V compounds prepared by particulate approaches where remanent porosity is an inherent feature.

* Polycrystalline ceramic with cubic crystal structure comprised of 90 percent Y_2O_3 and 10 percent ThO_2 or ZrO_2 in solid solution, produced at General Electric² Company.²

The mere presence of grain boundaries is not likely to present scattering problems for such optically isotropic materials as cubic I-VII halides and II-VI zinc blend crystal structures unless birefringence results from process-induced strain ⁽²⁾ whereby $\frac{\Delta n}{n} = \frac{(n^2 - 1)(n^2 + 2)}{6n^2} S$.

The induced variation may be expressed in terms of n , the refractive index, and S , the induced strain. This is likely to be a small effect in contrast to porosity and should be capable of being annealed out. In addition, scattering as a result of the presence of a second phase (likely to be at a grain boundary) is a function of size, distribution, and index of refractive difference. This second phase would probably affect absorption more significantly.

3. Mechanical Strength

It is generally accepted that materials potentially useful as laser windows in 10.6 μ m region display rather poor mechanical properties, particularly in terms of tensile strength. In fact single crystals of such materials (wherein the energy to move dislocations is rather low) can be significantly weaker than fine-grain-size polycrystalline counterparts (because of dislocation blocking). The difference in strength may be an order of magnitude between the two. Strength can be increased still further in polycrystalline material by coupling alloying with grain size reduction.

In general, for brittle polycrystalline materials, the strength increase has been observed to essentially

follow the Griffith relation⁽³⁾

$$\sigma_f \approx \frac{1}{(\text{G.S.})}^{\frac{1}{2}}, \quad (\text{IX-1})$$

σ_f = tensile strength ,

G.S. = grain size.

In this connection polycrystalline materials have an inherent advantage over single crystals of current interest.

4. Preparation and Production of Large Size Windows

A significant disadvantage of the II-VI and III-V compounds is that they are not available as large single crystals. As a result, the consideration of polycrystalline materials becomes important in view of the relative ease by which large samples may be made. The observed absorption coefficients of currently available polycrystalline samples, however, are generally higher by one to two orders of magnitude than those of corresponding single crystals.

Four processes are worth discussing in this connection and they include:

a) Standard Hot Pressing

This process has been employed to produce the commercially available IRTRAN (Trademark Eastman Kodak Co.) series of polycrystalline materials, e.g., ZnS, CdTe, ZnSe. The hot-pressing process is currently supported by

a major DoD-sponsored program⁽⁴⁾ involving preparation and characterization of ZnSe and CdTe. The most significant advantage in the hot-pressing process is that the availability of large presses makes it feasible to scale-up the size of windows. It is considered very difficult to prepare material with adequate absorption coefficient, however. Problems in contamination, resulting from powder synthesis, handling, and consolidation, as well as in residual porosity, remain to be solved.

This may be less of a problem for the I-VII compounds than for the II-VI and III-V varieties, although it is probably preferable to consider a forging process for the I-VII compounds as described below.

b) Mechanical Working (e.g., Press Forging, Rolling, etc.)

This process of slow compressive deformation is probably most significant for the I-VII compounds primarily as a means of raising the strength of high-purity single-crystal samples. This is accomplished by recrystallizing single crystals into fine-crystallite structure without degradation of optical properties. By such an in situ grain-boundary formation, associated second phases and porosity, leading to absorption and/or scattering, are minimized. An additional advantage is that the process forms a larger diameter, short cylinder from a longer but smaller diameter one, thus relaxing initial crystal diameter requirements. The process has been successfully applied to such materials as magnesia and alumina⁽⁵⁾ as well as sodium chloride.⁽⁶⁾

c) Sonic Casting

The development and application of this process is currently sponsored under a DoD contract.⁽⁴⁾ It is a modification of melt-growth single-crystal processes and involves sonically irradiating a melt, e.g., CdTe during solidification. The vibrations are believed to assist in reducing the porosity of the casting, improve homogeneity, and assist in developing finer grain morphology than without vibratory casting.

The process has the advantage of being more easily scaled-up to produce large size windows than single crystal methods but difficulty in controlling resulting grain sizes and pore removal rates are anticipated in any scale-up operation. The process is currently being evaluated for CdTe.

d) Chemical-Vapor Deposition

This technique has been demonstrated for ZnS and ZnSe but has yet to be carried out successfully for CdTe.⁽⁴⁾ Chemical-vapor deposition offers potential scale-up and the control of impurities by selective distillation. Currently, it appears to be the most promising method of polycrystalline material preparation aside from the recrystallization of single crystals by mechanical working.

In this process, volatile compounds or other volatile species of the materials to be deposited are passed into the deposition zone of a furnace maintained at a given temperature and pressure. The volatile compounds

are directed to a substrate, e.g., pyrolytic graphite, and are then allowed to thermally decompose and react at the substrate to form solid material. Typical deposition rates are .005 to .010 in/hr. The reaction products are pumped away and disposed of by scrubbing, etc.

The process has been successfully applied in producing the purest single crystals of Al_2O_3 ⁽⁷⁾ and MgO ⁽⁸⁾ known.

4. Surface Coatings

No investigations of anti-reflection or protective surface coatings have been published for the II-VI and III-V compounds that have come to the attention of the Committee.

Coating work has been started for I-VII compounds and a combination of layers of BaF_2 and vitreous As_2S_3 looks promising.⁽⁹⁾

5. Radiation Damage

No investigations of the influence of radiation damage to absorption behavior for the II-VI, III-V, and I-VII compounds have come to the attention of the Committee.

6. Outlook at 2-6 μ m

A whole range of mechanically stronger and environmentally more resistant compounds become worthy of consideration in this spectral range.

These additional compounds to be considered include such fluorides as MgF_2 , CaF_2 , BaF_2 , PbF_2 , as well

as other materials; e.g., Si, Al_2O_3 , and MgO.

It is not likely that the preparation of suitable polycrystalline samples of these compounds by particulate processing, e.g., sintering or hot pressing, is any brighter.

Problems of pore removal and impurity contamination are still severe with no apparent solution. The chemical vapor deposition process as described in Section 3 does offer the potential of excellent impurity control as cited for MgO and alumina and ZnSe. In these particular instances, the products have been either single crystal material or highly oriented polycrystalline material.

C. SHORT- AND LONG-RANGE-RESEARCH PLANS

The short-range probability of success in developing suitable polycrystalline materials is not high unless one considers the recrystallization of single crystals by press forging (most suitable for large I-VII alkali-halide crystals currently available). The motivation here is to improve the mechanical-strength properties and a funding level of \$100,000 is recommended.

In this connection, particular attention should be given to evaluating press forging techniques applied to I-VII compounds in single-crystal form, with emphasis on resultant recrystallization, mechanical strength, and optical properties.

Long-range interest should give consideration to II-VI polycrystalline materials as large-size windows.

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