INFRARED TRANSMITTING MATERIALS

William B. White

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I. RESEARCH MISSION

This project concerns a search for oxide materials which may have useful properties as infrared windows in the range of 8-12 microns. Below this wavelength there are many good window materials and above it, oxides would certainly be poor candidates. In the intermediate range there seems some hope of finding oxides from the lower part of the periodic table which have useful transmission properties. Oxides in general have certain advantages over the IR transmitting chalcogenide materials, which justifies a careful search. These include high strength, better thermal stability, possibly lower cost, and chemical stability under ambient conditions.

Previous knowledge suggests that candidate materials should be sought among structures with high cation mass and high coordination number. Among the ionic solids, the 8-coordinated fluorite structure is a possibility. Since the infrared cut-off frequency increases with the ionicity of the compound, a second area of search is among the heavy metal oxides whose bonding is known to be partly covalent. The candidate materials here are the oxides of lead and bismuth.

It must be realized that the desired physical properties of high strength, high melting point, and high hardness intrinsically imply strong bonds and low coordination numbers. Thus we are really seeking an optimum trade-off between the infrared properties and the other physical properties.

II. FLUORITE STRUCTURE MATERIALS

The fluorite structure is face-centered cubic with the metal cation in 8 fold coordination. Simple oxides with this structure include such materials as ZrO_2, HfO_2, CeO_2, ThO_2, and UO_2. Of these, ThO_2 has one of the highest cation masses and is not beset with problems of valence state change, chemical stability, or polymorphic phase changes. The fundamental vibrational spectrum of ThO_2 was measured by Axe and Petit (1966). This structure permits 2 triply degenerate vibrational modes, T_{2g} active only in the Raman effect, and T_{1u} active in the infrared. The transverse optic mode is 279 cm^{-1} (36 µm) and the longitudinal mode is 568 cm^{-1} (17.6µm) according to Axe and Petit.

Our work with ThO_2 has been to measure the infrared absorption cut-off on thick pieces.

Single crystals of ThO_2 were obtained from the Norton Company. A semiquantitative spectrochemical analysis showed only trace impurities (0.01%) of Fe, Mg, Si, La, Y and Ca. Transmittance in the infrared, from 2.5 to 30 microns, was measured on a Perkin Elmer spectrometer (Model 621). Results show about 80-85% transmittance (uncorrected for reflectivity losses) out to 6.5 microns but beyond this the transmittance rapidly drops with complete cut-off occurring at 9.5 microns. The transmittance vs wavelength curve is shown in figure 1 for a 1.73 mm thick sample. No appreciable shift of the IR cut-off was observed for thinner samples of 1.59 and 1.07 thicknesses.

The cut-off curve conforms fairly well to the rule of thumb that the cut-off frequency should be about twice the longitudinal mode frequency.

It would appear from these initial results that the main application of ThO_2, if any, would be as a protective coating. Additional efforts to measure the transmission of ThO_2 in film thicknesses will be made.

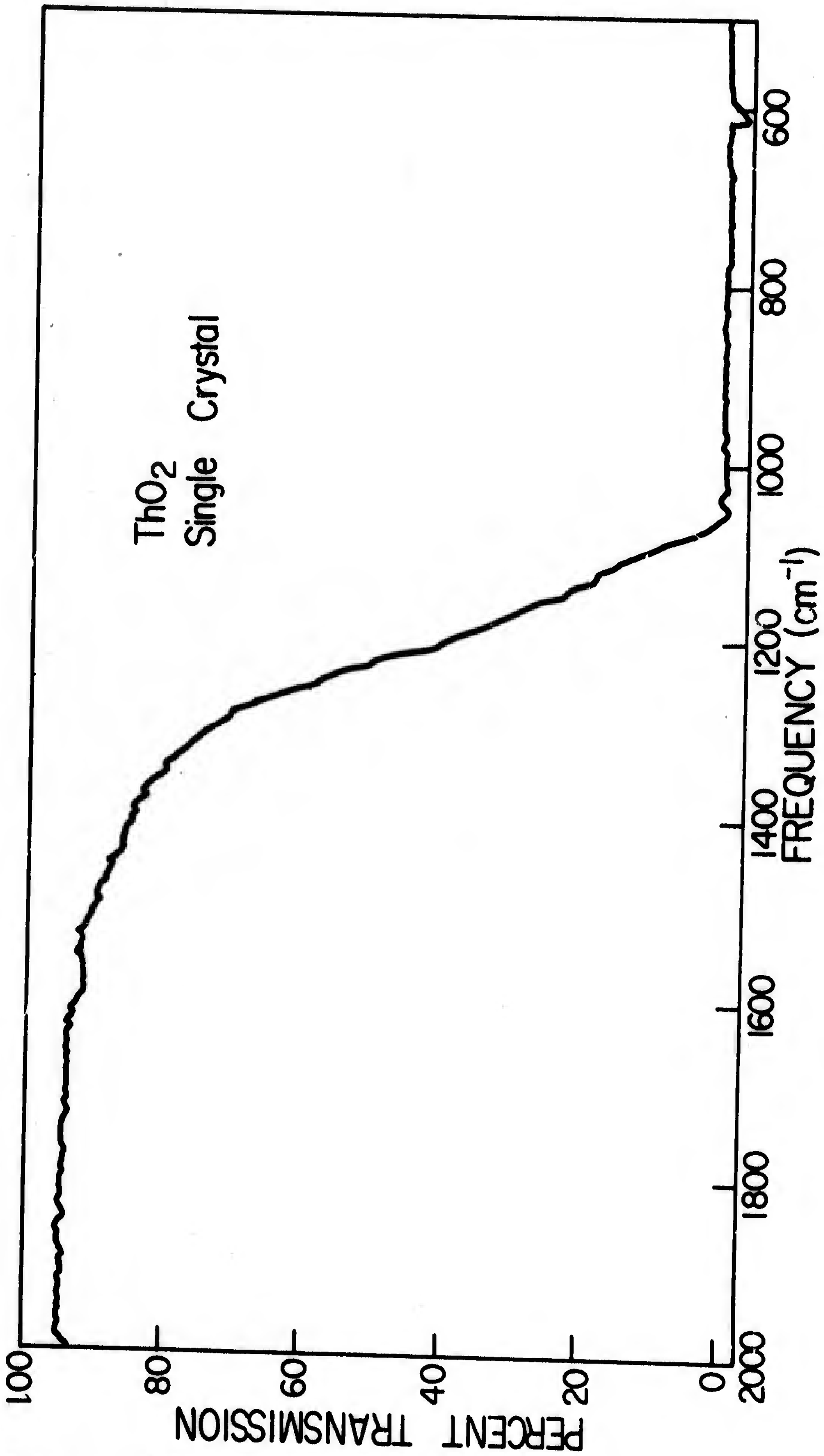

Fig. 1 Infrared cut-off of single crystal ThO_2

III. BISMUTH OXIDE MATERIALS

Introduction

Bismuth oxide is a yellow material with a high refractive index. It melts at 850°C to a highly fluid liquid. Above 730°C there is a phase transition to a stable cubic form. In addition, metastable tetragonal and body-centered cubic forms have been proposed (Levin and Roth 1964-a). The stable low temperature form is monoclinic, space group $P\ ^{2}1/c$, C^{5}_{2h} with 4 Bi_2O_3 per unit cell (Sillen, 1940). The only infrared data on this compound known to the writer are in the survey report on oxide spectra by McDevitt and Baun (1964).

Also of interest are a series of bismuth-rich compounds with divalent oxides (Levin and Roth, 1964-b). The system $PbO\text{-}Bi_2O_3$ contains a body-centered cubic compound, $PbO.6Bi_2O_3$ which melts incongruently at 730°C. No infrared data are known for this compound.

Our work with the bismuth oxides includes measurement of the vibrational modes on powders, preparation of Bi_2O_3 films for more precise determination of optical parameters, and growth of Bi_2O_3 and $PbO.6Bi_2O_3$ crystals for measurement of the infrared cut-off.

Preparation of Materials

A vacuum bell jar assembly has been adapted for depositing films of Bi_2O_3 on substrates suitable for subsequent spectroscopic measurements (e.g. on KBr single crystals for infrared transmission measurements). A diffusion pump capable of attaining pressures to 10^{-5} torr is used for evacuating the bell jar system which contains a platinum strip heater, appropriate mounts for supporting the substrate, and thermocouples for monitoring temperatures of the substrate and source material.

A series of experiments has been made to determine the effect of the variable parameters (pressure, temperature, heater to substrate distance, rate of evaporation, and crucible material) on the quality of the deposited films. Source material (Baker reagent grade Bi_2O_3 powder) was placed in either a platinum or ceramic crucible which was in direct contact with the platinum strip heater. For these preliminary tests, to determine optimum conditions, glass slides were used as substrates. These permit convenient evaluation of the films by x-ray diffraction and optical microscopy.

Since there are at least five parameters which can be varied, a large number of runs is required to bracket the optimum conditions producing high quality films. The most uniform and mechanically homogeneous films were deposited when the Bi_2O_3 powder and crucible were first heated for several hours in the evacuated bell jar at about 500°C. This, coupled with a substrate to source distance of about 2 inches eliminates splatter which occurs from faster heating and/or lowering of the substrate. After the bake-out process, power to the platinum strip was raised until melting was observed. The thermocouple, placed about 2 mm below the strip, read 710°C, but the actual temperature of the crucible and melt was undoubtedly somewhat higher. A yellow film began to deposit almost immediately on the substrate and the color gradually darkened with increasing thickness. Substrate temperature during deposition under the above conditions was about 225°C. Since the substrate does not have a separate heating unit, the temperature was controlled by the distance from the platinum strip. No obvious attack of the ceramic or platinum crucible was detected for the relatively short heating times used. X-ray diffraction patterns of all the films prepared to date indicate Bi_2O_3 as the principal phase. Some bismuth metal was present in each sample. Additional anomalous peaks were also observed. Some of these may be due to the presence of the beta and/or delta form of Bi_2O_3. Identification of these phases as well as the assignment of other unidentified reflections is difficult due to the large number of alpha Bi_2O_3 and Bi reflections which overlap and mask major peak positions of suspected contaminants.

Concurrent efforts are also being made to pull crystals of Bi_2O_3 from the melt. Results to date, however, have not provided sufficiently coarse-grained samples to be suitable for cutting and subsequent spectroscopic measurements.

Spectra of Bi_2O_3 Powder

The monoclinic form of Bi_2O_3 belongs to space group $P2_1/c$, C_{2h}^5. There are 4 Bi_2O_3 per unit cell. All atoms (Sillen, 1940) lie on the 4 (e) general positions. The 60 degrees of freedom of the 20 atoms in the cell are thus distributed uniformly over the 4 irreducible representations of C_{2h}.

Table 1

Factor Group Analysis of αBi_2O_3

C_{2h}	Total Modes	Acoustic	Vibrations	Selection Modes
A_g	15	-	15	Raman
B_g	15	-	15	Raman
A_u	15	z	14	IR, E ‖ b
B_u	15	x,y	13	IR, E ⊥ b

The analysis predicts a total of 27 infrared active modes.

The IR spectrum of αBi_2O_3 pressed in a CsI pellet is shown in Figure 2. At least 6 bands appear in the region above 200 cm^{-1} and many of these could easily represent more than one fundamental mode.

The infrared cut-off in the pellets is encouragingly low, absorption beginning at ~15 µm. These pellets contain about 1 mg Bi_2O_3 in 300 mg of CsI. The equivalent thickness of Bi_2O_3 alone would be about 0.01 mm based on an average thickness of the pellets themselves of 3 mm. How far the edge will shift with increasing thickness must await measurements on single crystals or thick films.

The compound $PbO.6Bi_2O_3$ was synthesized by direct reaction of the oxides. The identity and phase purity of the product was established by x-ray diffraction. This compound is body-centered cubic with a unit cell edge of 10.25 Å. The number of vibrational modes in this cell is large and a factor group analysis has not yet been performed.

The infrared spectrum on powdered $PbO.6Bi_2O_3$ pressed in a CsI pellet is shown in figure 3. Only 4 or 5 broad intense bands are observed in this spectrum but much more fine detail would be expected. The absorption edge begins at 12.5 µm in this preparation - somewhat higher than in the pure Bi_2O_3.

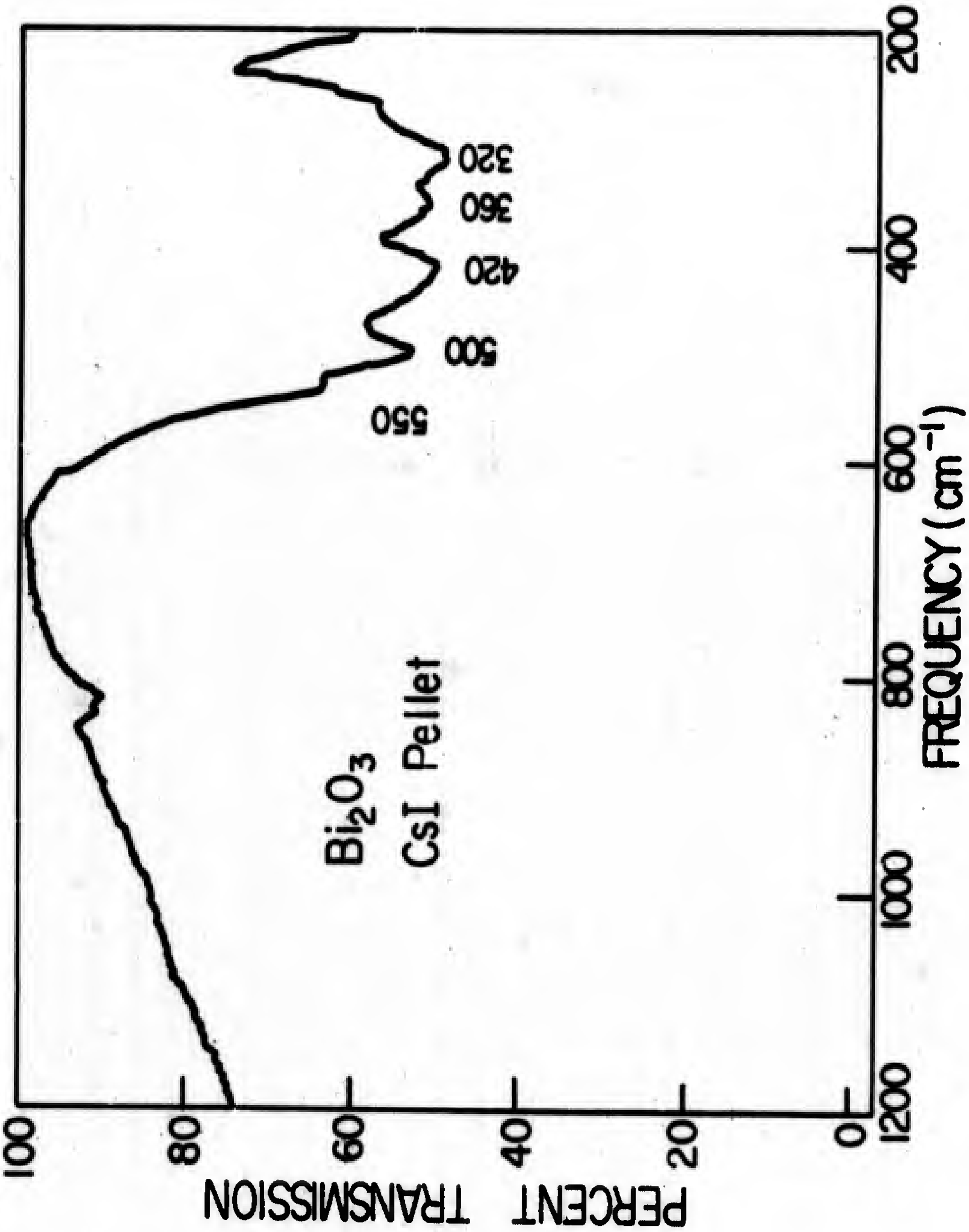

Fig. 2 Powder spectrum of Bi_2O_3

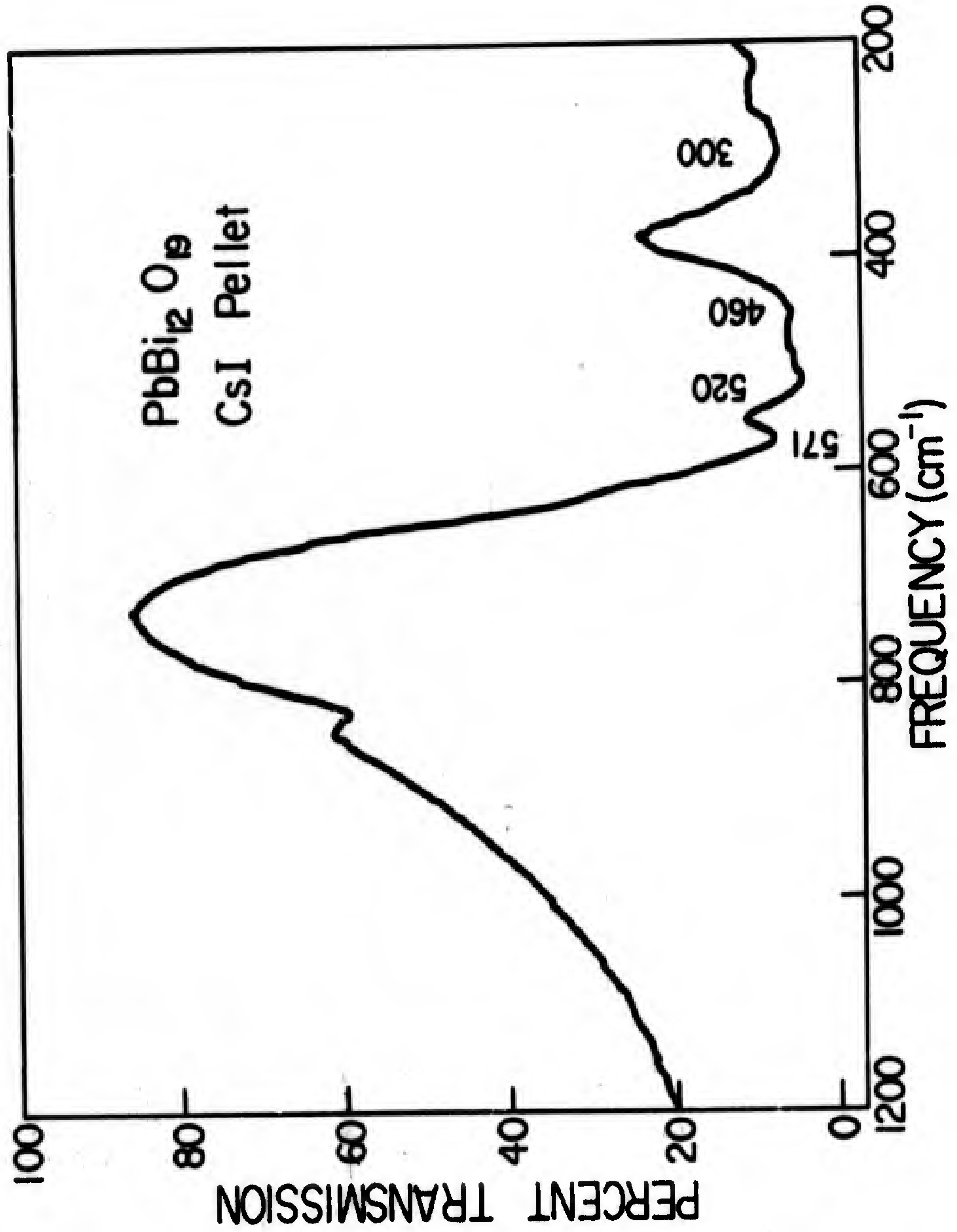

Fig. 3 Powder spectrum of $PbO \cdot 6Bi_2O_3$

IV. LEAD OXIDE MATERIALS

Introduction

Lead monoxide, PbO, exists in two different polymorphic forms, one a low-temperature tetragonal modification known as red lead oxide (litharge) and the other, a high-temperature orthorhombic phase, yellow lead oxide (Massicot). The temperature of transition under atmospheric conditions is about 580°C. Both forms can be prepared under high temperature conditions and after quenching will remain stable under ambient conditions. Large crystallites of the yellow orthorhombic phase are pressure-sensitive with even moderate grinding in a mortar causing it to revert to the red tetragonal form. The pressure (O_2)-temperature dependence of this transition at low to moderately high pressures has been determined by White and Roy (1964-a). Phase relations at low to less than atmospheric pressures have been reported by Otto (1966). Infrared spectra of both tetragonal and orthorhombic PbO in the KBr range were published by White and Roy (1964-b). These spectra were measured on powders only and extended only to 400 cm^{-1} (25 μm).

Preparation of Materials

Reagent grade PbO which is obtainable from chemical suppliers is never phase-pure, i.e. it is always a fine-grained mixture of the two polymorphs, litharge and massicot. A number of methods have been tried in order to obtain separate polymorphs.

Massicot, the yellow form is easily obtainable in a stable form by heating reagent grade PbO (Fisher Certified Reagent) for several hours at a temperature just above the litharge→massicot transition. Even then, though, the product is slightly sintered. With careful screening, a fine powder of this pure polymorph can be obtained without grinding. Mechanical abrasion causes the yellow form to partially revert to the red form.

Attempts were made to grow sizeable, (i.e. cm size) crystals of yellow massicot by slow cooling of a melt. Large crystals are always formed on solidification, however, on passing through the transition temperature (yellow→red) always spontaneously transform. This may be due to thermally induced strain in the crystallized massicot relieving itself as the stress required to activate the transition.

Some attempts have also been made to grow PbO crystals by the Bridgeman technique. Here again the phase transition disrupts the crystals.

Yellow massicot has also been obtained by hydrothermal methods. The starting material consisted of $3PbO.H_2O$ prepared by precipitation from lead acetate solution with concentrated NH_4OH. Temperatures used were around 500°C or less and about 10,ppp psi H_2O pressure. In about 3" long by 1/4" diameter gold tubes, up to mm sized equant thin crystals have been prepared. None were suitable for infrared transmission measurements. Transparent, colorless crystals of a new lead oxide hydrate were also found coexisting with these yellow crystals in some runs.

Red lead oxide (litharge) is much more difficult to prepare. When one tries to prepare it dry, analogous to the above dry preparation but heating at 525°C, only a mixture of Pb_3O_4 and yellow PbO was obtained with but a trace of red PbO. Inspection of the composite diagram for the Po_2-T phase relations reveals that the stability field for red PbO at 0.2 atmos. O_2 is very narrow and that it widens (temperature-wise) markedly for reduced O_2 pressures. To take advantage of this greater stability range, the same furnace was then purged with a small flow of nitrogen (both before and during heating). Experiments in this atmosphere over a temperature range 516° to 561°C did not result in red PbO but rather mixtures of yellow PbO and Pb_3O_4.

Red litharge for this study was prepared by hydrothermal methods. One run (12,000 psi H_2O, 230 °C) showed small amounts of minute red flakes intimately mixed with yellow PbO flakes at the bottom of the gold capsule. Careful hand selection of these red flakes under a binocular microscope provided a sample for the infrared spectrum, estimated at about 98% purity. This was then prepared for IR work by grinding to a fine powder under acetone.

Several investigators report growing thin films of PbO under vacuum conditions, Drift, Horsman and Langereis (1968) report growing only yellow massicot and while effects of substrate temperature and its orientation are rather well investigated, many other parameters were left undescribed. They do, however, report the minute pressure in their vacuum as oxygen. Kramarenko et al (1968) give only very sketchy experimental descriptions of thin film preparation but claim either red or yellow modifications form depending on substrate temperature.

The same vacuum deposition apparatus described in the Bi_2O_3 section, similar techniques, and similar experimental conditions were tried. All efforts to date have failed to produce a clear transparent film of PbO. Only glass substrates have been used. Yellow PbO was the only form observed to deposit regardless of substrate temperature and it was always intergrown with metallic lead. Some conditions, such as high vacuum, give only a lead film. PbO-containing films have been grown only with ceramic feed boats in agreement with vapor pressure measurements on PbO (Nesmeyanov, et al 1960). Platinum feed boats give lead vapor rather than oxide vapor. We also confirm findings on the orientation of yellow PbO crystals in these films.

There appear to be a number of experimental variables that must be maximized before films of either polymorph can be obtained. These are: composition of remaining gas in evacuated bell jar, feed boat composition, shape and height of walls of feed boat, temperature of feed boat, temperature of substrate, distance of substrate from feed, and polymorphic form of feed material.

Spectra of the Polymorphic

Factor group analyses to predict the number of normal modes of both PbO polymorphs were performed. Tetragonal PbO belongs to space group P_4/nmm, D_{4h}^7, with 2 PbO per unit cell (Leciejewicz, 1961). The Pb atoms are at the apex of a square pyramid with 4 oxygens for a base. The Pb atoms are on the 2 (c) sites with site symmetry C_{4v}. The oxygen atoms are on the 2 (a) sites with site symmetry D_{2d}. The invariance properties of the structure and its reducible representation are summarized in table 2. The reduction by factor group analysis yields the normal modes and selection rules shown in table 3. This analysis predicts only two modes active in the infrared from this compound.

The yellow, high temperature, crthorhombic form of PbO belongs to space group Pbcm, D_{2h}^{11} with 4 PbO per unit cell (Leciejewicz, 1961). Both kinds of atoms are on 4 (d) sites with c_s point symmetry. The coordinate system convention has been adopted which places the true mirror plane perpendicular to the b-crystallographic axis. The invariance conditions are then given in table 4 and the selection rules for the normal modes in table 5. Seven infrared and twelve Raman active modes are predicted by this analysis. Of the infrared bands, three of symmetry B_{1u} are polarized along the a-axis, one B_{2u} polarized along the b-axis, and three B_{3u} polarized along the c-axis.

Table 2

Invariance behavior of tetragonal PbO

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
C_{4v}	E	$2C_4$	C_2	-	-	-	-	-	$2\sigma_v$	$2\sigma_d$
2Pb	2	2	2	0	0	0	0	0	2	2
D'_{2d}	E	-	C_2	-	$2C_2''$	-	$2S_4$	-	$2\sigma_v$	-
$2O_x$	2	0	2	0	2	0	2	0	2	0
Total w_r	4	2	4	0	2	0	2	0	4	2
X(r)	12	2	-4	0	-2	0	-2	0	4	2

Table 3

Vibrational modes and selection rules for tetragonal PbO

D_{4h}	Total Modes	Acoustic	Vibrations	Selection rules
A_{1g}	1	-	1	Raman
A_{2g}	0	-	0	-
B_{1g}	1	-	1	Raman
B_{2g}	0	-	0	-
E_g	2	-	2	Raman
A_{1u}	0	-	0	-
A_{2u}	2	z	1	IR, $E \parallel c$
B_{1u}	0	-	0	-
B_{2u}	0	-	0	-
E_u	2	(xy)	1	IR, $E \perp c$

Table 4

Invariance conditions for orthorhombic PbO

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
C_s	E	-	-	-	-	-	σ_h	-
4Pb	4	0	0	0	0	0	4	0
C_s	E	-	-	-	-	-	σ_h	-
$4O_x$	4	0	0	0	0	0	4	0
Total w_r	8	0	0	0	0	0	8	0
X(r)	24	0	0	0	0	0	8	0

Table 5

Normal modes and selection rules for orthorhombic PbO

D_{2h}	Nt	Translation modes	Selection rules	Vibrations
A_g	4		R +	4
B_{1g}	2		R +	2
B_{2g}	4		R +	4
B_{3g}	2		R +	2
A_u	2		Inactive	2
B_{1u}	4	x	IR +	3
B_{2u}	2	y	IR +	1
B_{3u}	4	z	IR +	3

Absorption spectra for both red and yellow PbO over the range 2.5 to 50 microns were obtained on a Perkin Elmer Model 621 Spectrophotometer. Specimens were prepared in a manner analogous to the KBr pellet technique with several modifications in the method.

a) ~1000 mg CsI powder substituted for ~300 mg KBr.

b) pellets were pressure-annealed

c) shaking rather than grinding to mix sample with CsI

(a) Cesium iodide was used as a pellet medium so as to more closely match the high refractive indices of the lead oxides. This cuts down light scattering and facilitates transmission through the sample. (b) Three cycles of 5 minutes pressure followed by 5 minutes with no pressure were performed on the pellet while in the sample die. The technique is recommended for maximum clarity of CsI discs. (c) Sample powder was mixed by shaking to preclude pressure transformation that might take place under mechanical grinding.

Spectra of the powders are shown in figures 4 and 5. The tetragonal polymorph indeed exhibits only two infrared bands as predicted by the theoretical analysis. Measurements with polarized radiation on single crystals will be required to further assign these two bands. The 7 modes predicted for the orthorhombic form are not all observed in this frequency range. Whether some lie below 200 cm^{-1} or whether they are merely unresolved remains to be determined.

Tetragonal PbO has the lowest-lying frequencies of any materials yet examined. The cut-off of the dilute powder sample is ~17 µm. The orthorhombic phase is only slightly higher. Measurements on thick specimens will be required to test this further.

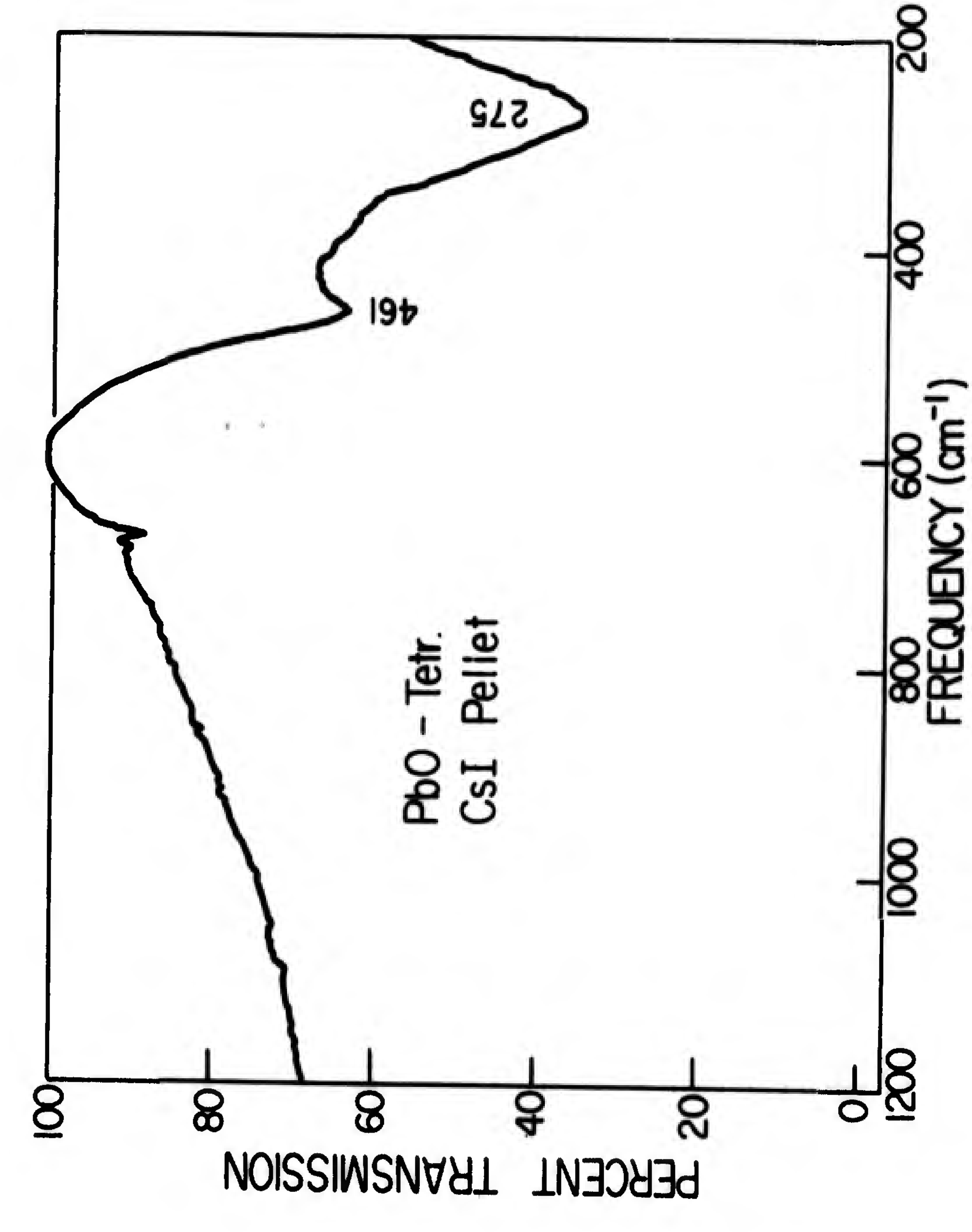

Fig. 4 Powder spectrum of tetragonal PbO (litharge)

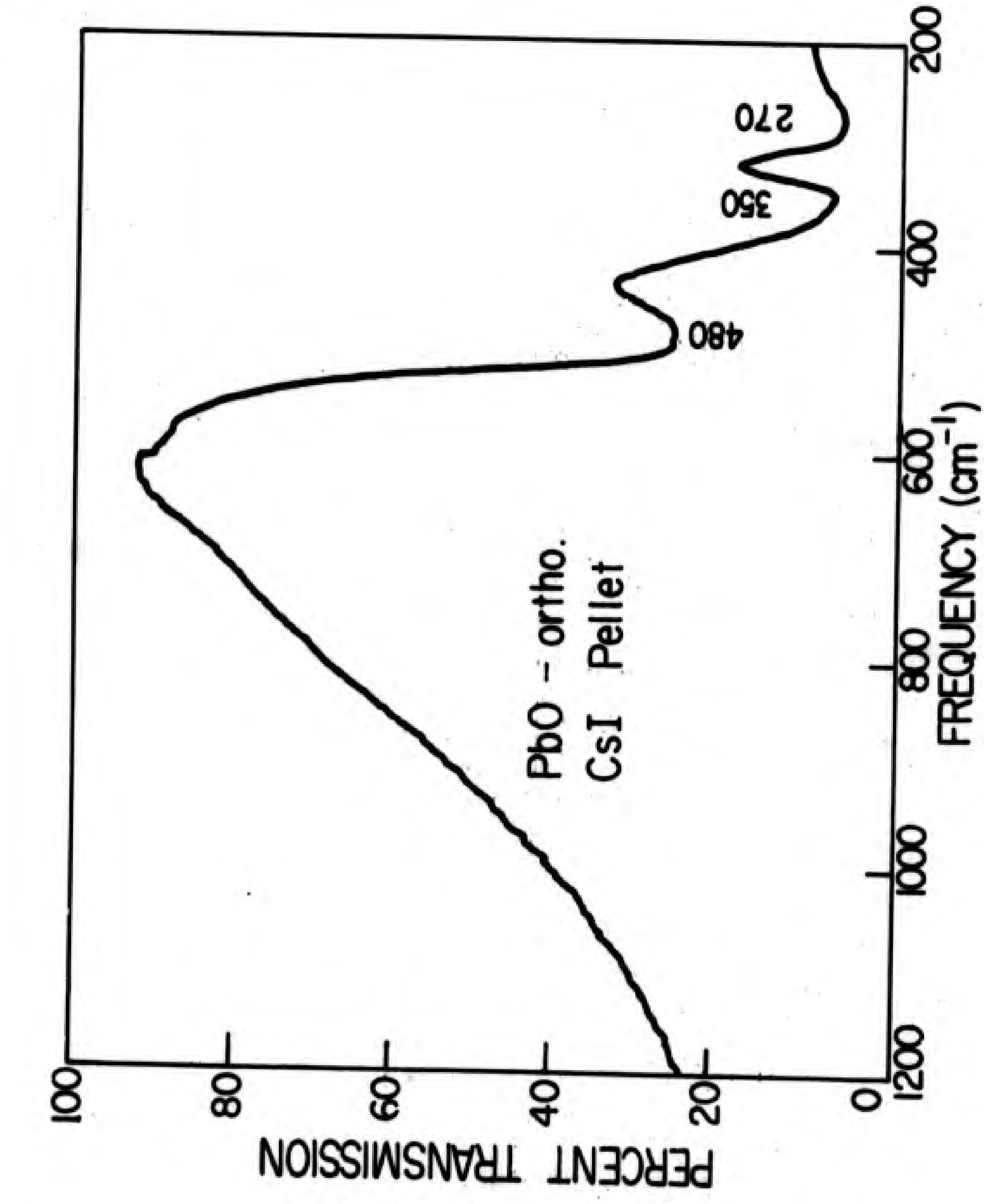

Fig. 5 Powder spectrum of orthorhombic PbO (massicot)

Spectra of Other Lead Compounds

Infrared spectra have been examined of some other heavy element lead compounds including $SrPbO_3$ and Sr_2PbO_4. $SrPbO_3$, although orthorhombically distorted, gives an infrared spectrum very similar to those known for other perovskites. $SrPb_2O_4$ is more interesting. It is the type compound for a structural family whose members include Cd_2PbO_4, Ca_2PbO_4, Cd_2SnO_4, Ca_2SnO_4, Ca_2SnO_4 and the high pressure form of Mn_2GeO_4. The space group is Pbam, D_{2h}^9, with 2 Sr_2PbO_4 per unit cell. The site occupations of the ions are

Ion	Equipoint	Symmetry
Sr^{++}	4(h)	C_s
Pb^{4+}	2(a)	C_{2h}
O^{-2}	4(h)	C_s
O^{-2}	4(g)	C_s

This leads to the invariance conditions given in table 6 and the normal modes and selection rules shown in table 7.

The infrared spectrum of Sr_2PbO_4 obtained in a CsI pellet is shown in figure 6. Of greatest interest is the 515 cm^{-1} high frequency band. It is very sharp, which usually indicates highly covalent bonding, even in the spectrum of pressed powder. The absorption cut-off is almost as low as the lead oxides. This is somewhat unusual, since the lead ion is tetravalent, which would normally indicate a strong force constant and thus a high-frequency vibration.

Table 6

Invariance conditions for Sr_2PbO_4

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
C_s	E	-	-	-	-	σ_h	-	-
4Sr	4	0	0	0	0	4	0	0
C_{2h}	E	C_2	-	-	i	σ_h	-	-
2Pb	2	2	0	0	2	2	0	0
C_s	E	-	-	-	-	σ_h	-	-
4 O_1	4	0	0	0	0	4	0	0
C_s	E	-	-	-	-	σ_h	-	-
4 O_2	4	0	0	0	0	4	0	0
Total w_r	14	2	0	0	2	14	0	0
XR	42	-2	0	0	-6	14	0	0

Table 7

Normal modes and selection rules for Sr_2PbO_4

D_{2h}	Total modes	Acoustic	Vibrations	Selection rules
A_g	6	-	6	Raman
B_{1g}	6	-	6	Raman
B_{2g}	3	-	3	Raman
B_{3g}	3	-	3	Raman
A_u	4	-	4	-
B_{1u}	4	z	3	IR, E || c
B_{2u}	8	y	7	IR, E || b
B_{3u}	8	x	7	IR, E || a

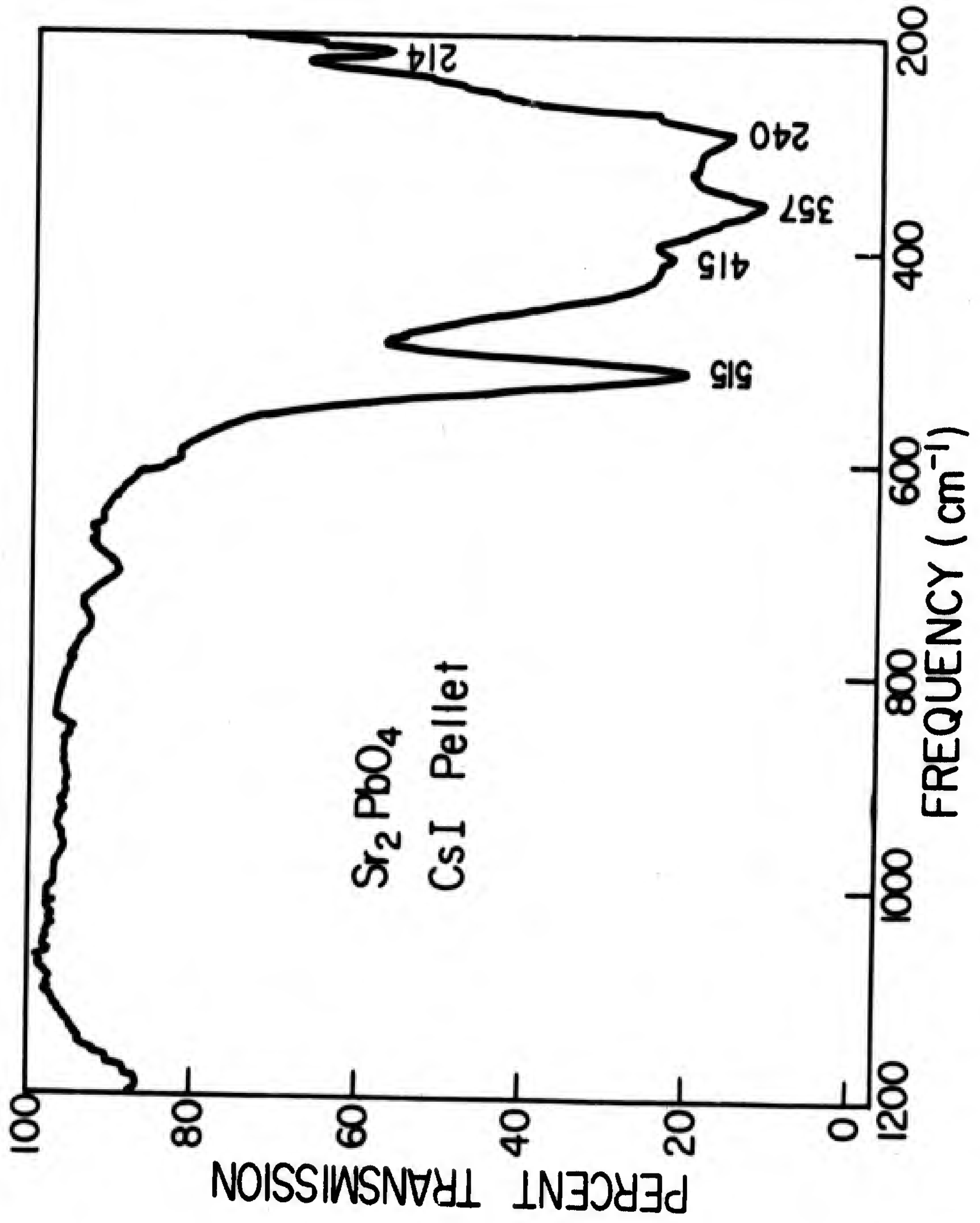

Fig. 6 Spectrum of powdered Sr_2PbO_4

V. GUIDELINES FOR THE SELECTION OF INFRARED TRANSMITTING MATERIALS

Although data on infrared vibrational frequencies, longitudinal mode frequencies, and infrared cut-offs are plentiful, few attempts have been made to relate these numbers to other crystallographic or crystal chemical properties of the materials. A small portion of the present effort is in this direction. During the first six months, the effort has been mainly in stock-piling new and more reliable data from the literature. This is a necessary task before any analysis can be attempted.

Relation of Vibrational Frequency to Structure

It has long been known that there is a general inverse relationship between the highest frequency transverse optic mode [presumably with mainly stretching character] and coordination number. More detailed relations of the vibrational frequency with interatomic distances and bond type are less well known. Many of the attempts at finding such correlations were based on spectra measured on powders. Some materials give reliable frequencies measured by powder methods, and some are inaccurate in treacherous ways. [See the comments by Axe and Pettit (1966) on this point.] During the past perhaps four years, many precise mode frequencies measured on single crystals have been published. These data are gradually being assembled and the relationships with crystal chemical parameters will be tested.

Relation of Absorption Cut-off to Vibrational Frequency

As can be seen from the data on ThO_2 at the beginning of this report, low transverse mode frequencies may be a poor guide to long wavelength transmitting materials. Several "rules-of-thumb" such as νcut-off = 2 ν_{LO} exist. These and other possible relationships will be tested with the accumulated collection of highly selected data.

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13. ABSTRACT

This report deals with the infrared transmitting properties of fluorite structure oxides and the heavy metal covalent oxides of bismuth and lead. Transmission data for single crystal ThO_2 are given. A theoretical analysis of the vibrational modes, selection rules and IR spectra of the powders are given for alpha-Bi_2O_3, $PbO \cdot 6Bi_2O_3$, tetragonal PbO, orthorhombic PbO, and Sr_2PbO_4. ( )

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
IR transmitting materials						
Bi_2O_3						
Lead oxides						
Thorium oxide						
Infrared windows						