

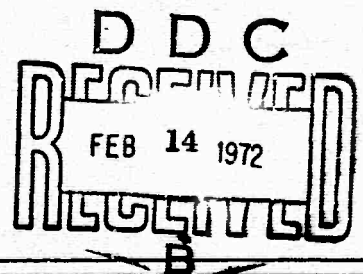
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TECHNICAL SUMMARY REPORT
TO
ADVANCED RESEARCH PROJECTS AGENCY
ON
MATERIALS PREPARATION AND CHARACTERIZATION RESEARCH

For the Period 1 July 1971 to 31 December 1971

Contract No. DA-49-083 OSA 3140, Amendment No. P00004

ARPA Order No. 338/6



THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

UNIVERSITY PARK, PENNSYLVANIA

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Part 1: INTRODUCTION

1.1 FORMAT

This semi-annual report reports briefly the work supported under the ARPA contract dealing with "Materials Preparation and Characterization Research". The Annual Report of the Laboratory issued at the end of the fiscal year reports the results obtained in this ARPA supported work as well as all other research on materials carried out by the faculty of the Materials Research Laboratory. The scope of this report is therefore considerably narrower than that of the Annual Report, while at the same time it generally contains more detail than the latter.

In a major departure from previous years, the research reported here represents a much more task-oriented study in three defined areas. The principal rationale underlying all three major areas is the theme that the chemical side of materials science has reached a maturity where it is increasingly within the reach of the laboratory to tailormake materials with designed properties.

Parts 2, 3 and 4 summarize the results of research in the areas of new transducer and detector materials, ferroelectric and ferroelastic materials, real surface manipulation and glass surface coatings.

1.2 SUMMARY OF HIGHLIGHTS

During this past half year the cast of our research has been very substantially altered. Whereas for the past decade we have been concerned with the development of the science of the preparation and characterization of wide band gap materials, often pursuing the applications which beckoned on the basis of our new results, we are now more tightly coupled to a set of defined objectives or target materials. While the change is not a major

one, there is a re-orientation period as one mode takes over from another.

In this change the 'preparation' side of our research has undergone somewhat less of a change than the characterization. We now have a substantially diminished effort in the latter. Some of the work in progress was being wound up and is reported in this report, but apart from that, the research in structural and compositional characterization such as development of new instruments with new capabilities or sensitivities precision, is now greatly reduced. In the preparation - synthesis and crystal growth area - the new contract entails a focusing of the effort into selected material groups of special importance with no change in level of effort. However, we have branched out our preparation work into two wholly areas and our rationale and progress deserves special comment.

1.2.1 Tailormade Organic Crystalline Materials.

For two decades the principal investigator has developed a school and research group of high temperature crystal chemistry of inorganic materials. This "science" has now reached the maturity, that it is reasonable to demand that if we seek a particular property in a material we can proceed along the sequence.

Desired PROPERTY	via known principles relating to structure	→	Desired STRUCTURE	via empirical crystal chemical rules	→	Desired COMPOSITION
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In recent years as many organic materials have become prominent in electronic devices, there is clearly a need to establish a similar link in the organic world. We are confronted here with an amazing total blank on previous studies of systematic organic crystal chemistry. The difference can be very simply put: We can predict with good accuracy what will happen to structure if we substitute K^+ for Na^+ or Ge^{4+} for Si^{4+} in any given phase.

But there are absolutely no data to help us say what happens when an ethyl group is substituted for a methyl, or NO_2 for OH etc., etc. Our new venture here which will provide some insight on this general problem is tied to very specific useful materials chiefly triglycine sulfate, an important ferroelectric and lithium thallium tartrate. Here by understanding the principles of substitution we may well be able to control and improve these detector and transducer properties.

1.2.2 Coatings for Non-Metallics.

We have been studying the 'Real Surfaces' of materials by a multi-technique approach for some years. It has been clear that in the oxygen + water ambient of spaceship earth a very large number of properties - especially electrical and mechanical - are determined by the properties of this unintended oxide "coating". We have long advocated a study of surfaces with controlled coatings and hence in the redirection of our work we have initiated a new effort in the preparation of controlled coatings for non-metallic materials by a variety of methods. Here sputtering and CVD look like the obvious candidates but we are not lacking in exclusively on these as yet, but rather looking at some rather different methods such as high temperature high pressure reactions.

In both these new areas progress has been reasonably good, with a few specially interesting results appearing. However, it is too early to place too much weight on these.

1.3 DISSEMINATION OF RESULTS

A significant number of publications describing research supported by this contract over the last several years have appeared or went to press during the last half year. These are listed below.

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- Jindal, G. R., J. W. Faust, Jr. Materials Problems in Lithium-Drifted Germanium Radiation Detectors - II. *J. Appl. Phys.* 42, 2508 (1971).
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- Liaw, H. M., J. W. Faust, Jr. Growth Kinetics of Lead Dendrites Grown in Gels. *J. Cryst. Growth* 13-14, 471 (1972) (in press).
- McCarthy, G. J., R. Roy. Gel Route to Homogeneous Glass Preparation: II, Gelling and Desiccation. *J. Am. Ceram. Soc.* 54, 639 (1971).

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Part 2: NEW TRANSDUCER AND DETECTOR MATERIALS

Most available infrared detector materials operate through photoconductivity activated across a narrow band gap. Such materials require cryogenic cooling. Triglycine sulfate is one of the first materials to show promise as a broad band pyroelectric detector and does not require cooling. It does, however, require a high degree of crystal perfection for operation at or near the thermodynamic limit; a perfection that has not yet been achieved. Our research on organic detector materials, therefore, has been of two kinds. We have sought to improve the physical properties of TGS, and other transducer materials such as lithium thallium tartrate through habit modification and improved perfection. This is done by using novel growth techniques such as non-aqueous solvents under hydrothermal or epithermal conditions. The second approach is to improve the materials themselves through systematic modification of the crystal structure. This route has lead us into the unexplored territory of organic crystal chemistry and the preparation of analog compounds to TGS and LTT.

2.1 ORGANIC PYROELECTRIC DETECTOR MATERIALS ANALOGOUS TO TRIGLYCINE SULFATE

(Susan J. Countess and W. B. White)

This project involves attempts to synthesize compounds similar to TGS. It is thought that these analogs might have similar electrical properties to TGS, and that from this work might come a systematic approach to predicting the structure and properties of such organic compounds.

The problem of preparing analogs of TGS was attacked on two fronts: first, by trying to replace the inorganic sulfate group with similar inorganic anions and, second, by trying to replace the organic glycine moiety with

other amino acid molecules. Products were analyzed using x-ray powder diffraction, IR, and simple chemical means.

2.1.1 The Inorganic Groups.

The basic method that produces TGS was used; that is, reacting 3 moles of glycine in aqueous solution with 1 mole of the acid or anion involved. Reacting α -glycine with phosphoric acid gave γ -glycine. However, with $(\text{NH}_4)_2\text{HPO}_4$ and H_3PO_4 a product formed that had a positive qualitative test for PO_4^{3-} . The electrical properties of this compound are now being investigated. The γ -glycine was also submitted for evaluation, since the literature indicates that it is highly piezoelectric. Reacting glycine with phospho-tungstic acid produced the compound triglycine phosphotungstate $(\text{CH}_2\text{NH}_2\text{COOH})_3\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4] \cdot 5\text{H}_2\text{O}$, which proved to be centric and therefore uninteresting. There was no reaction between glycine and boric acid or between glycine and chromate. The anions VO_4^{3-} , MoO_4^{2-} , WO_4^{2-} , or MnO_4^{2-} were not tried, because they (as well as CrO_4^{2-}) exist only in basic solution in which the amino acid is itself in its anionic form. An attempt to react alanine and phosphoric acid by the TGS-like method also failed.

2.1.2 The Organic Groups.

The amino acids used to substitute for glycine in TGS were as follows: dl-alanine ($\text{CH}_3\text{CHNH}_2\text{COOH}$), dl-serine ($\text{HOCH}_2\text{CHNH}_2\text{COOH}$), l-valine [$(\text{CH}_3)_2\text{CHCHNH}_2\text{COOH}$], l-asparagine ($\text{NH}_2\text{COCH}_2\text{CHNH}_2\text{COOH}$), l-cystine ($\text{HOOCNH}_2\text{CHCH}_2\text{SSCH}_2\text{CHNH}_2\text{COOH}$), l-glutamic acid ($\text{HOOCCH}_2\text{CH}_2\text{CHNH}_2\text{COOH}$), dl-leucine [$(\text{CH}_3)_2\text{CHCH}_2\text{CHNH}_2\text{COOH}$], and l-tyrosine $\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2\text{CHNH}_2\text{COOH}$. These are chosen because they contain a representative sample of the organic functional groups and molecular weights of the amino acids.

Reactions analogous to that which form TGS were carried out with each of these amino acids. Only the dl-serine and l-valine react to form crystalline products. These products proved qualitatively to contain SO_4^{2-} and are being evaluated.

It was reported that serine forms a potassium sulfate salt when dissolved in 98% sulfuric acid at -6°C . All of the amino acids were dissolved in 98% H_2SO_4 and were cooled first in an ice/salt bath to -5°C , and then in dry ice. Crystalline products formed from both the leucine and the tyrosine mixtures. No progress has been made in drying these products. Both seem to be indefinitely soluble in water. Evaporation of the solvent under reduced pressure resulted in decomposition of the product. The tyrosine product may be a sulfonate of the phenolic group of the tyrosine and not a sulfate salt.

Studies on the possible dependency of the TGS-like reactions on pH were begun using Na_2SO_4 and NaHSO_4 to provide both the proper concentration of SO_4^{2-} and different pH values. The mixtures using Na_2SO_4 all had pH values around 6 and gave no products. The NaHSO_4 mixtures also gave negative results and had pH values around 2.7.

A paper on TGS doped with alanine [P. J. Lock, Appl. Phys. Lett. 19, 390 (1971)] led to an attempt to duplicate Lock's results. A reaction using 2 moles of glycine, 1 mole of dl-alanine, and 1 mole of H_2SO_4 gave a product that had an x-ray powder diffraction pattern analogous to TGS, as expected. This product is being studied further and also evaluated electrically.

2.2 ELECTRONIC DETECTOR MATERIALS BASED ON CdF_2

(M. P. O'Horo and W. B. White)

Trivalent doped CdF_2 , after appropriate chemical heat treatment, possesses unusual and apparently unique electrical and optical properties for such

a large band gap ionic material. Normally trivalent doped CdF_2 is a transparent insulator. However, after heat treatment it is a deeply colored semiconductor with a large absorption peak in the near IR. In order to clarify the crystal chemical basis for CdF_2 properties, various substituted crystals are being studied. CdF_2 crystals with various amounts of YF_3 , GdF_3 , HoF_3 , and InF_3 have been grown and are now being investigated to determine dependence of the electrical and optical properties on trivalent dopant concentration. Doped solid solution crystals of CdF_2 with ZnF_2 and PbF_2 are also being grown and studied, the phase diagrams for these binary systems having first been determined.

The growth of good quality single crystals suitable for physical properties measurements (especially solid solution crystals) is substantially impeded by oxide contamination. Oxide contamination is present in the starting material in varying degrees due to the nature of the material and methods of preparation. When present in sufficient amounts, the melts attack the graphite crucible during growth, resulting in graphite inclusions and in the doped crystals an uncontrolled conversion to the semiconducting state. In order to sufficiently eliminate oxide contamination and grow well characterized crystals, it was found necessary to heat all the various fluoride starting material in flowing HF gas for long periods of time. Conversion of the doped crystals is found to be a reversible process, whereby the semiconducting crystal can be completely returned to the transparent insulating state by heating the sample in a running vacuum. The temperature of the sample and not the metal vapor pressure is found to be the controlling factor in the conversion process, since above 300°C fluorine vacancy formation at the surface becomes important and diffuses into the interior of the crystal. Below 0.1 m% trivalent dopant the number of optically or thermally excited electrons follow the concentration of dopant. However, above 0.1% this is no longer true. The number of electrons between

0.1 and 1 m% is approximately constant then decreases drastically, so that above 2 m% conversion no longer occurs. Crystal field splitting of Ho^{3+} absorption spectra indicates that up to 0.1 m% the trivalent dopant is in cubic coordination, whereas above 1 m% cubic and tetragonal coordination is indicated. The electrical and optical properties of the Y, Gd, and Ho crystals show the same concentration dependence independent of dopant, whereas the In-doped crystals show significant departures in their behavior. Preliminary fluorescence and Raman scattering results show as yet unexplained changes in properties above 0.1% dopant and distinctive behavior in the In-doped samples. Work is continuing on the doped solid solution crystals of $\text{CdF}_2\text{:ZnF}_2$, PbF_2 .

Part 3: FERROELECTRIC AND FERROELASTIC MATERIALS FOR INFORMATION STORAGE AND RADIATION DETECTION

In the new areas of optical communications, optical information storage, processing and display and in integrated optics, it is clear that 'ferroic' crystals which offer a range of tailored electro-elasto-magneto-optic interactions will play a major role in future development. For optical information storage and display it has been shown that ferroelectric crystals with optically distinct domain states offer significant advantages in speed, and versatility over competing liquid crystal and thermo-magnetic systems.

Our object in this research has been to produce single crystals of one of the most promising storage media, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and to grow crystals of a new ferroelectric $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ for exploratory study.

Single crystal $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has the unique combination of ferroelectric and electro-optic properties which make it highly attractive for a number of optical storage, switching and display devices. With relatively simple photoconductor and direct electron writing address schemes, Cummins at Wright-Patterson AFB has shown resolution in the stored domain image of ~ 120 line pairs/mm. Switching at TV line frequencies appears to be practicable. A number of papers related to both direct and holographic storage of information in single crystal and thin films of bismuth titanate presented at the 1971 Symposium on the Applications of ferroelectrics attest to the importance of this material. A major stumbling block to further development work, however, is the lack of availability of high quality single crystals of reasonable surface area.

The mica-line morphology of bismuth titanate and its relative dielectric permittivity of $\epsilon_c = 140$ suggest that this material should have a

high electric breakdown strength and should be useful as an energy storage medium. Unfortunately, in pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ high electric fields lead to electrochemical degradation. Recent studies have shown, however, that this can be inhibited by the substitution of lanthanum to form solid solutions $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$. In this system, breakdown strengths up to 1.2 MV/cm have been measured on single crystals.

Lead germanate, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, is potentially of high importance; the ferroelectric species which we have shown to be $\bar{6}(1)\text{D}\bar{3}\text{F}3$ is distinguished by having only two possible domain states ($\pm P_c$) along the six-fold alternating axis. In the polar 3 symmetry, the domain has optical rotatory power, and changes hand on inversion of P_c . Since the domain wall is not strongly constrained to specific directions, limited area switching is possible, and a white light interrogation of the switched states yields patterns of high contrast.

We have demonstrated switching by extensive sideways motions of domain walls in this system, and together with optical evidence that the wall is rather broad it is probable that a wide range of domain control devices will become possible in this material.

3.1 BISMUTH TITANATE CRYSTAL GROWTH

The progress on bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) crystal growth research is briefly summarized in four sections: (a) phase equilibria, (b) compatibility tests, (c) flux crystal growth, and (d) sputtering. In spite of the considerable effort expended the last several years in growing bismuth titanate crystals from compositions in the Bi_2O_3 - TiO_2 system, the temperature-composition phase diagram of this important system is not accurately known. This fact lead to investigations of the phase equilibria in this pseudo-binary system. Platinum is the only container reported to have

been used in all previous flux growth studies on bismuth titanate, and even platinum is slowly attacked by the bismuth oxide-rich flux. Two possible container materials not previously tried were tested for possible use as an alternative to platinum. Flux experiments are planned to produce Pt free crystals for comparison purposes, and a flux furnace has been rebuilt to facilitate removal of molten flux from the crystals and for more accurate temperature profile measurements. The equipment modifications needed for the sputtering experiments will be installed shortly.

3. 1. 1 Phase Equilibria (R. L. Mohler and W. B. White).

Several discrepancies are present in the literature concerning the number of compounds that exist in the Bi_2O_3 - TiO_2 pseudo-binary system. Information about melting behavior and temperature, and liquidus curve data are also uncertain or lacking. Because of this, the phase equilibria in the Bi_2O_3 - TiO_2 system is being investigated, with particular emphasis being placed on the region of the diagram used in the growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystals from bismuth oxide-rich fluxes.

Various compositions were prepared and the samples annealed at constant temperatures below those needed to produce a liquid phase. The samples were then quenched from the annealing temperatures and examined by optical microscopy, x-ray diffraction, and differential thermal analysis techniques. X-ray diffraction data, however, have not been published for most of the reported compounds in this system.

Preliminary results indicate that some of the reported compounds with compositions rich in Bi_2O_3 may not exist, at least at temperatures above 700°C . The use of DTA methods has shown that some of the transition temperatures and solidus temperatures shown on the published phase diagram may be in error by as much as 20°C .

3.1.2 Compatibility Tests (D. Tiche and K. E. Spear).

The compatibility of liquid bismuth oxide with both BeO and ThO₂ has been examined to determine if either of these oxides would be suitable as a container material in the growth of Bi₄Ti₃O₁₂ from a bismuth oxide rich melt.

A piece of a BeO crystal was suspended with a platinum wire into a platinum crucible containing molten bismuth oxide. After heating at about 1300°C for several hours, the system was allowed to cool to 900°C and the Pt wire holding the sample was removed from the liquid oxide. The BeO completely dissolved in this experiment.

A sample of an impervious ThO₂ plate was suspended by a Pt wire in a similar experiment, and heated in molten bismuth oxide at 1100°C for 4 hours. The sample was removed from the molten oxide, and examined under a microscope. The bismuth oxide had not visually attacked the ThO₂ sample.

The bismuth oxide used in the ThO₂ experiment was leached from the crucible and examined for radioactivity with a detector system employing a thallium-doped sodium iodide scintillation crystal. The activity of the leached acid was not above that of the background. Because of the low activity and the fact that the ThO₂ sample did not appear etched, no attempts were made to quantitatively determine the amount of thorium dissolved in the bismuth oxide.

3.1.3 Flux Crystal Growth (D. Tiche and K. E. Spear).

Equipment is almost assembled for two types of crystal growth experiments involving a bismuth oxide-rich flux system. The first is a simple experiment to grow small bismuth titanate crystals out of a ThO₂ crucible using a ThO₂ rod as a cold finger and as a means of pulling the crystals out

of the molten flux. The ferroelectric behavior of these crystals will be compared with that of crystals grown from platinum crucibles to determine if dissolved Pt or ThO_2 has a measurable effect on the properties of bismuth oxide.

In the second type of experiment, an existing flux furnace with a four-inch diameter working region and temperature control to better than 1°C was rebuilt and equipped with a counter-weighted pulley-mechanism that allows one to raise and lower the furnace while the crystal growing crucible assembly remains stationary. The crystals grown in this system will be separated from the molten flux by raising the furnace off the hot crucible, the flux poured off, and the furnace lowered back onto the crucible so that the crystals can be annealed. This system will also provide an easier mechanism for accurate temperature measurements during an experiment.

3.1.4 Sputtering Experiments (R. Messier and R. Roy).

Preliminary tests have shown that high substrate temperatures are needed to produce good single crystal films. A new sputtering system with a substrate heater capable of 700°C is being ordered and will be in use within several weeks.

3.2 CRYSTAL CHEMISTRY OF THE FERROELECTRIC BISMUTH TITANATE FAMILY*

(R. E. Newnham, R. W. Wolfe and R. A. Armstrong)

More than fifty ferroelectrics belong to the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ family, and all consist of Bi_2O_2 layers interleaved with perovskite-like $\text{M}_{n-1}\text{R}_n\text{O}_{3n+1}$

*This work is partially sponsored by the Advanced Electronics Devices Branch, Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio.

layers. With the solution of the crystal structures of Bi_2WO_6 , $\text{Bi}_3\text{TiNbO}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ described in previous reports, a sound understanding of the structural basis of ferroelectricity in the family has been developed. It is generally found that compounds with an odd number of perovskite layers crystallize in B2cb and show one phase transition, while even-layered members prefer $\text{A2}_1\text{am}$ and show two phase transitions. Bi_2WO_6 ($n = 1$) is orthorhombic, space group B2cb; $\text{Bi}_3\text{TiNbO}_9$ ($n = 2$) orthorhombic, $\text{A2}_1\text{am}$; $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$) monoclinic, Pc, but very nearly orthorhombic, B2cb. Similar distortions occur in all three structures, with large rotational motions accompanying the polarization along a. Below the transition, a strong Bi-O bond is formed to the apex oxygen of the perovskite layer, tilting the octahedra and producing antiparallel shifts along b. Symmetry differences in the even- and odd-layered compounds can be explained by the type of strains produced in the perovskite layer. The octahedral cations (W, Ti, Nb) are the major contributors to the spontaneous polarization, moving about $0.4\text{\AA}$ toward an octahedral edge.

3.2.1 $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Ta}_2\text{O}_9$

Several interesting problems remain to be resolved in the characterization of these materials, one of which is a crystal structure analysis of the intermediate phase common to the even-layered compounds.

$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Ta}_2\text{O}_9$ is a two-layer member of the $\text{Bi}_4\text{Ti}_2\text{O}_{12}$ family, belonging to the $\text{SrBi}_2\text{Ta}_2\text{O}_9$ - $\text{BaBi}_2\text{Ta}_2\text{O}_9$ solid solution series. The composition $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Ta}_2\text{O}_9$ lies in or very near the intermediate phase region at room temperature. The determination of the structure of this solid solution has been undertaken utilizing single crystal x-ray and neutron powder diffraction data.

3.2. Bismuth Titanate Compounds with $n = 5$.

This work which has been recently initiated is concerned with extending the study of the bismuth titanate family to include those members with the greatest number of perovskite-like layers. These compounds have c parameters about $50\text{\AA}$. Preliminary crystal growth runs have indicated that the growth of the five-layered compounds may prove to be difficult, due in part to the large number of phases possible in a system. As a result of these runs, small single crystals of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ have been produced. The morphology of the crystals and the lattice distortion appear to differ from that usually found in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ family.

3.2.3 Bismuth Titanate Solid Solutions.

The ferroelectric and electro-optic properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are drastically altered by even minor chemical changes. In previous reports, the substitution limits for the following series were presented:

$\text{Bi}_4\text{Ti}_{3-x}\text{M}_x\text{O}_{12}$ ($\text{M} = \text{Sn}, \text{Hf}, \text{Zr}$), $\text{Bi}_{4-x}\text{R}_x\text{Ti}_3\text{O}_{12}$ ($\text{R} = \text{rare earths and Y}$),
 $\text{Bi}_{4-x}\text{R}_x\text{Ti}_{3-x}\text{M}_x\text{O}_{12}$ ($\text{R} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$; $\text{M} = \text{Nb}, \text{Ta}$).

The mismatch between the perovskite and bismuth oxide layers appears to be principally responsible for the observed limits. The size of the Bi_2O_2 layer can be estimated from various bismuth oxide structures, and a formula for the perovskite cell parameter was derived empirically from a survey of 60 oxides in the perovskite family. The cubic cell constant a is related to the ionic radii of the cubo-octahedral cation (r_A) and octahedral cation (r_B) by

$$a = 0.51 r_A + 1.33 r_B + 2.40. (\text{\AA})$$

Hard-sphere models based on ideal- and distorted-perovskite structures can be used to explain the coefficients in this equation. The equation is used to predict the cell dimension of the perovskite layer in the bismuth

titanate compounds, which is then compared with that of the Bi_2O_2 layer. The instability of compounds such as $\text{Bi}_4\text{Zr}_3\text{O}_{12}$ results from lattice mismatch since the perovskite layer is much too large. On the other hand, large substitutions for Bi in the perovskite layer are tolerated because of the insensitivity of lattice parameter to r_A .

Part 4: COATINGS: MANIPULATION AND CHARACTERIZATION OF REAL SURFACES

The potential in technology - of manipulating a surface to give a desired surface - is almost as great as in preparing new materials. Indeed if we consider the potential of improving existing materials, controlled coatings may offer some of the highest benefit/cost ratios in materials research.

Our efforts are concentrated in the most neglected area - the coating of oxides and other non-metallics including glasses.

4.1 PREPARATION OF COATINGS

4.1.1 Deposition of High Oxidation State and Hard Coatings by Sputtering (R. Messier, A. Gallagher and R. Roy).

In the course of the characterization of variable valence transition metal oxide films prepared by sputtering, it was noticed that there were differences in some films even though they all had an x-ray diffraction pattern of the highest valence oxide. These differences were in color (NiO films), lattice spacings (NiO and V_2O_5 films), and IR and visible transmission spectra (NiO, V_2O_5 , TiO_2 , Fe_2O_3 films) notably. It is presently believed that these differences are due to variations in either stoichiometry or stress in the films. Tests are under way to determine the exact cause of these variations.

To date, films (0.1 to 1μ thick) of V_2O_5 , Fe_2O_3 , NiO and TiO_2 have been successfully deposited onto glass, fused silica, quartz, α -alumina, spinel, silicon, and rutile substrates by rf-sputtering from the various metal oxides powders which are hot pressed into sputtering targets. In every case we have obtained highly adherent films which have shown no aging effects

over at least a six month period. In all cases the films were polycrystalline, except TiO_2 (non-crystalline).

SiC and carbon films have been deposited with preliminary x-ray results showing both materials being non-crystalline over a wide range of sputtering conditions. Tests are being performed on their hardness and chemical inertness.

4. 1. 2 New Glass Coating Processes and Materials.

The purpose of this research is to explore novel methods of preparing coated glass. Coatings are one of the best methods of maintaining the high strength and increasing the durability of freshly prepared or "acid fortified" glass. The desirable properties to be sought in these glass coatings are adherence, resistance to corrosive ambients, uniform dense coverage, hydrophobicity (the ability to repel water) and increased strength when compared to uncoated glass with an identical heat treatment. Results from the research on the three new coating processes or materials initiated in the last six months are summarized below.

(a) Impregnation of the glass surface with organic molecules (S. P. Faile, G. J. McCarthy and R. Roy). Silica, soda lime silica and boro silicate glass rods were treated with various alcohols and other organics in stellite cold seal pressure vessels generally in the temperature range of 300°C to 500°C and at pressures up to two kilobars. After the treatments, the glasses were examined for changes in surface properties and adherence of the coating.

The alcohols which are of interest range from methanol to tetradecanol. Treatments with these often alter the glass surface as indicated by greater lubricity, resistance to wetting (hydrophobic properties), and increased resistance to breakage during bending tests of the glass rods. In-

frared spectra, electron probe, ellipsometry and mass spectrometry studies are being or will be used for characterization of the glass surface and identification of the actual organic species which cause the property changes. Treatments of the glass surface have also been started using those likely breakdown products of the alcohols such as the alkenes, ketones, and H_2O which may polymerize and form complexes that react with the glass surface. Several other organics (alkanes, catechol, 3-amino-1-propanal, and glycerol) have been investigated but so far have not produced the properties of lubricity, and the hydrophobic characteristics associated with the increased resistance to breakage found for the alcohol treated glasses.

Etched borosilicate glass, when treated with several mixtures of the long and short chain alcohols, such as a mix of 2-propanal and decyl alcohol, showed a 3-fold increase in strength when compared to a reference glass subjected to a similar thermal history. Treatments of the borosilicate and silica glass rods with many of the alcohols routinely produces rods that are 50% stronger than the reference glasses.

The surface properties resulting from an alcohol treatment are not destroyed by a Co^{60} dose of 10^8 rads or by an immersion of the glass rods in NH_4OH . The surface properties, however, are rapidly destroyed by immersion of the glass in many types of acid and by heating above $300^\circ C$ in an argon atmosphere. Excessively long alcohol treatments can also destroy the surface properties since a large proportion of the alcohol dehydrates and thereby increases the H_2O concentration to such an extent that the steam reacts with the glass and penetrates the glass to depths exceeding a couple of microns.

(b) Coatings from microwave excitation of organic molecules (R. Shaw, S. P. Faile, G. J. McCarthy and R. Roy). We know from recent

work on chemically excited luminescence that the excess energy stored in electronic levels can, in certain cases, be transferred to the lattice ions. If processes such as these can lead to the conversion of thermal energy locally, we may be able to develop a wholly new way to form adherent coatings. Dense adherent coatings of several forms of carbon can be prepared from cracking of simple hydrocarbon over the approximate temperature range 1400° to 2200°C. However, these temperatures are many hundreds of degrees above the softening points of common glasses. What we are attempting to do is to produce these coatings from simple hydrocarbons in the 300-600°C range appropriate to glass systems with the extra energy being supplied by microwave excitation of the hydrocarbon plasmas. The plasma is produced using a McCarroll Microwave cavity operating at 12.2 cm and 60-90 watts on flowing gas at 6-12 torr. pressures.

Preliminary experiments using methane and acetelene have been encouraging. Visible darkening of borosilicate glass is produced after 5-20 minutes of treatment at 300-500°C. No tests have yet been performed on these glasses. Other hydrocarbon gases are now being investigated.

(c) R. F. sputtering of coatings. With this technique, glass can be given a coating of virtually any solid material while the bulk of the glass is maintained at or near room temperature. The high energy and therefore the high effective temperature of the sputtered species gives the adherence of the coatings. This work is presently in progress utilizing SiC, TiO₂, and Al₂O₃ as coating materials. It will be expanded to include other materials which would be expected to impart strength, hydrophobicity, chemical resistance, and other desirable properties to glass.

4.1.3 Radiation Protection of Glasses by Surface Impregnated Hydrogen (R. DiSalvo, L. N. Mulay and D. M. Roy).

A study has been underway to determine the role played by interstitial

hydrogen near the surface of glass in prevention of radiation damage in basic oxide glass. The "damage" under consideration is the formation of color centers in the glass upon exposure to 1.27 MeV gamma radiation from the University's Co^{60} source.

Boric oxide glass rods are drawn from an 1100°C melt. It is then possible to control to some extent the impregnation of these rods with hydrogen gas by proper control of temperature and pressure in cold seal bombs. The various rods are then subjected to gamma radiation on the order of 10^7 rads, which has been shown to be a dose which will saturate the untreated rod with color centers.

The characterization techniques being employed in the study are primarily magnetic. An electron paramagnetic resonance spectrometer has been calibrated with standard solutions of the free radical DPPH and used to estimate the concentration of color centers (i. e. unpaired electrons trapped at defect sites). Saturation concentration is on the order of 10^{17} free spins/cc. Decay curves have been obtained which indicate the recombination of these color centers as a function of time.

At the same time magnetic susceptibility studies at room temperature using the Faraday technique are being employed. Thus far this method has been unable to detect any differences in irradiated and non-irradiated glasses due to the relatively small concentration of free spins produced, but it is felt that temperature dependence studies may yield better results.

In addition to this, preliminary broadline NMR studies are being performed by Varian Associates on a series of samples. Both H^1 and B^{11} resonances are being observed in attempts to study local symmetry conditions. It is hoped that this combination of magnetic techniques will result in a synergistic relationship.

This work is being continued. In addition, attempts will be made to study conditions at radiation doses, below and well above the saturation dose on glasses of varying composition in order to obtain more quantitative information. The Co^{60} facility is currently being modified to increase its output to approximately 10^8 R/hr. Temperature dependence studies promise to be informative in yielding activation energies for the recombination hydrogen reaction processes. Also more information is to be obtained, from the hyperfine structure of the EPR spectra.

4.2 CHARACTERIZATION OF REAL SURFACES

4.2.1 Characterization of Real Surfaces by Ellipsometry (K. Vedam, M. Malin and E. W. White).

The ellipsometric measurements on single-crystal silicon surfaces subjected to various surface treatments such as mechanical polishing, chemical etching, sputtering by argon ions, cleavage, and annealing have been completed. Because of the consistency and reproducibility of the results on chemically etched silicon samples by other workers as well as our own, these results are believed to be truly representative of the bulk sample of silicon without any damaged surface layer even though there is always a thin oxide film present on the surface of the sample. Ellipsometric measurements on both mechanically polished and argon ion bombarded surfaces have shown considerable increase in the values of the ellipsometric parameter ψ and the pseudo-normal reflectance $\bar{R}$ as compared with those of the etched samples. This is obviously caused by the presence of the damaged surface layers on these samples. It is observed that the variation in ψ between different cleaved samples is much larger than the possible experimental errors. This discrepancy has been attributed to the presence of dislocations on or near the cleaved surfaces created in the process of cleavage. These fresh disloca-

tions can be taken into account by an effective average value of the refractive index of silicon or, more meaningfully, by an effective thin damaged surface layer with different optical parameters, on the bulk silicon. The annealing of cleaved silicon samples at high temperatures and ellipsometric measurements on such annealed samples show that the fresh dislocations introduced in the sample during cleavage can be removed by annealing. These studies reveal that ellipsometry provides another means of detecting surface defects and yields information concerning the optical properties and average film thickness of the damaged surface layer as well as those of the film and the substrate.

Currently, a combined ellipsometer and oxygen x-ray spectrometer system is under construction for simultaneous studies of oxide film formation under carefully controlled conditions of PH_2O and PO_2 .

4.2.2 Characterization of Real Surfaces by Laser Mass Spectrometry (B. E. Knox).

The laser mass spectrometer is a powerful tool for chemical analysis of solid materials. In some cases structural analysis can also be done with this instrument. Because this instrument is relatively new in the field of materials characterization, its full potential has not yet been realized. The principal objectives of this project are to determine the effectiveness and possible special capabilities of the laser mass spectrometer as a surface analysis tool and microprobe. Of special interest are some of the oxide surfaces which have been studied by soft x-ray spectroscopy and ellipsometry.

There has been a continuous effort to further the understanding of the laser-solid interactions occurring, including both possible condensed phase and plasma reactions. A study of the alkali halide system is nearly complete. This was undertaken to help elucidate the nature of the process(es)

responsible for ionization of the laser-produced vapor species. This study has shown that ion-molecule reactions are more prevalent than expected. These are of the types: $M^+ + MX = M_2X^+$; $M^+ + M_2X_2 = M_3X_2^+$; $M^+ + M_3X_3 = M_4X_3^+$; etc. All of these reactions have been demonstrated to occur in the plasma and not in the condensed phase.

Preliminary studies of pure germanium have pointed to the importance of an oxide surface in the vaporization process. Oxide species, such as GeO , GeO_2 , are important components of the vapor over laser-impacted germanium. Large polymeric structures of germanium also exist in the plasma, as do ion-molecule produced $GeOK^+$, GeO_2K^+ , etc.

The importance of the oxide surface layer is also being studied with various types of silicon surfaces. Preliminary results show the same kind of behavior as in the case of germanium.

4.2.3 Measurement of Residual Strain and Microstructure.

(a) Residual strain in refractory materials by Raman spectroscopy (V. G. Keramidas and W. B. White). The objective of this study was to determine whether Raman spectroscopy could be used as an adequate tool in deducing the strain rate of refractory materials.

The hot pressing of commonly used refractories introduces strain induced deformations to their lattices. Such deformations, if large enough, may result in changes of the selection rules of the vibrational behavior of the solids. These changes will in turn manifest themselves in the Raman spectrum of the material by the appearance of forbidden modes, the removal of the existing degeneracy in allowed modes and the resulting splitting of peaks, the shift of vibrational frequencies or the change of linewidth. Representative structures of the most widely used refractory materials were studied. Hot pressed pellets of ThO_3 , $\alpha-Al_2O_3$ (corundum) and TiO_2

(rutile) were investigated. First the single crystal Raman data were obtained at both room temperature and liquid nitrogen temperature, where the signal to noise ratio was substantially improved. They were used as reference. Then the Raman spectra of hot pressed pellets were obtained again at room and liquid nitrogen temperature.

An analysis of the obtained results showed that the residual strain induced lattice deformations, if any, are not substantially large to manifest themselves in changes of the Raman spectrum.

(b) Residual strain by x-ray techniques (C. W. Gregg and H. A. McKinstry). The current phase of this research is essentially complete. During the course of this work micro-strains and x-ray coherent domain sizes were measured in three different materials. A method was developed for the separation of overlapping peaks which arise from different sets of reflecting planes. The measured micro-strains in lanthanum doped lead zirconate - lead titanate and in potassium niobate - sodium niobate solid solutions were unusually large, while the effect of coherent domain size was found to predominate in alumina. The effect of the diffractometer on the observed line broadening was successfully accounted for by a calculated profile, for the case where the sample contained large micro-strains.