

AD-A073 815

CASE WESTERN RESERVE UNIV CLEVELAND OHIO

F/G 20/5

DIPOLAR DEFECT STRUCTURE OF LASER AND OTHER TRANSPARENT MATERIA--ETC(U)

JUL 79 C ANDEEN, D E SCHUELE

DAAG29-76-6-0222

UNCLASSIFIED

ARO-13440.7-P

NL

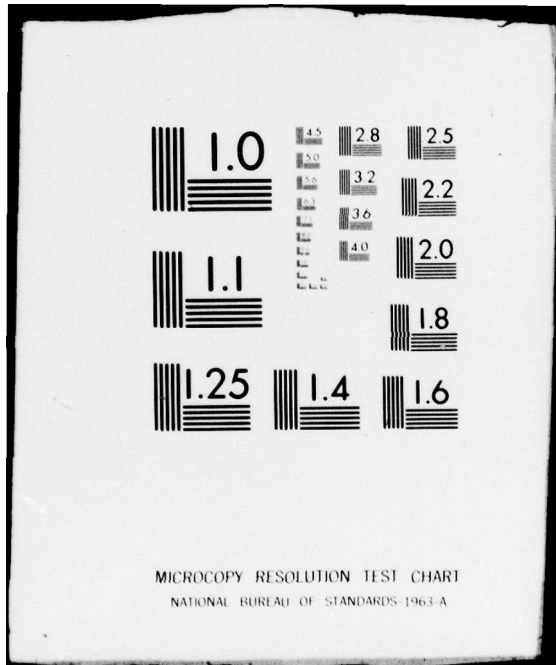
| OF |

AD  
A073815

1 OF 15



END  
DATE  
FILMED  
10-79  
DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

Unclassified

18 ARO

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER 19 13440.7-P		2. JOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER Rept.
4. TITLE (and Subtitle) 6 Dipolar Defect Structure of Laser and Other Transparent Materials		5. TYPE OF REPORT & PERIOD COVERED 9 Final May '76 - May '79	
7. AUTHOR(s) C. Andeen D.E. Schuele		8. CONTRACT OR GRANT NUMBER(s) 15 DAAG29-76-G-0222	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Case Western Reserve University/ 10900 Euclid Avenue Cleveland, Ohio 44106		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 11 15 July 1979	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 14	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 12 19p.		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 10 Carl Andeen Narald E. Schuele			
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) optical glasses      alkaline earth fluorides      dielectric relaxation alkali metals      laser materials semiconductors      transparent materials fluorides      dipolar defects			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → The dipolar defects resulting from rare-earths doped in alkaline earth fluorides have been measured by the method of dielectric relaxation. These measurements have been made over the temperature range 5K to 400K and, in some cases, as a function of pressure. New relaxation peaks were discovered, particularly at low temperatures. The strengths of the various defects did not scale monotonically with dopant concentration. Measurements on crystals with two or more dopants enabled a positive identification of clustering. Studies →			

DDA 073815

DDC FILE COPY

DDIC RECEIVED SEP 17 1979

Block 20

→ were also carried out on alkaline earth fluorides doped with alkali metals, a series of optical glasses, and some semiconductors. A microprocessor controlled automatic capacitance bridge was developed and constructed and is operational. Advancements were made on the high pressure dielectric gauge. ←

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	<input type="checkbox"/>
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	



DIPOLAR DEFECT STRUCTURE OF LASER AND  
OTHER TRANSPARENT MATERIALS

FINAL REPORT  
JULY 15, 1979

U. S. ARMY RESEARCH OFFICE  
DAAG 29-76G-0222

CASE WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO 44106

CO-PRINCIPAL INVESTIGATORS

C. ANDEEN  
D. E. SCHUELE

APPROVED FOR PUBLIC RELEASE  
DISTRIBUTION UNLIMITED

79 09 - 4 314

THE FINDINGS OF THIS REPORT ARE NOT BE BE CONSTRUED AS AN OFFICIAL  
DEPARTMENT OF THE ARMY POSITION, UNLESS SO DESIGNATED BY OTHER AUTHORIZED  
DOCUMENTS.

TABLE OF CONTENTS

	<u>Page</u>
STATEMENT OF THE PROBLEM -----	1
EXPERIMENTAL INVESTIGATIONS -----	1
OVERVIEW OF EXPERIMENTAL RESULTS -----	2
RESUME OF RESULTS	
1. Pure Materials -----	4
2. Alkaline Earth Fluorides -----	5
3. Fused Silica -----	9
4. $As_2S_3$ and $As_2Se_3$ -----	10
5. Automatic Capacitance Bridge -----	10
6. Dielectric Pressure Gauge -----	11
PUBLICATIONS SUPPORTED BY ARO GRANT -----	12
PRESENTATIONS MADE UNDER ARO SPONSORSHIP -----	13
TECHNICAL REPORT -----	14
PERSONNEL ASSOCIATED WITH GRANT -----	14



## STATEMENT OF THE PROBLEM

The purpose of this research was a systematic study of the dielectric properties of insulators containing dipolar entities. In particular, the measurements were of the dielectric constant,  $\epsilon$ , and the dissipation factor,  $\tan \delta$ , as a function of temperature (4.2K to 400K), pressure (0 to 3k bar from dry ice to room temperature) and frequency (five fixed frequencies -  $10^2$ ,  $10^{2.5}$ ,  $10^3$ ,  $10^{3.5}$ ,  $10^4$  Hz). The system of interest included AER:RE<sup>3+</sup>, AEF:AM<sup>+1</sup>, and optical and infrared transmitting glasses. AEF represents the alkaline earth fluorides such as CaF<sub>2</sub>, and RE<sup>3+</sup> and AM<sup>+1</sup> stand for rare earth and alkali metal ions respectively, with the symbol : meaning "doped with."

Also in the course of this investigation, continual development of experimental methods and techniques were undertaken. Of special note is the design and construction of an automatic capacitance bridge with computer interface and control. This bridge enhances the development of an automatic high pressure gauge with capability of being a secondary transfer standard.

## EXPERIMENTAL INVESTIGATIONS

### A. Systems Studied

- I. Dielectric Measurements [at five audio frequencies over the temperature range 5.5K to 400K]
  1. Pure materials CaF<sub>2</sub>, BaF<sub>2</sub>, SrF<sub>2</sub>, MgO.
  2. CaF<sub>2</sub> doped with rare earths [Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu] and Y, La at various dopant concentrations.
  3. SrF<sub>2</sub> doped with Ce, Eu, Gd and Er and two concentrations.
  4. BaF<sub>2</sub> doped with Er.
  5. Double doped CaF<sub>2</sub> [Er-Sm, Nd-Tb, Tb-Tm] over temperature range of 150K to 400K.
  6. Annealing studies in alkaline earth fluorides doped with Er.
  7. Neutron and x-ray radiation on rare earth doped CaF<sub>2</sub>.
  8. CaF<sub>2</sub> doped with Li, Na, K, Rb, Cs.
  9. SrF<sub>2</sub> doped with Na and K.
  10. Diamond.
  11. Fifteen kinds of fused silica.

12. Effects of radiation on fused silica.

13.  $As_2S_3$  and  $As_2Sc_3$ .

II. Pressure Dependence [high pressure measurements on selected relaxation peaks]

1.  $CaF_2$  doped with Er.

2.  $SrF_2$  doped with Er.

III. Combined Pressure and Temperature Dependence

1. Diamond

2. Anisotropic Materials -- quartz, sapphire, calcite and magnesium fluoride.

B. Development and Construction of an Automatic Capacitance Bridge

#### OVERVIEW OF EXPERIMENTAL RESULTS

Point defects play an important role in the mechanical, optical, and electrical properties of materials. In recent years, a number of experimental techniques have been applied to defect systems in order to better our understanding of the nature of the defect as well as the motion of the defect. Among these are electron paramagnetic resonance, nuclear magnetic resonance, electron nuclear double resonance, optical absorption, ionic conductivity, ionic thermocurrent, dielectric relaxation, anelastic relaxation and radioactive tracer techniques. Each of these techniques has its own advantages and disadvantages in elucidating the nature of the defect structure and its motion within a particular material. During the course of these studies and after examining past measurements and the present state of theoretical models for the alkaline earth fluoride system doped with trivalent impurities, it became quite evident that if there was hope of our understanding of the point defect nature of these materials that a systematic study would have to be undertaken. In particular, it is important to note that in many of the previous studies, theoretical models were postulated from measurements on only a couple of materials.

Because of the complexity of the defect structure which depends not only on the particular dopant but also on past thermal history as well as dopant concentration, it became clear that systematic studies over a large number of dopants and varying levels of concentrations would be required. The dielectric relaxation technique as developed in this laboratory lends



itself to such a study because of its inherent accuracy and precision and also because of our ability to make measurements in situ on eight samples. This technique allows for an accuracy in the measurement of the activation energy as well as the pre-exponential factor to a degree which is equal to or better than any of the above mentioned experimental techniques.

The major results of our experimental investigation have been in the calcium fluoride system. In particular, we have uncovered relaxation phenomena at low temperatures which have previously not been observed and have also shown the interplay between the various relaxation peaks as a function of concentration and past thermal history. Because of the measurements on a large number of different doped samples, we have been able to unambiguously identify the various relaxation peaks in this family of materials. A major problem in the understanding of the point defect nature in these materials is to identify the structure of the defect. We have advanced the knowledge in this area through the measurements for the first time of mixed crystals, that is, a crystal which contains two dopants. This has enabled us to show unambiguously that one of the relaxation peaks must arise from a dimer -- that is, a defect which involves two impurity atoms. The measurements and analysis on these mixed crystals are by no means complete. Also, we have observed that the relaxation spectrum for strontium fluoride is vastly different from that for calcium fluoride and, while the measurements on barium fluoride are minimal, we can also extend the above statement to that system. At present, the theoretical calculations on these systems are not accurate enough to differentiate between them. We believe that the trends shown in these measurements will allow for further theoretical advance since the nature of some of these sites are better known. In particular, point defects probe in a very critical way the short range interaction between the constituents in the solid as well as the electrical polarization of the configuration in the neighborhood of the defect. The measurements to date have resulted in a major advance in the determination of the properties of some of the point defects.

In order to complete the study of the alkaline earth fluoride system doped with rare earths as well as other systems will require a tremendous amount of data taking. In view of this, it became apparent quite early in our study that if we were to complete our studies on the alkaline earth fluorides it would require that we be able to take data in an automated fashion

while maintaining our accuracy and precision. To this end, an automatic capacitance bridge has been designed and constructed, and is now operational. This instrument is unique in its capabilities and reduces the data taking time by better than a factor of ten. Besides this, it extends our capability in the dynamic range of measuring the imaginary part of the dielectric constant which will allow us to extend our measurements to higher temperatures and to probe the ionic conductivity portion of the dielectric spectrum. This capability will enable us to extend our measurements from bound defects to unbound defects which determine the high temperature electrical conductivity of many insulating materials.

In conjunction with the bridge development, we have continued to investigate the use of a dielectric sensor in the measurement of high pressure. The automatic bridge allows for direct readout and, because it is microprocessor controlled, will enable us to reduce the stringent requirements on temperature control from our previously designed capacitance pressure gauge. This advance will allow for the development of a high pressure gauge which is completely automatic and which is extremely simple to run from an operator standpoint. Its accuracy is such that it should qualify as a secondary transfer standard. Because the sensitivity and accuracy of the automatic bridge is the same as that for our manual bridges, the employment of the automatic bridge into the capacitance pressure gauge will result in no loss of accuracy or sensitivity from our previously designed capacitance pressure gauge.

## RESUME OF RESULTS

### 1. Pure Materials

The temperature dependence of the dielectric constant of pure calcium fluoride, strontium fluoride, barium fluoride and magnesium oxide have been measured over the temperature range 5.5 to 380K. Tables have been prepared listing the dielectric constant at 20<sup>0</sup> intervals from 5K to 380K. Corrections to the data have been made in the case of CaF<sub>2</sub> due to low residual impurities.

Besides being an important parameter in itself, the dielectric constant is important as an input parameter for the various lattice dynamical models for these materials.

The temperature and pressure variation of the dielectric constant for diamond has been measured. Measurements were made at atmospheric pressure

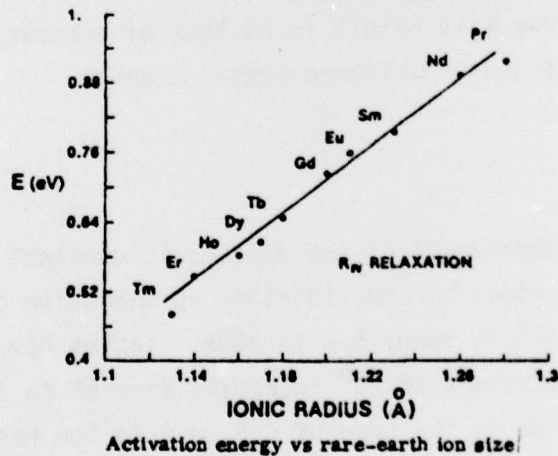
over the temperature range of 5.5 to 340K and at room temperature at pressures up to 1.4 kilobars. The curvature of the dielectric constant with temperature has also been determined. Pressure measurements based on many techniques such as capacitance, optical interference, and photo-elasticity agree surprisingly well. The theoretical value for the pressure derivative is approximately a factor of two smaller than the experimental result. Also, the dielectric constant has been measured as a function of temperature and pressure on the anisotropic materials -- quartz, sapphire, calcite and magnesium fluoride.

## 2. Alkaline Earth Fluorides

A:  $\text{CaF}_2$

The complex dielectric constant has been measured for calcium fluoride individually doped with 13 rare earths and yttrium, lanthanum and double-doped with several pairs of rare earths. Five relaxations have been identified and, because of this systematic study, an unambiguous labeling of the spectra has been obtained for the first time. The activation energies range from 0.03 electron volts to 1.9 electron volts, though care must be exercised in the interpretation for some peaks which are not Debye like.

The activation energy of the relaxation denoted as  $R_{IV}$  scales directly with the rare earth ion size as shown in the figure below. Concentration dependence studies as well as annealing studies indicate this to be a cluster.



Correlation with optical absorption studies in conjunction with annealing studies gives evidence that this defect has a modified trigonal symmetry.

In an attempt to understand the nature of some of these relaxation peaks, measurements were undertaken with calcium fluoride doped with two rare



earths. In the mixed crystal the  $R_{IV}$  relaxation peaks associated with the single doped crystals have been observed along with an  $R_{IV}$  peak slightly shifted from the relaxation peak associated with single doped crystal containing the small rare earth. The results strongly suggest that  $R_{IV}$  is dimer associated, the new peak being due to a mixed dimer! This shows that the rare earths in the dimer do not participate equally in the reorientation of the fluorine ion. In order to obtain these results, it was necessary to supplement the dielectric results with measurements using the ionic thermocurrent technique, employing the method of peak enhancement. The ITC measurements were carried out for us at the Naval Research Laboratory. These mixed crystal measurements unambiguously substantiate the existence of the dimer formation.

The measurements on yttrium were carried out to see if there would be a major effect on the relaxation spectrum due to the mass of the dopant. The  $R_{IV}$  relaxation activation energy for yttrium scales with the ionic radius as found for the rare earth dopants as well as the pre-exponential factor. Thus, at present it is felt that there is no mass dependence on the relaxation parameters.

Some preliminary work has been carried out on the pressure dependence of the  $R_I$  and  $R_{IV}$  relaxations. The results for the  $R_I$  relaxation indicate that the activation volume is 3 cc/mole and that it is significantly smaller for the  $R_{IV}$  relaxation. It should be emphasized that the pressure work is in the early stages and these are only preliminary results.

Crystals have been irradiated with gamma rays at room temperature and the resultant relaxation spectrum is similar to that observed for an annealed crystal followed by a quench for  $R_I$ ,  $R_{III}$ , and  $R_{IV}$ . The  $R_{II}$  relaxation appears to be anomalous with a new relaxation peak occurring in the neighborhood of  $R_{II}$ . In addition, two new peaks anneal out at room temperature which is not the case of any of the peaks of the non-irradiated material. The crystals must be maintained below 200K for stability of these induced peaks.

Measurements have been carried out on the dielectric relaxation spectrum for calcium fluoride doped with lithium, sodium, potassium, rubidium and cesium. The main defect structure is thought to be a fluorine vacancy motion which results in the charge compensation when the alkali metal ion replaces the calcium ion substitutionally. The results show one relaxation peak which is attributed to vacancy motion. The shape of the relaxation peak with lithium

as the dopant appears anomalous and this may be a result of the extremely small ion size. Pressure measurements will be extremely important in this system in order to calculate the activation volume for bound vacancy motion. Measurements should be carried out on the DC conductivity to obtain the activation energies for both bound and unbound vacancy motion.

B: SrF<sub>2</sub>

Measurements on this system have been completed for four rare earths (Ce, Eu, Gd and Er) in two different concentrations. It is found that three relaxations are characteristic of the rare earths in strontium fluoride. The two main relaxation peaks are thought to be associated with type one and type two dipoles (nearest neighbor and next nearest neighbor interstitials respectively). In cerium doped material, only the nearest neighbor dipole is observed while in Er and Gd both the nearest neighbor and next nearest neighbor dipoles are observed. Er shows only the next nearest neighbor. The third relaxation peak is found in the low temperature region below 40K and, at present, its nature is unknown. From the amplitudes of the relaxation peaks, the nearest neighbor relaxations appear to be in thermal equilibrium. The identification of the two more prominent dipoles correlates well with electron spin resonance results which show that the site symmetry goes from tetragonal to mixed to trigonal as one goes from Ce to Er.

The low temperature peak is analogous to the R<sub>III</sub> relaxation found in calcium fluoride and, to our knowledge, has not been reported previously. It appears to be associated with clustering since it is only seen in crystals with concentrations greater than 0.1 mole %. In comparison to calcium fluoride, it requires a higher concentration of the dopant before it is observed.

Crystals of strontium fluoride doped with sodium and potassium have been measured. As in the above system, one main peak is observed. However, in the low temperature region there is a large amount of structure with at least three new peaks being observed. There is some evidence that sodium and potassium go in interstitially in these materials and further measurements will be required.

The complex dielectric constant for erbium doped strontium fluoride has been measured at pressures up to 0.4 GPa over the temperature range 300-360K. Consequently, the reorientation of Type II dipole (substitutional rare-earth and next-nearest neighbor interstitial fluorine charge compensator) has been



studied. The activation volume for the motion is found to be  $4.7 \pm 0.1 \text{ cm}^3/\text{mole}$ . It is argued that this value should be similar to the migration volume for "free" interstitials. Excellent agreement is found between a value for the migration volume for "free" interstitials calculated from Flynn's dynamical diffusion model and the experimental value for bound interstitials. The compressibility of the activation volume is found to be more than an order of magnitude greater than the compressibility of the host lattice.

C: BaF<sub>2</sub>

Only preliminary measurements have been made on this system with one rare earth, namely Er. It is difficult to make extrapolations from a single material; however, this one material does indicate that the defect structure is entirely different from those previously observed. The relaxation spectrum shows only one very broad relaxation peak for concentrations up to 1 mole %. Ionic thermocurrent measurements show four relaxation peaks to be associated with this single broad relaxation in the dielectric spectrum. The activation energy is found to be around 0.57 electron volts and the dominant defect structure is thought to be trigonal. There appears to be no clustering and it should be borne in mind that these measurements are preliminary in nature.

D: Anneal Studies

Samples of CaF<sub>2</sub>:Er, SrF<sub>2</sub>:Er and BaF<sub>2</sub>:Er having nominal concentrations of 0.01, 0.1, and 1.0 mole % were annealed in vacuum at 1120K and quenched by withdrawing the annealing tube from the furnace. The samples remained clear after this treatment. The crystals were examined before and after treatment using optical and dielectric spectroscopy. The optical spectra were taken on a Cary 17 recording spectrophotometer.

Five relaxations were studied in CaF<sub>2</sub>:Er. The lowest temperature, 0.03 ev, relaxation, which grows monotonically with concentration and is thought to be cluster-associated, was observed to decrease when the samples were annealed and quenched. In the 0.3 mole % sample, for example, the 0.03 ev relaxation decreased by a factor of three. The 0.15 ev relaxation, on the other hand, grew by a factor of three. The optical absorption bands recently associated with clustered rare-earth ions showed a decrease. An increase in absorption bands associated with relaxations having tetragonal symmetry was observed. The magnitude of the increase in the tetragonal absorption bands was close to three.

In the  $\text{SrF}_2:\text{Er}$  where the low temperature dielectric relaxation is not observed until higher concentrations than in the  $\text{CaF}_2:\text{Er}$ , the samples show little change upon annealing and quenching at concentrations less than 0.1 mole %. The 1.0 mole % samples show a decrease in the low temperature relaxation spectra upon annealing and quenching. Some growth has been observed at intermediate temperatures. No substantial change in the principal relaxation was observed. The DC conductivity was significantly enhanced at high temperatures. The optical absorption spectra showed a substantial decrease in spectral regions similar to the  $\text{CaF}_2:\text{Er}$ . No growth in absorption was observed.

In the  $\text{BaF}_2:\text{Er}$  samples, where no low temperature, cluster-associated relaxation is observed up to concentrations of 1.0 mole %, the dielectric spectrum showed no significant changes other than an increased DC conductivity. The optical spectra, on the other hand, showed a decrease in absorption similar to that observed for  $\text{CaF}_2:\text{Er}$  and  $\text{SrF}_2:\text{Er}$ . No increase in absorption was observed.

Further experiments were conducted to attempt to restore the samples to their original state. Samples of  $\text{CaF}_2:\text{Er}$  having concentrations of 0.3 mole % and 1.0 mole % were annealed in vacuum at temperatures of 620K, 645K, 670K, and 695K for 15 minutes and quenched in the same manner as the original quenching. In the 0.3 mole % sample, the changes in the optical spectrum were found to be reversible. The dielectric spectra, however, showed no changes in the three peaks which grew after the original annealing and quenching.

### 3. Fused Silica

Measurements of the dielectric constant and dielectric loss have been performed on fifteen kinds of fused silica over the temperature range 5.5 to 380K. The dielectric relaxation spectrum is characteristic of the production process used in making the materials. All of the materials have a low temperature peak characteristic of the glass structural relaxation. For those materials with substantial  $\text{OH}^-$  impurity, an extremely low temperature relaxation peak is observed. This is indicative of tunneling and a lower temperature capability will be required to complete this study. Materials were subjected to gamma radiation and the resultant radiation darkening appears to be directly related to the existence of a particular loss peak in the virgin material. The 240K relaxation is attributed to an aluminum alkali center and the gamma ray induced relaxation is attributed either to an aluminum

oxygen hole center or to a non-local alkali atom. Isochronal annealing of the samples in conjunction with ESR and further dielectric measurements are currently underway to test these identifications. Also, accurate values for the real part of the dielectric constant were presented for many of the samples for the first time.

#### 4. As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>Se<sub>3</sub>

The complex dielectric constant has been measured over the temperature range 5.5 to 300K at zero pressure and at pressures up to 3k bar over the temperature range 260-300K for various samples of vitreous As<sub>2</sub>Se<sub>3</sub> and As<sub>2</sub>S<sub>3</sub>. In addition, the pressure dependence of the refractive index at optical frequencies has been measured for vitreous As<sub>2</sub>S<sub>3</sub>. In both materials a broad maximum is found in the real part of the dielectric constant at low temperatures. There appear to be no corresponding anomalies in the conductivity. In addition, a Debye type relaxation is observed in the sample of As<sub>2</sub>Se<sub>3</sub> studied. Optical absorption measurements have also been carried out on this material.

#### 5. Automatic Capacitance Bridge

An automatic capacitance bridge has been designed and constructed. It is now operational and in the last month has replaced our manually balanced bridge. It has been built around a GR-1615 three terminal capacitance bridge and retains all of the accuracy and range. This bridge operates with three volts across the sample at all of the frequencies. It has a lower sensitivity of  $3 \times 10^{-6}$  picofarads and a loss capability of 1 part in 10,000 or  $3 \times 10^{-6}$  pf equivalent in loss. The system has eight digit readout on the capacitance and four-1/2 digit readout on the loss with the 1/2 digit being an internal interpolation by the microprocessor. An example of the power of employing a microprocessor control in the bridge has been a reduction in the noise level by an order of magnitude through microprocessor sampling of the signal to eliminate 60 cycle line related noise.

The bridge can be operated in several different modes. For example, one mode cycles through all five frequencies and, by controlling an external electronic switching system, will cycle through eight samples. This reduces the time to take data at a single temperature from 25 minutes to approximately two minutes.

A future development will allow for control of the cryostat temperature so that the entire system will be automatic with direct interface to computer



for data storage and analysis. This will allow a much finer temperature scan which is necessary for complete data analysis.

#### 6. Dielectric Pressure Gauge

One of the goals of the present research program was to investigate the feasibility of dielectric materials to be used as pressure transducers. Prior to the present research, a dielectric pressure gauge was developed which used a calcium fluoride sensor. A goal of the present work was the investigation of other possible materials to be used as the transducer material as well as the development of an automatic bridge so that the pressure could have direct readout. With respect to materials, two advances have been made. It has been found that the "unclamped" dielectric constant for  $\alpha$ -quartz has a zero temperature coefficient at just about room temperature. While there is a piezoelectric contribution to the dielectric constant, (which is, in fact, responsible for cancelling the intrinsically positive temperature coefficient) there is no a priori reason to expect difficulties with this material for use in a hydrostatic pressure system. The second recent advance concerns the use of dipoles to cancel the temperature coefficient of capacitance. This has resulted from the study of rare earth doped strontium fluoride wherein the dipolar complexes have a very large dipole moment. In addition, large concentrations of the dipoles can be incorporated into the lattice. The problem initially was that the relaxation occurred at too high a temperature. (For Er doped  $\text{SrF}_2$ , the temperature coefficient is zero at about 350K.) However, for large rare earths (Ce), the authors have found a single, strong relaxation below room temperature. Consequently, it should be possible to cancel the intrinsically positive temperature coefficient of  $\text{SrF}_2$  (which is smaller than that for  $\text{CaF}_2$  to begin with) at room temperature. This possibility is currently being investigated. Finally, with the microprocessor controlled bridge, one is now able to correct internally for the non-linearity of the capacitance as a function of pressure. Consequently, the readout is direct in any pressure units.

PUBLICATIONS SUPPORTED BY ARO GRANT

1. "Temperature and Pressure Variation of the Refractive Index of Diamond", Appl. Optics, 16: 2949 (1977).
2. "Cluster Associated Relaxations in Rare-Earth Doped Calcium Fluoride," Phys. Rev., B16: 3762 (1977).
3. "Temperature and Pressure Dependence of the Single-Crystal Elastic Constants of  $^6\text{Li}$  and Natural Lithium", Physical Review B16: 5173 (1977).
4. "Dielectric Relaxation in Yttrium and Lanthanum Doped Calcium Fluoride", Phy. Rev., B17: 3429 (1978).
5. "Dipolar Complexes in Rare-Earth Doped Strontium Fluoride", Phys. Rev., B18: 4454 (1978).
6. "Electric Dipole Relaxation of Mixed Clusters in Double Doped Calcium Fluoride", Phys. Rev., B19: 5293 (1979).
7. "The Dielectric Properties of As-Received and Gamma Irradiated Fused Silica", J. Non-Cryst. Solids, 31, 401 (1979).
8. "The Low Temperature Electrical Properties of Some Anisotropic Crystals", J. Phys. Chem. Solids (to be published).
9. "The Temperature Variation of the Dielectric Constand of 'Pure' Calcium Fluoride, Strontium Fluoride, Barium Fluoride and Magnesium Oxide", J. Appl. Phys. (to be published).
10. "Activation Volume for Interstitial Motion in Strontium Fluoride" submitted to Physical Review.
11. "Annealing Studies in Erbium Doped Alkaline Earth Fluorides" submitted to Physical Review.



PRESENTATIONS MADE UNDER ARO SPONSORSHIP

1. "Temperature and Pressure Variation of the Refractive Index of Diamond", Topical Meeting on Optical Phenomena in Infrared Materials, 1-3 December 1976, Annapolis, Maryland.
2. "Electrical and Optical Properties of Vitreous Arsenic Sulphide and Arsenic Selenide", 1977 March Meeting of the APS, San Diego, California, Bull. APS, 22: 335 (1977).
3. "Dipolar Relaxation in Rare-Earth Doped Calcium Fluoride", 1977 March Meeting of the APS, San Diego, California, Bull, APS, 22: 351 (1977).
4. "Dielectric Relaxation in Rare-Earth and Alkali Metal Doped Alkaline Earth Fluorides," International Conference on Defects in Insulating Crystals, 9-14 October 1977, Gatlinburg, Tennessee.
5. "Radiation Effects in Rare-Earth Doped Calcium Fluoride", 1978 March Meeting of the APS, Washington, D.C., Bull, APS, 23: 254 (1978).
6. "Optical and Dielectric Absorption Studies in Erbium Doped Calcium Fluoride", 1978 Spring Meeting of APS, Washington, D.C., Bull, APS, 23: 548 (1978).
7. "Electrical Dipole Relaxation of Mixed Clusters in Double Doped Calcium Fluoride", 1979 March Meeting of the APS, Chicago, Illinois, Bull. APS, 24: 377 (1979).
8. "The Dielectric Properties of As-Received and Gamma Irradiated Fused Silica", 1979 March Meeting of the APS, Chicago, Illinois, Bull. APS, 24: 494 (1979).

TECHNICAL REPORT

1. Preliminary Report of an Automatic Capacitance Measuring System  
issued June 30, 1978.

PERSONNEL ASSOCIATED WITH GRANT

1. Dr. Carl G. Andeen
2. Dr. John Fontanella
3. Dr. Donald Schuele

(Also, a number of undergraduate students worked on the various projects.)