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NEW MATERIALS FOR INFRARED TRANSMITTING ELECTROOPTIC FILTERS

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The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have an EO coefficient an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our

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approach will overcome these obstacles by first synthesizing approximately 20 polycrystalline samples. Subsequently, their dielectric constants at low and ambient temperatures will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

During the last quarter, synthesis work included preparation of $ZnIn_2S_4$, $ZnIn_2Se_4$, $CdIn_2S_4$, $GeSe_2$, and $NbGe_2$. Reaction kinetics for the synthesis of $ZnIn_2Se_4$ presented some problems in obtaining that compound, but an alternate approach is promising enough to suggest that the material will be successfully synthesized next quarter. $ZnIn_2S_4$ and $CdIn_2S_4$ were reacted in the vapor phase using the binary end members (ZnS, In_2S_3) and HCl. This reaction is strongly dependent on HCl pressure, which was increased accordingly in the last runs.

Samples of $GeSe_2$ and $ZnGa_2S_4$ were measured to determine the dielectric constant and dissipation factor over a range of frequencies. $ZnGa_2S_4$ showed a large low-frequency dielectric constant (the largest yet obtained on this program) and a relatively high dissipation factor. $GeSe_2$ showed a lower dielectric constant than the previously measured samples.

$ZnGa_2S_4$ appears to be a favorable candidate for single-crystal growth and subsequent measurement of the electrooptic coefficient. This is expected to get under way in the next quarter.

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SECTION 1

INTRODUCTION AND SUMMARY

A. PROGRAM OBJECTIVES

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have EO coefficients an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our approach will overcome these obstacles. First, we will synthesize 20 polycrystalline samples. Then the dielectric constant of each, at both low and ambient temperatures, will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

B. SUMMARY

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SECTION 2

MATERIALS PREPARATION AND CRYSTAL GROWTH

A. PREPARATION OF $ZnIn_2S_4$ AND $CdIn_2S_4$

For the preparation of $ZnIn_2S_4$ and $CdIn_2S_4$, the starting materials were the respective compounds encapsulated in a silica tube with 380 mm HCl at ∿25°C. To clean its tip, the tube was placed vertically in a hot furnace for one day so that the collection end of the tube was hotter than the source end. The temperature was then reversed, and the tube was pulled slowly (0.8 mm/hr) through the temperature profile until it was several centimeters out of the furnace. For the zinc compound, the maximum temperature was 1000°C and the "growth" time was 18 days; for the cadmium compound, the maximum temperature was 960°C and the "growth" time was 19 days. After the run, the tube was air quenched to room temperature.

In previous runs with HCl, the pressure of HCl was calculated to give 1 atm of pressure at the operating temperature. These runs were filled with 380 mm HCl at room temperature. The HCl pressure was ∿2 atm for each run at maximum temperature. The increase in HCl pressure was suggested by results from our previous runs, in which the amount of material transported had been relatively low. An inspection of the reaction equations,

$$ZnS + In_2S_3 + 8HCl \rightleftharpoons ZnCl_2 + 2InCl_3 + 4H_2 + 2S_2 \rightleftharpoons ZnIn_2S_4 + 8HCl,$$

indicated that the reaction is pressure dependent, and that it may be possible, to increase the amount of transported material by increasing the pressure. This was later verified. The material was submitted for X-ray analysis. The compound $CdIn_2S_4$ was identified by X-ray powder diffraction analysis. The pattern is shown in Figure 1.

B. PREPARATION OF $GeSe_2$

$GeSe_2$ was synthesized by mixing stoichiometric amounts of Ge and Se in two vitreous silica ampoules under a flow of nitrogen. An excess of

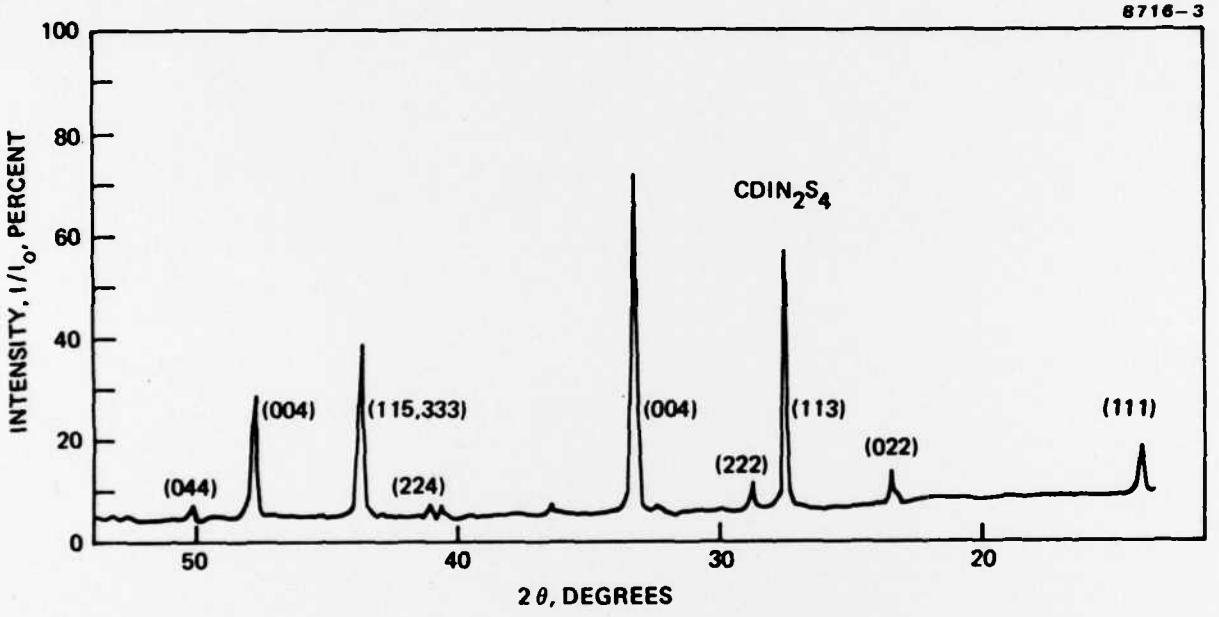

Figure 1. X-ray diffraction pattern of $CdIn_2S_4$.

1.0 g of Se was added to provide 1 atm of Se_2 vapor at the processing temperature. The tube was then evacuated and sealed.

The setup was heated to 410°C over a period of 16 hr, and 690°C for 30 hr (boiling point of Se is 688°C). The color of the Se_2 vapor was used as an indicator of the extent of completion of the reaction. When the color of the vapor appeared to become lighter, the temperature was raised to 725°C for 18 hr, then to 740°C (melting point of $GeSe_2$) for four days. After this time, no Se_2 vapor was observed and the material sublimed to the colder ends of the tube. Part of the tube was pushed out of the furnace to attempt to nucleate and grow crystals. The temperature of the furnace was increased to 765°C in two days, after which the setup was slowly cooled to room temperature.

The material obtained was a mica-like mixture of gray, red, and yellow. However, X-ray analysis showed the material to be $GeSe_2$. The color differences were caused by variations in thickness.

The material was transferred into a vitreous SiO_2 crystal growth tube, evacuated, and sealed. Crystal growth by the vertical Bridgman method was attempted at 800°C. The resulting material was polycrystalline. Samples were sliced and submitted for dielectric constant measurements.

C. PREPARATION OF $ZnIn_2Se_4$

In the first attempt to prepare $ZnIn_2Se_4$ a two-boat, two-temperature process was used. Stoichiometric amounts of In and Zn were placed in a SiO_2 boat under a nitrogen flow. The stoichiometric amount of Se plus an excess of 0.49 g (to provide 1 atm Se_2 at the processing temperature) was placed in the second boat. The tube was evacuated and sealed.

The temperature of both the metal end and the Se end was varied from 500 to 1050°C, to ensure that one end would always be at or below 688°C, the boiling point of Se. Because the reaction was so slow, this procedure was stopped and the approach was redesigned.

A second synthesis attempt involved mixing stoichiometric amounts of Zn, In, and Se (0.40 g excess) in an ampoule, which was subsequently evacuated and sealed. The tube was heated gradually; the heating rate

was determined by the intensity of Se_2 vapor color. The processing temperatures were 370°C for 16 hr, 680°C for 8 days, 700°C for 13 days, 730°C for 6 days, and 770°C for 7 days. Since, once again, the reaction was proceeding too slowly, this run was stopped.

The third attempt, which is planned for the next quarter, will involve the synthesis of the binary compounds In_2Se_3 and ZnSe and subsequently combining them in stoichiometric quantities.

D. PREPARATION OF $NbGe_2$

The preparation of $NbGe_2$ utilized the constituent elements powdered into an intimate mixture. The mixture was placed in a vitreous carbon boat inside an alundum tube. Under a nitrogen atmosphere, the setup was heated to 1400°C for 1.5 hr and 1450° for 2 hr. The material was sintered. X-ray analysis showed the material to be a mixture of $NbGe_2$ and Ge.

SECTION 3

MATERIALS EVALUATION

A. DIELECTRIC CONSTANT MEASUREMENTS

In the past quarter, dielectric measurements were made on two new materials: zinc thiogallate ($ZnGa_2S_4$) and germanium diselenide ($GeSe_2$). The properties studied were dielectric constant and dissipation factors as a function of frequency. Measurements were performed over the range 5 to 500 kHz using blocking contacts (consisting of mylar sheets with one silvered surface) and a Boonton 540C capacitance bridge. A detailed description of the measurement and analytical techniques was reported in Quarterly Report No. 4. The measured dielectric constants for these materials are shown in Table 1.

Table 1. Dielectric Constants at Indicated Frequency

Material	Frequency, kH				
	6	10	50	100	400
$ZnGa_2S_4$	62.1	40.9	21.3	18.1	13.5
$GeSe_2$	5.32	5.31	5.30	5.30	5.26

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Reproducibility of $ZnGa_2S_4$ was checked by measuring two separate samples from the same as-grown ingot at two different low frequencies. The results are shown in Table 2.

The reproducibility of measurements is fairly good. The small sample-to-sample variations are probably caused by minor local variations in structure, impurity, or defect, concentrations.

Table 2. Dielectric Constant Measured on Different Samples of $ZnGa_2S_4$

Sample	Frequency	
	10 kHz	20 kHz
$ZnGa_2S_4$-1	39.04	35.8
$ZnGa_2S_4$-2	40.88	31.0

B. DIELECTRIC RELAXATION

Figure 2 shows the variation of dissipation factor versus frequency of $GeSe_2$; the same plot for $ZnGa_2S_4$ is shown in Figure 3. In the case of $GeSe_2$, two dielectric relaxation peaks corresponding to 8.5 kHz and 70 kHz are observed. The plot for $ZnGa_2S_4$ shows less pronounced features, a small peak at 27 kHz. The dielectric constant of $ZnGa_2S_4$ is much higher at low frequencies (6 kHz) than similar constants for other materials that we have previously investigated in this project. For example, we have measured the following low frequency dielectric constants:

GeS_2 10.7

$CuInSe_2$ 37

$ZnSeAs_2$ 35

$GeSe_2$ 5.3

The dissipation factors, on the order of 10^1, are fairly high as compared with the chalcogenides (listed above), which are on the order of 10^{-3}. At present we do not understand these relaxation phenomena because of a lack of knowledge of the details of the local atomic arrangements and defect structures in this material.

By using lock-in techniques, we plan to measure the dielectric constant at low temperatures and even lower frequencies (200 Hz) than the available capacitance bridge offers.

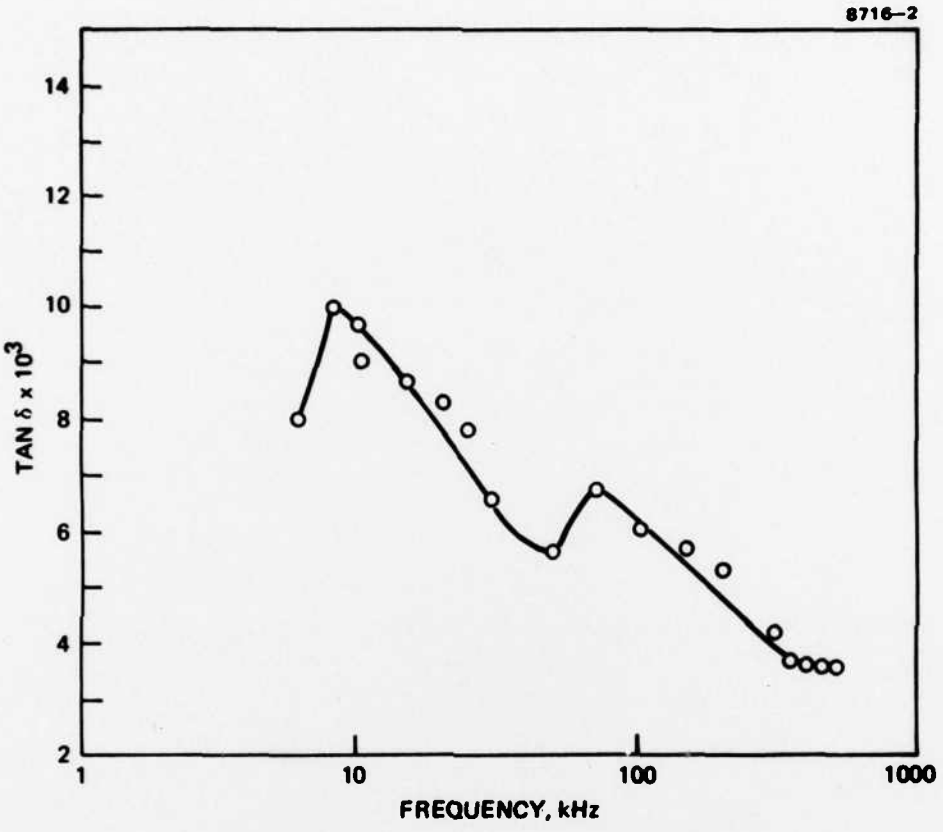

Figure 2. Tanδ versus frequency for $GeSe_2$.

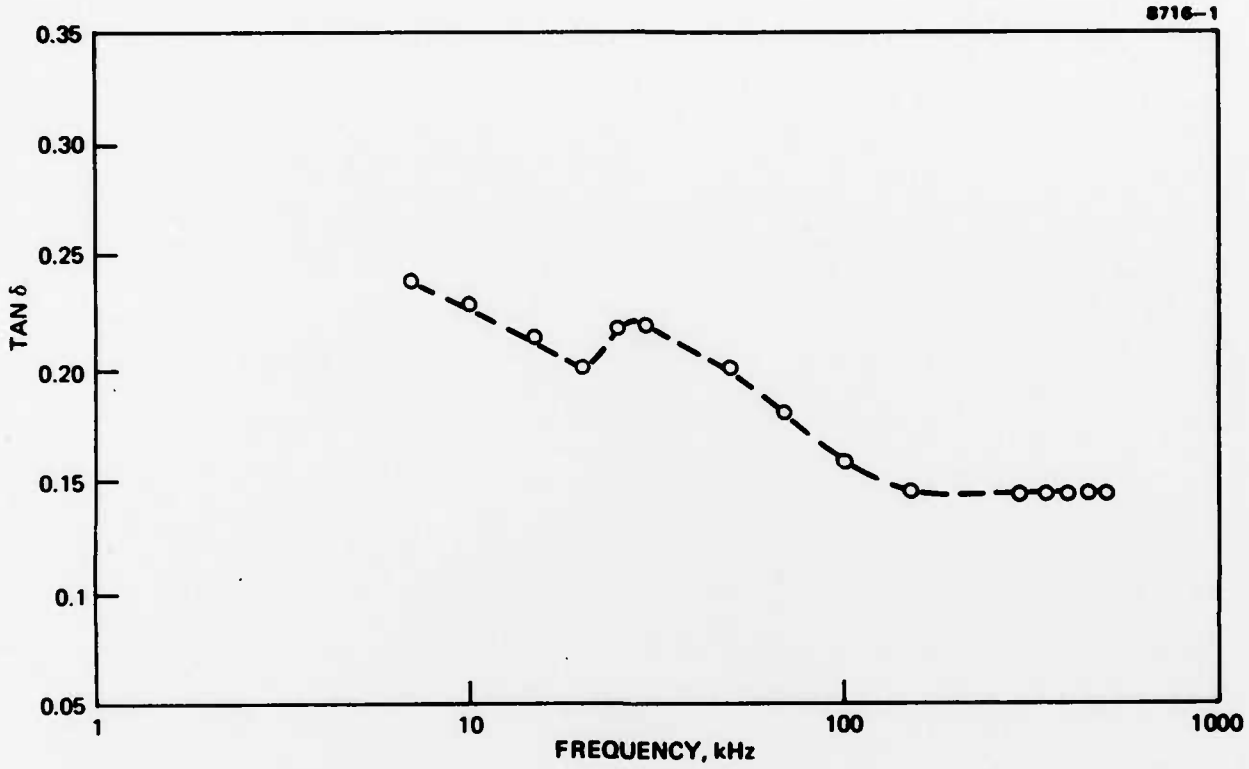

Figure 3. Dissipation factor versus frequency for $ZnGa_2S_4$ (zinc thiogallate).