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NEW MATERIALS FOR INFRARED TRANSMITTING ELECTROOPTIC FILTERS

Quarterly Technical Report No. 3

For period 01 August 1978 through 31 October 1978

Contract MDA 903–78–C–0180

Program Code Number 8D10

Program Element Code 61101E

Hughes Research Laboratories

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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

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) characterized and others have high melting points or melt incongruently. Our 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, $CdIn_2Se_4$ was prepared using vapor transport with iodine as the transport medium. The lack of successful synthesis of many ternary chalcogenides by the use of I_2 led to the investigation of HCl as a transport medium. Using HCl, we synthesized $ZnIn_2S_4$, $CdIn_2S_4$, and $CdGa_2Se_4$. The $ZnIn_2S_4$ run also contained $Zn_9In_8S_{21}$ and $Zn_3In_2S_6$. Attempts to synthesize $CdGaS_2$ using HCl came close in composition to the desired stoichiometry, as indicated by x-ray diffraction analysis, but some free Ga_2S_3 was also identified. Problems encountered with contacts on some samples delayed the evaluation of dielectric constant until next quarter.

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REPORT SUMMARY

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 approach will overcome these obstacles by first synthesizing 20 polycrystalline samples; subsequently, 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, $CdIn_2Se_4$ was prepared using vapor transport with iodine as the transport medium. The lack of successful synthesis of many ternary chalcogenides by the use of I_2 led us to investigate HCl as a transport medium. Using HCl, we synthesized $ZnIn_2S_4$, $CdIn_2S_4$, and $CdGa_2Se_4$. The $ZnIn_2S_4$ run also contained $Zn_9In_8S_{21}$ and $Zn_3In_2S_6$. Attempts to synthesize $CdGaS_2$ using HCl yielded a compound close in composition to the desired stoichiometry, as indicated by x-ray diffraction analysis, but some free Ga_2S_3 was also identified. Problems encountered with contacts on some samples delayed the evaluation of dielectric constant until next quarter.

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

During the last quarter, $CdIn_2Se_4$ was prepared using vapor transport with iodine as the transport medium. The lack of successful synthesis of many ternary calcogenides by the use of I_2 led us to investigate HCl as a transport medium. Using HCl, we synthesized $ZnIn_2S_4$, $CdIn_2S_4$, and $CdGa_2Se_4$. The $ZnIn_2S_4$ run also contained $Zn_9In_8S_{21}$ and $Zn_3In_2S_6$. Experiments aimed at the sythesis of $CdGaS_2$ using HCl yielded a compound close in composition to the desired stoichiometry, as indicated by x-ray diffraction analysis, but some free Ga_2S_3 was also identified. Problems encountered with contacts on some samples delayed the evaluation of dielectric constant until next quarter.

SECTION 2

MATERIALS PREPARATION AND CRYSTAL GROWTH

A. VAPOR TRANSPORT OF TERNARY CHALCOGENIDES

1. Iodine as Transport Medium

Initial results in vapor transport reaction, using II-VI and III-VI binary compounds as starting materials followed by the addition of iodine into the ampoule, were not universally successful in forming the desired ternary compound (i.e., $A^{II}B_2^{III}C_4^{VI}$) or in the complete transport of material to form an ingot. This is described in detail in Quarterly Report No. 2 of this program. Those compounds that did not previously yield usable samples for evaluation (either by reaction and recrystallization in situ or by vapor transport) were repeated using CdI_2 and ZnI_2 as starting materials. In these cases, iodine is still the transport medium, but advantages are gained by (1) minimizing the loss of the very volatile elemental iodine in the preparation stages and (2) having constituent elements in a more volatile form (i.e., the iodide, which yields a highly reactive metal atom on decomposition).

This procedure was followed, to synthesize $CdIn_2S_4$, $CdIn_2Se_4$, and $ZnIn_2S_4$, using 1-cm-diameter ampoules and calculating iodine concentration to obtain 1 atm of iodine at the run temperature; stoichiometry was balanced using appropriate II-VI binary compounds. Runs typically were carried out around 1000°C at the source with a large thermal gradient on the order of 400°C.

Successful results in transporting and forming $CdIn_2Se_4$ were obtained; the compound was identified by x-ray analysis (Figure 1). A small amount of ZnS + In_2S_3 transported, but not enough for identification. No transport was observed in the $CdIn_2S_4$ experiment.

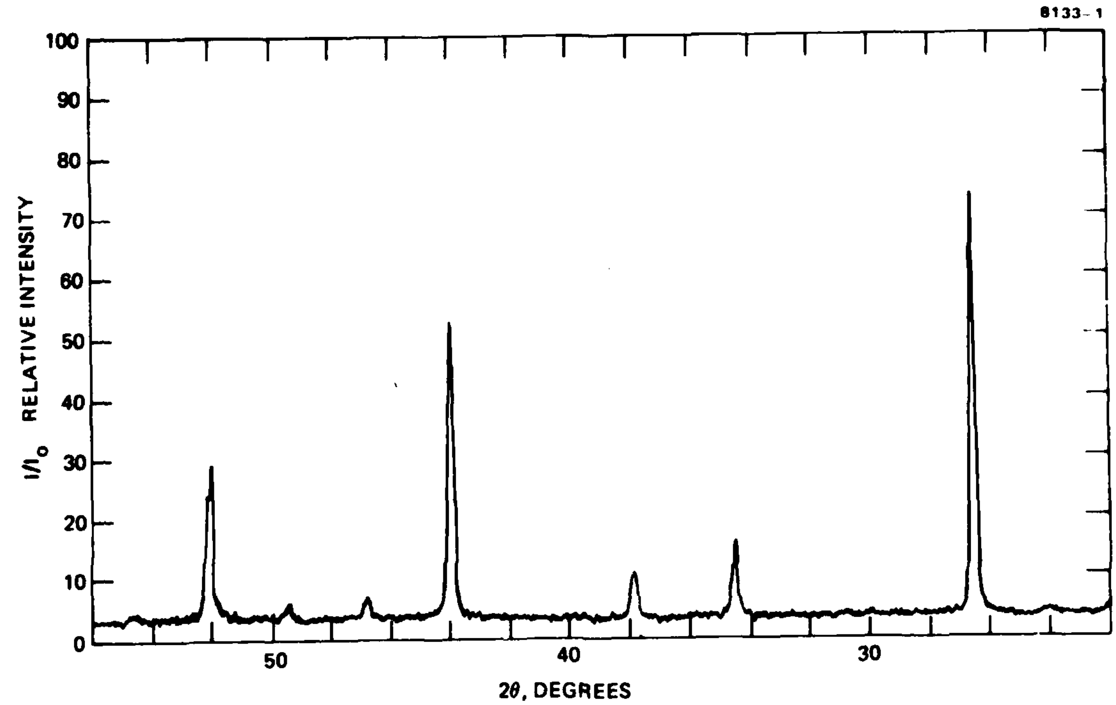

Figure 1. X-ray diffraction pattern of $CdIn_2Se_4$.

2. HCl as Transport Medium

Early observations of little or no transport using iodine as a carrier gas led to the search for a more efficient carrier. Based on optimistic reports in the literature, we selected HCl for this carrier gas. Special equipment for loading this corrosive gas into the ampoule had to be acquired. The only additional significant change in these runs was to increase the tube diameter from 1 cm to 2 cm in accordance with theories that the trasnport rate increases exponentially with increased ampoule diameter. This idea was discussed in the last quarterly report. Using HCl as the transport medium at a pressure calculated to be 1 atm at run temperature, $CdIn_2S_4$ was prepared and confirmed by x-ray diffraction analysis.

Initial runs using HCl for the preparation of $ZnIn_2S_4$ indicated that there was a substantial amount of the desired ternary compound present and that $Zn_9In_8S_{21}$ and $Zn_3In_2S_6$ were also present. A ternary compound close to $GdGa_2S_4$, as identified by x-ray analysis, was also formed by HCl vapor transport reactions. Some free Ga_2S_3 (a volatile component) was collected and identified from the run. In addition, the formation of $CdGa_2Se_4$ from its binary constituents (CdSe and Ga_2Se_3) was accomplished using this procedure.

We plan to continue investigating HCl vapor transport reactions to synthesize additional samples of the ternary compounds of the type $A^{II}B_2^{III}C_4^{VI}$ for subsequent measurement of the dielectric constant. No further runs using iodine are planned.

The results of all vapor transport reaction studies are summarized in Table 1.

Table 1. Vapor Transport Reaction Studies

Desired Compound	Starting Materials	Temperature Range, °C	Carrier	Tube Diameter, cm	Amount of Source Left	Transport	X-Ray	Remarks
$CdIn_2Se_4$	$CdSe + In_2Se_3$	990 to 550	I_2	1	None	Yes	Yes	
$CdIn_2S_4$	$CdS + In_2S_3$	990 to 550	I_2	1	All	No	——	
$ZnIn_2S_4$	$ZnS + In_2S_3$	990 to 550	I_2	1	Much	Little	——	Two sections of tube coated: yellow crystalline in high temperature section; red, yellow, white coatings in low temperature region.
$ZnIn_2S_4$	$ZnS + In_2S_3$	1010 to 625	HCl	2	Much	Yes	Yes (Black)	Also $Zn_9In_8S_{21}$ and $Zn_3In_4S_6$
$CdIn_2S_4$	$CdS + In_2S_3$	1010 to 625	HCl	2	Some	Yes	Yes (Black)	
$CdGa_2S_4$	$CdS + Ga_2S_3$	650	HCl	2	Much	Yes	Yes	Close to $CdGa_2S_4$, some free Ga_2S_3
$CdGa_2Se_4$	$CdSe + Ga_2Se_3$	900	HCl	2	Much	Yes	Yes	

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SECTION 3

MATERIALS EVALUATION: DIELECTRIC CONSTANT MEASUREMENTS

Measurements have been delayed because of contact problems. Attempts to use silver paint contacts yielded anomalous results: the contacts were non-Ohmic and measurements showed extremely high capacitance. Evaporated contacts using constituent metals (e.g., Zn for $ZnIn_2S_4$, Cd for $CdGa_2Se_4$) are being processed. We anticipate results in the next quarter.