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RAYTHEON COMPANY
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20. ABSTRACT (Continue on reverse side if necessary, and identify by block number) The objective of this program was to extend basic knowledge of the structure and properties of significant new infrared materials. Two materials were synthesized and studied: Gallium phosphide, which is of potential importance as a high durability multispectral window surfacing material and zinc selenide, the current state-of-the-art material for high quality long wavelength infrared and laser components.		

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A new microcrystalline form of gallium phosphide was synthesized by chemical vapor deposition. It exhibited high infrared transparency and no evidence of free carrier absorption. Spectroscopy was carried out on single crystals of gallium phosphide and gave new detailed information on the 3 and 4 phonon spectra at wavelengths below 12 μm . Similar spectroscopy on the infrared absorption edge of ZnSe better defined its 3 and 4 phonon spectral features and separated them from instrumental effects.

A low temperature form of ZnSe synthesized by the CVD process showed impurity spectral features at wavelengths below 13 μm . They were attributed to the presence of ZnH_2 , H_2Se and H_2S complexes.

Broadband internal reflection spectroscopy was carried out on ZnSe samples subjected to various organic cleansing procedures. Spectral absorption at wavelengths below 13 μm were attributed to CH_2 and H_2O - other features were not identifiable.

Heat treatment and compression tests on standard CVD ZnSe caused its infrared absorption coefficient to change. Initial heating to 300°C reduced its 10.6 μm absorption. The material showed non-recoverable distortion at stress levels as low as 5000 psi.

Finally, a new laser calorimetry technique using polarized laser radiation and a prismatic sample was established. It permits the unambiguous separation of surface and bulk absorption coefficients on a single sample and represents a significant advance in calorimetry technique.

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1.0 RESEARCH OBJECTIVES

This program was conceived originally as part of a five year effort to consolidate the scientific advances that underlay the very successful technical development of high transparency infrared materials for use in high power laser windows. That development program concentrated its attention primarily on the production of zinc selenide, the alkali halides and alkaline earth fluorides in high purity forms that minimized both scatter and absorption effects. The result was a very significant increase in the power handling capacity of high power infrared optics. It created an active research community engaged in the fabrication, characterization and understanding of the fundamental optical and mechanical properties of these materials.

The objectives of the present program were set down in very broad terms intended to extend these and similar considerations to materials used in a wider range of infrared optics, as follows:

- 1) Synthesis of polycrystalline forms of chalcogenide, oxide and fluoride materials that exhibit high transparency in the infrared spectral range.
- 2) Investigation of the factors, intrinsic and extrinsic, that limit the infrared transparency of polycrystalline forms of chalcogenide optical materials.
- 3) Exploration of linear and nonlinear scatter and absorption mechanisms in chalcogenide oxide and fluoride infrared materials.
- 4) Identification of the absorption mechanisms active at surfaces and in sub-surface structures in transparent chalcogenides, oxides and fluorides.

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A. D. BLOSE

Technical Information Officer

5) Investigation of the infrared absorption properties of these materials at elevated temperatures and analysis of their linear and non-linear interaction with high power laser radiation.

2.0 STATUS OF RESEARCH EFFORT

Raytheon Company's contribution to this field has been primarily experimental, in the actual fabrication of materials now used in airborne lasers and in air-to-air and air-to-ground missiles. In the two year period of this contract we have worked exclusively on materials already in development for other Air Force programs; namely, chemically vapor deposited zinc selenide and gallium phosphide. Zinc selenide is still the prime material for use in high power CO₂ laser systems and is also important in infrared imaging optics. Gallium phosphide has been considered as a high durability companion material for use with zinc selenide in airborne imaging systems. A variety of optical and mechanical experiments have been carried out on these two materials. They can be grouped as follows:

1. Synthesis and Characterization of Microcrystalline Gallium Phosphide
2. Infrared Spectroscopy of GaP
3. Infrared Spectroscopy of CVD ZnSe
4. Thermo-Mechanics of ZnSe
5. Laser Calorimetry in High Transparency Materials.

Each subject is covered in more detail in the following sections.

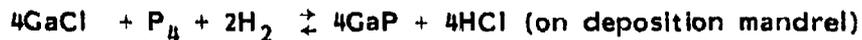
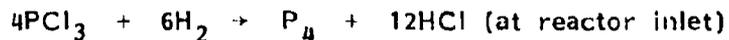
2.1 Synthesis and Characterization of Microcrystalline GaP

This project was carried out in part with funding under this program, and in part under a parallel Air Force contract (Contract No. F33615-78-C-5073). Gallium phosphide is a relatively wide band gap III-V semiconductor material that is transparent at the longer visual wavelengths and,

in addition, shows good transparency at infrared wavelengths in the intervals between well defined lattice vibration bands. In addition, it is the hardest of the common III-V group materials. As such it has been considered as a leading candidate for high durability surface layers on multispectral infrared windows designed to withstand rain and sand erosion to a greater degree than the state-of-the-art ZnS material.

It was of interest, therefore, to study the feasibility of synthesizing GaP by the vapor deposition technique already proven successful for ZnS and ZnSe. If the CVD technique can be successfully applied to a new material, it immediately offers the possibility for the fabrication of the large size blanks needed for practical infrared optics. In this context, success implies the formation of polycrystalline material with a porosity of less than 10 ppm to ensure uniformity of refractive index and low scatter coefficients, and at the same time a material that is highly stoichiometric in order to avoid free carriers and conduction losses. In order to maximize the mechanical strength of the material very fine grain size is also desired.

CVD runs were made to form GaP based on the technology developed at Raytheon for fabricating GaAs films for microwave devices. The reaction chamber was formed from a fused silica tube and was heated by a 4-zone Lindberg furnace, 4 inches in diameter. A solid GaP source was contained in a quartz boat in the hot zone of the furnace and was reacted and transported into the deposition area by a mixture of phosphorous trichloride (PCl_3) vapors and purified hydrogen (H_2) gas. The deposition mandrel was fabricated from vitreous carbon plates. Pyrex wool loosely filled the exhaust end of the reactor tube and effectively filtered out particulate byproducts (P and GaCl). The vapor pressure of the halide reactant was controlled by controlling the bubbler temperature which, in turn, established the PCl_3/H_2 molar ratio. The bubbler was contained in a nitrogen filled glove box for safety purposes. During deposition of GaP, the following reactions are thought to take place.



A typical deposition lasted 80 hours, limited usually by the volume of the solid source material.

The physical properties of CVD GaP were found to depend on deposition temperature. The material becomes increasingly transparent with increasing deposition temperature. At a deposition temperature near 820°C, it is completely transparent, orange in color, and shows a transmittance curve identical with that of single crystal material. In lower temperature materials, transparency is reduced by absorbers located mostly at grain boundaries. They are as yet unidentified, but may depend on deviations from stoichiometry. In some cases, also, an increased absorption appears at long infrared wavelengths and is characteristic of free carrier effects.

In the fully transparent form, the average grain size was some 50-100 μm in cross-section and ranged up to 300 μm in the growth direction. The measured Knoop hardness (834 kg/mm^2) is similar to single crystal material. Rain erosion testing carried out on samples of this material bonded onto zinc selenide substrates showed that the durability of the composite was essentially the same as the conventional zinc sulfide material. As such, the composite design has little to recommend it over monolithic ZnS as a multispectral window.

2.2 Infrared Spectroscopy of GaP

Investigations over the past 10 years have provided a great deal of information about and understanding of the intrinsic absorption

processes that define the infrared transmittance limits of halide and chalcogenide material and of elemental materials such as germanium and silicon. The long wavelength limits of these materials is set by an exponential absorption edge made up of high order lattice vibrations, or "multiphonon" spectra. At room temperature, these edges show very little structure, in general, and are best described by a spectral density distribution of mode pairs, triplets, quartets, and so on, whose excitation is governed by the crystal lattice symmetry, its ionicity and the nonlinear vibratory characteristics of the lattice.

Gallium phosphide stands out in the group of III-V and II-IV material with the zinc blende structure in exhibiting a very rich and well defined spectrum associated with both the fundamental lattice vibrations and with its 2-phonon spectrum. In this investigation, we have been able to display the corresponding 3-phonon spectrum for the first time, along with several of the major 4-phonon peaks. In this case the individual 1, 2, 3, and 4-phonon line groups are well delineated and separated from each other, with a spectral range of relative transparency between each group.

It is possible to make assignments of specific peaks based on a knowledge of the 1-phonon dispersion data derived from diffraction and/or second order Raman scattering. In principle, the spectrum could be accurately computed from a knowledge of the 1, 2, 3, and 4-phonon density-of-states spectra, modified by a function that defines the oscillator strength for each mode. In practice, such a calculation is too difficult to make. However, considerable success has been achieved in matching the sharp spectral factors of such spectra, if not their relative intensities, by simply calculating the n-phonon density of states. Such a calculation is being attempted for GaP to fit our new spectral data.

2.3 Infrared Spectroscopy of ZnSe

The spectroscopic and calorimetric studies carried out in the past on CVD ZnSe have shown the infrared absorption edge at wavelengths beyond 11 μm to be formed by 3-phonon processes. In the past two years, subtle features on this edge have been assigned to various 3 and 4 phonon characteristics. A further examination of this spectral edge has been made using very long samples to better distinguish between real features and instrumental artifacts. This work has been partially successful, but in the light of variations induced in the 10.6 μm absorption coefficient by annealing, described below, we believe that a further attempt to define these edge features is necessary using annealed material.

The object of this work is to establish the degree to which absorption measured at wavelengths less than 11 μm is determined by extrinsic mechanisms, to define the specific absorbing species and to evolve ways for their elimination. Typically absorption coefficients lie in the range of $3\text{-}10 \times 10^{-4} \text{ cm}^{-1}$. At this level it is extremely difficult to observe spectral features that would help in identification. We have had some success in this identification by using material deliberately formed under conditions that lead to large concentrations of defect centers. The spectra of this material show peaks that we identify with ZnH_2 , H_2S and H_2Se complexes in ZnSe. Whether these same centers are present in the standard material at the $1 \sim 10$ ppm concentration level needed to account for its extrinsic absorption is not proven but is certainly a real possibility.

In attempting to establish the actual bulk absorption coefficients by laser calorimetry, it is important to be able to distinguish them from absorption at the surfaces. Typical surface absorption coefficients for ZnSe lie between $2 \sim 5 \times 10^{-4}$ per surface, and introduce considerable uncertainty in cases where the bulk coefficient is below 10^{-3} cm^{-1} . A series of broadband spectral analyses were carried out to assess the effects of various cleaning techniques on surface absorption. This was done using

total internal reflection plates wherein multiple reflections from the surfaces enhance the relative strength of the surface absorptions. A variety of organic spectral lines were seen, together with an ill-defined spectrum near 6 μm that can be easily confused with the ZnH_2 band previously seen in bulk ZnS and ZnSe spectra. An unidentified band in the 10-11 μm region also appeared that affects CO_2 laser calorimetry.

2.4 Thermo-Mechanics of ZnSe

A series of experiments were carried out to find the effects of compressional stress on the optical properties of ZnSe . They were done both at room temperature and at temperatures up to 500°C . Two effects are predominant; the first is a reduction in the bulk absorption coefficient of the material, the second is a permanent deformation of test body, seen primarily in the development of a residual stress-optical pattern.

More extensive tests have shown that the reduction in bulk absorption depends on the thermal annealing process, and not on the presence of mechanical stress. The effect represents a reduction of bulk absorption by an amount of $5.7 \times 10^{-4} \text{ cm}^{-1}$. Previous calorimetry set the original level at $9.3 \times 10^{-4} \text{ cm}^{-1}$. The final value of $3.6 \times 10^{-4} \text{ cm}^{-1}$ achieved after thermal anneal is comparable to the lowest values ever recorded in CVD ZnSe . The intrinsic value at 10.6 μm is believed to be near $2 \times 10^{-4} \text{ cm}^{-1}$ with the remainder due to hydrogen complexes present either in the body of the ZnSe grains or at intergrain boundaries. While it is plausible that the thermal annealing either changes the structure of these complexes, or removes them by diffusion, it is difficult to understand why the annealing action did not occur during the cool-down stage of the original vapor deposition sequence itself. In any case, the achievement of bulk absorption values below $5 \times 10^{-4} \text{ cm}^{-1}$ by post deposition anneal is a very significant finding and should prove of great value in the preparation and use of ZnSe in laser optical systems.

The findings on the effects of compressive stress, on the other hand, are somewhat disquieting. As a rule, materials that fail by brittle fracture due to accelerated growth of pre-existing flaws tend to withstand compressive stresses many times greater than their tensile strength. Thus for ZnSe, whose tensile strength is in the range of 5000-8000 psi, depending on grain size, one would expect a stable and elastic response to compressive stresses up to 40 - 50 kpsi. In fact, our experiments at room temperature show that a large scale irreversible deformation takes place at compressive stress levels greater than 5000 psi and possibly as low as 3000 psi. At elevated temperatures, the large scale pattern is not observed, but is replaced by a fine scale pattern that appears at stress levels as low as 1000 psi.

These findings have serious implications in the design and use of optical components such as window and lens elements that act as high pressure windows or are subjected to compressive stress in their mounting, in temperature cycling, or when they are heated by the passage of high power laser beams. A progressive reduction in optical performance might occur under these conditions. It is clear that an effort should be made to reduce the plasticity of CVD ZnSe, possibly by the introduction of aliovalent dopants, a technique that has been applied with greater success in the case of the alkali halides.

2.5 Laser Calorimetry In High Transparency Materials

The separation of bulk and surface absorption in laser calorimetry is important in the characterization of high transparency materials. The technique first used in this field involved independent measurements on a set of samples of different lengths. These gave a measure of the bulk loss as the slope of the loss versus length curve, and a measure of surface loss as the zero length intercept. The success of the method depends on the uniformity of bulk loss, sample to sample, and the repeatability of the surface finishing and cleaning steps. Two other techniques have evolved to allow separation of bulk and surface absorptions with measurements taken

on only one sample. The first technique uses "long" bars and examines the time dependence of the temperature rise at the center of the bar. The initial temperature rise is determined by bulk losses only, and is followed by a temperature surge as thermal diffusion from the end surfaces comes into play. A second technique records the sound pulses produced by pulse heating of a sample and deduces the separate absorption sites from pulse propagation effects.

In considering other possibilities for surface/bulk separation, we examined the possibility of using standard ballistic calorimetry but on specially prepared prismatic samples wherein a laser beam is made to traverse a fixed pattern of paths and surface intercepts, but wherein the relative intensity of the light at each surface and along each segment of the path can be varied by changing the polarization and/or the direction of propagation of the beam. A simple 60° equilateral prism will suffice for materials with a refractive index less than 2. For materials with $n > 2$, the prism design and internal path is more complicated and takes the form of a truncated isosceles triangle. It is clear from even a cursory analysis that in principle, the removal of the degeneracy of a parallelepiped sample allows separation of surface and bulk losses, and could lead to a reduction in the number and size of sample test pieces needed in calorimetry. The practicality of the technique, though, has not been assessed. Clearly more care must be taken in the fabrication of prismatic samples and a more flexible calorimeter equipment is required. An experimental test of this method is in progress.

3.0 PUBLICATIONS IN PROFESSIONAL JOURNALS

The work carried out under this contract has explored possibilities in some eight different areas. Materials for professional publications has been accumulated in each, but no completed manuscripts have been submitted. Partial manuscripts exist for four papers.

- 1) Extrinsic Absorption Spectra in Zinc Selenide
- 2) Three and Four-Phonon Spectra in GaP
- 3) Effects of Heat Treatment on Infrared Absorption in CVD ZnSe
- 4) Polarization Sensitive Laser Calorimetry.

4.0 PROFESSIONAL PERSONNEL ASSOCIATED WITH RESEARCH EFFORT

The following staff were associated with this effort:

- 1) Mr. R. Donadio
- 2) Dr. P. A. Miles
- 3) Dr. J. Pappis
- 4) Dr. R. W. Tustison
- 5) Dr. C. B. Willingham

5.0 INTERACTIONS

Papers based directly on work performed under this program:

"Extrinsic Absorption Spectra in Zinc Selenide," by P. A. Miles, Optical Society of America, October 1979, Rochester, New York.

"Erosion Resistant FLIR Windows," by P. A. Miles and R. W. Tustison, IRIS Specialty Group Meeting, June 1980, Seattle, Wash.

In addition, this project is closely connected with a very active program in the design, fabrication, test and evaluation of new infrared materials in Air Force and DoD laboratories. Professional activities of the staff linked with this project include the following:

P. A. Miles

Related Papers

"Hardened Sensor Optics," (J. L. Hopson, W. T. Beachamp) Proc. 3rd DoD Conference on High Power Laser Technology, 1979.

"Erosion Resistant Infrared Windows - Thermal, Mechanical and Optical Aspects of Composite Designs," Proc. SPIE 23rd Annual Technical Symposium, 1979.

"Compressive Failure of Sapphire Under CO₂ Laser Irradiation" (R. L. Gentilman), 11th Annual Symposium on Optical Materials for High Power Lasers, October 1979.

"Multilayer Dielectric Reflectors for Laser Hardened Optical Systems," (J. L. Hopson, W. T. Beauchamp), High Power Laser Optical Components Meeting, November 1979.

"Tactical Missile Countermeasures," (J. E. Hopson), Proc. 4th DoD Conf. on Laser Vulnerability, Effects and Hardening, September 1980.

"Laser Hardened Infrared Missile Domes," (R. L. Gentilman, E. A. Maguire, J. E. Hopson), Proc. 4th DoD Conf. on Laser Vulnerability, Effects and Hardening, September 1980.

Professional Activities

Review Workshop for ONR Advanced Materials Program. Philadelphia, May 7, 1979. Cognizant Individuals: R. Pohanka, A. Diness (ONR).

Member, E.I.A. Critical Technology Expert Group to Advise Department of Defence on Technology Export Policy, Washington, April 24, May 22, October 25, 1979. Cognizant Individuals: William T. Sackett Jr., Honeywell Research Center, Minneapolis; Col. John A. Hager, Office of Undersecretary of Defense-DDR/E.

Review Workshop for ONR Advanced Materials program. Philadelphia, May 8-9, 1980. Cognizant Individuals: R. Pohanka, W. Savage (ONR).

Program Reviews at Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. Cognizant Individuals: D. W. Fischer and J. R. Koenig (AFML/LP).

J. Pappis and R. Donadio

Related Papers

"Infrared-Active Phonons in Cubic Zinc Sulfide," (C. Klein). To be published in Journal of Applied Physics (1979).

"Specifications of RAYTRAN[®] Materials," (J. Connolly and B. diBenedetto), Proc. Soc. of Photo-Optical Instrumentation Engineers, Vol. 181, Washington, DC (April 1979).

"Lattice Absorption, Index Homogeneity, and Image Spoiling Characteristics of CVD ZnS in the Infrared," (C. Klein, B. diBenedetto, and T. Kohane), Proc. Laser Damage Sym., Boulder, Colorado (Sept. 1979).

"Chemical Vapor Deposition of Ceramics for Infrared Windows," (R. Gentilman, B. diBenedetto, R. Tustison). Proc. Am. Ceram. Soc. Annual Meeting, Chicago, Illinois (April 1980).

"Fabrication of CVD ZnS and ZnSe Optical Components," (B. diBenedetto), Optical Soc. of Am. Workshop, Falmouth, MA (September 1980).

Professional Activities

Program Reviews at Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. Cognizant Individuals: L. Kopell, W. Frederick, J. Koenig, A. Hopkins, E. Kuhl, J. Strecker.

Review of High Durability IR Transparent Materials, Office of Naval Research, Washington, DC, February 22, 1980. Cognizant Individuals: R. Pohanka, W. Savage.

Roadmap Review Meeting, Wright-Patterson AFB, Ohio. June 25-27, 1980. Cognizant Individuals: AF Materials Lab Staff.

"Graded Optics," Army Research Office, Raleigh, N. C., October 20, 1980. Cognizant Individuals: Dr. B. D. Guenther, Dr. J. D. Duthie.

6.0 MISCELLANEOUS

During the period of this research effort there were no new discoveries, inventions, patent disclosures or specific applications.