

**REPORT DOCUMENTATION PAGE**

Form Approved OMB No. 0704-0188

maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.  
**PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

**1. REPORT DATE (DD-MM-YYYY)**      **2. REPORT TYPE** Final Report      **3. DATES COVERED (From - To)**  
 8 February 2002 - 08-Feb-03

**4. TITLE AND SUBTITLE**  
 Polarization Effects In Optical Properties Of Gase Crystal Bulk And Surfaces

**5a. CONTRACT NUMBER**  
 F61775-02-WE008

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**  
 Professor Kerim Allahverdi

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5e. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**  
 TUBITAK, Marmara Research Center  
 P.K. 21 41470 Gebze/Kocaeli  
 Gebze/Kocaeli P.K.21  
 Turkey

**8. PERFORMING ORGANIZATION REPORT NUMBER**  
 N/A

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**  
 EOARD  
 PSC 802 BOX 14  
 FPO 09499-0014

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**  
 SPC 02-4008

**12. DISTRIBUTION/AVAILABILITY STATEMENT**  
 Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**

20040625 088

**14. ABSTRACT**

This report results from a contract tasking TUBITAK, Marmara Research Center as follows: The contractor will investigate the anisotropy of the optical properties of quasi two-dimensional crystals, specifically of GaSe, using IR absorption and exciton photoluminescence spectroscopy over a wide frequency range. The results obtained will be used to determine the mechanism of free carrier scattering and its anisotropy; to identify the nature of peaks observed in the anisotropy of IR absorption spectra; and to construct the equations describing the spectral dependence of the absorption coefficients for two polarization in the spectral range of 1-25 mm.

**15. SUBJECT TERMS**  
 EOARD, Photonics, optical materials, Nonlinear Optics

<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b> UL	<b>18. NUMBER OF PAGES</b> 53	<b>19a. NAME OF RESPONSIBLE PERSON</b> Alexander J. Glass, Ph. D.
<b>a. REPORT UNCLAS</b>	<b>b. ABSTRACT UNCLAS</b>	<b>c. THIS PAGE UNCLAS</b>			<b>19b. TELEPHONE NUMBER (Include area code)</b> +44 (0)20 7514 4953

**FINAL REPORT FOR THE PROJECT  
“POLARIZATION EFFECTS IN OPTICAL  
PROPERTIES OF GaSe CRYSTAL BULK AND  
SURFACES”**

**MATERIALS AND CHEMICALS TECHNOLOGIES RESEARCH  
INSTITUTE  
MARMARA RESEARCH CENTRE  
TURKISH SCIENTIFIC AND TECHNICAL RESEARCH COUNCIL  
GEBZE/KOCAELI  
TURKEY  
DECEMBER 2002**

Dr. Alex GLASS

December 16, 2002

European Office of Aerospace

Research and Development

(EOARD)

223/231 OLD MARYLEBONE ROAD

LONDON, NW1 5TH

UNITED KINGDOM

Subject: The Final Report (Stage 4) for the Project "POLARIZATION EFFECTS IN OPTICAL PROPERTIES OF GaSe CRYSTAL BULK AND SURFACES" (SPC 02-4008 and CON F61775-02-WE008).

Dear Dr. GLASS,

Please find enclosed the Final Report (Stage4) for the Project 9SPC 02-4008 and CON F61775-02-WE008 that have been prepared according to a Final Work Plan for entire Project and a Final Budget of Suppliers and Equipment. The report is prepared according the requirement to include the declarations, disclaimers and acknowledgment specified by the terms of my contract.

Yours sincerely,



Prof.Dr. Kerim ALLAHVERDI

Principle Investigator  
Materials and Chemicals Technologies  
Research Institute, Materials Division

## **CONTENT**

<b>LIST OF RESEARCHERS PARTICIPATED IN PROJECT.....</b>	<b>4</b>
<b>INTRODUCTION.....</b>	<b>5</b>
<b>OBJECTIVES STATED.....</b>	<b>7</b>
<b>EXPERIMENTAL.....</b>	<b>8</b>
<b>RESULTS AND DISCUSSION.....</b>	<b>9</b>
<b>CONCLUSION.....</b>	<b>19</b>
<b>ACKNOWLEDGMENTS OF SUPPORT AND DISCLAIMER... </b>	<b>21</b>
<b>REFERENCES.....</b>	<b>23</b>
<b>ATTACHMENTS AND TABLES.....</b>	<b>25</b>
<b>PAPER SUBMITTED TO THE JOURNAL OF APPLIED PHYSICS.....</b>	<b>38</b>

## **LIST OF RESEARCHERS PARTICIPATED IN PROJECT**

From the Marmara Research Centre, Materials and Chemicals Technologies  
Research Institute, Turkish Scientific and Technical Research Council,  
Gebze/Kocaeli, Turkey:

Prof.Dr. Kerim ALLAHVERDÍ -	Principle Investigator
Doc.Dr. AliArslan KAYA-	Researcher
Doc.Dr. Esin GÜNAY-	Researcher
Dr. Zehra SALAEVA-	Researcher (was invited to MKTAE, MAM, TUBITAK from the Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan)
Dr. Havva Kazdal ZEYTIN-	Researcher

From the US AF Wright-Patterson Laboratory, Materials Directorate, Ohio, USA:

Prof.Dr. Nils FERNELIUS-	Researcher
Dr. Jonathan GOLDSTEIN-	Researcher

## INTRODUCTION

Gallium selenide is one of the best laser frequency generation material in the mid IR. Outstanding non-linear optical properties (high value of the non-linear optical coefficient  $d_{22} \geq 72 \pm 6 \text{ pm/V}$ , birefringence, that makes it possible to satisfy the phase-matching conditions, high optical quality, wide transparency range of  $0.65 - 18 \mu\text{m}$  and high damage threshold  $30 \text{ MW/cm}^2$  [1-3]) make this material very useful for sum- and difference- frequency generation, second harmonic generation, optical parametric oscillation, bi-stable switching devices, laser light modulators, polarized optical filters, optical filters tunable by the electric fields etc. Recently a new possibility was found to use this material in the THz range [4]. The type-II difference laser frequency generation with the kilowatt peak power and output wavelength continuously tunable in the range of  $4.14 - 28 \mu\text{m}$  has been achieved in [4]. This opens new perspectives to use this material in atmosphere monitoring, countermeasures, space signal detection etc.

The binding energy of the direct free excitons  $Ry = 19.5 \text{ meV}$  [5] makes it possible to observe them in optical absorption (reflection) spectra at room temperature.

More than 1300 papers were devoted the physical properties of GaSe. Most of them describe the optical and electrical properties when the wave vector of the incident light was directed along the optical  $c$ - axis and the current flow in the plane of layers, respectively. About 11 papers were devoted the optical properties of

GaSe in the mid IR ( $400 - 10000 \text{ cm}^{-1}$ ). Most of them describe the results of experiments when the wave vector of incident light was parallel to  $c$ - axis.

The results of theoretical band structure calculations revealed that GaSe is an indirect gap material ( $E_g^d = 2.02 \text{ eV}$ ,  $E_{exc}^d = 2.00 \text{ eV}$ ,  $E_g^i \approx 2.00 \text{ eV}$  [5], where  $d$  is for direct,  $exc$  is for excitons,  $i$ - for indirect gap, respectively). Energy position of the direct free excitons is in resonance with the indirect gap and they are considered as the *resonance* free excitons. The valence band of GaSe is not degenerate and the second valence band is about  $1 \text{ eV}$  lower from the top of the valence band at  $k = 0$  [19,20].

Due of the layered structure plane-parallel crystals between about  $20 \mu\text{m}$  (and thick) and several millimeters in thickness are easily cleaved with a razor blade. The cleavage plane of GaSe is parallel to the layers so that the samples with excellent surfaces are obtained. Yet in another directions cutting is very problematic. At the same time the value of the angle of synchronism  $\theta$  is beyond the critical angle of total reflection. Latter extremely limits efficient application of GaSe in non-linear optical laser frequency converters. This makes necessary to cut and polish the crystals under different angle to the cleavage plane into plane-parallel plates with good optical quality.

## OBJECTIVES STATED

They are as follows:

to develop the technology of obtaining the plane-parallel plates of GaSe with at least  $5 \times 5 \text{ mm}^2$  or larger faces, which contain the optical  $c$ - axis;

to study optical anisotropy in two polarization ( $E \perp c$  and  $E // c$ , where  $E$  is the electric field vector of the electromagnetic wave) in the mid IR;

to construct accurate equation that describe the wavelength dependence of the absorption coefficient  $\alpha$  in  $E // c$  polarization in the mid IR;

to explain the anisotropy of absorption mechanism in the mid IR and the mechanism of the free carriers scattering;

to study room-temperature anisotropy of the photoluminescence (PL) spectra of the direct free excitons.

## **EXPERIMENTAL**

Equipment and facilities used in the present research:

X-ray diffraction (Shimadzu XDR-600) and X-ray fluorescence (Philips PW 2404;

high resolution transmission TEM (JEOL - JEM100C) and scanning SEM (JSM - 840) microscopes;

IR Fourier transform spectrometers (Perkin Elmer Spectrum 1 FTIR and Bomem DA-3);

Ar<sup>+</sup> laser and DFS-24 spectrometer;

facilities and powders for cutting and polishing the crystals, visual microscopes, digital micrometer.

## RESULTS AND DISCUSSION

Four distinct modifications, the  $\beta$ -, the  $\varepsilon$ -, the  $\gamma$ - and the  $\delta$ - type were reported for GaSe, differing by the stacking order of two-dimensional Se-Ga-Ga-Se sheet [5]. The difference between types arises from the stacking of layers and from the number of layers per unit cell. The  $\varepsilon$ - type [ $(D_{3h}^1$  space group (SG), contains 2 layers per unit cell] is the most common and best investigated. Up to now the existence of the  $\beta$ - type ( $D_{6h}^4$  SG, two layers per unit cell) has not yet been confirmed. The  $\gamma$ - type has three layers ( $C_{3v}^5$  SG), the  $\delta$ - type contains four layers per unit cell ( $C_{6v}^4$  SG). Normally the crystals grown by the Bridgman method are the mixture of  $\varepsilon$ - and  $\gamma$ - types, with the predominant content of former.

Starting the project *first* we characterized the crystal by help of XDR-600 Shimadzu X-ray diffractometer. Observed diffraction peaks at  $11.10^\circ$ ;  $22.26^\circ$ ;  $28.60^\circ$ ;  $32.30^\circ$ ;  $39.76^\circ$ ; (broad weak);  $45.62^\circ$ ;  $48.54^\circ$ ;  $54.10^\circ$ ;  $57.92^\circ$  [see Attachment XDR to the present report. Same Figure with more detailed description of the results has been presented in the Interim Report (Stage2), which have been sent to EOARD in June 17, 2002)] were identified according to the Data Base: Hanawalt Search Manual, Inorganic Phases, Powder Diffraction Files, Sets 1-45, International Centre for Diffraction Data, Pennsylvania 19073-3273, USA, Copyright JCPDS- International Centre for Diffraction Data, 1995. The results of identification showed that the crystals belong to  $\varepsilon$ - modification with the lattice parameters  $a = b = 3.74 \text{ \AA}$ ,  $c = 15.907 \text{ \AA}$ ,  $c/a = 4.243$ . Attachment XDR1 represents the results of identification of the observed diffraction peaks according to corresponding Muller's indexes. The results of X- ray fluorescence measurements showed the next content of the initial components: Ga in the range from 45.914 % (Se- 54.084 %) to 45.742

(Se- 54.258 %). Some samples had the composition Ga- 47.174 %, Se- 52.826 %). Unintended impurities were detected also in some samples: Ni (0.220 %), Mn (0.049 %). No noticeable difference was observed in the optical properties of samples with different content of chalcogenide atoms.

Characterization using the thermoelectric power measurements showed that all crystals were p- type.

The hexagonal symmetry was confirmed also by the TEM and SEM measurements technique. To study the crystals by TEM technique a method was developed to obtain thin (less than 500 Å) films of GaSe. *Method developed opens new perspectives for experimental investigations of quantum sized effects in the layered GaSe- type crystals.* The details of this method were described in the interim Report (Stage2). In some cases non-identified features perturbed the pattern. This fact says in a favor that the crystals consist of the mixture of different modifications with predominant content of  $\epsilon$ - type (in agreement with the results of optical measurements using confocal Raman and PL microscopy [6]).

*Special attention* at the beginning of project we made on developing a technique of preparing the plates of GaSe crystals (aperture 5 x 5 mm<sup>2</sup> or larger), containing the optical *c*- axis. Main steps of developed technology include:

1. Embedding the single crystal blocks into some binder.
2. Cutting the crystal blocks into plane-parallel plates.
3. Polishing the plates.

Detailed description of above mentioned 3 steps were described in the Interim Report (Stage2), that has been sent to EOARD on June 17, 2002.

We found that good results were obtained when using the Buchler Epoxide Resin as a binder. Cutting with a sewing wire (with the wire thickness about 250  $\mu$ m) and

with commercial Struers Minton device with rotating diamond coated wheel gave nearly the same results, the latter being more fast and productive. Final polishing of surfaces were performed with Buchler Matermet Colloidal Silica ( $\text{SiO}_2$ ) suspension with a partial diameter  $0.05 \mu\text{m}$ . Polished surface were examined by ZEISS AXIOYTECH optical microscope in reflected and transmitted light. Obtained surfaces were compared with freshly cleaved one oriented in the (001) plane. Freshly cleaved surfaces were more perfect. Nevertheless, polished plates were quite good optical quality. They had mirror-like plane-parallel surfaces that allowed to read the printed text onto the polished surface in the reflected light. Good optical quality was confirmed also when comparing the transmission spectra of our samples (for  $E // c$  in the range of  $400 - 700 \text{ cm}^{-1}$ ) with those presented in Ref. [7]. Maximum transmission for  $8.78 \text{ mm}$  thick sample was  $\sim 55 \%$  (see Attachment **IR1**), whereas for  $0.84 \text{ mm}$  plate presented in Ref. [7] it was  $\sim 20 \%$  (we understand that the transmission is dependent also from the impurity content).

The transmission spectra of freshly cleaved samples were compared with the spectra of polished samples. For  $E \perp c$  the spectra were identical with a small difference in transmission. Transmission of freshly cleaved sample was about 5 to 7 % higher for the sample with same thickness. The transmission spectra of  $1.061 \text{ mm}$  thick freshly cleaved sample measured in  $E \perp c$  at room temperature is presented in Attachment **IR2**.

5 samples were prepared. These samples have been sent to the Materials Directorate of the WPAFB, Ohio to Dr. Nils FERNELIUS for polarized spectra measurements in the mid IR. The samples were as follows:

$8 \times 6.3 \times 8.78 \text{ mm}^3$  (length x width x thickness) *Sample No1.*

$8 \times 3.8 \times 6 \text{ mm}^3$  ----- *Sample No2.*

10 x 15 x 2.66 mm<sup>3</sup> ----- *Sample No3.*

15 x 5 x 0.468 mm<sup>3</sup> ----- *Sample No4.*

10 x 5 x 0.274 mm<sup>3</sup> ----- *Sample No5.*

Each of these samples may be used for anisotropy measurements of the absorption spectra in  $E \perp c$  and  $E // c$  at room temperature. Some of them that were not fully embedded in epoxy binder along the perimeter (sample *No2, No3, No5*) may be used also for the low-temperature experiments.

Detailed explanation how to handle these samples and recommendations how to mount them onto the sample holder in case of low-temperature measurements were presented in the Interim Report (Stage2).

Attachment **IR1** shows non-polarized room-temperature transmission spectrum of 8.78 mm thick crystal (*Sample No1*) when the wave vector of the incident light was perpendicular to polished plane. The absorption bands at 621, 889, 1073 (seen as a weak shoulder) and 1270  $cm^{-1}$  are clearly resolved. Bands in the range below 600  $cm^{-1}$  are not seen due of high thickness of the sample. Transmission spectrum of 2.48 mm thick sample measured at the same conditions as for 8.78 mm thick GaSe is presented in Attachment **IR3**. Besides the bands mentioned above the bands at 540, 945, 1095  $cm^{-1}$  are seen. The prominent feature (when analyzing the number and the shape of the lines) of these spectra is a sharp line 891  $cm^{-1}$ . To our knowledge, this line was observed for the first time. Nature of this line will be discussed later.

Measurements of the transmission spectra of samples (from freshly cleaved surface and the surface containing the optical axis) with different thickness in non-polarized and polarized light revealed the bands that are shown in **Table 1**. **Table 1** summarizes the data published in Ref. [7-15] and the results obtained in the present Project. 8 and 5 absorption bands were observed at 420, 448, 482, 488, 512, 540,

551, 619  $cm^{-1}$  and 498, 891, 945, 1095, 1270  $cm^{-1}$  in  $E \perp c$  and  $E // c$  geometry, respectively. Nature of these bands will be discussed later. Our results are in a fairly good agreement with those published by different authors.

### **Anisotropy of the mid IR absorption**

Room-temperature transmission spectra of 8.78 mm thick GaSe in two polarization  $E \perp c$  (“o-ray”) and  $E // c$  (“e-ray”) is given in Attachment **IR4**. The absorption band at 498  $cm^{-1}$  is not seen due to a higher thickness of sample when comparing with that of 2.48 mm thick sample (Attachment **IR3**). The absorption bands at 891  $cm^{-1}$  and 1093  $cm^{-1}$  are clearly resolved, whereas the bands at 945 and 1093  $cm^{-1}$  are seen as a weak shoulder. Different character for the transmission-wavelength dependencies for *o*- and *e*- rays follows from the Attachment **IR4**, especially in the spectral range below  $\sim 2250$   $cm^{-1}$ . The transmission for *e*- ray decreases gradually to longer wavelength starting from  $\sim 2250$   $cm^{-1}$ , whereas for *o*-ray transmission decreases sharply from  $\sim 750$   $cm^{-1}$ . To reveal the origin of such anisotropy we performed the calculations of the absorption coefficient  $\alpha$ . The absorption coefficient was calculated by using the formulae given in Ref. [16]:

$$\alpha = (1/d) \ln \left[ 2TR^2 / \sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2 \right] \quad (1)$$

where  $d$  is the sample thickness,  $T$  and  $R$  is the transmission and reflection, respectively.

According to Ref. [16], in the transparency range reflection coefficient may be calculated according to formulae:

$$R = (n - 1)^2 / (n + 1)^2 \quad (2)$$

where  $n$  is the refractive index.

To calculate  $R$  we used  $n = 2.8$  which is the average value of sum for the ordinary and extraordinary refractive indexes in the transparency range. Room-temperature wavelength dependencies of the absorption coefficients for both orientations (polarization of the incident electromagnetic light relative to the optical  $c$ - axis) are shown in the Attachment **IR5**. These dependencies were calculated using the formulae (1) and the data of Attachment **IR4**.

To explain the anisotropy in the transmission spectra we first supposed, that the absorption in  $E // c$  in the spectral range below  $2250 \text{ cm}^{-1}$  are due of the free carriers that move along the optical  $c$ - axis.

In case when the relaxation time  $\tau$  does not depend on time, for the free carriers absorption Drude theory gives [16]:

$$\alpha = Nq^2\lambda^2/m^*8\pi^2nc^3\tau \quad (3)$$

where  $N$  is the carriers concentration,  $q$  is the electron charge,  $\lambda$  is the wavelength,  $m^*$  is the effective mass of the free carriers,  $c$  is the speed of light.

Scattering mechanism for the case when  $\tau$  depends on the electron energy brings about the following wavelength dependent terms:

$$\alpha = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5} \quad (4)$$

where  $A$ ,  $B$  and  $C$  are constant.

The dominant term depends on the scattering mechanism. Scattering by the acoustic, optical phonons and by the ionized impurities gives  $A\lambda^{1.5}$ ,  $B\lambda^{2.5}$  and  $C\lambda^{3.5}$ ,

respectively. It was found that the wavelength dependence of the absorption coefficient in the spectral range of 2 – 18  $\mu m$  obeys the formulae:

$$y = y_0 + A |x - x_c|^P \quad (5)$$

with  $y_0 = 0.239$ ,  $x_c = 3.91$ ,  $A = 0.048$  and  $P = 1.40$ .

The power law dependence of the absorption coefficient on the wavelength allows concluding that it is due of the free carriers.  $P = 1.40$  says in a favor of fact, that the dominant scattering mechanism at room temperature is the acoustic-mode scattering. Those given in Ref. [17] supplement this results. The authors of Ref. [17] have been measured the temperature dependencies of the electrical resistance and the Hall constant  $R_H$  for  $n$ - and  $p$ - type GaSe ( $n$ - type crystals were grown by the vapor transport method using iodine as a transporter). All measurements were performed in geometry when the current was flowing in the plane of layer (perpendicular to  $c$ - axis). The temperature dependence of the Hall mobility derived from these measurements allowed to conclude that in the temperature range of  $\sim$  (700 – 300 K) the holes scatter mainly due of the homopolar optical phonons [17]. Attentive examination of Fig. 4 (see mobility=temperature dependence marked by symbol  $\nabla$  in Fig. 4 [12]) shows however that for  $p$ - type crystal the scattering mechanism is different in the range of 500 – 300 K. For some  $p$ - type crystals the mobility-temperature dependence changes the slope at  $\sim$  300 K. We believe that the difference in the free carriers scattering mechanism obtained in the present research and in Ref. [17] is due of the different geometry of measurements. This says in a favor of fact that the scattering mechanism is different in two mutually perpendicular directions. By the other words the carriers moving in the plane of layers and in the direction of the optical  $c$ - axis reveal different scattering

mechanism. Scattering for the carriers moving in the layer plane (current flow in the cleavage plane  $XY$ ) is due of homopolar optical phonons, whereas the acoustic vibrations are predominant scattering for the carriers moving in the direction parallel to  $c$ - axis (results of the present research). This conclusion reflect the anisotropy of the physical properties of GaSe and important when creating different devices. Due to difficulty to prepare good quality crystals the authors of Ref. [17] could not measure the electrical resistance and the Hall coefficient when the current flows parallel to  $c$ - axis.

Anisotropy of the  $R_H$  coefficient measurements in the temperature range from 100 to 500 K was reported in Ref. [18]. The holes mobility derived from these measurements in the range of 110 - 238 K and 238 - 500 K exhibited temperature dependence of the form  $\mu \sim T^n$ , where  $n = 2.1$  (current flows in the plane of layer) and  $n = - 1.62$  (current flows parallel to  $c$ - axis), respectively.  $n = 2.1$  and  $n = - 1.62$ , say in a favor of optical and acoustic phonons scattering mechanism, respectively. Stron0g anisotropy  $R_{H\perp}/R_{H\parallel} \approx 18$  was reported in Ref. [18].

Acoustic-mode scattering mechanism at room temperature for the carriers moving along the optical  $c$ - axis [18] is in fairly good agreement with our conclusion, obtained from the optical measurements.

The wavelength dependence of the absorption coefficient for  $E // c$  when the free carriers absorption has been subtracted from the spectrum shown in Attachment **IR5** is presented in the Attachment **6a**. It is seen that maximum of the absorption coefficient does not exceed  $2.5 \text{ cm}^{-1}$ . The bands at  $7.9 \text{ }\mu\text{m}$  ( $1270 \text{ cm}^{-1}$ ),  $9.1 \text{ }\mu\text{m}$  ( $1093 \text{ cm}^{-1}$ ),  $10.5 \text{ }\mu\text{m}$  ( $949 \text{ cm}^{-1}$ ) and relatively strong band at  $11.2 \text{ }\mu\text{m}$  ( $891 \text{ cm}^{-1}$ ) are clearly seen. Most probably the origin of these band and the other absorption bands observed in the present research are due of the multi-phonon absorption and the

localized mode of vibrations induced by uncontrolled impurities. This question is beyond the scope of the present project and may a question of separate investigation.

Especially attention was made to the absorption band at  $891\text{ cm}^{-1}$  ( $110\text{ meV}$ ). This was made because this line when comparing with others is quite sharp and relatively strong. The origin of this line may arise also due of the hole transitions from the first lower lying valence band in the center of the Brillouin zone to the top of the valence band ( $\Gamma_6^+ \rightarrow \Gamma_4^-$  transition [19,20]). The results of the band structure calculation do not contradict this. According to Ref. [19,20] two upper lying valence bands are formed due of the interlayer splitting. At the same time it is possible to suppose that the splitting is about several hundred  $\text{meV}$ . To clarify nature of this band further research is necessary (e.g. low-temperature measurements, measurements under high hydrostatic pressure etc.).

### **PL anisotropy**

The spectra were excited with  $5145\text{ \AA}$  ( $E = 2410\text{ eV}$ ) line of an  $\text{Ar}^+$  laser (power  $< 20\text{ mW}$ ). The emitted light was dispersed through a spectrometer DFS – 24 and detected with liquid nitrogen cooled CCD detector. To get the energy positions and the intensity of the PL peaks, the experimental spectra were fitted by a Lorentzian line shape. The PL spectra of GaSe from the surface containing the optical c- axis are shown in the Attachment 6. Left Figure shows the spectra when the c- axis of the sample was vertically oriented relative to the ground and the analyzer was oriented horizontally, relative to the c- axis ( $\theta = 90^\circ$ ).  $\theta$  is the angle between the optical c- axis and the polarization of the emitted light. Right Figure represents the PL spectra measured at the same conditions as in left Figure, but the analyzer was

oriented vertically to the optical c- axis ( $\theta = 0^\circ$ ). The measurements were done in the range of  $0^\circ < \theta < 180^\circ$ .

Variation of the PL peak wavelength and the PL intensity versus angle  $\theta$  is shown in the Attachment 7 and Attachment 8, respectively. As it is seen (Attachment 8) when the laser light was oriented horizontally (perpendicular to c-axis), then the peak position of the light emitted by sample does not noticeably depend on the position of the analyzer. At the same time when the excited light is vertical (parallel to c- axis), then the peak center depends on the position of the analyzer. For  $E // c$  the peak position is at 632 nm, in comparing with 627 nm when  $E \perp c$ . The 5 nm shift is beyond the accuracy of our measurements and this value reflects the anisotropy of the PL peak position in GaSe at room temperature in two different geometries.

The anisotropy of the PL intensity for both polarizations are shown in Attachment 8. As it is seen they are less informative and look like similar with a small difference at small angles.

## CONCLUSION

X-ray diffraction analysis showed that the melt-grown crystals used in the present Project belong to  $\epsilon$ -modification and reveal  $p$ -type conductivity. The lattice parameters are  $a = b = 3.74 \text{ \AA}$ ,  $c = 15.907 \text{ \AA}$ ,  $c/a = 4.243$ , space group  $D_{3h}^1$ , contains two layers per elementary unit cell.

We have developed a simple but effective technology to achieve optical-quality cutting and polishing of GaSe at an arbitrary angle to the optical axis. Several samples containing the optical axis were prepared and the quality of these samples was analyzed by mid IR absorption spectroscopy and visual inspection under the microscope. The technology developed opens new perspectives for practical applications of GaSe in laser wave generation and mixing experiments.

Five slabs of GaSe containing the optical  $c$ -axis have been sent to the Materials Directorate of the US Air Force Wright-Patterson Laboratory to Dr. N. Fernelius for further measurements and characterization.

The anisotropy of the mid IR absorption spectra of GaSe was measured at room temperature for the radiation polarized perpendicular and parallel to the optical  $c$ -axis. It is shown that the anisotropy of absorption arises due to the free carriers absorption recorded in  $E // c$ . The carriers that move along the optical  $c$ -axis are mainly scattered by the longitudinal acoustic vibrations.

New absorption bands were recorded in  $E // c$  at 891, 945, 1093 and  $1270 \text{ cm}^{-1}$ . Most probably, these bands are due to the multi-phonon absorption and the localized mode of vibrations induced by uncontrolled impurities. To clarify the nature of these bands further research is necessary.

Polarization anisotropy of the PL spectra studied in the present work are less informative and interesting. The only feature we may stress on is that the peak center difference between the spectra measured in  $E // c$  and  $E \perp c$  is about 5 nm.

The results of present research were submitted for publication to the Journal of Applied Physics. Submitted paper by K. Allakhverdiev, N. Fernelius, F. Gashimzade, J. Goldstein, E. Salaev, Z. Salaeva entitled "Anisotropy of Optical Absorption in GaSe Studied by mid-IR Spectroscopy" are given at the end of the present Report.

*As a perspectives for future to explain the anisotropy of the absorption and the origin of lines observed in  $E // c$  spectrum one needs to obtain plates for optical measurements with the optical  $c$ - axis in the plane of face. Using these plates the optical absorption will be measured at different temperatures. Using these plates at a variety of temperatures should obtain data for explaining the anisotropy of optical absorption in GaSe. Theoretical model should be developed to predict the vibration frequencies of the impurity atoms. The results of calculation will be compared with the experimental data. The results of this effort will be useful for creating some prototype devices, such as optical parametric oscillators, tunable laser sources in the mid-IR and others.*

## **ACKNOWLEDGMENTS OF SUPPORT AND DISCLAIMER**

This material is based upon work supported by the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory, under Contract No. F61775-02-WE008. The authors gladly acknowledges the European Office of Aerospace Research and Development (EOARD) for financial support. The authors express their thanks to Dr. Alex GLASS and Mrs. Beth WANN for fruitful collaboration.

The authors are indebted to Dr. Tarik BAYKARA, the Director of the Materials and Chemicals Technologies Research Institute of the Marmara Research Center of TUBITAK, for support and attention.

We would like to point out the following disclaimers: all described results, findings, conclusions and recommendations for future research are belong to the authors and do not necessarily reflect the views of the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory.

In accordance with Defence Federal Acquisition Regulation 252.227-7036, Declaration of Technical Data Conformity (Jan 1997) "The Contractor, TUBITAK, Marmara Research Center, hereby declares that, to the best of our knowledge and belief, the technical data delivered here with under Contract No. F61775-02-WE008 is complete, accurate, and complies with all requirements of the Contract".

In accordance with the requirements in Federal Acquisition Regulation 52.227-13, Patent Rights-Acquisition by the U.S. Government (Jun 1989) "I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this Contract".



Prof. Dr. Kerim ALLAHVERDI

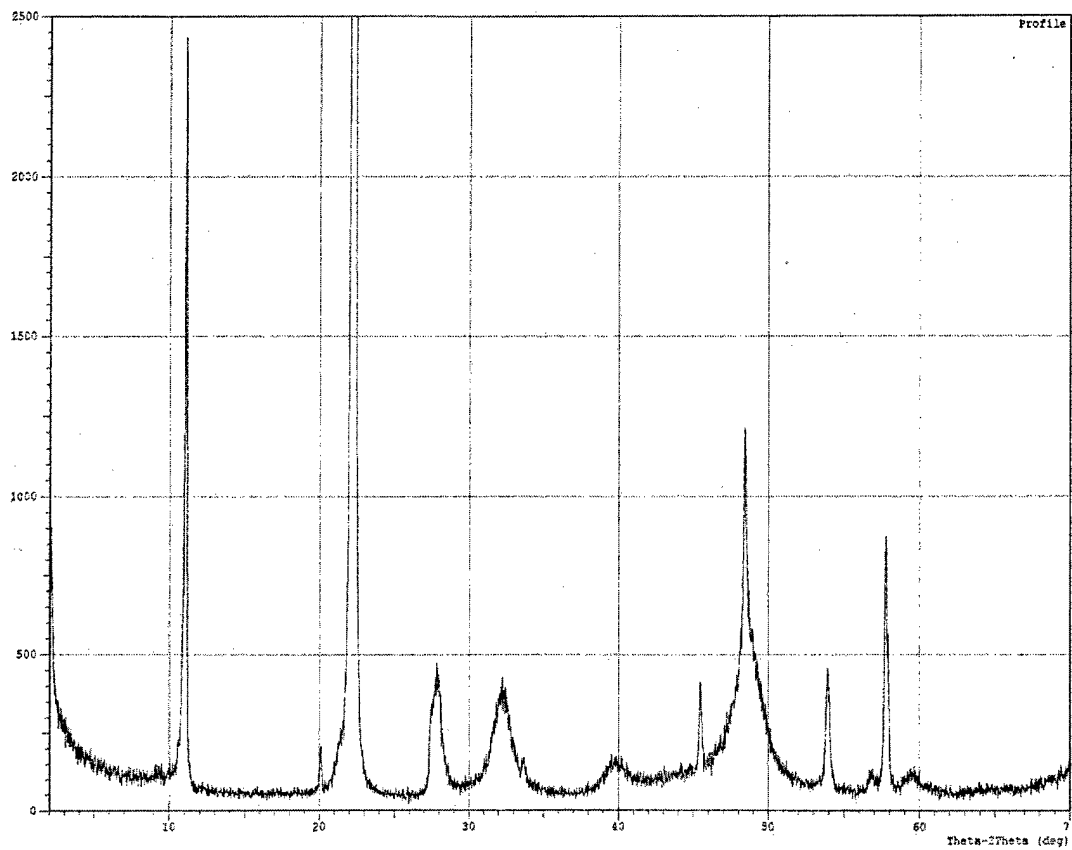
Principle Investigator

## REFERENCES

1. G.B. Abdullaev, L.A. Kulevskii, A.M. Prokhorov, A.D. Savel'ev, E.Yu. Salaev, V.V. Smirnov, JETP Lett., 16, 90 (1972).
2. L. Kador, M. Braun, K.R. Allakhverdiev, E.Yu. Salaev, Optics Commun., 143, 62 (1997).
3. G.B. Abdullaev, K.R. Allakhverdiev, L.A. Kulevskii, A.M. Prokhorov, E.Yu. Salaev, A.D. Savel'ev, V.V. Smirnov, Sov. J. Quant. Electron., 5, 665 (1975).
4. W. Shi, J. Ding, X. Mu, N. Fernelius, Applied Physics Letter, 80, 3889 (2002).
5. Landölt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie/Gesamtherausgabe: Group III. Kristall- und Festkörperphysik, Band17, Ed. K.H. Hellwege and O. Madelung, Springer-Verlag, Berlin/Heidelberg/New York/Tokyo 1983 (p.530).
6. Y. Fan, M. Bauer, L. Kador, K. Allakhverdiev, E.Yu. Salaev, J. Appl. Phys., 91, 1081 (2002).
7. P.C. Leung, G. Andermann, W.G. Spietzer, J. Phys. Chem. Solids, 27, 849 (1966).
8. N. Kuroda, Y. Nishina, T. Fukuroi, J. Phys. Soc. Japan, 28, 981 (1970).
9. T. J. Wieting, J.L. Verble, Phys. Rev., B5, 1473 (1972).
10. H. Yoshida, S. Nakashina, A. Mitsuishi, Phys. Stat. Sol., b59, 55 (1973).
11. E. Finkman, A. Rizzo, Solid State Commun., 15, 1841 (1974).

12. R.Le. Toullec, N. Piccioli, M. Mejatti, M. Balkanskii, *IL Nuovo Cimento*, **38B**, 159 (1977).
13. V.M. Burlakov, E.A. Vinogradov, G.N. Zhizhin, N. Melnik, D.A. Rzaev, V.A. Yakovlev, *Sov. Phys. Solid State*, **21**, 1477 (1979).
14. K.R. Allakhverdiev, "Optical Properties and Vibration Spectra of Layered and Chained Crystals of  $A^3B^6$ ,  $A^3B_3C_2^6$  Group and the Solid Solutions on their Basis", Dissertation, Doctor of the Physical-Mathematical Sciences, Baku, 1980, p.313.
15. C. Julien, M. Eddrief, M. Balkanski, A. Chevy, *Materials Science and Engineering*, **B13**, 253 (1982).
16. J. Pnakove, *Optical Processes in Semiconductors*, Prentice-Hall, Englewood Cliffs, New Jersey.
17. R. Fivaz, E. Mooser, *phys. Rev.*, **163**, 743 (1967).
18. A.T. Nagat, S.A. Hussein, Y.N. Gameel, A.A. Belal, *Indian J. Pure Appl. Phys.*, **28**, 586 (1990).
19. M. Schlüter, *Nuovo Cimento*, **B13**, 313 (1973).
20. M. Schlüter, J. Camassel, S. Kohn, J. Voitchovsky, Y. Shen, M. Cohen, *Phys. Rev.*, **B13**, 3534 (1976).

Group: Endustri 4 Data: GaSe(Kerim Allahverdi) >



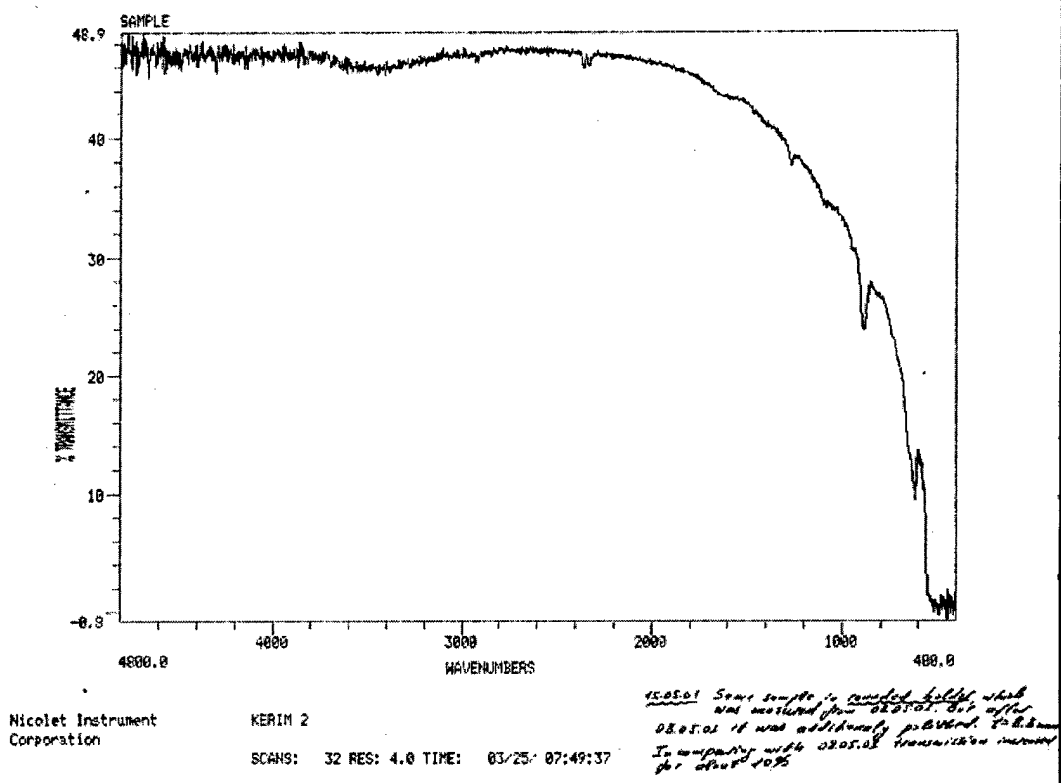
**Attachment XRD.** Room-temperature X-ray diffraction pattern of GaSe powder versus the angle  $\theta$ .

37-0931		Wavelength= 1.54056				i
GaSe	2 $\theta$	Int	h	k	l	
Gallium Selenide	11.100*	62	0	0	2	
	22.261*	100	0	0	4	
	27.601*	4	1	0	0	
	28.001*	6	1	0	1	
	32.301*	5	1	0	3	
	33.801*	2	0	0	6	
	39.762*	1	1	0	5	
	45.622*	10	0	0	8	
	48.542*	17	1	1	0	
	54.102*	5	1	1	4	
56.903*	1	0	2	0		
57.923*	27	2	0	2		
59.502*	1	1	0	9		
59.502*	1	0	2	3		
71.023*	17	0	0	12		
78.803*	2	1	1	10		
78.803*	2	2	1	2		
85.365*	20	0	0	14		
90.784*	5	1	1	12		
Rad.: CuK $\alpha$	$\lambda$ : 1.5417	Filter: Mono	d-sp: Diffractometer			
Cut off:	Int.: Diffract.	I/cor.:				
Ref: Anis, M., Nazar, J. Mater. Sci. Lett., 2, 471 (1983)						
Sys.: Hexagonal	S.G.:					
a: 3.749	b:	c: 15.907	A:	C: 4.2430		
$\alpha$ :	$\beta$ :	$\gamma$ :	Z:	mp:		
Ref: Ibid.						
Dx:	Dm:	SS/FOM: $\bar{1}7=6(.051, 60)$				

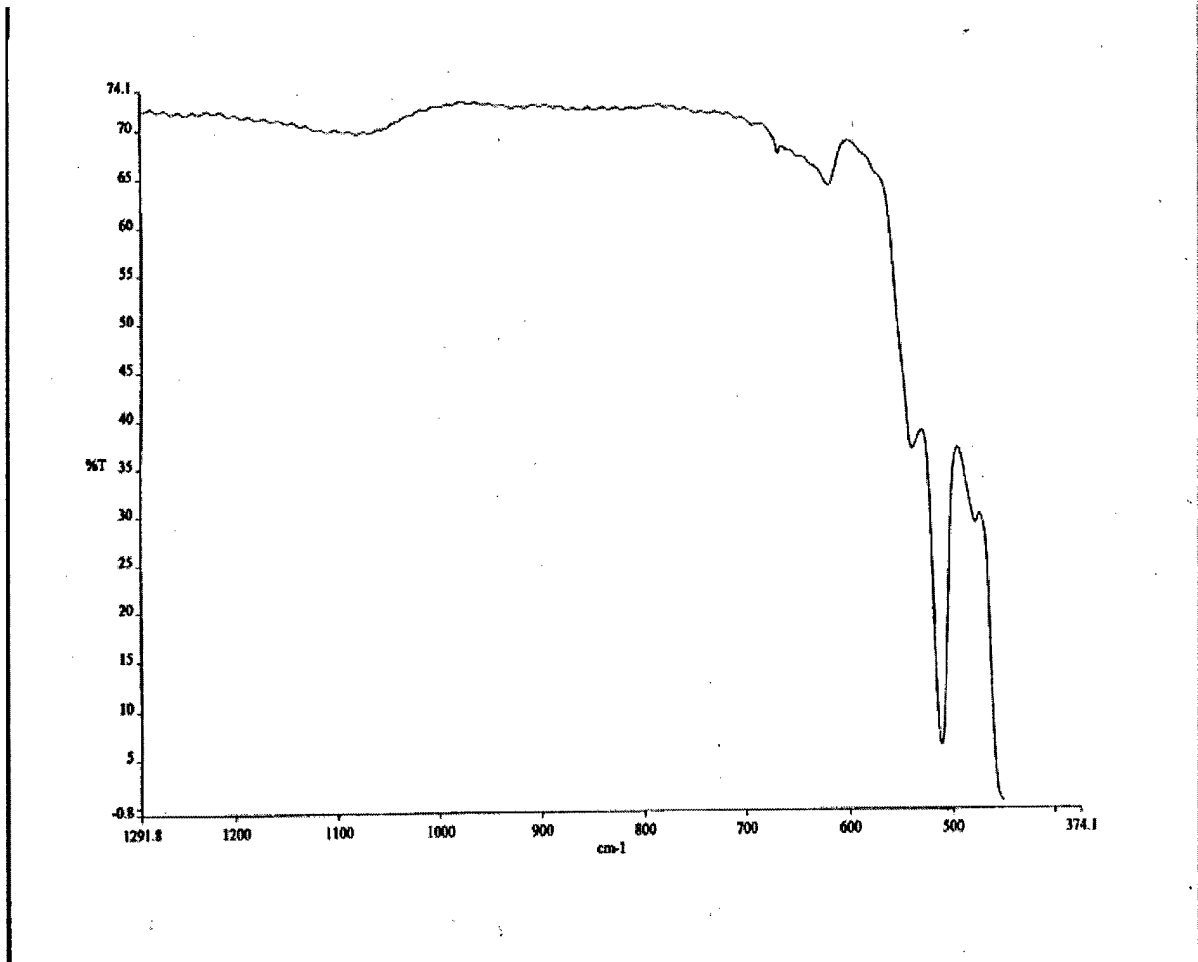
p-type single crystals were grown by a Bridgman-Stockbarger method. Reference reports a=3.750(3) and c=15.950(5). Mwt: 148.68. Volume[CD]: 193.62.

©1996 JCPDS-International Centre for Diffraction Data. All rights reserved.

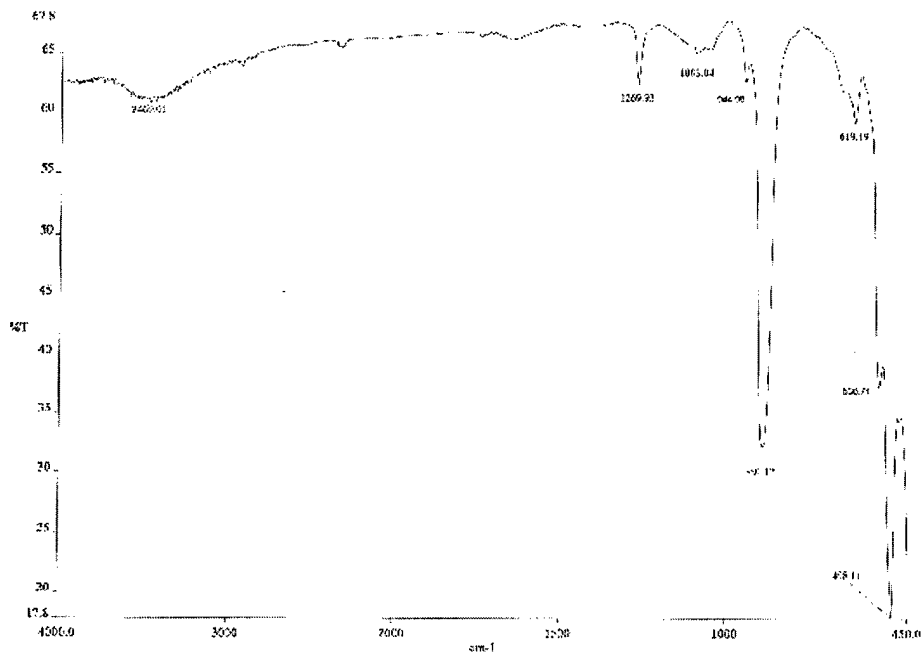
Attachment XDR1. The result of identification of the diffraction peaks, given in the Attachment XDR.



**Attachment IR1.** Room-temperature transmission spectrum of 8.78 mm thick GaSe sample (*Sample No1*) measured in non-polarized light when the wave vector of the incident light was perpendicular to polished plane (110).

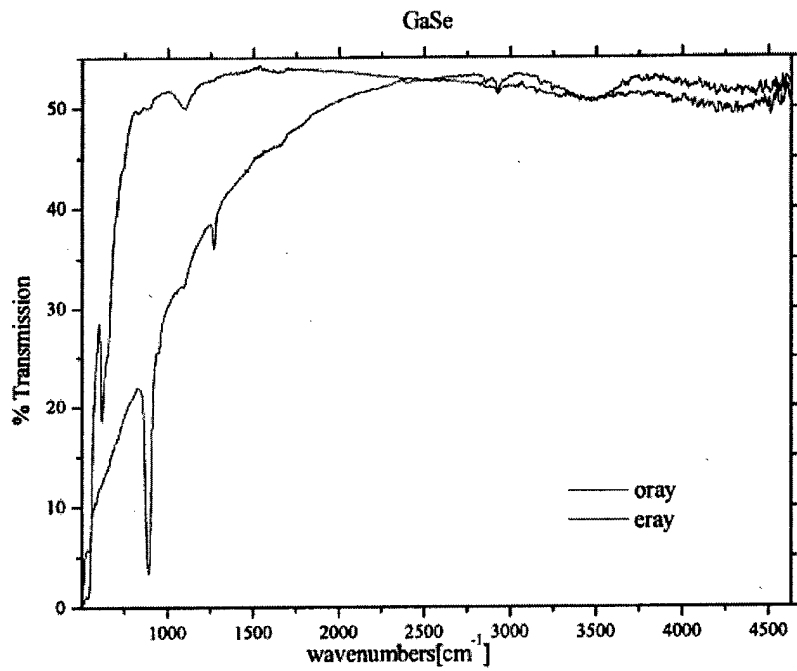


**Attachment IR2.** Room-temperature transmission spectrum of 1.061 *mm* thick GaSe measured from freshly cleaved surface in non-polarized light.

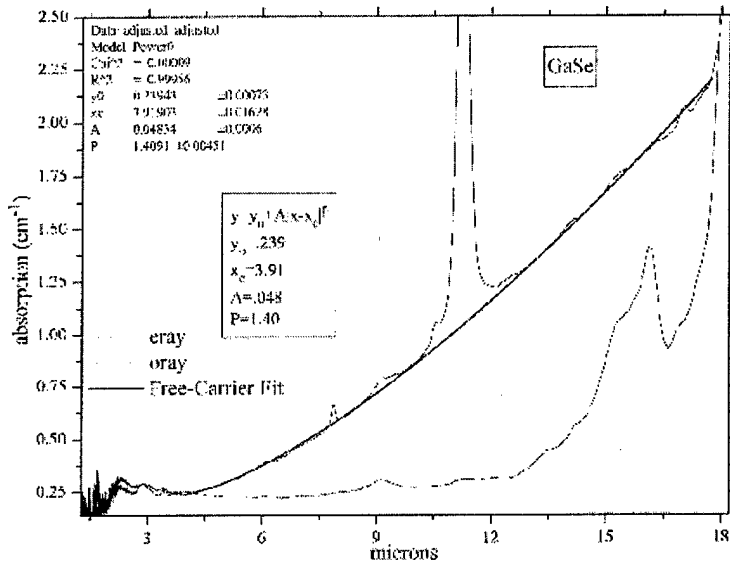


C:\behele\infrared\spctra\transm\248mm-GaSe2.48mm  
 16.01.01, CaSe and polished, then polished light 2.48 mm

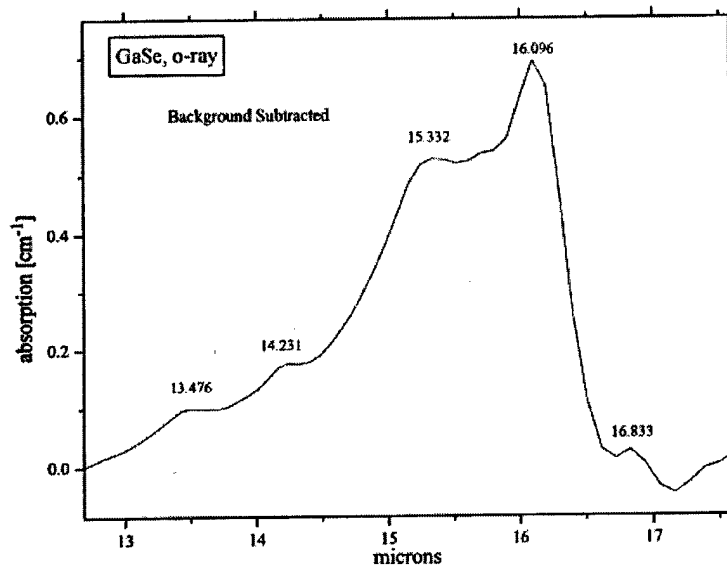
**Attachment IR3.** Transmission spectrum of 2.48 mm thick GaSe plate. Conditions of measurements are same as in Attachment IR1.



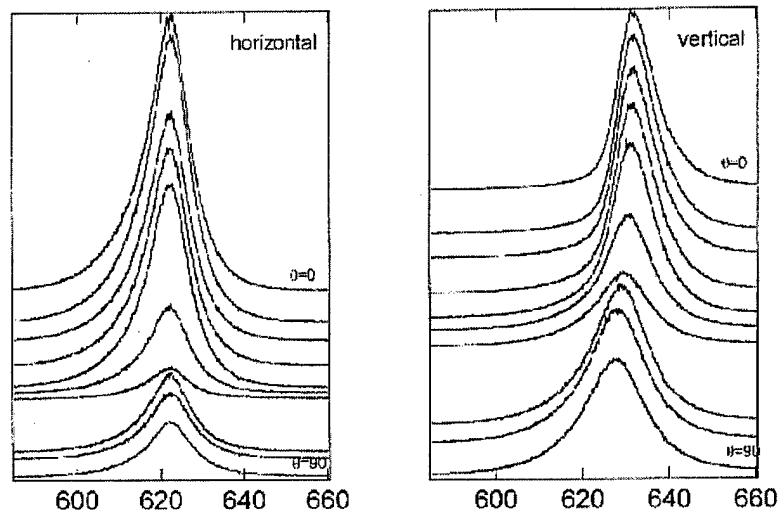
**Attachment IR4.** Room-temperature transmission spectra for 8.78 mm thick GaSe plate for  $E \perp c$  ("o-ray") and  $E \parallel c$  ("e-ray") geometry.



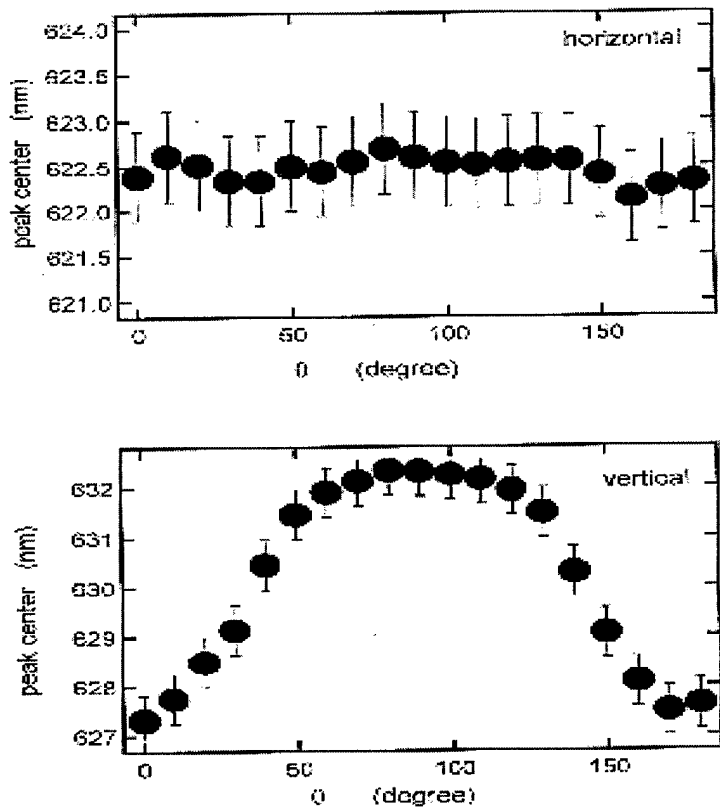
**Attachment IR5.** Room-temperature absorption coefficient for GaSe in  $E // c$  (bolded line), calculated using formulae 1 using the data of the Attachment IR4. Insert shows the formulae and the value of parameters according which the wavelength dependence for the absorption coefficient for “eray” is adjusted.



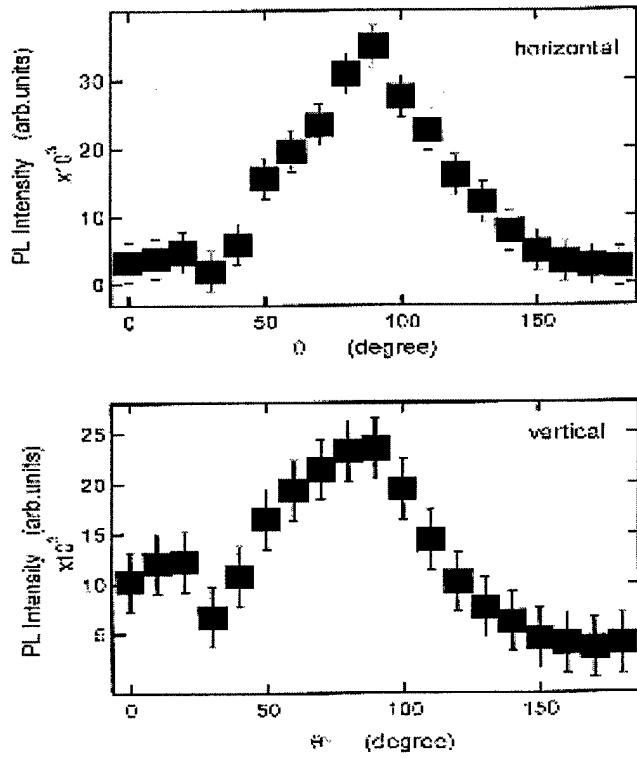
**Attachment 6a.** Room-temperature absorption coefficient for GaSe in  $E // c$  geometry for case when the free carriers absorption has been subtracted from the spectrum shown in the Attachment **IR5**.



**Attachment 6.** Room-temperature PL spectra of GaSe plate containing the optical c- axis and excited with a 5145 Å line of an Ar<sup>+</sup> laser, when the analyzer was oriented horizontally (left) and vertically to the optical c- axis (right).  $\theta$  is the angle between the optical c- axis and the polarization of the light emitted.



**Attachment 7.** Polarization dependence of the PL peak center of GaSe slab containing c- axis for horizontally polarized excited light.



**Attachment 8.** Polarization dependence of the PL peak center of GaSe slab containing c- axis for horizontally and vertically polarized excited light.

**Table 1.** IR absorption (reflection) bands of GaSe. \*Data for freshly cleaved crystal  
<sup>1</sup>Data for  $\nu_{TO}$  (transverse optical) and  $\nu_{LO}$  (longitudinal optical) phonons obtained from IR reststrahlen spectra (freshly cleaved and surfaces containing the optical c-axis). References are mentioned according to that given at the end of the Final Report.

Ref.	Band position [ $\text{cm}^{-1}$ ], $E \perp c$	Ref	Band position [ $\text{cm}^{-1}$ ], $E \parallel c$
[7] <sup>1</sup> [8]*	231 <sub>TO</sub> , 254 <sub>LO</sub> , 423, 445, 476, 511, 539 211 <sub>TO</sub> , 420, 448, 481, 488, 512, 539, 551, 619	[7] <sup>1</sup>	237 <sub>TO</sub> , 246 <sub>LO</sub> , 318, 360, 416, 495
[9] <sup>1</sup> [10]*	214 <sub>TO</sub> , 255 <sub>LO</sub> 20, 20K		
[11] <sup>1</sup>	215 <sub>TO</sub> , 252 <sub>LO</sub>	[11] I	236 <sub>TO</sub> , 247 <sub>LO</sub>
[12] <sup>1</sup>	214, 254		
[13]*	214 <sub>TO</sub> , 252 <sub>LO</sub>		
[14] <sup>1</sup> [15] <sup>1</sup>	212 <sub>TO</sub> , 254 <sub>LO</sub> 212, 255	[14] I	237 <sub>TO</sub> , 245 <sub>LO</sub>
Present work	420, 448, 482, 488, 512, 540, 551, 619		498, 891, 949, 1095, 1270

**PAPER SUBMITTED TO THE JOURNAL OF APPLIED PHYSICS**

For submission to Journal of Applied Physics

**Anisotropy of Optical Absorption in GaSe Studied by mid-IR Spectroscopy**  
K. Allakhverdiev<sup>b,c)</sup>, N. Fernelius<sup>a)</sup>, F. Gashimzade<sup>c)</sup>, J. Goldstein<sup>a)</sup>, E. Salaev<sup>c)</sup>, Z. Salaeva<sup>b,c)</sup>

<sup>a</sup> *Materials Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 4533-7707, USA*

<sup>b</sup> *Marmara Research Centre of TÜBİTAK, Materials and Chemicals Technologies Research Institute, P.K. 21, 41470 Gebze/Kocaeli, Turkey*

<sup>c</sup> *Institute of Physics, Azerbaijan National Academy of Sciences, H. Javid ave. 33, 370143 Baku, Azerbaijan Republic*

#### ABSTRACT

Slab samples of  $\epsilon$ -GaSe have been prepared with the optical axis (the c-axis) in the plane of the face. Previously, most optical studies were made on slabs cleaved from crystals, which have the c-axis perpendicular to the face. The infrared absorption spectra of  $\epsilon$ -GaSe has been measured at room temperature in the spectral range from 4000 to 400  $\text{cm}^{-1}$  for the e-ray (polarized parallel to the optical axis), and the o-ray (polarized perpendicular to the optical axis). The maximum value of the optical absorption coefficient,  $\alpha$ , for both geometries, does not exceed 2.5  $\text{cm}^{-1}$  ( $E \parallel c$ ). We find an anisotropy in the transmission, in the spectral range below  $\sim 2250 \text{ cm}^{-1}$ , due to the free carrier absorption, seen only in the e-ray. At  $T = 300 \text{ K}$ , acoustic lattice vibrations are the dominant scattering mechanism for carriers moving parallel to the c-axis. New absorption bands were observed in the e-ray spectrum at 891, 945, 1093 and 1270  $\text{cm}^{-1}$ . These bands may be due to multi-phonon absorption, or to localized vibrational modes stemming from unintentional impurities. It is suggested that a sharp absorption at 891  $\text{cm}^{-1}$  may be due to hole transitions from the lowest-lying valence band in the center of the Brillouin zone, to the top of the valence band ( $\Gamma_6^+ \rightarrow \Gamma_4^-$  transition).

## I. INTRODUCTION

Several different properties are required of a crystal if it is to be of practical use in nonlinear optical (NLO) devices. These include a high nonlinear optical coefficient, a high damage threshold, a suitable transparency range, and a low absorption coefficient. For purposes of serving as an NLO material in the mid-IR, GaSe possesses excellent values for all these properties, as has been extensively documented in the literature. Yet, its practical implementation in NLO devices remains limited due to a fatal flaw – its softness. To achieve birefringent phase-matching, it is generally necessary to be able to cut and polish the faces of an NLO crystal at an arbitrary angle to the optical axis (for GaSe, this is the c-axis, along the [001] direction). However, GaSe has a layered structure, with weak van der Waals-like bonds between the layers, making it extremely difficult to cut and polish, except for crystal faces in the plane of cleavage (perpendicular to the optic axis). This feature drastically reduces GaSe's utility as an NLO crystal of practical use, and also complicates access to measurement of its basic properties. For example, although over 1300 papers have been published on GaSe<sup>1-10</sup>, we are aware of only four which investigate transmission of the crystal's e-ray to any extent, and these focused only on the vicinity of the Reststrahlen band (see Table 1 for details).

In the present article we report mid-IR absorption measurements on  $\epsilon$ -GaSe single crystals which were grown from the melt. In Sec. II we describe our original method of preparation of the plane-parallel samples, which contain the optical c-axis, and the experimental procedures. The results of the mid-IR absorption measurements are presented and discussed in Sec. III. Finally in Sec. IV we give the conclusions.

## II. EXPERIMENT

Over the last few years, we have developed a simple but effective technology to achieve optical-quality cutting and polishing of GaSe at an arbitrary angle to the optical axis. Specifically, we encase the uncut GaSe boule within a firm polymer resin, forming a hard "puck". The puck is then cut and polished, as a whole. The re-enforcement provided by the polymer resin prevents the deformation of the GaSe. With careful polishing methods, we have reproducibly obtained mirror-smooth surfaces, on faces of area greater than  $1\text{cm}^2$ , parallel to the optical axis. (The polymer resin can then be trimmed away, or left on, depending on one's purpose). As a result of this technology, we have been able to measure and compare the transmission of both the o- and the e-ray of GaSe.

Undoped, p- type GaSe crystals were grown in evacuated quartz ampoules ( $10^{-5}$  Torr) by the Bridgman method. From the boules (diameter 15 mm), slabs of different thickness were easily cleaved with a razor blade. The slabs were embedded in a special polymer resin, and were cut into plane-parallel plates of different thickness. The slabs were cut by means of a low-speed diamond saw. The plates were gently polished using alumina grit to reach mirror-like surfaces. The resulting surfaces were sufficiently mirror-smooth to permit easy reading of printed text reflected from their surfaces. However, their overall smoothness is not quite as perfect as that obtainable by cleavage. Room-temperature transmittance was measured in the mid IR ( $1.5 - 18 \mu\text{m}$ ) using a Bomem DA-3 spectrometer.

## III. MID-IR ABSORPTION SPECTRA

First, we compared the transmission spectra of freshly cleaved samples with the spectra of our specially-polished plates. For the o-ray ( $E \perp c$ ), the spectra were identical with a small difference in transmission. Transmission of freshly cleaved

samples was about 5 to 7 % higher for samples of the same thickness. The optical quality of our samples also compared favorably with the highest-quality samples reported in the literature<sup>2</sup>. Maximum transmission for our 8.8-mm thick sample (Fig. 2) was ~ 55 %, whereas for the 0.84-mm plate reported in the literature it was ~ 20 %.

Fig. 1 presents non-polarized transmission spectrum of 2.66-mm thick GaSe crystal, with the wave vector of the incident light parallel to the layer planes. New absorption bands are clearly resolved at 891, 945, 1093 and 1270 cm<sup>-1</sup>. These lines are listed in Table 1. The e- and o- ray transmission spectra of our 8.8 mm thick GaSe plate are shown in Fig. 2. The absorption bands at 891 cm<sup>-1</sup> and 1270 cm<sup>-1</sup> are clearly resolved, whereas the bands at 945 cm<sup>-1</sup> and 1093 cm<sup>-1</sup> are seen as weak shoulders. The character of the transmission's wavelength dependence differs for the two polarizations in the spectral range below ~ 2250 cm<sup>-1</sup>. The transmission of the e-ray decreases gradually to longer wavelength starting from ~ 2250 cm<sup>-1</sup>, whereas the o-ray transmission decreases sharply from ~ 750 cm<sup>-1</sup>.

The absorption coefficient  $\alpha$  was calculated using the equation<sup>11</sup>:

$$\alpha = (1/d) \ln \left[ 2TR^2 / \sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2 \right] \quad (1)$$

where  $d$  is the sample thickness;  $T$  and  $R$  are the transmission and reflection, respectively. In the transparency range,  $R$  was calculated using the equation<sup>11</sup>:

$$R = (n - 1)^2 / (n + 1)^2 \quad (2)$$

where  $n$  is the refractive index. To calculate  $R$  we used  $n = 2.8$ . Room-temperature wavelength dependencies of the absorption coefficients, for both geometries, are shown in Fig. 3. The dependencies were calculated using Eqn. (1), and the data of Fig. 2.

For free-carrier absorption, when the relaxation time,  $\tau$ , is time-independent, Drude theory gives<sup>11</sup>:

$$\alpha = Nq^2\lambda^2/m^*8\pi^2nc^3\tau \quad (3)$$

where  $N$  is the carrier concentration,  $q$  is the electron charge,  $\lambda$  is the wavelength,  $m^*$  is the effective mass of the free carriers, and  $c$  is the speed of light. When  $\tau$  depends on the electron energy,  $\alpha$  can be expected to exhibit a wavelength dependence of the form:

$$\alpha = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5} \quad (4)$$

where  $A$ ,  $B$  and  $C$  are constants. The dominant term depends on the scattering mechanism. Scattering by acoustic phonons, optical phonons and ionized impurities gives rise to the terms  $A\lambda^{1.5}$ ,  $B\lambda^{2.5}$  and  $C\lambda^{3.5}$ , respectively. For GaSe, we found that the wavelength dependence of the absorption coefficient, in the spectral range of 2 - 18  $\mu\text{m}$ , obeys the equation:

$$y = y_0 + A(x - x_c)^P \quad (5)$$

with  $y_0 = 0.239$ ,  $x_c = 3.91$ ,  $A = 0.048$  and  $P = 1.40$ . The power law dependence of the absorption coefficient on the wavelength indicates that the long-wavelength absorption is due to free carriers. Moreover the value of  $P = 1.40$  implies that the dominant scattering mechanism at room temperature is due to acoustic phonons.

Our results complement Hall effect measurements found in the literature<sup>12,13</sup>. Hall measurements indicate that, for electrons propagating perpendicular to the  $c$ -axis, homopolar optical phonons are the primary scattering mechanism<sup>12</sup>, while for carriers propagating parallel to the  $c$ -axis acoustic phonons dominate the scattering interactions<sup>13</sup>. The Hall measurements indicated an anisotropy in the Hall coefficient,  $R_H$ , of  $R_{H\perp}/R_{H\parallel} \approx 18$ . The conclusions from these electrical measurements are in agreement with those reached through our optical work.

The wavelength dependence of the e-ray absorption coefficient, with the free carrier absorption subtracted out, is shown in Fig. 4. We find that the maximum absorption coefficient does not exceed  $2.5 \text{ cm}^{-1}$ . The bands at  $1270 \text{ cm}^{-1}$ ,  $1093 \text{ cm}^{-1}$ ,  $945 \text{ cm}^{-1}$  and the relatively strong band at  $891 \text{ cm}^{-1}$  are clearly evident. The most likely origin of these bands would be multi-phonon absorption, and localized vibration modes due to unintentional impurities. The results of the X-ray fluorescence measurements indicated the presence of Ni (0.220 %) and Mn (0.049 %) atoms in our crystals, unintentionally introduced during synthesis and growth.

It is possible that the sharp absorption at  $891 \text{ cm}^{-1}$  (110 meV) is due to a hole transition from a low-lying valence band in the center of the Brillouin zone to the top of the valence band (the  $\Gamma_6^+ \rightarrow \Gamma_4^-$  transition<sup>14,15</sup>). This would be in agreement with published band structure calculations, which indicate that the two uppermost valence bands in GaSe are split, their degeneracy removed due to interlayer splitting. The calculations indicate that the energy difference between these bands is on the order of several hundred meV. Although it is not possible to calculate the exact value of the splitting, the value indicated by the calculations would be in agreement with such an assignment. Admittedly, clarifying the origin of this band requires further research, and is beyond the scope of the present work.

#### IV. CONCLUSIONS

In conclusion, the room-temperature mid-IR absorption spectra of GaSe were measured for both the e-ray (polarized parallel to the optical axis) and the o-ray (polarized perpendicular to the optical axis). It is shown that the anisotropy of the absorption arises due to free carrier absorption, seen only in the e-ray. The free carriers that move parallel to the optical c- axis are mainly scattered by the

longitudinal acoustic vibrations. New absorption bands were recorded in the e-ray at 891, 945, 1093 and 1270  $\text{cm}^{-1}$ . The most likely origin of these lines would be multi-phonon absorption and the localized vibrational modes of unintentional impurities. It is not excluded that the sharp absorption band at 891  $\text{cm}^{-1}$  is due to  $\Gamma_6^+ \rightarrow \Gamma_4^-$  hole transitions in the center of the Brillouin zone.

#### **ACKNOWLEDGMENTS**

The authors would like to thank the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, Air Force Research Laboratory for financial support under Contract No. F61775-02-WE008.

## REFERENCES

1. For a review of the entire GaSe literature, see N. C. Fernelius, *Prog. Crystal Growth Charact.* 28, 275 (1994).

The following references, 2 – 10, are papers that focus on transmission measurements of GaSe, in the mid-IR range of 1 - 20  $\mu\text{m}$ .

2. P.C. Leung, G. Andermann, W.G. Spitzer, *J. Phys. Chem. Solids*, 27, 849 (1966).
3. N. Kuroda, Y. Nishina, T. Fukuroi, *J. Phys. Soc. Japan*, 28, 981 (1970).
4. T.J. Wieting, J.L. Verble, *Phys. Rev.*, B5, 1473 (1972).
5. H. Yoshida, S. Nakashima, A. Mitsuishi, *Phys. Stat. Sol.*, b59, 55 (1973).
6. E. Finkman, A. Rizzo, *Solid State Commun.*, 15, 184 (1974).
7. R.Le. Toullec, N. Piccioli, M. Mejatti, M.Balkanski, *IL Nuovo Cimento*, 38B, 159 (1977).
8. V.M. Burlakov, E.A. Vinogradov, G.N. Zhizhin, D.A. Rzaev, V.A. Yakovlev, *Sov. Phys. Solid State*, 21, 1477 (1979).
9. K.R. Allakhverdiev, "Optical Properties and Vibration Spectra of Layered and Chained Crystals of  $A^3B^6$ ,  $A^3B^3C_2^6$  Group and the Solid Solutions on

- their Basis", Dissertation, Doctor of the Physical-Mathematical Sciences,  
Baku, 1980, p.313.
10. C. Julien, M. Eddrief, M.Balkanski, A. Chevy, Materials Science and  
Engineering, B13, 253 (1992).
  11. J. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood  
Cliffs, New Jersey (1971).
  12. R. Fivaz, E. Mooser, Phys. Rev., 163, 743 (1967).
  13. A.T. Nagat, S.A. Hussein, Y.N. Gameel, A.A. Belal, Indian J. Pure Appl.  
Phys., 28,  
586 (1990).
  14. M. Schlüter, Nuovo Cimento, B13, 313 (1973).
  15. M. Schlüter, J. Camassel, S. Kohn, J. Voitchovsky, Y. Shen, M. Cohen,  
Phys. Rev. B13, 3534 (1976).

#### **FIGURE CAPTIONS.**

**Fig 1** Non-polarized room-temperature transmission spectra of 2.66 mm thick GaSe plates. The thin line is from a plate obtained by cleaving a boule, such that the c-axis is perpendicular to the face of the sample. The thick line is from a plate created by our polishing method, for which the c-axis is parallel to the face of the sample.

These two samples were obtained from two separate boules.

**Fig.2** Room-temperature polarized transmission spectrum of 8.8 mm GaSe plate for  $E \perp c$  ("o-ray") and  $E \parallel c$  ("e-ray", bolded line) geometry.

**Fig. 3** Room-temperature wavelength dependence of the absorption coefficient for the  $E \parallel c$  and  $E \perp c$  geometries (bolded and thin line, respectively), calculated using the Eqn. 1 and the data of Fig. 2.

**Fig. 4** Room-temperature absorption coefficient for GaSe in the E || c geometry, with the free carriers absorption subtracted out.

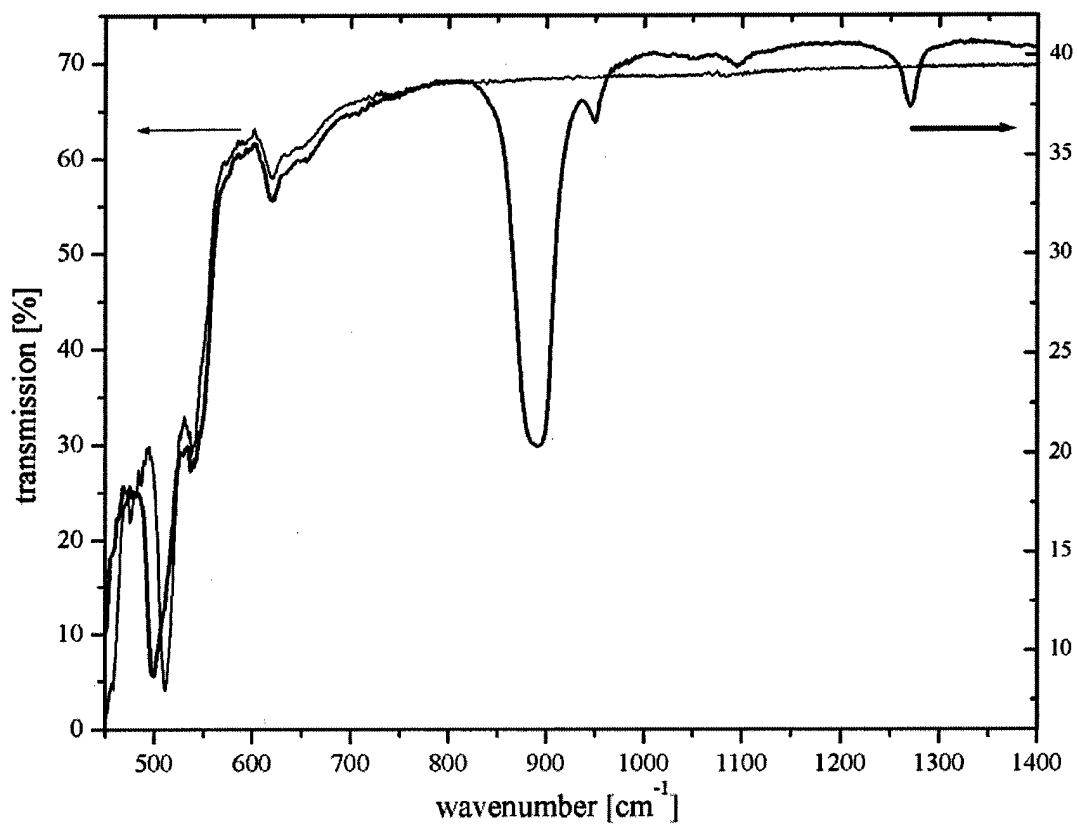


Figure 1

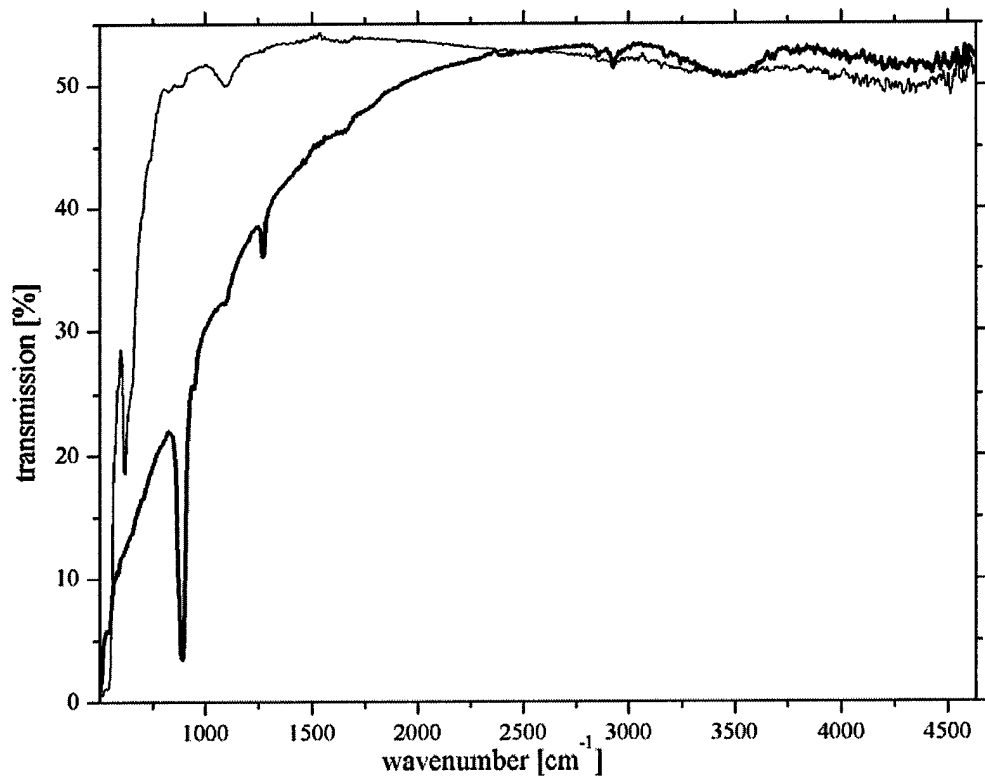


Figure 2

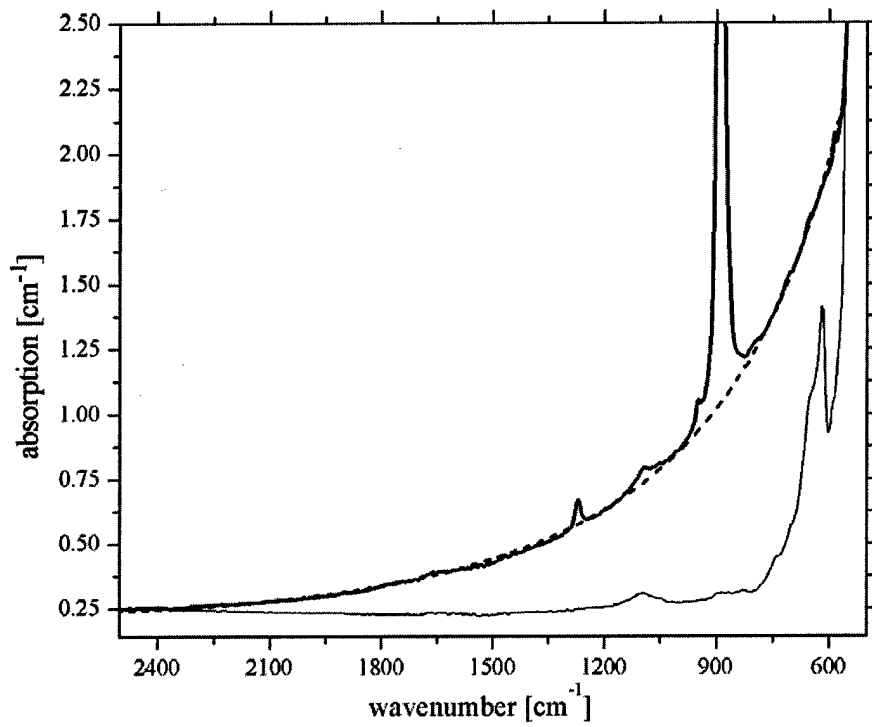


Figure 3

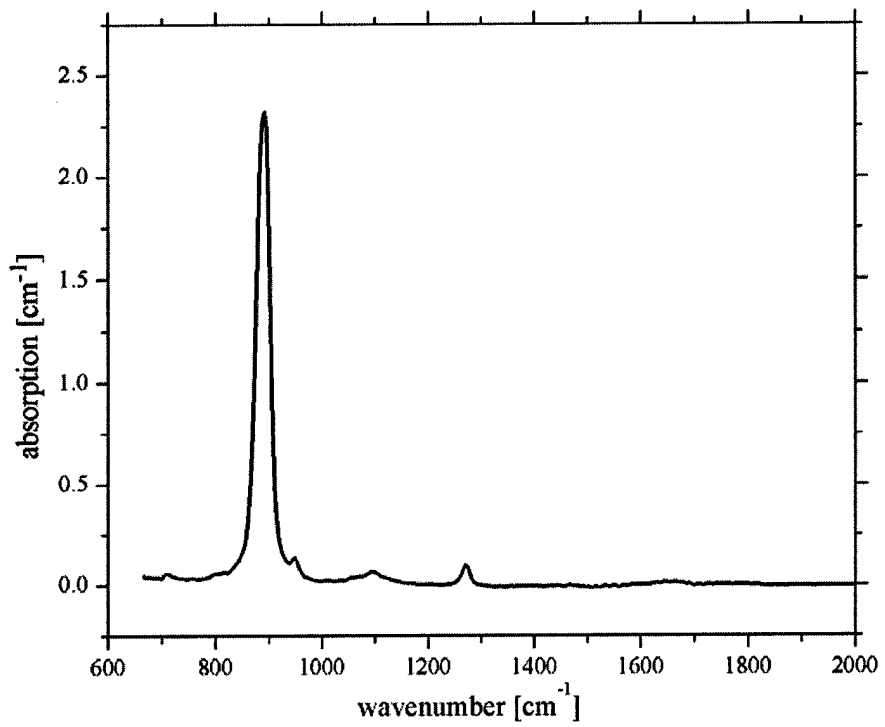


Figure 4

**Table 1.** Room-temperature IR absorption (reflection) bands of GaSe.

\*\*Data obtained from the IR reflection and transmission spectra from freshly cleaved surface and surface containing the optical c- axis. Subscripts <sub>TO</sub> and <sub>LO</sub> denote the transverse and longitudinal phonon, respectively.

\*Data obtained from the absorption spectra of freshly cleaved crystals, measured in non-polarized light in the geometry when the wave vector of the incident light was parallel to the optical c- axis.

Ref.	Band position, cm <sup>-1</sup> , E ⊥ c (o-ray)	Ref.	Band position, cm <sup>-1</sup> , E    c (e-ray)
[2]**	231 <sub>TO</sub> , 254 <sub>LO</sub> , 423, 445, 476, 511, 539	[2]**	237 <sub>TO</sub> , 246 <sub>LO</sub> , 318, 360, 416, 495
[3]*	40, 211 <sub>TO</sub>		
[4]**	214 <sub>TO</sub> , 255 <sub>LO</sub>		
[5]*	20 (2K), 211 <sub>TO</sub> , 254 <sub>LO</sub>		
[6]**	215 <sub>TO</sub> , 252 <sub>LO</sub>	[6]**	236 <sub>TO</sub> , 247 <sub>LO</sub>
[7]**	214 <sub>TO</sub> , 254 <sub>LO</sub>		
[8]*	214 <sub>TO</sub> , 252 <sub>LO</sub>		
[9]**	212 <sub>TO</sub> , 254 <sub>LO</sub>	[9]**	237 <sub>TO</sub> , 245 <sub>LO</sub>
[10]**	212 <sub>TO</sub> , 255 <sub>LO</sub>		
present work	499, 512, 540, 619, 655		891, 945, 1093, 1270