



TEMPERATURE VARIATION OF LATTICE PARAMETERS AND THERMAL EXPANSION COEFFICIENTS OF THE COMPOUND $ZnGa_2Se_4$

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Abstract—X-ray powder diffraction measurements on $ZnGa_2Se_4$, a II-III₂-VI₄ semiconductor compound, were made in the temperature range between 300 K and 700 K, a region in which this material has a defect tetragonal structure. From the analysis of the X-ray diffraction lines, accurate lattice parameter values were determined as a function of temperature. These results allowed the evaluation of the thermal expansion coefficients of the corresponding parameters. The observed increase, with the temperature, of the tetragonal deformation $\delta(=2 - c/a)$ as well as of the crystal anisotropy $A_\alpha(= \alpha_a - \alpha_c, \text{ with } \alpha_a > \alpha_c)$ was then explained by using the relations proposed by Abrahams and Bernstein. © 1997 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

A wide range of semiconducting compounds have been studied in recent years, with emphasis on the II-IV-V₂ and I-III-IV₂ compounds which have an adamantine structure [1]. A third class of ternary compounds which have received considerable attention are the II-III₂-VI₄ semiconductor compounds, which again have an adamantine structure but are defect structures with only three of every four cation sites occupied. The compound $ZnGa_2Se_4$, which is a member of this class and has possible applications in device technology, has been studied in some detail. This compound was first studied crystallographically by Hahn *et al.* [2] using an X-ray method, and it was reported that the tetragonal unit cell had the space group symmetry $I\bar{4}$ with cell parameters $a = 5.485 \text{ \AA}$, $c = 10.97 \text{ \AA}$ and $c/a = 2$. Latter work [3] carried out on the T - z phase diagram of the $Zn_{1-z}Mn_zGa_2Se_4$ alloy system showed that, at room temperature, this compound has the α ordered defect $I\bar{4}$ tetragonal structure which is stable up to $T \approx 400^\circ\text{C}$, in the range between 400°C and 940°C has the α' partially disordered tetragonal structure and from 940°C to 1140°C , the former temperature being the melting

point of the material, the β disordered zinc-blende structure occurs. Up to now, neither single crystal X-ray diffraction work nor lattice parameter measurements as a function of the temperature have been reported for this material. Hence, in the present work, X-ray powder diffraction measurements have been carried out on the $ZnGa_2Se_4$ compound to determine values of a , c and c/a as well as the corresponding thermal expansion coefficients in the temperature range between 300 K and 700 K.

EXPERIMENTAL DETAILS

Samples of $ZnGa_2Se_4$ were prepared by the melt and anneal technique using different heat treatments, the components of 1.5 g sample were sealed under vacuum in small quartz ampoules. In each case, the components were melted together at 1150°C for about 2 h, annealed to equilibrium at 600°C , 500°C and 370°C . The samples were finally either brine-quenched or slowly cooled to room temperature. Previous experience indicates that for this type of materials, this procedure usually gives samples showing conditions corresponding to equilibrium near room temperature. Guinier X-ray photographs were used to check the conditions of each of the resulting samples at room temperature.

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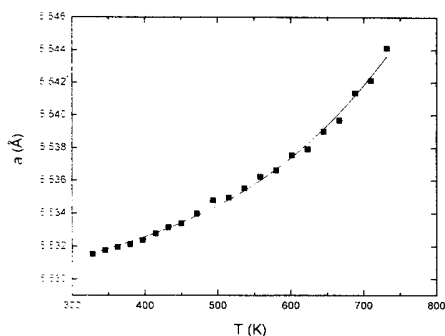


Fig. 1. Variation of the lattice parameter a with temperature T for ZnGa_2Se_4 . Full squares: experimental values; full curve: fitted curve.

The X-ray powder photograph was obtained, in the temperature range 300 K to 700 K, using a Guinier–Lernne high temperature camera with a speed of (2 mm h^{-1}) for 40 h and the radiation was $\text{Cu K}\alpha$ ($\lambda_{\text{Cu}}^* = 1.5418 \text{ \AA}$). The Bragg angles were corrected by using NH_4Br powder as standard material. The lattice parameter values at different temperatures were calculated by using the usual least squares method together with all of the diffraction lines that could be clearly measured from the temperature X-ray pattern. The accuracy in the determination of the parameters a and c was estimated to be $\pm 0.001 \text{ \AA}$ and $\pm 0.005 \text{ \AA}$, respectively.

RESULTS, ANALYSIS AND DISCUSSION

The samples, grown using different heat treatments, were investigated at room temperature by Guinier X-ray powder photographs. In each case, the diffraction patterns were found to be very similar, and it was observed that splitting of the (220/204), (312/116), (400/008), etc. structure lines occurred, indicating that the ratio c/a of this compound is less than two. The sample annealed at 500°C and slowly cooled to room temperature gave the sharpest diffraction lines and hence this sample was selected for the X-ray measurements as a function of T . The Guinier–

Lernne X-ray powder photograph taken on this sample showed the expected α defect tetragonal structure with space group symmetry $\bar{I}4$, where the vacancies and the Zn and Ga ions are all ordered on the cation sublattice [2]. It was found that after approximately 700 K, the line quality became too diffuse as to make any accuracy measurement of the Bragg angle of these lines, so that the line measurements were made up to 700 K. The lattice parameter values were determined, at each temperature as described above, and at 320 K these values were $a = 5.532 \text{ \AA}$, $c = 10.914 \text{ \AA}$ and $c/a = 1.973$, with a standard deviation of the experimental points of $\sigma = \pm 0.0001 \text{ \AA}$. It is observed that the values of a , c and c/a are different from those reported by Hahn *et al.* [2]. As it was indicated above, in the present work, the value of the ratio c/a is found to be less than two, this is an important information when the valence band structure and optical properties of a semiconducting material are being studied. The variations of the crystallographic parameters a , c and c/a with temperature are shown in Figs 1, 2 and 3, respectively. The scattering of the experimental data observed in the case of the lattice parameter c , Fig. 2, is due to the poor quality of the high Bragg angle lines as the temperature was increased. It is seen from these figures that the values of a and c increase nonlinearly, while the ratio c/a decreases nonlinearly with temperature. It is found that, within the limits of experimental error, the variations of a and c/a can be very well fitted to a cubic polynomial relation, while the parameter c can be fitted to a quadratic relation, the equations obtained are:

$$a(T) = 5.5250 + 4 \times 10^{-5} T - 7.5927 \times 10^{-8} T^2 + 8.4542 \times 10^{-11} T^3 \quad (\text{\AA}) \quad (1)$$

$$c(T) = 10.9086 + 2 \times 10^{-5} T + 2 \times 10^{-9} T^2 \quad (\text{\AA}) \quad (2)$$

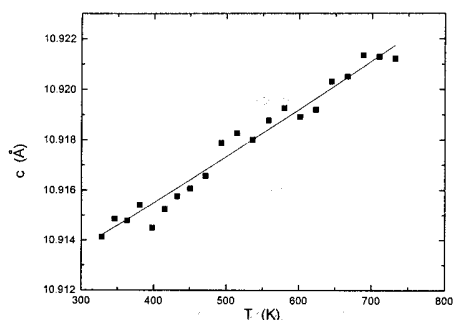


Fig. 2. Variation of the lattice parameter c with temperature T for ZnGa_2Se_4 . Full squares: experimental values; full curve: fitted curve.

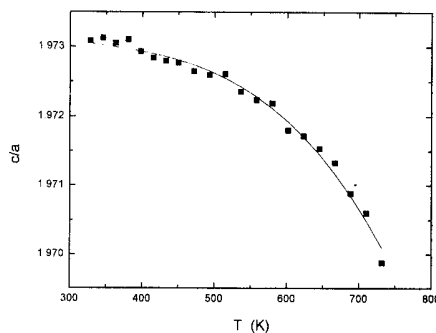


Fig. 3. Variation of the ratio c/a with temperature for ZnGa_2Se_4 . Full squares: experimental values; full curve: fitted curve.

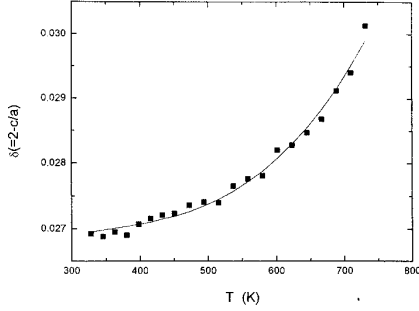


Fig. 4. Variation of the tetragonal deformation δ with temperature for ZnGa₂Se₄.

$$c/a(T) = 1.9749 - 1 \times 10^{-5} T + 3.8266 \times 10^{-8} T^2 - 3.7914 \times 10^{-11} T^3 \quad (3)$$

the standard deviations of the fitted points being $\pm 0.0002 \text{ \AA}$, $\pm 0.0004 \text{ \AA}$ and ± 0.0001 , respectively, the resulting curves are shown in Figs 1, 2 and 3 as solid lines. These relations were used to calculate the tetragonal deformation δ along the z axis, the volume V and the X-ray density D_x , the values so obtained are shown plotted in Figs 4 and 5. It can be seen from Fig. 4 that the values of δ increase with temperature, this is consistent with the reduction of c/a , shown in Fig. 3, which leads to the increase of the tetragonal deformation. Regarding to the variations of V and D_x , it is observed that the decrease of the values of D_x is consistent with the increase of V with T , Fig. 5.

The thermal expansion coefficient α_p of a given crystalline parameter p can be determined by using the relation given by:

$$\alpha_p(T) = (1/p_0) dp/dT \quad (4)$$

where p_0 is the value of the parameter p at 300 K. Then, the expressions for the parameters of interest, obtained

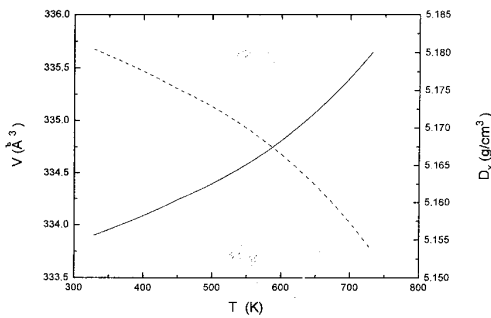


Fig. 5. Variations of the volume V (solid curve) and the X-ray density D_x (dashed curve) with temperature T for ZnGa₂Se₄.

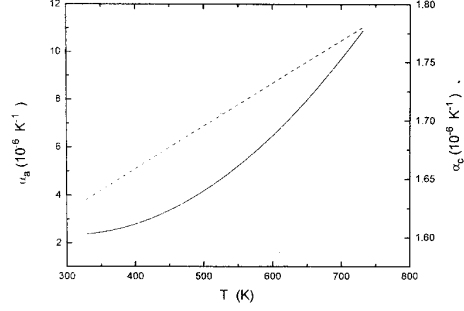


Fig. 6. Variation of the thermal coefficients α_a (solid curve) and α_c (dashed curve) with temperature T for ZnGa₂Se₄.

by using relation (4) with eqs (1), (2) and (3) are:

$$\alpha_a(T) = 6.4389 \times 10^{-6} - 2.7456 \times 10^{-8} T + 4.5857 \times 10^{-11} T^2 \quad (\text{K}^{-1}) \quad (5)$$

$$\alpha_c(T) = 1.5120 \times 10^{-6} + 3.6656 \times 10^{-10} T \quad (\text{K}^{-1}) \quad (6)$$

$$\alpha_{c/a}(T) = -7.2978 \times 10^{-6} + 3.8788 \times 10^{-8} T - 5.7646 \times 10^{-11} T^2 \quad (\text{K}^{-1}) \quad (7)$$

$$\alpha_\delta(T) = 5.4 \times 10^{-4} - 2.8440 \times 10^{-6} T + 4.2267 \times 10^{-9} T^2 \quad (\text{K}^{-1}) \quad (8)$$

the corresponding results are plotted in Figs 6 and 7. It is observed from these figures that, α_a , α_c and α_δ increase with T , while the values of $\alpha_{c/a}$ are negatives and their absolute magnitudes increase with temperature, this is consistent with the variation with T of the parameters shown in Figs 1–4. It is also observed that $\alpha_a > \alpha_c$ in the whole temperature range, this indicates that the crystal anisotropy A_α increases with temperature, this is shown in Fig. 8. These results are to be compared with those reported previously for the I–III–VI₂ chalcopyrite materials as well as for the MnGa₂Se₄, a II–III₂–VI₄ semi-magnetic semiconductor compound which has space

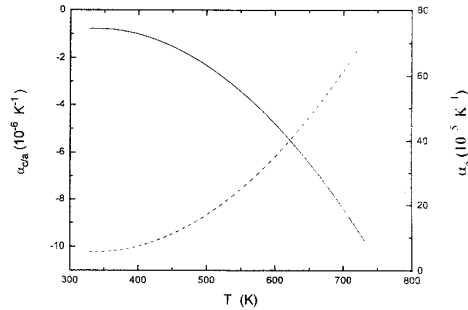


Fig. 7. Variation of the thermal coefficients $\alpha_{c/a}$ (solid curve) and α_δ (dashed curve) with temperature T for ZnGa₂Se₄.

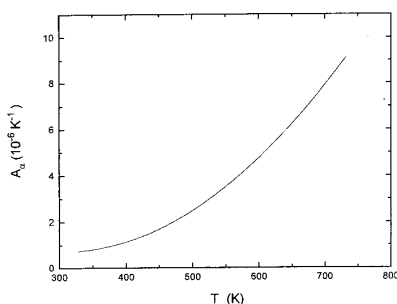


Fig. 8. Variation of the crystal anisotropy A_α with temperature T for ZnGa_2Se_4 .

group $\bar{1}42m$. In the case of Cu-II-VI_2 compounds [4], it is found that α_a and α_c are positives and $\alpha_a > \alpha_c$, but the axial thermal coefficient $\alpha_{c/a}$ is negative. However, for the Ag-III-VI_2 [5] and for the MnGa_2Se_4 [6] compounds, it was shown that α_a is positive but α_c and $\alpha_{c/a}$ are both negatives and also $\alpha_a > |\alpha_c|$. The behaviour corresponding to the Cu-III-VI_2 chalcopyrite compounds is similar to the one described above for the ZnGa_2Se_4 compound.

The increase of δ and A_α with temperature could be explained by considering the method proposed by Garbato *et al.* [7], which takes into account the displacement ($\sigma_x, \sigma_y, \sigma_z$) of the anion from the ideal equilibrium position (1/4, 1/4, 1/8) as well as the cation-anion distances $d(\text{Zn-Se})$ and $d(\text{Ga-Se})$. However, since the powder X-ray method gives only a few diffraction lines and intensity measurements were not made, these parameters were not determined here, hence, this model could not be used in the present work. Another point of interest is to use, as a first approximation, the relations proposed by Abrahams and Bernstein [8], which were determined for crystals with the chalcopyrite structure, such as the II-IV-V_2 and I-III-VI_2 compounds. These relations are given by

$$\chi = 0.5 - [c^2/32a^2 - 1/16]^{1/2} \quad (9)$$

$$d(A-C) = [a^2\chi^2 + (4a^2 + c^2)/64]^{1/2} \quad (10)$$

$$d(B-C) = [a^2(0.5 - \chi)^2 + (4a^2 + c^2)/64]^{1/2} \quad (11)$$

where in the present case χ is the Se anion coordinate and $d(A-C)$ and $d(B-C)$ are assumed to be the Zn-Se and Ga-Se distances, respectively. These equations were used together with eqns (1) and (2) to determine the corresponding thermal expansion coefficients of these parameters, and the resulting curves are shown in Fig. 9. It is seen from this figure that the values of α_χ and $\alpha_{d(\text{Zn-Se})}$ are positives and increase with T , while that $\alpha_{d(\text{Ga-Se})}$ is positive and constant with

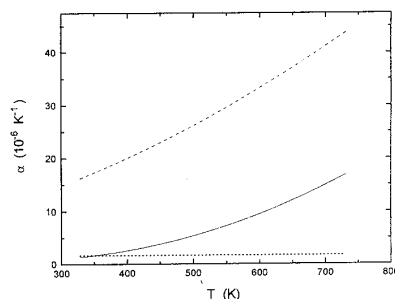


Fig. 9. Variation of the thermal coefficients α_χ (solid curve), $\alpha_{d(\text{Zn-Se})}$ (dashed curve) and $\alpha_{d(\text{Ga-Se})}$ (dotted curve) with temperature T for ZnGa_2Se_4 .

temperature, also, $\alpha_{d(\text{Zn-Se})}$ is higher than $\alpha_{d(\text{Ga-Se})}$ in the whole temperature range. These results mean that, as the temperature is increased, the χ coordinate of the Se anion increases as expected for increasing δ and that the Zn and Ga cations move far away from their Se anion. As explained by Abrahams and Bernstein, the thermal coefficient along the z axis, α_c , will depend largely on the strength of the $B-C$ bonds and in the perpendicular direction the thermal coefficient, α_a , will depend on the strength of the $A-C$ bonds. Thus, the fact that, in the whole temperature range, $\alpha_{d(\text{Zn-Se})} > \alpha_{d(\text{Ga-Se})}$ indicates that α_a is higher than α_c , so that the tetragonal distortion δ and the crystal anisotropy A_α are enhanced.

CONCLUSIONS

The results showed that the values of a and c increase nonlinearly, while c/a decreases nonlinearly with temperature and that the variation of these parameters can be very well fitted to a parabolic relation. It is found that the thermal coefficients α_a and α_c , are positives while the values of $\alpha_{c/a}$ are negatives and also $\alpha_a > \alpha_c$, these results could be explained in terms of the temperature variation of the cation-anion distances as described by Abrahams and Bernstein.

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