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Lattice thermal expansion of silver indium disulphide

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Abstract. Lattice parameters of chalcopyrite type compound silver indium disulphide ($AgInS_2$) were determined as a function of temperature by the x-ray method in the temperature range 28 to 685°C. Using these data, the coefficients of thermal expansion, $\alpha_\perp$ and $\alpha_\parallel$, were evaluated by a graphical method. The temperature dependence of $\alpha_\perp$ and $\alpha_\parallel$ is represented by a suitable equation. The anisotropic thermal expansion of $AgInS_2$ is explained in terms of the thermal expansion of the Ag-S and In-S bonds of the $AgInS_2$ lattice.

Keywords. X-ray diffraction; thermal expansion; silver indium disulphide.

1. Introduction

The present investigation constitutes part of our general studies on the lattice thermal behaviour of ternary semiconductors of the type $A^I B^{III} C_2^{VI}$ (superscripts denote groups in the periodic table and subscripts the number of atoms). These ternary compounds crystallize in the tetragonal chalcopyrite structure with the space group I $\bar{4}2d$ (D_{2d}^{12}) (Berger and Prochukhan 1969). Silver indium disulphide ($AgInS_2$), a member of this family of compounds, exhibits interesting optical and electrical properties which make it a promising candidate in opto-electronic device applications Shay and Wernick 1975; Wagner 1977). No systematic data concerning the lattice thermal behaviour of $AgInS_2$ have been published to date. We have therefore investigated the temperature variation of the lattice parameters and the coefficients of thermal expansion of $AgInS_2$ and the results are reported in this paper.

2. Experimental procedure

The melt-grown sample of chalcopyrite $AgInS_2$, made available by professor Brian R. Pamplin, Bath University, London, England, was used. The details of its preparation and analysis have been reported by Pamplin *et al* (1979). The powder photographs were obtained at different temperatures up to 685° C using a high temperature powder camera (Unicam 19 cm) and CuKα radiation. Four pairs of

reflections recorded in the Bragg angle region 62°-78° were used to determine the lattice parameters of $AgInS_2$ applying Cohen's (1935) analytical method. The experimental arrangement and the procedure to evaluate the lattice parameters, the standard error in the lattice parameters and the coefficients of thermal expansion etc have been detailed elsewhere (Kistaiah *et al* 1981).

3. Results and discussion

The lattice parameters of $AgInS_2$ determined at room temperature in the present study are given in table 1 along with other values taken from the literature. The values of a and c now obtained agree with those reported by Hahn *et al* (1953) and Roth *et al* (1973).

The lattice parameters obtained at different temperatures are shown graphically in figure 1. It can be seen that both the lattice parameters a and c increase non-linearly with increasing temperature.

The coefficients of thermal expansion, $\alpha_\perp$ and $\alpha_\parallel$, perpendicular and parallel to the principal axis respectively, obtained at various temperatures are shown graphically in figure 2. Their temperature dependence is represented by the following equations:

$$\alpha_\perp = (10{\cdot}206 + 3{\cdot}912 \times 10^{-4} T + 3{\cdot}624 \times 10^{-6} T^2 \pm 0{\cdot}3) \times 10^{-6}, \quad (1)$$

$$\alpha_\parallel = (8{\cdot}949 + 4{\cdot}338 \times 10^{-3} T + 3{\cdot}939 \times 10^{-6} T^2 \pm 0{\cdot}3) \times 10^{-6}, \quad (2)$$

Table 1. Comparison of the lattice parameters of $AgInS_2$ at room temperature.

Source	Lattice parameter (Å)	
	a	c
Hahn *et al* (1953)	5·829	11·19
Goryunova (1965)	5·81	11·16
Roth *et al* (1973)	5·8292	11·203
	± 0·0004	± 0·002
Present study	5·8360	11·1789
	± 0·0002	± 0·0004

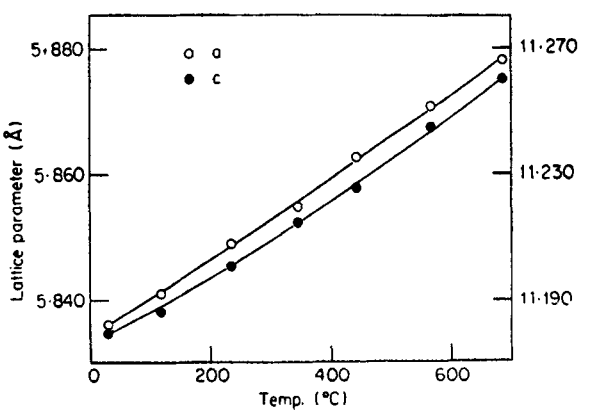

Figure 1. Variation of the lattice parameters of $AgInS_2$ with temperature.

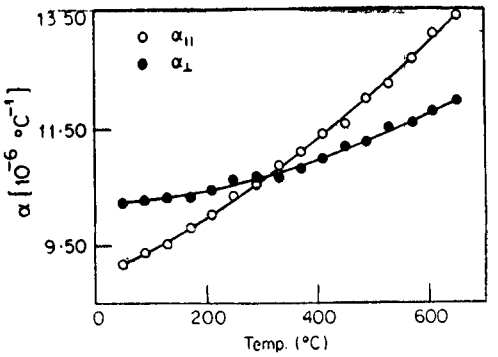

Figure 2. Variation of the coefficients of thermal expansion of $AgInS_2$ with temperature.

where T is in °C and α is in $°C^{-1}$. The values of these coefficients at room temperature (28°C) and the mean values over the temperature range 28-685°C are found to be

$$\alpha_{\perp}(28°C) = 10{\cdot}22 \times 10^{-6}\,°C^{-1} \text{ and } \alpha_{\parallel}(28°C) = 9{\cdot}06 \times 10^{-6}\,°C^{-1}$$

$$\alpha_{\perp}(28 - 685°C) = 10{\cdot}75 \times 10^{-6}\,°C^{-1}$$

$$\text{and } \alpha_{\parallel}(28 - 685\,°C) = 11{\cdot}26 \times 10^{-6}\,°C^{-1}$$

The thermal expansion behaviour of $AgInS_2$ observed at room temperature is similar to its isotypic compounds of I-III-VI_2 group in that it has a relatively small coefficient of expansion along the c-axis and a large coefficient of expansion in the perpendicular direction ($\alpha_{\parallel} < \alpha_{\perp}$) (Kistaiah *et al* 1981). However, in $AgInS_2$ (figure 2) both the coefficients $\alpha_{\perp}$ and $\alpha_{\parallel}$ are equal at about 320°C and above this temperature $\alpha_{\parallel}$ is greater than $\alpha_{\perp}$. Among the I-III-IV_2 chalcopyrites so far studied, $AgInS_2$ is the only compound which shows this unusual thermal expansion. This is explained below:

As pointed out earlier (Kistaiah *et al* 1981), the difference in interactions (including ionic and covalent forces) perpendicular and parallel to the principal axis of an $A^{I}\,B^{III}\,C_2^{VI}$ tetragonal chalcopyrite lattice can be approximated by the difference between the interactions of the A-C and B-C bonds, respectively. This implies that in $AgInS_2$, the In-S bond affects the coefficient of expansion along the c-direction while the Ag-S bond affects along the a-direction. Since the In-S bond is more covalent than the Ag-S bond at room temperature (Levine 1973), a smaller coefficient of expansion is to be expected along the c-direction than that along a-direction. This is confirmed by the present results at room temperatue. However, the unusual thermal expansion of $AgInS_2$ at elevated temperatures may be due to a larger dilation of the In-S bond than the Ag-S bond with temperature. This is also confirmed by the study of the bond expansion of $AgInS_2$ lattice. The thermal expansion of the Ag-S and In-S bonds of $AgInS_2$ compound is determined by using the relations given by Abrahams and Bernstein (1973) and its temperature variation is shown in figure 3. It can be seen that the expansion of the Ag-S bond is greater than the In-S bond upto about 350°C and above this temperature the expansion of the Ag-S bond is smaller than the In-S bond. This means that the In-S bond becomes weaker than the Ag-S bond above 350°C and it supports the unusual lattice thermal expansion of $AgInS_2$.

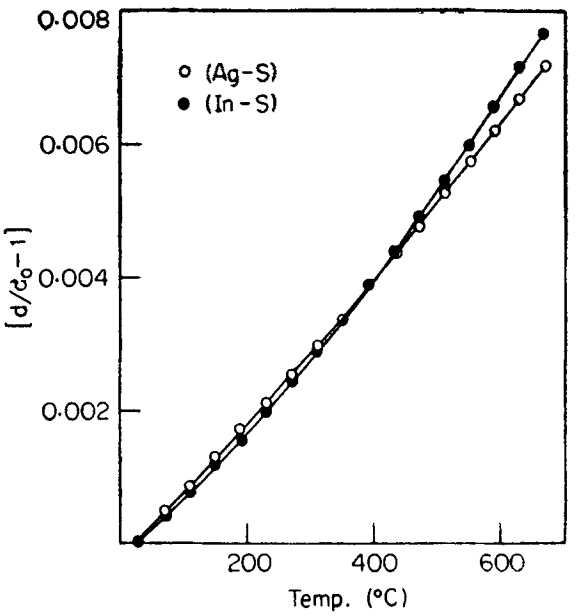

Figure 3. Variation of thermal expansion of the Ag-S and In-S bonds of $AgInS_2$ with temperature.

To conclude, we have determined the temperature variation of the lattice parameters and thermal expansion of the compound $AgInS_2$. The observed lattice thermal expansion behaviour of this compound is as expected on the basis of its structure and bond expansion.

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