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Lattice thermal expansion of cupric thiogallate

The I–III–VI_2 ternary compounds which crystallize in the uniaxial calcopyrite structure are potentially interesting as non-linear optical materials as well as semiconductors [1, 2]. The compound cupric thiogallate, Cu–Ga–S_2, a member of this class of materials, is probably the most interesting because of its potential use for many technological applications [2, 3]. Under a programme of studies on some chalcopyrite ternary semiconducting compounds by X-ray diffraction analysis the authors have previously reported the lattice thermal expansion of a number of compounds within this class of materials [4–8]. The present note gives the results of a similar X-ray study of cupric thiogallate. While the work was in progress, Yamamoto *et al.* [9] reported the temperature variation of lattice parameters and the average coefficients of thermal expansion of Cu–Ga–S_2 using X-ray diffraction analysis. In their study they made use of a Rigaku high-temperature powder camera. However, in their work [9] no details of the accuracy of their results was given and, further, the accuracies with which the lattice parameters and the temperatures were determined were poor compared to our earlier studies [4–8]. Hence, it was thought worthwhile to proceed and to determine the accurate lattice parameters and the coefficients of thermal expansion for Cu–Ga–S_2 at various temperatures, as a part of the programme.

The Cu–Ga–S_2 sample used in the present study was kindly supplied by Dr B. Tell of Bell Laboratories. The details of the growth method

TABLE I Lattice parameters of Cu–Ga–S_2 at room temperature

Lattice parameter		Reference number
a (nm)	c (nm)	
0.5349	1.047	[13]
0.5351	1.0484	[10]
0.534 741 ± 0.000 007	1.047 429 ± 0.000 006	[14]
0.5347	1.0474	[15]
0.5359	1.049	[3]
0.534 74 ± 0.000 01	1.048 25 ± 0.000 02	Present study

TABLE II Lattice parameters of Cu–Ga–S_2 at different temperatures

Temperature (° C)	Lattice parameter	
	a (nm)	c (nm)
28	0.534 74	1.048 25
116	0.535 15	1.048 58
234	0.535 66	1.048 91
346	0.536 26	1.049 45
442	0.536 85	1.049 74
566	0.537 48	1.050 42
685	0.538 17	1.051 10

and purity analysis of the sample were described by Tell *et al.* [10]. The crystal sample was crushed to a powder of appropriate particle size. The powder sample for the study was then placed in a thin-walled quartz capillary. Using a Unicam 19 cm high-temperature X-ray powder diffraction camera and CuKα radiation, powder diffraction photographs were taken at different temperatures ranging from room temperature (28° C) to 685° C. Temperature control was facilitated by the use of a voltage stabilizer and variac and the temperature could be held constant to within about 2° C. The details of the experimental set-up and the construction of the camera were described in an earlier paper [11].

Eight reflections, recorded in the Bragg diffraction angle region from 64 to 72°, were used to determine the accurate lattice parameters at different temperatures. The data have been used to evaluate the coefficients of thermal expansion, $\alpha_{\parallel}$ and $\alpha_{\perp}$, respectively parallel and perpendicular to the principal axis, at various temperatures. The method of evaluating the accurate lattice parameters, the standard error in the lattice parameters and the coefficients of thermal expansion have been described in an earlier paper [12].

The lattice parameters of Cu–Ga–S_2 at room temperature obtained in the present study are given in Table I together with the other values available in the literature. The value of the lattice parameter, a, from the present study agrees well with those of the two recent determinations [14, 15] while the value of the lattice parameter, c, is slightly higher than the values of [14, 15].

The lattice parameters obtained at different temperatures are given in Table II and Fig. 1a and b. It can be seen that both the lattice parameters a and c increase non-linearly with increasing temperature. The mean standard error of the lattice parameters in the range of temperatures covered in this investigation is about 1×10^{-5} nm in the a-parameter and about 2×10^{-5} nm in the c-parameter. The coefficients of thermal expansion, $\alpha_{\perp}$ and $\alpha_{\parallel}$ obtained at various temperatures are shown in Fig. 2. It can be seen that both coefficients increase non-linearly with increasing temperature. Over the range of temperatures studied in the present investigation, these coefficients of thermal expansion, $\alpha_{\perp}$ and $\alpha_{\parallel}$, in $^{\circ}\,C^{-1}$, are represented by the following equations:

$$\alpha_{\perp} = 7.97519 \times 10^{-6} + 6.09366 \times 10^{-9} T - 2.47084 \times 10^{-12} T^2; \quad (1)$$

$$\alpha_{\parallel} = 2.89500 \times 10^{-6} + 2.01764 \times 10^{-9} T + 3.13378 \times 10^{-12} T^2, \quad (2)$$

where T is the temperature expressed in ° C.

The mean expansion coefficients of cupric thi-

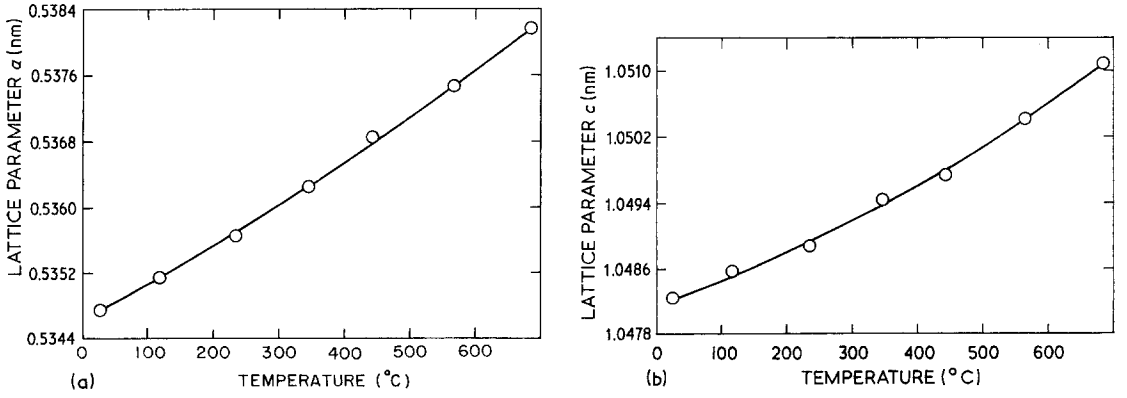

Figure 1 Variation of the lattice parameters of cupric thiogallate with temperature. (a) a and (b) c.

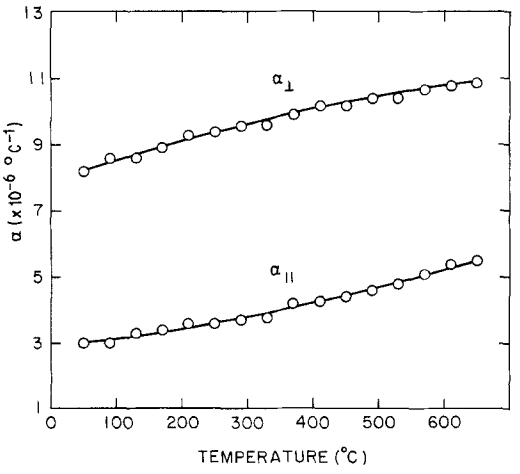

Figure 2 Variation of the coefficients of thermal expansion, $\alpha_{\parallel}$ and $\alpha_{\perp}$, of cupric thiogallate with temperature.

ogallate, over the range of temperatures covered in the present investigation, are $\bar{\alpha}_{\perp} = 9.76 \times 10^{-6}\,^{\circ}\,C^{-1}$ and $\bar{\alpha}_{\parallel} = 4.14 \times 10^{-6}\,^{\circ}\,C^{-1}$; those obtained by Yamamoto *et al.* [9] are $\bar{\alpha}_{\perp} = 11.2 \times 10^{-6}\,^{\circ}\,C^{-1}$ and $\bar{\alpha}_{\parallel} = 4.1 \times 10^{-6}\,^{\circ}\,C^{-1}$. Even though there is agreement in the values of $\bar{\alpha}_{\perp}$ and $\bar{\alpha}_{\parallel}$ there is a large difference in their measured temperature variations. In [9] the thermal expansion coefficients, $\alpha_{\perp}$ and $\alpha_{\parallel}$, are constant throughout the temperature range. In the present study the thermal expansion coefficients increase non-linearly with increasing temperature. This discrepancy may result from the greater accuracy of measurements of the lattice parameters and the temperature in the present study. The lattice thermal behaviour of Cu–Ga–S_2 is similar to that of its isotypic compounds, such as Cu–In–Se_2 [7] and Cu–In–S_2 [8], having a relatively large coefficient of expansion along the *a*-direction ($\alpha_{\perp}$) and a relatively small coefficient of expansion along the *c*-direction ($\alpha_{\parallel}$).

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