

Determination of lattice parameters and thermal expansion of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ at elevated temperatures

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Received 12 December 2005, revised 21 February 2006, accepted 6 March 2006

Published online 15 August 2006

Key words semiconductor, x-ray diffraction, lattice parameter, thermal expansion.

PACS 08.15.Bh

CuGe_2P_3 is a p-type semiconductor with zincblende structure. Ge_3P_4 is soluble up to 35 mole % in CuGe_2P_3 . Lattice parameters of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ have been determined at elevated temperatures from room temperature to 873 K using the x-ray diffraction profiles (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) obtained from high temperature diffractometer. It is found that the lattice parameter increases linearly from 0.53856 nm at RT to 0.54025 nm at 873 K. The data on lattice parameter is used and coefficient of lattice thermal expansion of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ was determined at different temperatures. It is found that the coefficient of thermal expansion of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ is $5.48 \times 10^{-6} \text{K}^{-1}$ and is independent of temperature.

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1 Introduction

Copper germanium phosphide CuGe_2P_3 is a p-type semiconductor having zinc blend structure with the space group. $F\bar{4}3m$. In the unit cell, the copper and germanium atoms are randomly distributed on the cation sites [1]. Germanium is soluble up to 6 mol.% in CuGe_2P_3 . At this composition CuGe_5P_3 is formed [2]. It is also reported that Cu_2GeS_3 dissolves up to 90 mol.% while hypothetical adamantine compound Ge_3P_3 dissolves up to 35 mol.% in CuGe_2P_3 forming zincblende structure[3] in CuGe_2P_3 . As a part of the general program of the determination of lattice parameters and coefficient of thermal expansion of several semiconducting materials, the ternary semiconductors of $\text{CuGe}_2\text{P}_3\text{-Cu}_2\text{GeS}_3$ and $\text{CuSi}_{2+x}\text{P}_3$ ($x=1,2$) systems of different compositions have been reported earlier[4-8] from x-ray diffraction studies at elevated temperatures. In the present paper, the authors report lattice parameters and coefficient thermal expansion of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ at elevated temperatures.

2 Experimental

The compound $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ was prepared using a melt growth technique of modified Bridgman method. The details of preparation are given elsewhere [2,3]. Preliminary x-ray diffraction data has been collected at room temperature for the purpose of indexing. It is found that all the profiles recorded are sharp and indexed to FCC zinc blend structure. For the x-ray diffraction study at high temperature, the crystals of

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$\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ were ground, and specimen was prepared by filling powder on 10mm x 10mm diffractometer sample holder with a suitable binder. Then the sample was dried for an hour. The x-ray diffraction data were collected using the specimen with scanning speed of 1° per minute on a Philips 3121 x-ray diffractometer with a proportional counter using Cu $K\alpha$ radiation with Ni filter. The x-ray data on profiles (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) have been recorded using the divergence, scattering slits of 1° each and receiving slit of 0.2 mm in the Bragg angle region ranging from 14° to 50° . The x-ray diffraction data were collected at different temperatures from room temperature (298 K) to 873 K with an interval of 100 K. A high temperature attachment supplied by Anton Paar was used for this purpose. The error in the measurement of temperature was $\pm 2\text{K}$.

3 Results and discussion

The lattice parameter of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ at different temperatures was calculated by the method of Cohen's least squares analysis [9] of the x-ray diffraction profiles and are given in table 1. The error in the lattice parameters was calculated by the method suggested by Jette and Foote [10] and found to be $\pm 4.0 \times 10^{-5}$ nm. The experimental data on lattice parameter are fitted to the equation:

$$a_T = 0.53763 + 2.9525 \times 10^{-6} T \quad (1)$$

where T represents the temperature in Kelvin and a_T is the lattice parameter in nano meters at any arbitrary temperature in the temperature range studied. The lattice parameters calculated using equation (1) are also included in table 1.

Table 1 Lattice parameters of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ at elevated temperatures.

Temperature (K)	Lattice parameter (nm)	
	experimental	calculated (eq.1)
298	0.53856 ± 0.00004	0.53851
373	0.53872	0.53879
473	0.53906	0.53908
573	0.53942	0.53938
673	0.53965	0.53967
773	0.54000	0.53997
873	0.54025	0.54026

It is convenient to fit the temperature variation a_T to the equation of type

$$\ln a_T = -0.6205854 + 5.4738 \times 10^{-6} T \quad (2)$$

as its first derivative directly would give the coefficient of thermal expansion (CTE), (α_T) of the lattice as:

$$\alpha_T = \frac{1}{a_T} \frac{da_T}{dT} = \frac{d}{dT} (\ln a_T) \quad (3)$$

The variation of lattice parameter of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ with temperature is shown in figure 1.

From figure 1, it can be seen that the lattice parameter of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ increases linearly from 0.53856 nm at RT to 0.54025 nm at 873 K. The coefficient of thermal expansion of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ is found to be $5.48 \times 10^{-6} \text{K}^{-1}$ (eq.3) and constant throughout the temperature range studied.

Compounds having covalent bonds normally have low coefficient of thermal expansion whereas compounds having ionic bonds have higher values, because covalent bonds are stronger than ionic bonds. For example, the mean value of CTE of silicon between 273 and 873 K is $2.0 \times 10^{-6} \text{K}^{-1}$ [3] while for NaCl it is $5.0 \times 10^{-6} \text{K}^{-1}$. Generally, it is considered that the integrated thermal expansion from absolute zero to melting point is of the order of 0.7% for the covalent bonded crystals and is 3 to 4 times larger for the ionic and metallic 3 to 4 times larger for the ionic and metallic crystals [11].

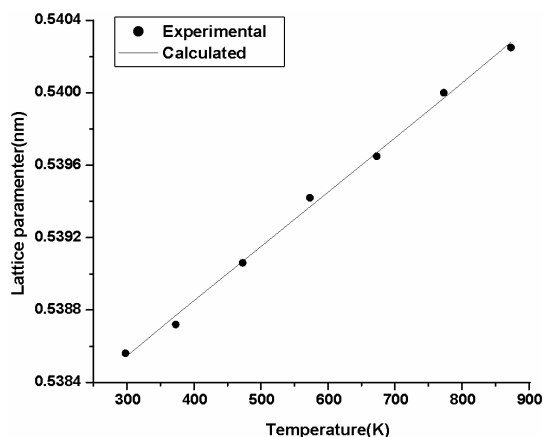


Fig. 1 Variation of lattice parameter of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ with temperature.

Higher thermal expansion coefficients are observed for compounds such as CuGe_2P_3 and $\text{CuGe}_2\text{P}_3\text{-Cu}_2\text{GeS}_3$ mixed crystals when compared to other covalent compounds of the III-V group such as GaP and GaAs and other semiconductors such as silicon and germanium [8]. Similarly, CTE of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ mixed crystals ($5.48 \times 10^{-6} \text{K}^{-1}$) obtained in the present study is comparable with GaP, GaAs and $\text{CuSi}_{2+x}\text{P}_3$ ($x = 0, 1, 2$) semiconductors and lies between CTE of silicon or germanium and $\text{CuGe}_2\text{P}_3 - \text{Cu}_2\text{GeS}_3$ mixed crystals [8]. This indicates that the present substance $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ has more ionic nature compared to silicon or germanium and less ionic than that of $\text{CuGe}_2\text{P}_3 - \text{Cu}_2\text{GeS}_3$ mixed crystals.

4 Conclusions

- 1 The lattice parameter of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ increases linearly with temperature.
- 2 The CTE of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ is 5.48K^{-1} and found to be independent of temperature in the range 298 – 873 K.
- 3 The ionic character of $\text{CuGe}_2\text{P}_3 + 0.2 \text{Ge}_3\text{P}_4$ lies between ionic character of Si or Ge and $\text{CuGe}_2\text{P}_3 - \text{Cu}_2\text{GeS}_3$ mixed crystals.

Acknowledgements The authors also thank Dr. M. S. Omar, Dept. of Physics, College of Science, University of Salahadden, Arabia, Iraq for providing sample for the present study. One of the authors (GB) thanks Prof. S. V. Suryanaryana, Dept. of Physics, Osmania University, Hyderabad, India for his encouragement.

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