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# Research on the thermal expansion of $AgGa_{1-x}In_xSe_2$ single crystals

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ABSTRACT

Thermal expansion coefficients of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals have been measured in the range from 323 K to 823 K. The values of $\alpha_a$ are positive and increase with temperature whereas the values of $\alpha_c$ are negative and their absolute magnitudes increase with the increasing temperature for different x. With the increase of x, thermal expansion coefficients $\alpha_a$ and $\alpha_c$ both decrease numerically. The mean linear thermal expansion coefficient $\alpha_L$ and the anisotropy of thermal expansion $\alpha_\eta$ have been calculated, and they are also decreasing numerically with the increasing x. The slope of the straight line $\alpha_{hkl}$ versus $cos^2\phi$ decreases as x increases at 473 K and 773 K, respectively. According to the variation of thermal expansion coefficients, the relationship between the thermal expansion coefficient, bond length, and melting point of $AgGa_{1-x}In_xSe_2$ satisfies the equation $\alpha_L = \frac{0.021}{T_m} - B(d-d_0)^3$. In addition, the mechanism of thermal expansion variation has been discussed in terms of crystal structure, bond lengths, and thermal vibration of bonds in $AgGa_{1-x}In_xSe_2$ single crystals.

## 1. Introduction

The ternary $A^IB^{II}C_2^{VI}$ compounds $AgGaSe_2$ and $AgInSe_2$ crystallize in chalcopyrite structure. $AgGa_{1-x}In_xSe_2$ crystal, which is obtained by mixing indium into $AgGaSe_2$ [1,2] and belongs to the $AgGaSe_2$-$AgInSe_2$ system, is a new promising mid-IR nonlinear optical material. $AgGa_{1-x}In_xSe_2$ crystal has application prospect in nonlinear optical frequency conversion devices widely. It can achieve noncritically phase-matched (NCPM) second-harmonic frequency (SHG) for 9.27 μm $CO_2$ laser [3,4] and three wave frequency mixing of NCPM [1,3–7].

With the different indium content, $AgGa_{1-x}In_xSe_2$ crystal presents various properties, and some of related studies have been reported. Hahn and Kim [8] measured lattice constants, photoconductivity, peak energy, and the energy gap of $AgGa_{1-x}In_xSe_2$ polycrystal in the composition range from x = 0.0–1.0. Vijayakumar et al. [9] reported supercooling temperature of $AgGa_{1-x}In_xSe_2$ (x = 0, 0.2, 0.5, 1). Cui et al. [10,11] studied Raman spectroscopy and photoluminescence of $AgGa_{1-x}In_xSe_2$ (x = 0, 0.1, 0.2). Moreover, with the increase of x, the birefringence coefficient gradually changes over a wide range from 0.033 ($AgGaSe_2$) to 0.003 ($AgInSe_2$) and the band gap energy of quaternary compound is tunable from 1.24 eV ($AgInSe_2$) to 1.80 eV ($AgGaSe_2$) [5–7,12]. Due to the mixing of indium, the thermal properties appear to change, and some related studies about the thermodynamic properties of $AgGaSe_2$ [4,13,14], $AgInSe_2$ [15], and $AgGa_{0.7}In_{0.3}Se_2$ [16] have been accomplished, respectively. However, there are only a few types of research available about thermal properties of $AgGa_{1-x}In_xSe_2$ with other different x. Furthermore, $AgGa_{1-x}In_xSe_2$ single crystal cracks easily when cooling from melting point to room temperature because it has a positive thermal expansion along a-axis while negative thermal expansion along c-axis. Therefore, it is significant to investigate the thermal expansion behavior of $AgGa_{1-x}In_xSe_2$ crystal for improving the growth conditions to obtain crack-free and large-size single crystals.

In this paper, the thermal expansion coefficients along a-axis and c-axis of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals have been measured in the range from 323 K to 823 K by using the thermal dilatometer. The mean linear thermal expansion coefficient $\alpha_L$, the anisotropy of thermal expansion $\alpha_\eta$, and the coefficient of the linear expansion $\alpha_{hkl}$ have been calculated. Based on the results, the relation between the thermal expansion coefficients, bond length, and melting points of $AgGa_{1-x}In_xSe_2$ have been discussed. What is more, the factors of the thermal expansion coefficients variation along the a-axis and c-axis for different x at different temperatures are also analyzed.

## 2. Experiment

The $AgGa_{1-x}In_xSe_2$ crystals used in this study were grown by the vertical Bridgman method. High-purity (6 N) elements of silver (Ag),

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gallium (Ga), indium (In) and selenium (Se) were weighed in accordance with the stoichiometric ratio of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) and an excess of 0.5 wt% Se as raw material. The raw materials were sealed in a quartz ampoule under $10^{-4}$ Pa and loaded into a vertical furnace. The $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) polycrystalline material was synthesized by the melt temperature oscillation method [17]. Then the temperature slowly cooled to room temperature at a rate of 1 ℃/min. $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals were successfully grown by the modified vertical Bridgman method [18] in a three-zone vertical furnace. Then the $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) polycrystal was ground to powder and loaded into a two-layer quartz growth ampoule with inner wall coated with carbon that was sealed under $1 \times 10^{-4}$ Pa. The sealed growth ampoule was loaded into the furnace. The temperature of the up-, mid-, and bottom sections of the furnace was raised to 930, 900, and 650 ℃, respectively. The ampoule was mechanically lowered at a rate of 3–8 mm/day until the solidification of the material.

According to the orientation of cleavage faces of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) ingots and X-ray diffractometric (XRD) measurement and analysis, we identified the c- and a-axes of the bulk crystal. The block samples were cut along the direction of [001] and [100], and the thermal expansion coefficients were measured between 323 K and 823 K at a heating rate of 5 K/min by WinTA100 dilatometer (Bähr company, Germany).

## 3. Results and discussion

### 3.1. XRD measurement of $AgGa_{1-x}In_xSe_2$ single crystal

The c- and a-axes of the block samples were analyzed using XRD technique. The XRD patterns of (001) and (100) faces on $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) crystals are shown in Fig. 1.

### 3.2. Thermal expansion measurement of $AgGa_{1-x}In_xSe_2$ single crystal

The thermal expansion coefficient $\alpha$ of c- and a-axes of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals were measured by WinTA100 dilatometer. According to the least square approximation, the lattice parameter $R$ can be described by the polynomial function of temperature as:

$$R(T) = A_0 + A_1T + A_2T^2 + A_3T^3 + \cdots \quad (1)$$

where $T$ represents temperature while $A_n$ represents the effect of temperature with the power of n. And the parameter $A_0$ is the value of the lattice parameter at 0 K.

It is more convenient to fit ln (R($T$)) to a polynomial form

$$\ln R(T) = A + BT + CT^2 + \cdots \quad (2)$$

The thermal expansion coefficient $\alpha$ of a given crystal parameter $R$ can be defined as:

$$\alpha_R(T) = \frac{1}{R_0}\frac{dR}{dT} = \frac{dlnR(T)}{dT} = B+2CT+\cdots \quad (3)$$

Therefore, we use linear fitting to do with the curve of thermal expansion $\alpha_a$ and $\alpha_c$ over the temperature range from 423 K to 823 K. The variation of thermal expansion coefficient $\alpha$ of c- and a-axes of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals are described in linear connection with temperature:

$$\begin{cases} \alpha_{a(x=0.2)} = 8.5921 \times 10^{-6}+1.29 \times 10^{-8} \\ \alpha_{c(x=0.2)} = -7.4547 \times 10^{-6}-6.87 \times 10^{-9} \\ \alpha_{a(x=0.3)} = 7.716 \times 10^{-6}+1.3 \times 10^{-8} \\ \alpha_{c(x=0.3)} = -6.8854 \times 10^{-6}-7.2 \times 10^{-9} \\ \alpha_{a(x=0.4)} = 6.5149 \times 10^{-6}+1.3 \times 10^{-8} \\ \alpha_{c(x=0.4)} = -6.1019 \times 10^{-6}-7.07 \times 10^{-9} \end{cases} \quad (4)$$

Mean linear thermal expansion coefficient $\alpha_L$, is obtained by the relation [19]:

$$\alpha_L \equiv \frac{1}{3}(2\alpha_a + \alpha_c). \quad (5)$$

The anisotropy of thermal expansion $\alpha_\eta$, is obtained by the relation:

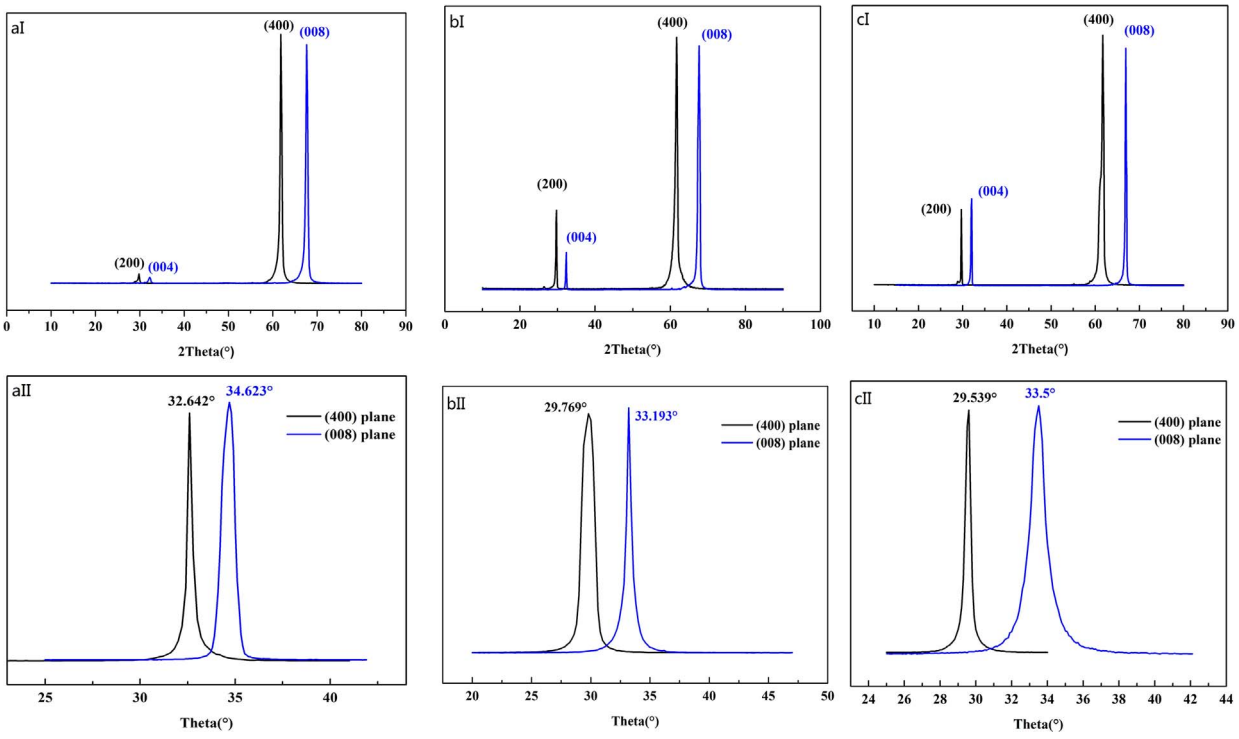


**Fig. 1.** XRD patterns of $AgGa_{1-x}In_xSe_2$ (x = 0.2, 0.3, 0.4) single crystals: (a) x = 0.2; (b) x = 0.3; (c) x = 0.4; (I) XRD patterns of (100) and (001) planes; (II) XRD rocking curves of (100) and (001) planes.