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X-ray powder diffraction, phase transitions and optical characterization of the $Cu(In_{1-x}Ga_x)_3Te_5$ semiconducting system

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Abstract

Ingots of several compositions of the $Cu(In_{1-x}Ga_x)_3Te_5$ semiconducting system were prepared by the Vertical Bridgman technique. X-ray powder diffraction, differential thermal analysis and optical absorption studies were used to characterize the fundamental structural aspects and phase transitions and determine the energy band gap E_G of this alloy system. It is found that a solid solution with a tetragonal chalcopyrite-related structure is formed over the entire range of composition for temperatures below 620 °C. The parameters *a* and *c* at room temperature of the tetragonal unit cell were found to vary linearly with composition *x* from 6.1639(4) and 12.346(6) Å for $x = 0$, to 5.93231(8) and 11.825(4) Å for $x = 1$. A phase transition to a cubic phase in the whole range of composition was observed above 620 °C. The energy band gap has been determined to be direct and varies linearly with composition *x*.

Keywords: Semiconductors; Crystal growth; X-ray diffraction; Light absorption and reflection; Thermal analysis

1. Introduction

There has been great progress in the development of high efficiency thin-film photovoltaic devices in the last 20 years [1]. One of the most interesting and promising advances has been the production of solar cells of the type $CdS/Cu(In,Ga)Se_2$. They exhibit the highest solar to electrical energy conversion efficiency recorded in a laboratory device [2,3]. This technologically important development has certainly played a major role in the increasing interest paid to ternary and multinary semiconducting compounds belonging to the Cu–In(Ga)–Se system. Since there have been consistent reports [4,5] that only stoichiometric and In-rich $CuInSe_2$ films produce good solar cells and that intermediate phases of the Cu_2Se–In_2Se_3 system, such as $CuIn_3Se_5$, appear as a secondary phase in In-rich $CuInSe_2$ films, several studies on the structure of bulk and thin film samples of these materials have been reported [6–9]. Structural and optical studies of the entire range of composition of the $Cu(In_{1-x}Ga_x)_3Se_5$ system have also been carried out [10,11]. Both $CuIn_3Te_5$ and $CuGa_3Te_5$, as well as $CuIn_3Se_5$ and $CuGa_3Se_5$, belong to the I III_3 VI_5 family of semiconducting compounds. This is one of the five-fold defect derivatives of the II–VI binary semiconductors in which the cation is substituted by two different types of cations and an array of vacancies is introduced [12]. In these materials, the vacancies might orderly occupy particular crystallographic sites in the structure. For this reason they have been called ordered vacancy compounds (OVC). After a comprehensive study of the defect physics of $CuInSe_2$, performed by Zhang et al. [13], it might be more appropriate to call them ordered defect compounds (ODC) since their formation can be rationalized in terms of units of $(2V_{Cu}^{-},In_{Cu}^{2+})$ defect pairs instead of a simple cation vacancy. In addition to their technological importance, these materials are also of academic interest because of the fundamental insights they could provide into the influence of their defect chemistry and the effects that defect-pairs play on their optical and electrical properties.

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To our knowledge, only a few reports on the structural characterization of $CuIn_3Te_5$ and $CuGa_3Te_5$ [14,15] exist in the literature and none on the mixed $Cu(In_{1-x}Ga_x)_3Te_5$ system. In this contribution, we present the crystal growth of several compositions of the $Cu(In_{1-x}Ga_x)_3Te_5$ system, their fundamental structural aspects, phase transitions and optical properties obtained by X-ray powder diffraction, differential thermal analysis and optical absorption techniques.

2. Experimental

Ingots of several compositions of the $Cu(In_{1-x}Ga_x)_3Te_5$ semiconducting system were prepared by the Bridgman technique in a multi-zone vertical furnace by solid-state reaction of stoichiometric mixtures of at least 5N pure constituent elements sealed in evacuated quartz ampoules. All ampoules were subjected to the same heat treatment in a multiple-zone furnace. The temperature was initially raised to 300 °C at a rate of 10 °C/h. The ampoule was kept at this temperature for 12 h and then heated to 1150 °C at 10 °C/h. The liquid phase of the reacting mixture was agitated thoroughly for 24 h by periodically rocking the furnace. The furnace was cooled down to 1050 °C at 10 °C/h, to 980 °C at 5 °C/h with a dwell at this temperature for 5 h and to 660 °C at 30 °C/h. The ingot was then annealed at this temperature for 48 h. Finally, the furnace was cooled down to room temperature at a rate of 40 °C/h.

Semi-quantitative elemental analysis was performed by EDX using a KEVEX model Delta-3 system connected to a Hitachi model S-2500 SEM. The results obtained from the central part of the ingots, from which the samples were cut for different types of analyses, were very similar to their nominal starting compositions.

The samples for the X-ray powder diffraction analysis were prepared by gently grinding a small portion of each composition in an agate mortar. A fraction of each alloy of the $Cu(In_{1-x}Ga_x)_3Te_5$ system was mounted on a zero background specimen holder, dusted on top of a thin film of paraffin.

The powder diffraction patterns were registered with a previously calibrated SIEMENS D-5005 diffractometer, operated at 45 kV and 30 mA using a Cu-target tube and a graphite monochromator. Fixed scatter and divergence slits of 1° and a 0.3 mm-receiving slit were used. The intensity data were recorded in a $2\theta/\theta$ mode from 5° to 90° with a step size of 0.02° and a scan speed of 0.3°/min. The JADE Plus 5.0 software was used to determine the positions of the diffraction maxima, to remove background, and to eliminate the $K\alpha_2$ component from each reflection. The position of each peak was established using the α_1 component (λ Cu $K\alpha_1 = 1.5406$ Å). Its intensity was measured as peak height above background and is expressed as a percentage of the strongest peak of the pattern.

The phase transitions of this alloy system were studied from differential thermal analysis (DTA) using silver or gold as reference material. Samples were contained in sealed silica tubes to prevent oxidation or loss of volatile phases. The transition temperatures were determined from the baseline intercept of the extrapolated tangent to the endothermic or exothermic peak. Last-to-melt temperatures were defined to be the maximum temperature when the endotherm began rapid return to the baseline. The first-to-freeze temperatures were defined to be the onset of the exothermic reaction. A heating rate of about 10 °C/min was used. The error in determining the transition temperature is estimated to be about 8 °C.

The optical transmittance spectra at room temperature were measured with a fully automated Cary-17I spectrophotometer using a tungsten lamp as a light source. The transmitted radiation was detected by a Ge photodiode and a PAR model 5208 lock-in amplifiers. The absorption coefficient α was obtained from the measured transmittance through the relation $\alpha = (1/t)\ln(I_0/I) + \alpha_R$, where t is the thickness of the sample, I_0 and I the incident and transmitted radiation, respectively, and α_R a nearly constant residual absorption observed in the low energy region of the spectra.

3. Results and discussion

The diffraction patterns recorded at room temperature (see Fig. 1) for the $Cu(In_{1-x}Ga_x)_3Te_5$ system were very similar to

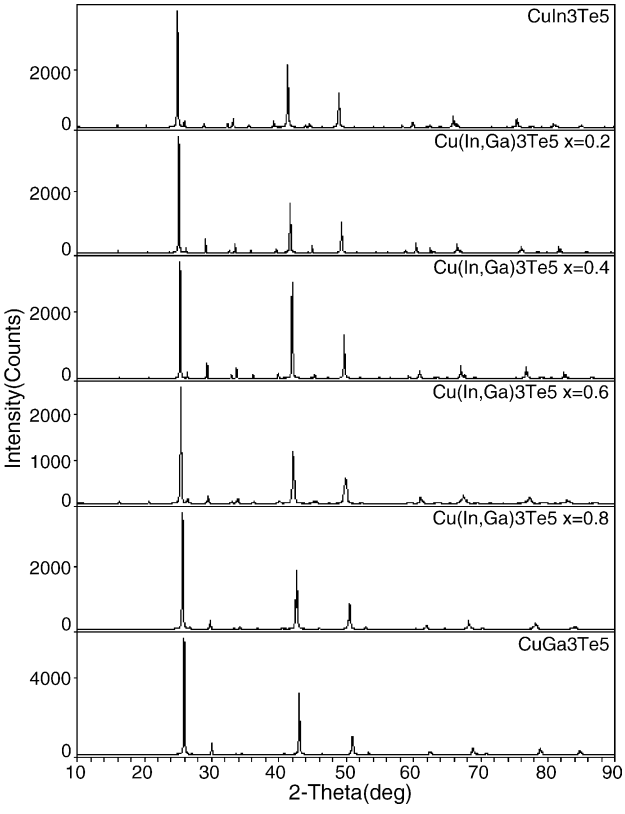

Fig. 1. Powder diffraction patterns obtained for different compositions of the $Cu(In_{1-x}Ga_x)_3Te_5$ system.