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Temperature-dependent structural transition, electronic properties and impedance spectroscopy analysis of Tl_2InGaS_4 crystals grown by the Bridgman method

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ABSTRACT

In this work, we report the temporary structural modifications associated with the in situ heating of the Tl_2InGaS_4 crystals in the temperature range of 300–420 K. The analysis of the X-ray diffraction patterns revealed the temperature-independent possible phase transformations between the monoclinic and triclinic phases. The temperature analysis of the lattice parameters, crystallite size, strain, dislocation density and stacking faults has shown a temporary enhancement in the crystallinity of this compound above 375 K. Significant increase in the grain size accompanied to decrease in the strain, defect density and stacking faults was observed above this temperature. The scanning electron microscopy imaging has shown that the crystals are layer structured with high quality layers of thicknesses of ~ 12 nm. In addition the energy dispersive X-ray analysis has shown that the crystal comprise no detectable impurity. Moreover, the room temperature optical characterizations has shown that the Tl_2InGaS_4 exhibit an energy band gap of 2.5 eV. The temperature dependent electrical resistivity measurements indicated highly resistive crystal with activation energy values of 0.84 and 0.19 eV above and below 375 K, respectively. On the other hand, room temperature impedance spectroscopy analysis in the frequency domain of 10–1800 MHz has shown that the crystal exhibits negative resistance and negative capacitance effects below and above 1580 MHz. The crystals are observed also to behave as band stop filter with notch frequency of 1711 MHz.

1. Introduction

The systems comprising $TlInS_2$ and $TlGaS_2$ crystals are of interest due to their wide range of physical applications. With the extremely high acousto-optic figures of merit, the $TlInS_2$ compound is nominated as an acousto-optic material that exhibits very high efficiency [1]. This crystal is also mentioned as an efficient magnetooptic material [2]. The $TlInS_2$ crystals are reported to exhibit both semiconducting and ferroelectric properties which makes it attractive for optoelectronics and sensorics [3]. Similar optoelectronic characteristics are also observed for the $TlGaS_2$ crystals [4]. For this reason, establishing crystalline systems that comprise both crystals have recently attracted the attention due to the interesting features they reveal. The compositional ratio of the $TlGaS_2$ and $TlInS_2$ in the content of the mixed crystal, significantly alters its physical properties. For example, the Raman spectral analysis of $TlGa_xIn_{1-x}S_2$ layered mixed crystals which were investigated in the compositional range of $0 \leq x \leq 1$ revealed significant effect of crystal disorder as observed from the line width broadenings of the Raman active modes [5]. In addition, the composition of 50% $TlInS_2$ and 50% $TlGaS_2$ mixed crystals that form Tl_2InGaS_4 layered crystals are reported to exhibit trapping centers that when onset can behave as optoelectronic switches. In addition to that they exhibit good optoelectronic performance [6–9]. In another work which comprise similar structural formations, the $Tl_2InGaSe_4$ was observed to exhibit a temperature dependent emission band which is located at 1.912 eV (648 nm) at 10 K [10]. This band red-shifted with increasing temperature or decreasing excitation intensity. In a similar manner, the emission band spectra of Tl_2InGaS_4 layered crystals revealed emission band at 1.754 eV (707 nm) at 10 K. This band blue shifts with increasing temperature [11].

In the light of the above reported properties and applications of the $TlInS_2$-$TlGaS_2$ system here in this work we target studying the crystallization process and electrical resistivity of the mixed crystals in the temperature range of 300–420 K and to report the room temperature

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optical absorption and response of these crystals to propagating electrical signals in the frequency domain of 10–1800 MHz. The effective applicability of these crystals as microwave cavity is also considered.

2. Experimental procedure

Tl_2InGaS_4 polycrystals were synthesized from high-purity elements (99.999%) including thallium (Fluka cat. no. 88202), indium (Fluka cat. no. 57077), gallium (Aldrich cat. no. 263273) and sulfur (Fluka cat. no. 84680) taken in stoichiometric proportions. The single crystals were grown by the Bridgman method from resultant polycrystalline ingots in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 55 cm in length) with a tip at the bottom in our crystal growth laboratory. We utilized three-zone furnace; each zone about 15 cm in length. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1} from 830° to 460°C at a rate of 1.0 mm h^{-1}. The resulting ingots (yellow-green in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The in situ temperature-dependent X-ray diffraction patterns were recorded in the temperature range of 300–450 K, using temperature exchanger attached to the Rigaku miniflex-600 × -ray unit. The morphology and nature of layers of the crystals were observed by the scanning electron microscopy technique using COXEM 200 scanning electron microscope. The compositional analysis were actiallized with the help of EDAX energy dispersive X-ray analyzer. The electrical and optical measurements were carried out with the help of a cryostat and spectrophotometer. The impedance spectroscopy was collected using Agilent 4291B 10–1800 MHz impedance analyzer.

3. Results and discussion

The X-ray diffraction patterns which were recorded in the temperature range of 300–420 K for the Tl_2InGaS_4 crystals are displayed in Fig. 1. As the figure shows, in addition to some minor peaks which are listed in Table 1, the patterns included three strong peaks located at 2θ values of 21.64, 23.88/24.06 and 48.84 ° corresponding to interplanner spacing (d) values of 4.103, 3.723/3.696 and 1.863 A°, respectively. The maximum intensity of the X-ray is observed for the peak which exhibits interplanner spacing of 3.723 A°. This peak is at the same position as we have previously reported for the same crystals in our early work [7]. However, the current X-ray diffraction studies which are carried out in more details displayed additional strong reflection peak located at interplanner spacing of 4.103 A°. This peak was not previously observed. The third strong peak which was observed at 1.863 A° represented 16% compared to the maximum peak in our previous work and 70% in the current study. Another interesting

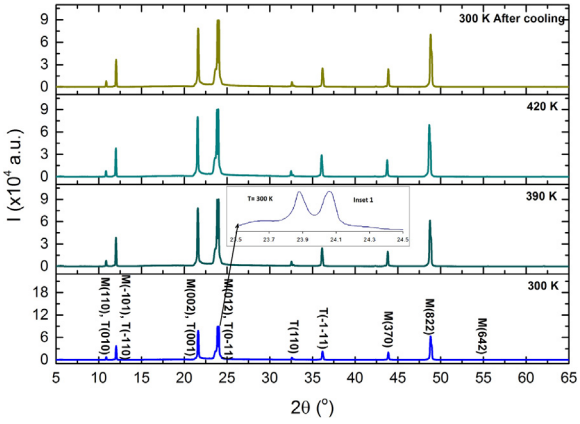

Fig. 1. The temperature-dependent X-ray diffraction patterns of the Tl_2InGaS_4 crystals. The inset show the phase transformation as observed in the most intensive peak located at $2\theta = 23.88^o$.

Table 1
The possible crystal structure and lattice paramters for Tl_2InGaS_4 crystals.

Monoclinic $a = 20.269A^o$, $b = 8.859A^o$, $c = 8.252A^o$, $\beta = 96.00^o$				Triclinic $a = 14.679A^o$, $b = 28.557A^o$, $c = 4.966A^o$, $\alpha = 121.970^o$, $\beta = 124.215^o$, $\gamma = 163.480^o$		
$2\theta_{obs.}$(°)	$2\theta Calc.$ (°)	$\Delta(2\theta)$(°)	$h\,k\,l$	$2\theta_{Calc.}$(°)	$\Delta(2\theta)$(°)	$h\,k\,l$
10.90	10.90	0.000	1 1 0	10.90	0.000	0 1 0
12.05	12.05	0.002	− 1 0 1	12.05	0.002	− 1 1 0
21.64	21.64	0.000	0 0 2	21.64	0.000	0 0 1
23.88	23.88	0.001	0 1 2	23.88	0.001	0 − 1 1
32.62	32.61	0.014	− 6 0 2	32.62	0.000	1 1 0
36.20	36.15	0.047	− 7 0 2	36.20	0.000	− 1 − 1 1
43.88	43.88	0.004	7 3 0	43.92	0.042	1 2 0
48.84	48.84	0.000	8 2 2	48.81	0.027	4 − 9 1
55.63	55.63	0.004	6 4 2	55.67	0.044	2 − 3 2

feature of the current reflection data is presented by the splitting of the maximum peak into two close peaks. The splitting of the peak is shown in the inset of Fig. 1. The peak shows two reflections at $2\theta = 23.88$ and 24.06 °. This behavior indicates that the Tl_2InGaS_4 crystals are exhibiting solid-solid phase transformation.

Careful analysis using "TREOR 92″ and "Crysdiff" software packages to solve the structure and determine the lattice parameters were carried out. The analysis included all possible types of structures and considered the differences between the observed and calculated $\Delta(2\theta)$ values. The analysis get benefit from the refinement by the least squares method. Among all the solutions two possible most appropriate solutions which relate to the monoclinic and triclinic unit cell types were determined. The results of the analysis are shown in Table 1. Except for the underlined $\Delta(2\theta)$ values, the correlations between the two structural types are very high. In accordance with the tabulated data, the maximum peaks are oriented in the (012) direction for the monoclinic phase and in the (0 − 11) direction for the triclinic phase. Previous investigations about the lattice parameters of the monoclinic unit cell reported values of $a = 10.639$ A^o,$b = 10.441A^o$, $c = 15.334A^o$and$\beta = 100.12^o$ for this crystal. These values were very close to those reported for the monoclinic $TlInS_2$ as $a = 10.942A^o$,$b = 10.484A^o$, $c = 15.070A^o$and$\beta = 99.66^o$ and for the monoclinic $TlGaS_2$ as $a = 10.310A^o$,$b = 10.430A^o$, $c = 15.070$ $A^o$and$\beta = 99.60^o$ [7]. Another monoclinc unit cell of paramters of $a = 9.133$, $b = 3.603$, $c = 11.604$ A^o and β = 95.2 0^o was also reported for Tl_2InGaS_4 crystals [12]. Even though the $TlInS_2$ exhibits four crystal modifications known as monoclinic, triclinic, tetragonal, and orthorhombic, it crystallizes in the triclinic and monoclinic forming layered planes and in orthorhombic and tetragonal forming chains [13]. Literature data almost rarely reported information about the triclinic type of structure for the $TlGaS_2$ or Tl_2InGaS_4. There is no ICDD or CIF cards available for this crystal. The only mentioned X-ray data is reported in our early work [7], for this reason, we found it worth of consideration as the triclinic lattice parameters reproduce the X-ray diffraction patterns of the Tl_2InGaS_4 crystals reported here.

The presence of possible phase transitions illustrated by the splitting of the maximum peak (inset of Fig. 1) may be assigned to too many reasons like the changes in temperature, pressure, chemical synthesis, cation disordering [14,15] in addition to topotactic transformation which involve internal atomic rearrangements [15]. The topotactic or pseudomorphic transformation relate to well-known relationships between axes of the two solids. Reports on phase transitions in $TlInS_2$ crystals assigned the structural transitions to the diffusion of Tl^+ ions towards vacancies in the Tl sub-lattice [16]. $TlInS_2$ is composed of layers that are made of In_4S_{10} (which in turn consist of four tetrahedrons InS_4) groups forming layers that extend perpendicular to the c-axis of the crystal. The negatively charged layers of In_4S_{10} are bonded together by Tl^+ ions. As a result of this bonding style a monoclinic