
Influence of Isomorphous Atom Substitution on Lattice Anisotropy of Thallium Dichalcogenide Layered Mixed Crystals

N.M. GASANLY*

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

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Compositional variation of the lattice parameters of $TlBX_2$ -type ($B = Ga$ or In and $X = S$ or Se) mixed crystals with monoclinic structure were studied by X-ray diffraction technique. The lattice anisotropy (c/b) of these mixed crystals changes linearly with substitution of the atoms located both at the centers and the vertices of the corresponding BX_4 tetrahedra. A brief survey of the important features of the effect of isomorphous atom substitution on the lattice anisotropy and the unit cell volume of $TlBX_2$ -type mixed crystals with layered structure was presented.

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1. Introduction

$TlBX_2$ -type compounds, where $B = Ga$ or In and $X = S$ or Se , crystallize in a monoclinic ($TlGaS_2$, $TlGaSe_2$, $TlInS_2$) or tetragonal ($TlInSe_2$) cell [1–3]. The lattice of the first three compounds consists of strictly periodic two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by 90° with respect to the previous one. Interlayer bonding is formed between Tl and B atoms while the bonding between B and X atoms is an intralayer. The views of the crystal structure in the ac - and ab -planes are presented in Figs. 1 and 2. The fundamental structural unit of a layer is the B_4X_{10} polyhedron representing a combination of four elementary tetrahedra BX_4 linked together by bridging X atoms. The Tl atoms are located in trigonal prismatic voids resulting from the combination of the B_4X_{10} polyhedra into a layer. These atoms form nearly planar chains along the $[110]$ and $[\bar{1}\bar{1}0]$ directions.

*e-mail: nizami@metu.edu.tr; on leave from Physics Department, Baku State University, Baku, Azerbaijan

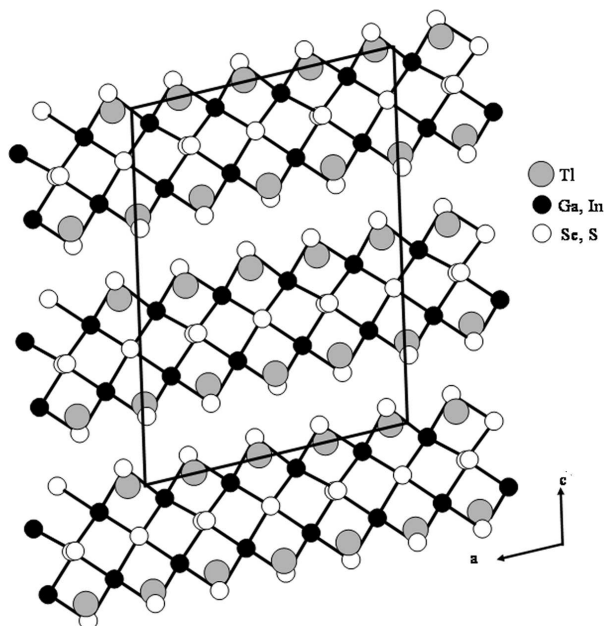


Fig. 1. Projection of the crystal structure of TlGaSe₂, TlGaS₂, and TlInS₂ on *ac*-plane.

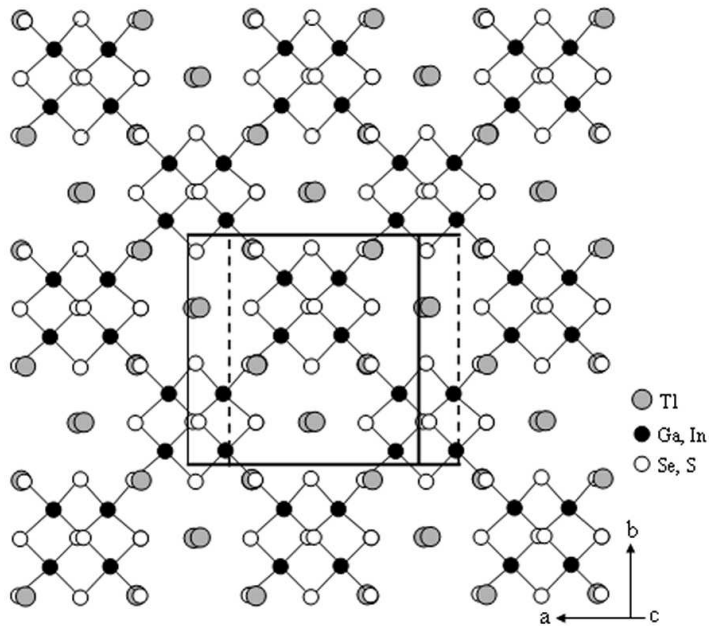


Fig. 2. Projection of the crystal structure of TlGaSe₂, TlGaS₂, and TlInS₂ on *ab*-plane.

The monoclinic TlGaS_2 and TlGaSe_2 , TlGaS_2 and TlInS_2 form a series of $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ and $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ mixed crystals, respectively, with no restrictions on the concentration of the components: $0 \leq x \leq 1$ [4, 5]. The tetragonal TlInSe_2 and monoclinic TlInS_2 compounds form a continuous series of mixed crystals $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ ($0 \leq x \leq 1$) [6]. The transformation from the tetragonal to monoclinic structure occurs at $x \approx 0.25$. The study of phase diagram in the $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ mixed crystals has shown that eutectic phase exists in the limited regions of 0–55.0 and 70.0–100 mol% TlInSe_2 [7]. In the first and second regions, $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystallize in the monoclinic and tetragonal structures, respectively.

The aim of the present paper was to study the influence of isomorphic atom substitution (gallium by indium and sulfur by selenium) on the lattice anisotropy and unit cell volume of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$, $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$, $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$, and $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ layered mixed crystals.

2. Experimental details

$\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0.5 \leq x \leq 1$), $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ ($0 \leq x \leq 1$), $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ ($0 \leq x \leq 1$), and $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ ($0.3 \leq x \leq 1$) polycrystals were obtained by direct fusion in evacuated capsules of particular high-purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals were grown by a modified Bridgman method from the polycrystals. The resulting ingots appear from dark red to yellow in color, and the freshly cleaved surfaces are mirror-like. In the X-ray powder diffraction experiment, a Philips PW1740 diffractometer with a monochromatized $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) was used at a scanning speed of $0.02^\circ 2\theta/\text{s}$. We have recorded X-ray powder diffractograms in the 2θ range from 10 to 75° of five $\text{TlGa}_{1-x}\text{In}_x\text{Se}_2$, nine $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$, eleven $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$, and seven $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ samples of mixed crystals having different compositions. The lattice parameters of the monoclinic unit cell were calculated by using a least squares computer program "Treor 90". The uncertainties in the calculated lattice parameters were in the range from 0.0003 to 0.012 nm .

3. Results and discussion

The variations of the lattice parameters (a , b , and c) and monoclinic angle β of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ (A), $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ (B), $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ (C), and $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ (D) mixed crystals with monoclinic structure as a function of their compositions are plotted in Figs. 3 and 4. Presently evaluated lattice parameters $a = 1.0312$, $b = 1.0431$, $c = 1.5072 \text{ nm}$ and $\beta = 99.61^\circ$ (TlGaS_2), $a = 1.0756$, $b = 1.0730$, $c = 1.5596 \text{ nm}$ and $\beta = 99.92^\circ$ (TlGaSe_2), and $a = 1.0942$, $b = 1.0484$, $c = 1.5606 \text{ nm}$ and $\beta = 100.70^\circ$ (TlInS_2) agree well with the corresponding data of Refs. [1, 2]. The main difference between mixed crystals A and C and mixed crystals B and D is the fact that in the mixed crystals A and C the substitution of atoms (gallium by indium) located at the centers of

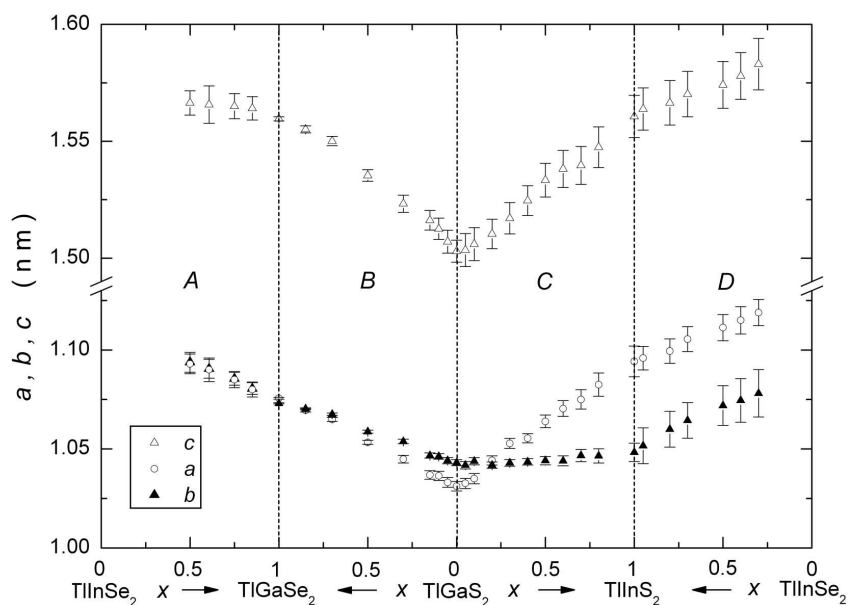


Fig. 3. Compositional variations of the lattice parameters (a , b , and c) of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ (A), $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ (B), $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ (C), and $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ (D) mixed crystals.

GaSe_4 , InSe_4 and GaS_4 , InS_4 tetrahedra, respectively, takes place; whereas in the mixed crystals B and D the substitution of atoms (sulfur by selenium) located in the vertices of the GaS_4 , GaSe_4 and InS_4 , InSe_4 tetrahedra, respectively, takes place. As seen from Figs. 3 and 4, the lattice parameters a , b , c and monoclinic angle β of A and C, and B and D mixed crystals increase at the substitution of gallium atoms by indium and of sulfur atoms by selenium, respectively. These observations may be accounted for considering the covalent radius of replacing atoms, which are equal to 0.126, 0.144, 0.104, and 0.114 nm for gallium, indium, sulfur, and selenium, respectively. The larger atoms replacing the smaller ones at the centers of the BX_4 tetrahedra (gallium by indium in A and C mixed crystals) and at the vertices of the BX_4 tetrahedra (sulfur by selenium in B and D mixed crystals) cause the observed lattice expansion in the mixed crystals studied.

The variations of the unit cell volume (V) and lattice anisotropy (c/b) of A, B, C, and D mixed crystals as a function of their compositions are presented in Fig. 4. As seen from this figure, the unit cell volume of A and C, and B and D mixed crystals also increase at the substitution of gallium atoms by indium and of sulfur atoms by selenium, respectively. As for the variations of the lattice anisotropy, these dependencies on composition of mixed crystals show quite different behavior. The lattice anisotropy for A and C mixed crystals noticeably decreases or increases at the substitution of gallium atoms by indium ones, re-

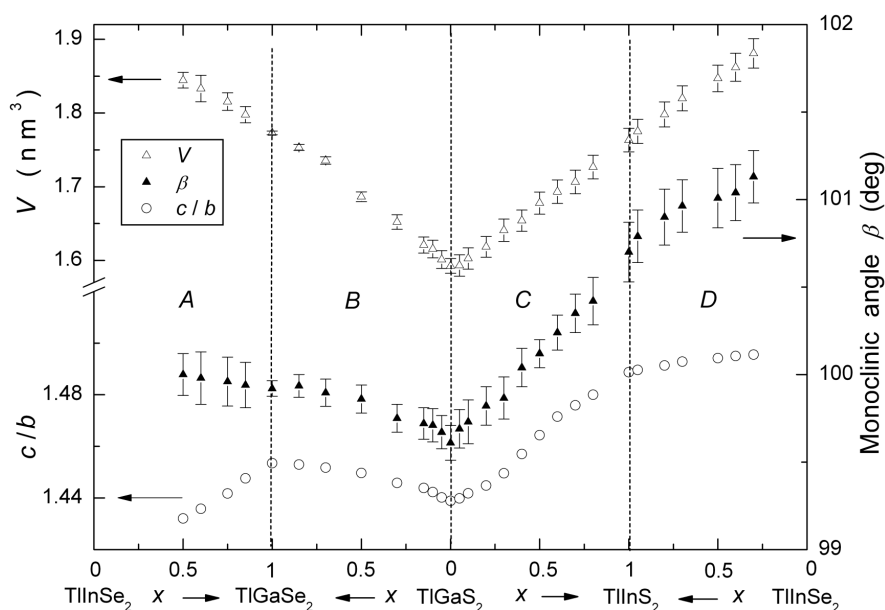


Fig. 4. Compositional variations of the unit cell volume (V), monoclinic angle (β) and lattice anisotropy (c/b) of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ (A), $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ (B), $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ (C), and $\text{TlIn}(\text{Se}_{1-x}\text{S}_x)_2$ (D) mixed crystals.

spectively. As for *B* and *D* mixed crystals, in both of them the lattice anisotropy shows slight increase at the substitution of sulfur atoms by selenium ones. Thus, when the atoms at the centers of $\text{Ga}(\text{In})\text{Se}_4$ and $\text{Ga}(\text{In})\text{S}_4$ tetrahedra are replaced by the larger atoms (gallium by indium) in *A* and *C* mixed crystals, the unit cell becomes less or more anisotropic, respectively, depending on the types of atoms (selenium or sulfur) located at the vertices of corresponding tetrahedra. On the other hand, when the atoms at the vertices of $\text{Ga}(\text{S}_4)\text{Se}_4$ and $\text{In}(\text{S}_4)\text{Se}_4$ tetrahedra are replaced by the larger atoms (sulfur by selenium) in *B* and *D* mixed crystals, the unit cell becomes somewhat more anisotropic, which does not depend on the types of atoms (gallium or indium) located at the centers of corresponding tetrahedra.

As we mentioned above, in the crystals studied interlayer bonding is formed between Tl and S(Se) atoms whereas the bonding between Ga(In) and S(Se) atoms is responsible for intralayer interaction (Figs. 1 and 2). In the case of *A* mixed crystals (Tl–Se interlayer bonding) replacement of Ga atoms by In atoms leads to the noticeable increase in lattice parameter b while for the parameter c this increase is less pronounced (Fig. 3). Therefore, the lattice anisotropy c/b decreases for *A* mixed crystals comprising selenium atoms (Fig. 4). On the other hand, for *C* mixed crystals (Tl–S interlayer bonding) replacement of Ga atoms by In atoms results in the slight increase in lattice parameter b while for the parameter c this

increase is more pronounced (Fig. 3). Hence the lattice anisotropy c/b increases for C mixed crystals comprising sulfur atoms (Fig. 4). These observations imply that the different behavior of the lattice anisotropy c/b with respect to the composition of mixed crystals is related to the chalcogenide atoms (selenium or sulfur) taking part in interlayer and intralayer bondings.

It is worthy noting that the rate of change in the lattice anisotropy c/b with composition for B and C mixed crystals, having monoclinic structure throughout the whole composition range, appears to be proportional to the covalent radii difference, ΔR , of atoms substituted ($\Delta R = R_{\text{Se}} - R_{\text{S}} = 0.010$ nm and $\Delta R = R_{\text{In}} - R_{\text{Ga}} = 0.018$ nm for B and C mixed crystals, respectively). The same tendency is also observed for A and D mixed crystals in the studied composition ranges of $0.5 \leq x \leq 1$ and $0.3 \leq x \leq 1$, respectively (Fig. 4).

Now let us consider the variation of the lattice volume on the compositions of the mixed crystals studied. It is well known from the literature that TlGaSe_2 and TlInS_2 sequentially undergo low-temperature transitions to an incommensurate phase and a ferroelectric phase at $T_i = 115$ K, $T_c = 108$ K and $T_i = 213$ K, $T_c = 189$ K, respectively [8–11]. However, in TlGaS_2 crystals no evidence for a soft mode behavior has been found. Yee and Albright [12] have studied the bonding and structure of TlGaSe_2 crystal by tight-binding calculations and have revealed that the ferroelectric phase transition is essentially associated with the slippage of the two thallium atom channels along the $[110]$ and $[1\bar{1}0]$ directions, respectively (see Figs. 1 and 2). Since in $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ and $\text{TlGa}_{1-x}\text{In}_x\text{S}_2$ mixed crystals the unit cells get smaller with increase in sulfur and gallium contents, respectively, the average distances between the thallium atom channels also get shorter as compared with those of TlGaSe_2 and TlInS_2 crystals. Therefore, the thallium atom channel slippages in the smaller unit cell do not easily take place so that they may not be sufficient for destroying the inversion center, which is necessary for the occurrence of ferroelectricity. This assumption is in agreement with the absence of ferroelectric phase transitions with soft mode features in TlGaS_2 crystal [13] and $\text{TlGa}(\text{S}_{1-x}\text{Se}_x)_2$ mixed crystals with compositions $x < 0.75$ [14].

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