Birefringence of In$_x$Tl$_{1-x}$I solid state solution

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The results of investigation of optical properties of the newly synthesized solid solution In$_x$Tl$_{1-x}$I in concentration range of $0.4 \leq x \leq 0.7$ are presented. Birefringence is measured for In$_x$Tl$_{1-x}$I solid state solution. Dependence of the birefringence Δn_i on the concentration of thallium iodide is investigated. Dielectric permeability distribution $\varepsilon(E)$ is calculated using pseudopotential method in the framework of density functional theory. The real ε_1 and imaginary ε_2 parts of the dielectric constant are calculated for polarization $E \| \mathbf{a}$ and $E \| \mathbf{c}$ over a range of photon energy from 0 to 14 eV. The spectra show pronounced anisotropy between these polarizations. Spectral dependences of the birefringence Δn_i of In$_x$Tl$_{1-x}$I crystals for various physical crystal directions are obtained based on these calculations. The experimental and theoretical birefringence spectra are in a good agreement.

Keywords: solid solution, optical constants, dielectric permittivity, birefringence.

Приведены результаты исследования оптических свойств новых твердых растворов In$_x$Tl$_{1-x}$I в области концентраций $0,4 \leq x \leq 0,7$. Двойное лучепреломление измеряли для твердотельного раствора In$_x$Tl$_{1-x}$I. Исследована зависимость двулучепреломления Δn_i от концентрации йодида таллия. Распределение диэлектрической проницаемости $\varepsilon(E)$ рассчитано с использованием метода псевдопотенциала в рамках теории функционала плотности. Для поляризации $E \| \mathbf{a}$ и $E \| \mathbf{b}$ в диапазоне энергий фотонов от 0 до 14 эВ рассчитаны действительная ε_1 и мнимая ε_2 части диэлектрической проницаемости. Спектры показали выраженную анизотропию между этими поляризациями. Спектральные зависимости двулучепреломления Δn_i кристаллов In$_x$Tl$_{1-x}$I для различных кристаллофизических направлений получены на основе данных расчетов. Экспериментальные и теоретические спектры двулучепреломления хорошо согласуются между собой.

Двопроменезаломлення твердих розчинів заміщення In$_x$Tl$_{1-x}$I. *А.І.Кашуба, А.В.Франів, О.В.Бовгира, Р.С.Брезвін.*

Приводяться результати дослідження оптичних властивостей нових твердих розчинів In$_x$Tl$_{1-x}$I в області концентрацій $0,4 \leq x \leq 0,7$. Подвійне променезаломлення виміряно для твердого розчину заміщення In$_x$Tl$_{1-x}$I. Досліджується залежність двопроменезаломлення Δn_i від концентрації йодиду талію. Розподіл діелектричної проникності $\varepsilon(E)$ розраховано з використанням методу псевдопотенціалу у рамках теорії функціонала густини. Дійсна ε_1 і уявна ε_2 частини діелектричної проникності розраховані для поляризації $E \| \mathbf{a}$ й $E \| \mathbf{b}$ у діапазоні енергій фотонів від 0 до 14 еВ. Спектри показали виражену анізотропію між цими поляризаціями. Спектральні залежності двопромене-заломлення Δn_i кристалів In$_x$Tl$_{1-x}$I для різних кристалофізичних напрямків отримано на основі даних розрахунків. Експериментальні та теоретичні спектри двопроменезаломлення добре узгоджуються між собою.

1. Introduction

Searching for the new functional materials and ways to control their properties belongs to the primary tasks of physics of semiconductors and insulators. For a rather long time, attention of scientists is attracted to studying the properties of semiconductors and insulators with a layered crystalline structure.

Optical properties of the layered crystals are of interest in many of investigations [1−4]. For a number of substitutive solid solutions (SSS), the characteristic features of influence of static crystal lattice disordering on their optical properties, namely the influence of crystal-field fluctuations on the optical spectra are known to be experimentally observed [5]. It appears that indium and thallium iodide combined SSS's are being promising objects for investigations.

Among III−VII compounds, cubic thallium halides (TlI_xCl_{1-x}, TlI_xBr_{1-x}) have been extensively investigated. Their optical and transport properties have been studied by Kobayashi [4]. Thallium iodide, on the other hand, crystallizes in orthorhombic structure for temperature up to $170°C$ but at higher temperature it transforms to cubic CsCl structure. Several investigations of this structural phase transition have been reported [6]. In indium halides the phase transition does not occur except for InCl. The crystals cleave perpendicular to the crystallographic **b**-axis [7].

Earlier studies [9] described methods of synthesizing these compounds, methods of growth, as well as some results on their physical properties. The crystal structure of $In_xTl_{1-x}I$ SSS's is described by space group D_{2h}^{17} (*Cmcm*), with different directions **a**- and **c**-lying within the layer plane [8−10]. The structure of $In_xTl_{1-x}I$ SSS's is layered, with the two layers of sandwich type in the elementary cell and four formula units in the cell [9].

For today we have not found in literature any work either theoretical or experimental on optical functions or birefringence of $In_xTl_{1-x}I$. In this paper, we present the results of calculations of the optical constants of $In_xTl_{1-x}I$ SSS's. New guidelines for selecting or synthesizing the crystals with the desired birefringence are established. Dependence of the birefringence versus concentration of TlI is presented.
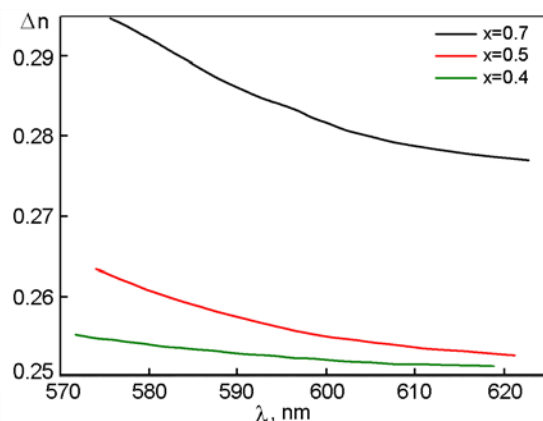

Fig. 1. Experimental spectral dependence of birefringence Δn of $In_xTl_{1-x}I$ crystals.

2. Experimental and calculations

One of the most important properties of optical materials is the refractive index and its dispersion behavior. The dispersion is a measure of change of the refractive index with wavelength.

The dispersion of the birefringence in the range of 570−630 nm was studied using changes in the interference pattern of polarized beams that was recorded using KSVU-23 spectral system [11, 12]. The samples were oriented on the diagonal in **ac** plane and placed into a cryostat between crossed polarizing filters.

Calculations of the total electron energy of the crystals were carried out self-consistently in the density functional theory framework. The electron energies and densities were determined by solving the Kohn-Sham equations [13]. The method of generalized gradient approximation (GGA) was used to describe the exchange-correlation potential. In this work, we used the Perdew-Burke-Ernzerhof (PBE) representation [14] for this potential. The inequality $\Delta E < 2 \cdot 10^{-6}$ eV for the electron energy difference between subsequent iterations was selected as a criterion for self-consistent procedure convergence.

In order to check how the experimental lattice parameters differ from their equilibrium values, the geometry optimization of a model structure was carried out. The relaxation procedure was considered to converge when the magnitudes of forces acting upon the atoms became less than 0.05 eV/A and the bulk stress was less than 0.1 GPa [8]. Using the Kramers-Kronig relations [15], the spectral dependence of the optical constants was calculated.
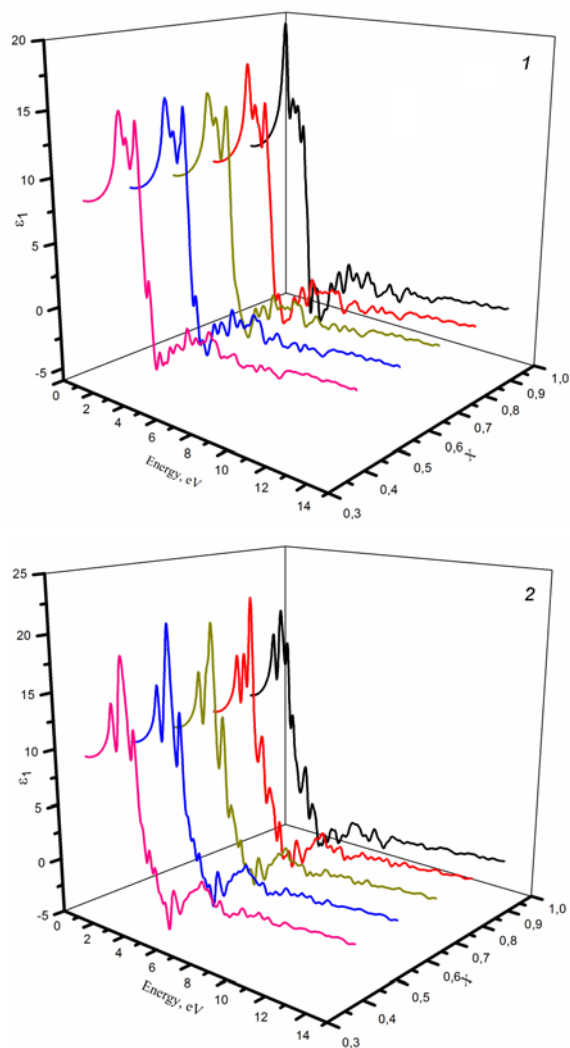
Fig. 2. The real part of dielectric permittivity ε_1 obtained on the basis of band calculations for $In_xTl_{1-x}I$ crystals ($E\|\mathbf{a}$ — *1*; $E\|\mathbf{c}$ — *2*).

Fig. 3. The imaginary part of dielectric permittivity ε_2 obtained on the basis of band calculations for $In_xTl_{1-x}I$ crystals ($E\|\mathbf{a}$ — *1*; $E\|\mathbf{c}$ — *2*).

3. Results and discussion

The experiments showed that the birefringence dispersion for the studied crystals is normal in the visible spectral region. A plot of the refractive index as a function of the wavelength for SSS is presented in Fig. 1. It can be seen that in the main spectral transmission region the refractive index increases towards shorter wavelength.

Such a behavior can be caused by increasing the exciton-phonon interaction and contribution of absorption coefficient in the process of formation of fundamental absorption edge of the solid solution [16].

The anomalous by large values of difference ($\Delta n > 0.25$) of the refractive indexes attract our attention [17]. To our mind this behavior is caused by strong anisotropy of
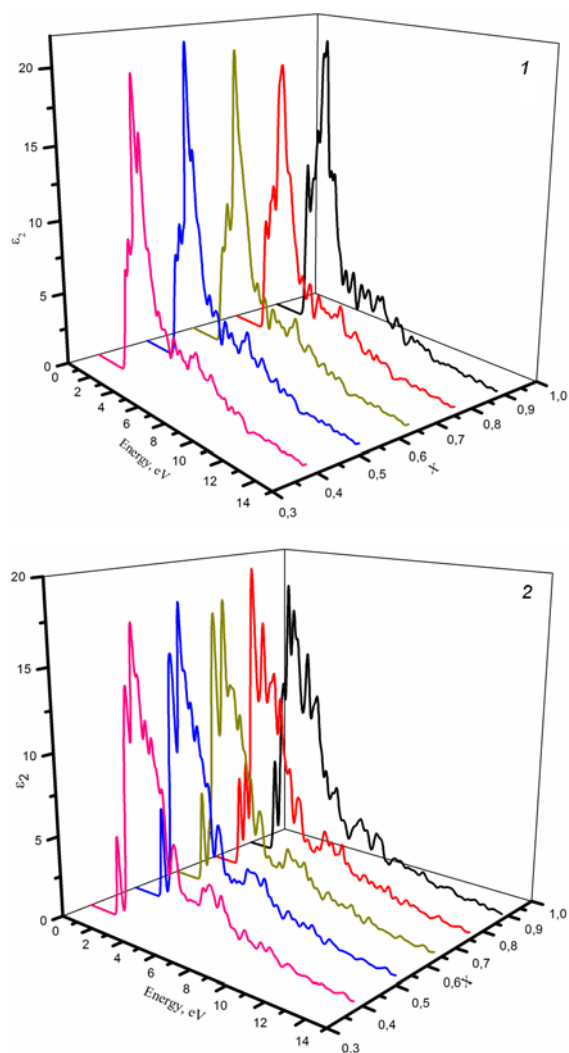
the optical functions ε_1, ε_2 (Fig. 2, 3). Similarly, such behavior is realized in pure binary compound InI and TlI and for SSS $In_xTl_{1-x}I$ crystals too. The optical constants, calculated on the basis of reflectivity curve, give the integral curve as a sum of contributions of all transitions throughout the volume of the Brillouin zone [18].

Spectra of the imaginary part of the dielectric function can be obtained from the results of band calculations of wave functions and energy eigen values of valence and virtual states. In the imaginary part the two types of electronic excitations have too contributions: intra- and inter-band ones.
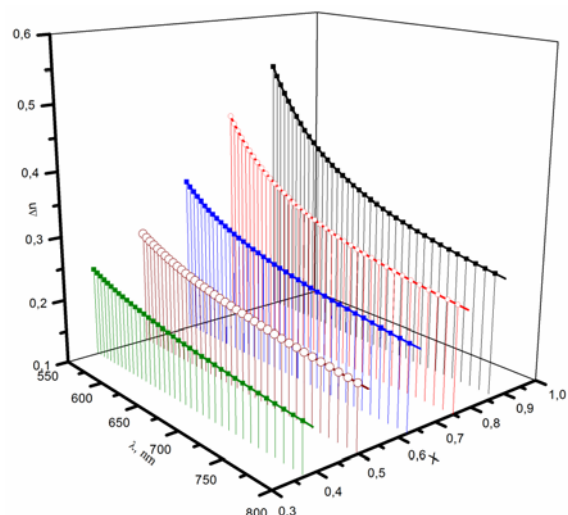
Fig. 4. Calculated spectral dependences of birefringence Δn of SSS $In_xTl_{1-x}I$.

Fig. 5. Experimental (*1*) and theoretical (*2*) spectral dependences of birefringence Δn of $In_{0.5}Tl_{0.5}I$ crystal ($d = 0.46$ mm).

The spectral dependences of the real ε_1 and imaginary ε_2 parts of the dielectric constant, calculated on the basis of the energy band results [8], show anisotropy which is confirmed by comparing the experimental data for two polarizations of light: $E\|\mathbf{a}$ and $E\|\mathbf{c}$ (Fig. 2, 3).

The dependences of optical constants of SSS $In_xTl_{1-x}I$ can be divided into three main groups of peaks localized in the spectral regions: 1.5−3 eV, 3−7 eV, and 7−14 eV.

Fig. 4 presents the calculated anisotropic birefringence dispersion for $In_xTl_{1-x}I$ SSS. The theoretical spectra show very good agreement with the experiment (Fig. 5).Concentration dependence of the birefringence shows that at increasing the concentration of TlI the Δn value decreases, that is associated with the structural changes (parameters $a \rightarrow c$). This is a consequence of the competition between two near band-gap optical processes contributing to the optical functions. Also, we do not exclude the possibility of the phase transition in $In_xTl_{1-x}I$, due to of the presence of TlI components.

4. Conclusions

The birefringence was measured for solid state solution of $In_xTl_{1-x}I$. It was found the anomalous by large values of difference ($\Delta n > 0.25$) of the refractive indexes in the visible region (570−680 nm).

The spectral dependence of the real ε_1 and imaginary ε_2 parts of the dielectric constant were calculated on the basis of the energy band results using the Kra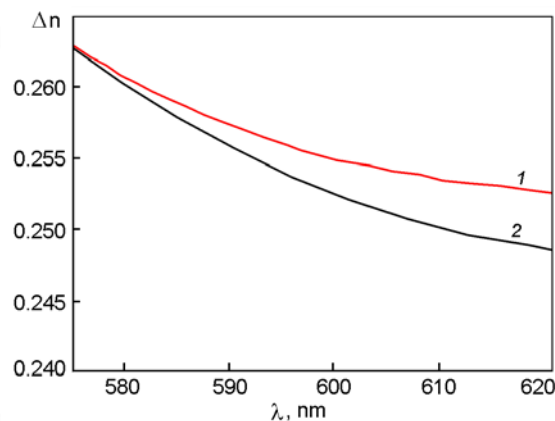mers-Kronig method. Dependence of the birefrin-gence Δn_i on concentration x was investigated. The experimental and theoretical birefringence spectra were in a good agreement. The concentration dependence of the birefringence shows that at increasing of TlI concentration there takes place decreasing of Δn. From the birefringence behavior of $In_xTl_{1-x}I$, we suppose, that this crystal in this phase transition is realized.

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