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Synthesis, Roentgenophase Analysis and Physical Properties of $TlIn_{1-x}Er_xSe_2$ Solid Solutions

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The results of high-frequency dielectric measurements on obtained $TlIn_{1-x}Er_xSe_2$ single crystals provided an opportunity to determine the mechanisms of dielectric losses and charge transport, and also to evaluate the density of states at the Fermi level; the average time of charge carrier hopping between localized states, average hopping distance, scattering of trap states near the Fermi level; concentration of deep traps.

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1. Introduction

$TlInSe_2$ single crystals are typical representatives of chain-layered semiconductors and attract a lot of attention due to their interesting physical properties. These properties include strong anisotropy of the electric parameters related to special features in the crystalline structure. $TlInSe_2$ single crystal has a wide range of physical characteristics of practical importance, such as high photo- and roentgenosensitivity [1–3]. Chain and layered crystals usually contain structural defects, such as vacancies and dislocations. The presence of these defects results in a high density of localized states near the Fermi level.

The states localized in the band gap are responsible for most electronic processes occurring in semiconductors. The large anisotropy in chemical bonding (strong, ionic-covalent bonds within the chains and weak, van der Waals forces between the chains) enables effective doping of $TlInSe_2$single crystals. The concentration and nature of dopants have a significant effect on the electrical properties of $TlInSe_2$ single crystals. The purpose of this work was to study the influence of partial erbium substitution for indium in $TlInSe_2$ crystals on their electric and dielectric properties.

2. Experimental technique

Investigated samples formed flat capacitors. Ohmic contacts of samples are made by Ag paste. Measurements of the dielectric coefficients of studied single crystals were performed at fixed frequencies in the range 5×10^4–3.5×10^7 Hz by the resonant method using a TESLA BM 560 Qmeter. For electrical measurements, the samples were placed in a specially constructed screened cell. An AC electric field was applied across the natural chains of single crystals. The amplitude of the applied field corresponded to the ohmic region of the current–voltage characteristics of the samples. All measurements were performed at $T = 300$ K. The accuracy in determining the resonance capacitance and the quality factor $Q = 1/\tan\delta$ of the measuring circuit was limited by errors related to the resolution of the device readings. The accuracy of the capacitor graduation was ± 0.1 pF.

The reproducibility of the resonance position was ± 0.2 pF in capacitance and $\pm(1.0-1.5)$ scale divisions in quality factor. The largest deviations from the average were 3–4% in ε and 7% in $\tan\delta$.

3. Results and discussion

$TlIn_{1-x}Er_xSe_2$ ($x = 0$, 0.001, 0.005 and 0.01) samples were prepared by reacting appropriate elemental mixtures, which were melted in silica tubes sealed off under vacuum of 10^{-3} Pa.

The annealed alloys were furnace-cooled to room temperature. The completion of the synthesis and the homogeneity and phase purity of the samples were checked by differential thermal analysis (DTA) and X-ray diffraction. $TlIn_{1-x}Er_xSe_2$ crystals were characterized by X-ray diffraction on a D8-Advance powder X-ray automatic diffractometer in the angular range $2\theta = 0.5°-80°$ (Cu K_α radiation, $\lambda = 1.5418$ Å, 40 kV, 40 mA). The X-ray diffraction results were analyzed using the EVA and TOPAZ programs and ICDD Powder Diffraction File data. X-ray diffraction characterization showed that the samples had a tetragonal crystal structure, $a = 8.0750$ Å, $c = 6.8470$ Å for $TlInSe_2$; $a = 8.0740$ Å, $c = 6.8430$ Å for $TlIn_{0.999}Er_{0.001}Se_2$; $a = 8.0679$ Å, $c = 6.8370$ Å for $TlIn_{0.995}Er_{0.005}Se_2$; $a = 8.0750$ Å, $c = 6.8470$ Å for $TlIn_{0.99}Er_{0.01}Se_2$, $Z = 4$. The used amount of the Er impurity element ($x = 0$, 0.001, 0.005 and 0.01) affects weakly the lattice parameters.

The electrical properties (loss tangent, real and imaginary parts of complex dielectric permittivity, and AC conductivity of Er-doped $TlInSe_2$ single crystals have been studied in the frequency range from 50 kHz to 35 MHz. The results demonstrate that the dielectric dispersion in the studied crystals has a relaxation nature (Figs. 1 and 2).

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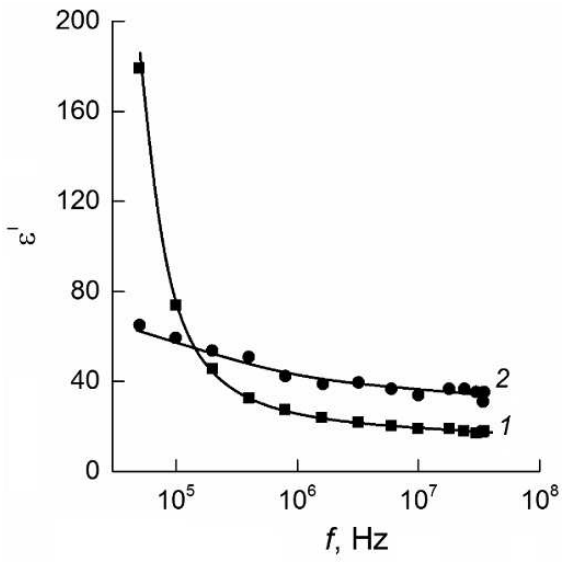

Fig. 1. Frequency dependences of real part of complex dielectric permittivity of $TlInSe_2$ (curve 1) and $TlInSe_2$:Er (1 mol% Er) (curve 2).

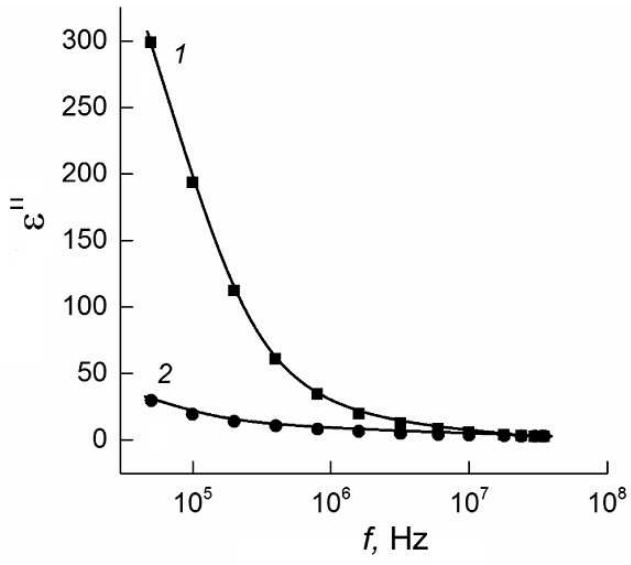

Fig. 2. Frequency dependences of imaginary part of complex dielectric permittivity of $TlInSe_2$ (curve 1) and $TlInSe_2$:Er (1 mol% Er) (curve 2).

It must be noted that after doping of $TlInSe_2$ single crystals with erbium the value and dispersion of dielectric permittivity decrease. For example, at f =50 kHz the value of dielectric permittivity of Er-doped $TlInSe_2$ single crystals is reduced by three times compared with the undoped $TlInSe_2$. At high frequencies the difference between values of ε' for doped and undoped $TlInSe_2$ single crystals decreases.

The experimental frequency dependence of the dissipation factor for $TlInSe_2$:Er (1 mol.% Er) single crystals

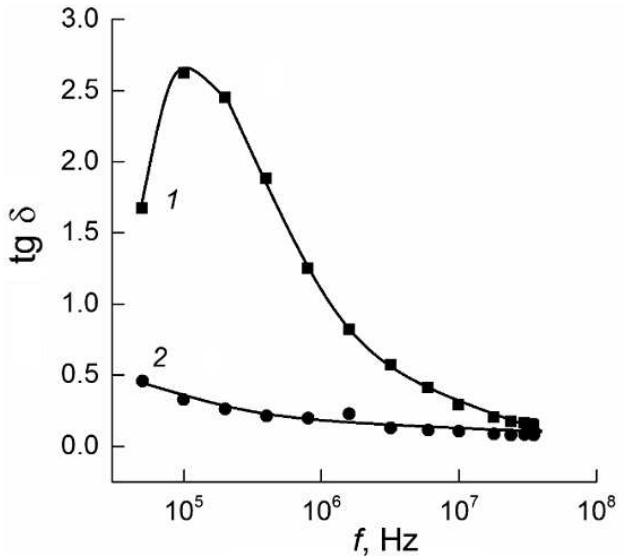

Fig. 3. Frequency dispersion of loss tangent in $TlInSe_2$(curve 1) and $TlInSe_2$:Er (1 mol% Er) (curve 2).

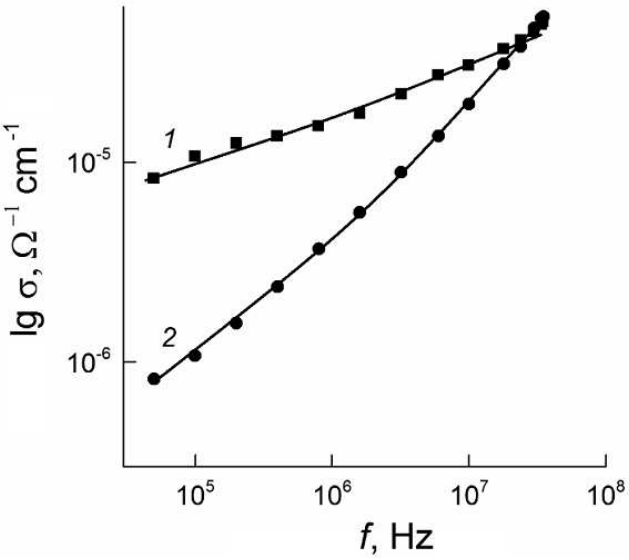

Fig. 4. AC-conductivity of $TlInSe_2$ (curve 1) and $TlInSe_2$:Er (1 mol% Er) (curve 2) vs frequency at $T = 300$ K.

is characterized with a monotonic descending with frequency (Fig. 3), which is evidence of the fact that conductivity loss becomes the main dielectric loss mechanism at studied frequency range [4].

As it is seen from Fig. 3 the experimental frequency dependence of the dissipation factor $\tan\delta$ for $TlInSe_2$ single crystal has maximum at $f = 10^5$ Hz and at $f > 10^5$ Hz is characterized with monotonic descending. Maximum on the $\tan\delta(f)$-curve points to relaxation losses in $TlInSe_2$.

At all studied frequencies the *ac*-conductivity of the Er-doped $TlInSe_2$ crystals (Fig. 4) varies according to the law $\sigma_{ac} \sim f^{0.8}$, characteristic of hopping conduction through localized states near the Fermi level [5]:

$$\sigma_{ac}(f) = \frac{\pi^3}{96} e^2 kT N_F^2 a^5 f \left[\ln \frac{\nu_{ph}}{f}\right]^4, \quad (1)$$

where e is the elementary charge, k is the Boltzmann constant, N_F is the density of localized states near the Fermi level, $a = 1/\alpha$ is the localization length, α is the decay parameter of the wave function of a localized charge carrier, $\psi \sim e^{-\alpha r}$, and ν_{ph} is the phonon frequency.

Using expression (1), we can calculate the density of states at the Fermi level from the measured experimental values of the conductivity $\sigma_{ac}(f)$. Calculated values of N_F for investigated $TlIn_{1-x}Er_xSe_2$ ($x = 0.005$ and 0.01) single crystals were equal to 8×10^{17} and 1.2×10^{18} eV^{-1} cm^{-3}, correspondingly (localization radius chosen as 58 Å, in analogy with the InSe single crystal [6]).

The theory of AC hopping conductivity provides an opportunity to determine the average time τ of charge carrier hopping from one localized state to another using the formula [5]:

$$\tau^{-1} = \nu_{ph} \exp(-2R\alpha) \quad (2)$$

where R is the average hopping distance,

$$R = \frac{1}{2\alpha} \ln \frac{\nu_{ph}}{f}. \quad (3)$$

Calculated values of τ and R for both $TlIn_{1-x}Er_xSe_2$ ($x = 0.005$ and 0.01) single crystals were equal to 5.7×10^{-2} μs and 320 Å, correspondingly.

Knowing N_F and R from [5]:

$$\frac{4\pi}{3} R^3 N_F \frac{\Delta E}{2} = 1, \quad (4)$$

we estimate energetic scattering of trap states near the Fermi level: $\Delta E = 0.018$ eV for $TlIn_{1-x}Er_xSe_2$ crystals with $x = 0.005$ and 0.012 eV for $x = 0.01$.

By formula

$$N_t = N_F \Delta E \quad (5)$$

we can determine the concentration of deep traps in Er-doped $TlInSe_2$ single crystals: $N_t = 1.4 \times 10^{16}$ cm^{-3} for both compositions $x = 0.005$ and 0.01.

4. Conclusions

The electrical properties (loss tangent, real and imaginary parts of complex dielectric permittivity, and AC conductivity of Er-doped p-type $TlInSe_2$ single crystals have been studied in the frequency range from 50 kHz to 35 MHz. The results demonstrate that the dielectric dispersion in the studied crystals has a relaxation nature. The experimental frequency dependence of the dissipation factor for $TlInSe_2$:Er single crystals is characterized with a monotonic descending with frequency, which is evidence of the fact that conductivity loss becomes the main dielectric loss mechanism at studied frequency range. At all studied frequencies the AC conductivity of the crystals varies according to the law, characteristic of hopping conduction through localized states near the Fermi level. The Fermi-level density of states, the spread of their energies, and the mean hop distance and time have been estimated.

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