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GROWING OF $SbO_xS_{1-x}I$ CRYSTALS AND INVESTIGATION OF VIBRATIONAL SPECTRA IN THE PHASE TRANSITION REGION

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$SbO_xS_{1-x}I$ ($x = 0-0.5$) crystals have been grown from the vapour phase. Reflection spectra of the $SbO_xS_{1-x}I$ ($x = 0.2$) crystals were studied by a modernized Fourier spectrometer at $\mathbf{E}\|\mathbf{c}$. Using an improved Kramers–Kronig technique with two confining spectral limits, the spectra of optical constants and optical functions were calculated. The vibrational frequencies $\omega_{\rm L}$ and $\omega_{\rm T}$ have been evaluated. The vibrational frequencies of $SbO_xS_{1-x}I$ ($x = 0.2$) chains in different phases have been calculated in the harmonic approximation. The theoretical results are compared with experimental data.

Keywords: $SbO_xS_{1-x}I$, growing crystals, vibrational spectra, Kramers–Kronig technique

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1. Introduction

A remarkable coexistence of ferroelectric and semiconducting properties and the possibility of their practical application cause a great interest in studying the semiconducting ferroelectric materials [1–4]. From this aspect, the mixed crystals $SbO_xS_{1-x}I$ are especially valuable, since their $T_{\rm C}$ exceeds that of pure SbSI with $T_{\rm C} = 293$ K [5]. The reasons of the $T_{\rm C}$ growth with increasing x in these crystals have not yet been explored. The IR vibrational and dielectric spectra and physical properties of mixed BiSI–SbSI, SbSI–SbSeI, SbSI–SbSBr crystals have been investigated by various groups for a long time [6–8]. However, the vibrational spectra were theoretically studied only for pure SbSI-type crystals [9]. There have been almost no experimental nor theoretical studies of IR vibrational spectra of mixed SbSI–SbOI crystals as yet.

The aim of the present work was to grow $SbO_xS_{1-x}I$ crystals with perfect mirror-like surfaces that would be suitable for experimental measurements of reflection IR spectra. Since in the IR spectral range of $\omega > 100$ cm^{-1} the total energy curves of vibrational modes are only slightly anharmonic (in contrast to the range of $\omega < 100$ cm^{-1}) [4], therefore, the vibrational frequencies of $SbO_xS_{1-x}I$ ($x = 0.2$) chains in different phases have been calculated in the harmonic approximation.

2. Growing $SbO_xS_{1-x}I$ crystals

Despite various attempts, only thin needle-like crystals or bundles of thin crystals were being obtained before [5, 6].

At the Solid State Optics Laboratory of the Vilnius Pedagogical University, we began to grow $SbO_xS_{1-x}I$ crystals with different values of x. The crystals are grown from the vapour phase, since at present this is the best way to get crystals suitable for studying their optical properties. For growing the crystals, we employed a vertical two-zone furnace (see Fig. 1).

In the upper part of the growth area, the temperature was 400 °C, and in the lower part it was 440 °C. As starting materials, we took Sb_2S_3, I_2, and Sb_2O_3 (as a source of oxygen). Before that, Sb_2S_3 was synthesized from a stoichiometric mixture of Sb and S. The synthesis took place in an evacuated quartz ampoule placed in a rotating furnace. The temperature slowly increased up to 700 °C and then was kept at this level for 12 hours. Afterwards Sb_2S_3, I_2, and Sb_2O_3 were put in a quartz ampoule, 22 mm in diameter and 200 mm long. Then the ampoule was evacuated and placed in

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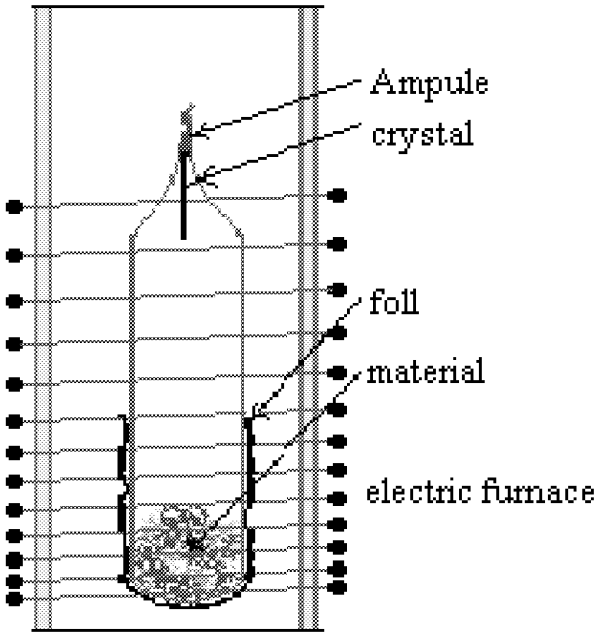

Fig. 1. The furnace for growing the crystals.

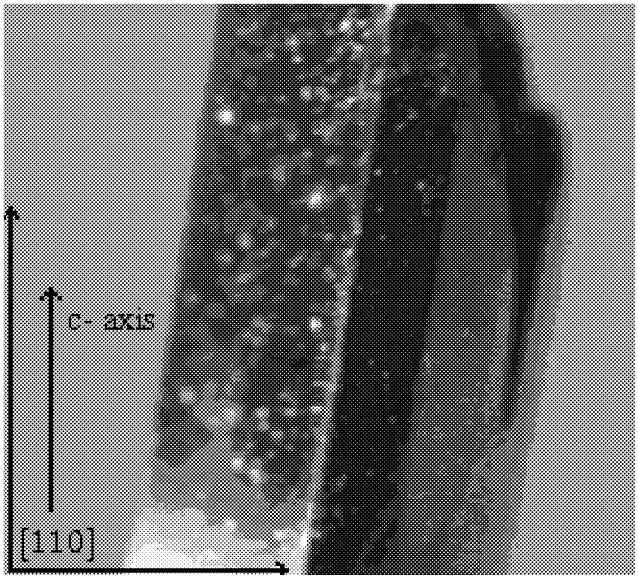

Fig. 2. The crystal with mirror-like surfaces.

the growth furnace. The total amount of the substance taken was 20 g.

In one or two days, the crystal seeds appear in the growth area, tiny crystallites that afterwards give rise to large crystals. The crystal length is parallel (and thickness perpendicular) to the c-axis. The growth rate along the c-axis attains 5 mm/day in the initial stage and about 0.1 mm/day in the final stage of the growth process. The growth rate in the directions perpendicular to the c-axis is about ten times slower. Employing this technique, during 50–60 days one can get crystals up to the dimensions of $5 \times 5 \times 25$ mm^3. The crystal surfaces are mirror-like, the largest is the [110]-plane, and the c-axis is always directed along the crystal (Fig. 2).

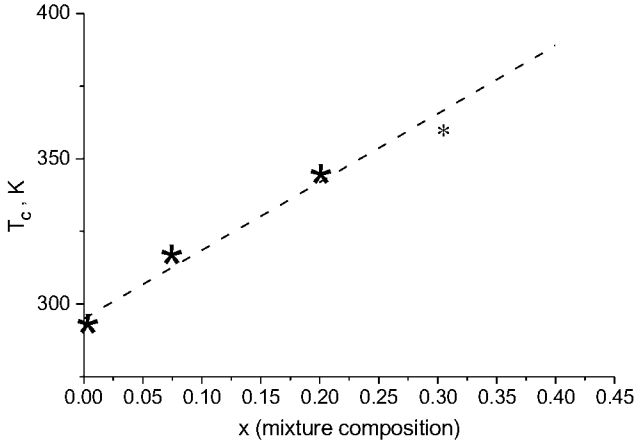

Fig. 3. The dependence of $T_{\rm C}$ for $SbO_xS_{1-x}I$ upon the mixture composition.

We determined the phase transition temperature $T_{\rm C}$ by measuring temperature dependences of reflection spectra and of the absorption edge of crystals.

Figure 3 shows the dependence of the phase transition temperature $T_{\rm C}$ of the grown crystals upon their stoichiometric composition x. Experimental results are shown by asterisks. The dependence of $T_{\rm C}$ on x is linear. The electronic structure of the crystal depends on x, because the average form factor $\overline{f}_{\rm VI}$ of the group VI atoms (S, Se, O) varies with x; here respectively $\overline{f}_{\rm VI} = f_{\rm S}(1-x) + f_{\rm O} \cdot x$ or $\overline{f}_{\rm VI} = f_{\rm S}(1-x) + f_{\rm Se} \cdot x$. In [10], it has been theoretically studied how the phase transition temperature $T_{\rm C}$ depends on the mixture composition x (or the average form factor) in SbSI-type mixed crystals. It has been found that when x grows, then the decrease of $\overline{f}_{\rm VI}$ causes $T_{\rm C}$ to increase. That is why in $SbO_xS_{1-x}I$ crystals the decrease of $\overline{f}_{\rm VI}$ also leads to an increase of $T_{\rm C}$.

3. IR vibrational spectra of the $SbO_xS_{1-x}I$ crystals in the phase transition region

For studying IR reflection spectra $R(\omega)$ of small crystals with perfectly reflecting surfaces, we applied a modernized Fourier spectrophotometer LAFS-1000 that was equipped with a small-crystal unit and a special cryostat with good temperature stabilization. The reflection spectrum of the $SbO_xS_{1-x}I$ crystals can be measured by the Fourier spectrophotometer in the region of $\omega > 20$ cm^{-1}. For calculating the

Table 1. Oscillator parameters of $SbO_xS_{1-x}I$ ($x = 0.2$) crystals obtained employing the Kramers–Kronig (KK) and oscillator parameter fitting (OP) techniques at $\mathbf{E}\|\mathbf{c}$.

Mode	KK		OP		Phase
No.	ω_T (cm^{-1})	ω_L (cm^{-1})	ω_T (cm^{-1})	ω_L (cm^{-1})	
1	49	125	43	122	PEF
2	170	272	173	274	$T = 360$ K
1	40	100	42	102	FEF
2	108	125	110	118	$T = 293$ K
3	148	156	149	155	
4	168	218	166	228	
5	243	271	245	275	

Table 2. Normal vibrational mode frequencies, IR intensities, optical activities in different phases (PEP and FEP) of $SbO_xS_{1-x}I$ ($x = 0.2$) crystals at $\mathbf{E}\|\mathbf{c}$.

Mode	PEP			FEP			Exper. FEP KK
No.	ω_L (cm^{-1})	IR intensity	Optical activity	ω_L (cm^{-1})	IR intensity	Optical activity	ω_L (cm^{-1})
1	64	0.000	R	60	0.002	IR	100
2	126	1.079	IR	95	0.778	IR	125
3	150	0.000	R	148	0.142	IR	156
4	219	0.439	IR	222	0.288	IR	218
5	260	0.000	R	270	0.235	IR	271

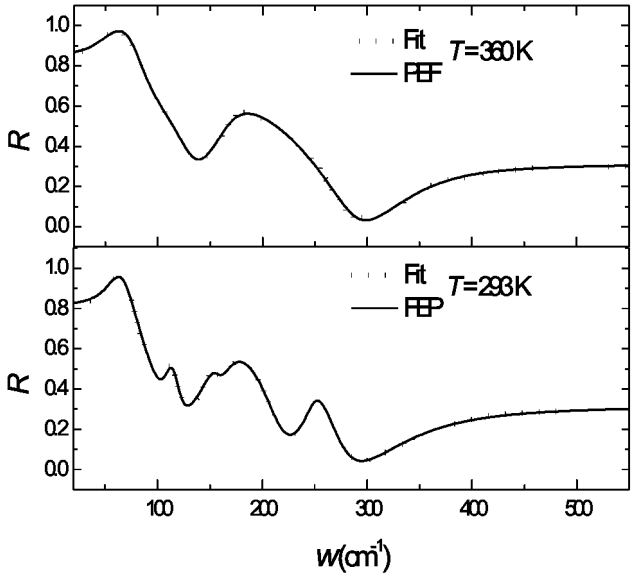

Fig. 4. The reflection spectrum $R(\omega)$ of the $SbO_xS_{1-x}I$ ($x = 0.2$) crystals studied by the OP technique at $\mathbf{E}\|\mathbf{c}$ and $T = 293$ K (FEP), $T = 360$ K (PEP).

optical constants $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, optical functions $\mathrm{Im}\,(\varepsilon^{-1})$, and frequencies ω_T and ω_L (Table 1) we employed an improved Kramers–Kronig (KK) technique with the spectral limits of $a = 20$ cm^{-1}, $b = 500$ cm^{-1}. The frequencies ω_T and ω_L were also found by means of oscillator parameter fitting (OP) technique (Fig. 4).

SbSI-type crystals are composed of chains in which atoms are connected by strong covalent–ionic bonds. These chains are directed along the z (**c**) axis. Between the chains, there are weak bonds of van der Waals type. Therefore, we performed calculations of normal mode frequencies of $SbO_xS_{1-x}I$ crystals for a single chain by considering a simplified unit cell.

Theoretical normal vibrational mode frequencies of $SbO_xS_{1-x}I$ ($x = 0.2$) in different phases have been calculated by means of dynamical matrix using the Born–von Karman model and the simplified elementary cell following Furman et al. [9] (Table 2). Force constants were calculated using a special program in the basis sets of atomic functions Hw [11].

4. Conclusions

Semiconductor-ferroelectric $SbO_xS_{1-x}I$ crystals grown from the vapour phase are suitable for optical investigations because they possess mirror-like surfaces. The phase transition temperature T_C depends on the average form factor $\overline{f}_{VI}$, which depends on their stoichiometric composition x (see Fig. 3).

The frequencies of normal modes ω_T and ω_L determined from the $R(\omega)$ spectrum by the Kramers–Kronig technique employing the spectral limits a and b are sufficiently accurate, because the error does not exceed ± 3 cm^{-1}. The same frequencies ω_T and ω_L deter-

mined by the oscillator parameter fitting technique coincide quite well with those derived by the Kramers–Kronig technique (see Table 1), which confirms the validity of the present results.

Sufficiently good agreement of the theoretical ω_{L} values with the experimentally measured ones (see Table 2) proves that the model of one chain of atoms directed along the z (**c**) axis with cyclic boundary conditions is acceptable for theoretical studies of vibrational spectra of SbSI-type mixed crystals.

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$SbO_xS_{1-x}I$ KRISTALŲ AUGINIMAS IR VIBRACINIŲ SPEKTRŲ TYRIMAS FAZINIŲ VIRSMŲ SRITYJE

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Santrauka

$SbO_xS_{1-x}I$ ($x = 0{-}0{,}5$) kristalai išauginti iš garų fazės. Šių kristalų atspindžio spektrai ištirti Fourier spektrometru, kai $\mathbf{E}\|\mathbf{c}$. Optinės konstantos, optinės funkcijos ir vibraciniai dažniai (ω_{T} ir ω_{L}) apskaičiuoti Kramers'o ir Kronig'o metodu. $SbO_xS_{1-x}I$ ($x = 0{,}2$) grandinėlės vibraciniai dažniai apskaičiuoti harmoniniame artėjime. Teoriniai rezultatai palyginti su eksperimentiniais.