GROWING OF SbO$_x$S$_{1-x}$I CRYSTALS AND INVESTIGATION OF VIBRATIONAL SPECTRA IN THE PHASE TRANSITION REGION

A. Audzijonis$^a$, L. Žigas$^a$, R. Žaltauskas$^a$, and A. Pauliukas$^a$

$^a$Department of Physics, Vilnius Pedagogical University, Studentu 39, LT-08106 Vilnius, Lithuania

E-mail: kkol@vpu.lt

Received 01 June 2004

Dedicated to the 100th anniversary of Professor K. Baršauskas

SbO$_x$S$_{1-x}$I ($x = 0–0.5$) crystals have been grown from the vapour phase. Reflection spectra of the SbO$_x$S$_{1-x}$I ($x = 0.2$) crystals were studied by a modernized Fourier spectrometer at E|=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 $\omega_1$ and $\omega_T$ have been evaluated. The vibrational frequencies of SbO$_x$S$_{1-x}$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$_x$S$_{1-x}$I, growing crystals, vibrational spectra, Kramers–Kronig technique

PACS: 81.10.–h, 81.10.Bk, 63.20.Dj, 77.80.Bh

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$_x$S$_{1-x}$I are especially valuable, since their $T_C$ exceeds that of pure SbSI with $T_C = 293$ $^\circ$C [5]. The reasons of the $T_C$ 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$_x$S$_{1-x}$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$_x$S$_{1-x}$I ($x = 0.2$) chains in different phases have been calculated in the harmonic approximation.

2. Growing SbO$_x$S$_{1-x}$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$_x$S$_{1-x}$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 $400$ $^\circ$C, and in the lower part it was $440$ $^\circ$C. As starting materials, we took Sb$_2$S$_3$, I$_2$, and Sb$_2$O$_3$ (as a source of oxygen). Before that, Sb$_2$S$_3$ 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 $700$ $^\circ$C and then was kept at this level for 12 hours. Afterwards Sb$_2$S$_3$, I$_2$, and Sb$_2$O$_3$ were put in a quartz ampoule, $22$ mm in diameter and $200$ mm long. Then the ampoule was evacuated and placed in
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 \( 5 \times 5 \times 25 \text{ mm}^3 \). The crystal surfaces are mirror-like, the largest is the \{110\}-plane, and the \( c \)-axis is always directed along the crystal (Fig. 2).

We determined the phase transition temperature \( T_C \) by measuring temperature dependences of reflection spectra and of the absorption edge of crystals.

Figure 3 shows the dependence of the phase transition temperature \( T_C \) of the grown crystals upon their stoichiometric composition \( x \). Experimental results are shown by asterisks. The dependence of \( T_C \) on \( x \) is linear. The electronic structure of the crystal depends on \( x \), because the average form factor \( f_{\text{VI}} \) of the group VI atoms (S, Se, O) varies with \( x \); here respectively \( f_{\text{VI}} = f_S(1-x) + f_O \cdot x \) or \( f_{\text{VI}} = f_S(1-x) + f_{\text{Se}} \cdot x \). In [10], it has been theoretically studied how the phase transition temperature \( T_C \) 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 \( f_{\text{VI}} \) causes \( T_C \) to increase. That is why in \( \text{SbO}_x\text{S}_{1-x}\text{I} \) crystals the decrease of \( f_{\text{VI}} \) also leads to an increase of \( T_C \).

3. IR vibrational spectra of the \( \text{SbO}_x\text{S}_{1-x}\text{I} \) 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 \( \text{SbO}_x\text{S}_{1-x}\text{I} \) crystals can be measured by the Fourier spectrophotometer in the region of \( \omega > 20 \text{ cm}^{-1} \). For calculating the
Table 1. Oscillator parameters of SbO$_x$S$_{1-x}$I ($x = 0.2$) crystals obtained employing the Kramers–Kronig (KK) and oscillator parameter fitting (OP) techniques at $E||c$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>No.</th>
<th>$\omega_T$ (cm$^{-1}$)</th>
<th>$\omega_L$ (cm$^{-1}$)</th>
<th>$\omega_T$ (cm$^{-1}$)</th>
<th>$\omega_L$ (cm$^{-1}$)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>49</td>
<td>125</td>
<td>43</td>
<td>122</td>
<td>PEF</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>170</td>
<td>272</td>
<td>173</td>
<td>274</td>
<td>$T = 360$ K</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>40</td>
<td>100</td>
<td>42</td>
<td>102</td>
<td>PEF</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>108</td>
<td>125</td>
<td>110</td>
<td>118</td>
<td>$T = 293$ K</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>148</td>
<td>156</td>
<td>149</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>168</td>
<td>218</td>
<td>166</td>
<td>228</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>243</td>
<td>271</td>
<td>245</td>
<td>275</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Mode</th>
<th>No.</th>
<th>$\omega_T$ (cm$^{-1}$)</th>
<th>IR intensity</th>
<th>Optical activity</th>
<th>$\omega_L$ (cm$^{-1}$)</th>
<th>IR intensity</th>
<th>Optical activity</th>
<th>Exp. FEP</th>
<th>KK $\omega_L$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>64</td>
<td>0.000 R</td>
<td></td>
<td>60</td>
<td>0.002 IR</td>
<td></td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>126</td>
<td>1.079 IR</td>
<td></td>
<td>95</td>
<td>0.778 IR</td>
<td></td>
<td>125</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>150</td>
<td>0.000 R</td>
<td></td>
<td>148</td>
<td>0.142 IR</td>
<td></td>
<td>156</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>219</td>
<td>0.439 IR</td>
<td></td>
<td>222</td>
<td>0.288 IR</td>
<td></td>
<td>218</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>260</td>
<td>0.000 R</td>
<td></td>
<td>270</td>
<td>0.235 IR</td>
<td></td>
<td>271</td>
<td></td>
</tr>
</tbody>
</table>

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$_x$S$_{1-x}$I crystals for a single chain by considering a simplified unit cell.

Theoretical normal vibrational mode frequencies of SbO$_x$S$_{1-x}$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$_x$S$_{1-x}$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 $f_{V1}$, which depends on their stoichiometric composition $x$ (see Fig. 3).

The frequencies of normal modes $\omega_T$ and $\omega_L$ 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 $\pm 3$ cm$^{-1}$. The same frequencies $\omega_T$ and $\omega_L$ deter-
mined by the oscillator parameter fitting technique co-
incide quite well with those derived by the Kramers–
Kronig technique (see Table 1), which confirms the va-
lidity of the present results.

Sufficiently good agreement of the theoretical $\omega_T$
values with the experimentally measured ones (see Ta-
ble 2) proves that the model of one chain of atoms di-
rected along the $z$ (c) axis with cyclic boundary condi-
tions is acceptable for theoretical studies of vibrational
spectra of SbSI-type mixed crystals.

References

[1] J. Grigas, E. Talik, and V. Lazauskas, Splitting of the
XPS in ferroelectric SbSI crystals, Ferroelectrics 284,
[2] B. Garbarz-Gloss, Dielectric properties of SbSI-
modified in phase transition region, Ferroelectrics 292,
137–143 (2003).
Peculiarities and properties of SbSI electroceramics,
L. Audzijonienė, Electronic potentials of normal vibra-
tional modes in SbSI crystals, Ferroelectrics 274, 1–15
(2002).
of Sb$\text{S}_1\text{O}_x\text{I}$, Ferroelectrics 51, 213–237 (1984).
and P. Ramasamy, Growth and electrical characteriza-
tion of SbSI and SbSOI crystals, J. Cryst. Growth 97,
[7] V. Kalesinskas, J. Grigas, A. Audzijonis, and K. Žič-
kus, Microwave resonance dielectric dispersion in
Sb$\text{S}_{0.7}\text{Se}_{0.3}\text{I}$ crystals, Phase Transitions 3, 217–226
(1983).
[8] V. Kalesinskas, J. Grigas, R. Jankevičius, and A. Au-
dzijonis, Soft mode in the microwave dielectric spectra
of the SbSI–BiSI system, Phys. Status Solidi B 115,
[9] E. Furman, O. Brafman, and J. Makovsky, Approxima-
tion to long-wavelength dynamics of SbSI-type crys-
[10] S. Kvedaravičius, A. Audzijonis, N. Mykolaitienė, and
J. Grigas, Soft mode and its electronic potential in
SbSI-type mixed crystals, Ferroelectrics 177, 181–190
(1996).
M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga,
K.A. Nguyen, S.I. Su, T.L. Windus, M. Dupuis, and
J.A. Montgomery, General atomic and molecular elec-
tronic structure system, J. Comput. Chem. 14, 1347
(1993).

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

A. Audzijonis, L. Žigas, R. Žaltauskas, A. Pauliukas

Vilniaus pedagoginis universitetas, Vilnius, Lietuva

Santrauka

SbO$_{x}$S$_{1-x}$I ($x = 0–0.5$) kristalai išauginti į garsų fa-
žes. Šiuos kristalų atspindžio spektra ištirti Fourier spektrometru,
kaip $\mathbf{E}||c$. Optinės konstantos, optinės funkcijos ir vibraciniai
dažniai ($\omega_T$ ir $\omega_L$) apskaičiuoti Kramers'o ir Kronig'o metodu.
SbO$_{x}$S$_{1-x}$I ($x = 0.2$) grandinės vibracinių dažnių apskaičiuoti
harmoniniam artėjime. Teoriniai rezultatai palyginti su eksperi-
mentiniai.