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# Optical properties of undoped and chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

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SbSI:Cr, SbSeI:Cr, BiSI:Cr, and BiSeI:Cr single crystals were grown by the vertical Bridgman technique using the ingots synthesized from the high-purity (99.9999%) elements antimony, bismuth, sulphur, selenium, iodine and chromium. The grown single crystals crystallized in the orthorhombic structure and had an indirect energy-band structure. The temperature dependence of the optical energy gap was well fitted by the Varshni equation. When chromium was doped into the single crystals, impurities in the optical absorption peaks appeared, and were attributed to the electron transitions between the energy levels of $Cr^{2+}$ ions sited at the $T_d$ symmetry point in the host lattice.

## 1. Introduction

SbSI, BiSI, SbSeI, and BiSeI single crystals, which are photoferroelectric semiconductors, have an indirect band-gap energy between 1.97 and 1.28 eV, so that they possess the opto-electronic response over the near infrared photon energy range. Of these single crystals SbSI and BiSI single crystals have first-order and second-order phase transitions, the others having only first-order one [1]. In these single crystals, the temperature at which the phase transitions take place, is dependent on the purity of the single crystals and the processing method of the samples. In addition, when the dopants are introduced into the single crystals, their phase transition temperature is changed due to the variation of atomic bonding, so that a study of the optical properties for the impurity-doped single crystals is important [2].

When chromium is doped in $V^A$–$VI^A$–$VII^A$ type semiconductor SbSI, BiSI, SbSeI, and BiSeI single crystals, it is anticipated that interesting optical properties will result because of the optical properties of chromium in the single crystals. However, the melting point of the chromium is higher than that of other elements, so that the doped chromium is isolated in the single crystals. Therefore, it is difficult to obtain high-quality single crystals. Because of this, no study has been reported on chromium-doped single crystals.

This is the first report on the optical properties of $V^A$–$VI^A$–$VII^A$ type semiconductor SbSI, BiSI, SbSeI, and BiSeI single crystals doped with chromium as an impurity. SbSI:Cr, BiSI:Cr, SbSeI:Cr, and BiSeI:Cr single crystals were grown by the vertical Bridgman technique. The optical absorption spectra of the grown single crystals were measured in the temperature range 10–300 K. The temperature dependence of the indirect energy gap and the relation between the temperature dependence and the phase transition temperature were specified. Finally, the impurity optical absorption properties by the chromium have been described by the cubic crystal field theory [3].

## 2. Experimental procedure

Undoped and chromium-doped SbSI, BiSI, SbSeI, and BiSeI single crystals were grown by the vertical Bridgman technique using ingots synthesized from mixtures of high-purity (99.9999%) elements antimony, bismuth, sulphur, selenium, iodine and chromium, and from an excess of iodine of 8.6 mol %. The excess of iodine of 8.6 mol % was added to obtain the single crystals satisfying stoichiometry, because iodine will exist in the gas state in the quartz ampoules during crystal growth, due to the relatively low boiling temperature; this iodine will consequently cause the deficiency of iodine from the stoichiometry in the grown single crystals. To grow the chromium-doped single crystals, 2 mol % chromium metal powder (purity 99.99%) was introduced into the mixtures. The grown single crystals were oriented with the *c*-axis along the vertical ampoule axis, and were about 50 mm long and 10 mm diameter. The plate-like samples, which had an optically flat glass surface and were 0.5 mm thick, were prepared by mechanical polishing and chemical etching after cutting the grown single crystals perpendicular to the *c*-axis.

The crystal structure of the grown single crystals was determined by the X-ray diffraction method. Optical absorption spectra were measured using

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a UV–VIS–NIR spectrophotometer (Hitachi, U-3501) at room temperature and a UV–VIS–NIR spectrophotometer (Hitachi, U-3400) equipped with the cryogenic system (Air Products, CSA-202B) at lower temperature.

## 3. Results and discussion

### 3.1. The crystal structure of chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

X-ray diffraction patterns of the grown single crystals were obtained using the powder X-ray diffraction method. Of the X-ray diffraction patterns, those of SbSI:Cr and SbSeI:Cr single crystals are shown in Fig. 1. The crystal structure was found to be orthorhombic from analysis of the X-ray diffraction patterns. The lattice constants were found to be $a = 0.8451$ nm, $b = 1.0181$ nm, $c = 0.4187$ nm for SbSI:Cr single crystal, and $a = 0.8692$ nm, $b = 1.0462$ nm, $c = 0.4049$ nm for SbSeI:Cr single crystal. Lattice constants of BiSI:Cr and BiSeI:Cr single crystals were found to have similar values to the above results. The lattice constants of $V^A$–$VI^A$–$VII^A$ and $V^A$–$VI^A$–$VII^A$:Cr (2 mol %) single crystals are listed in Table I. We can see from Fig. 1 and Table I that the crystal structure does not change in spite of the difference of the lattice constants between the undoped and chromium-doped single crystals.

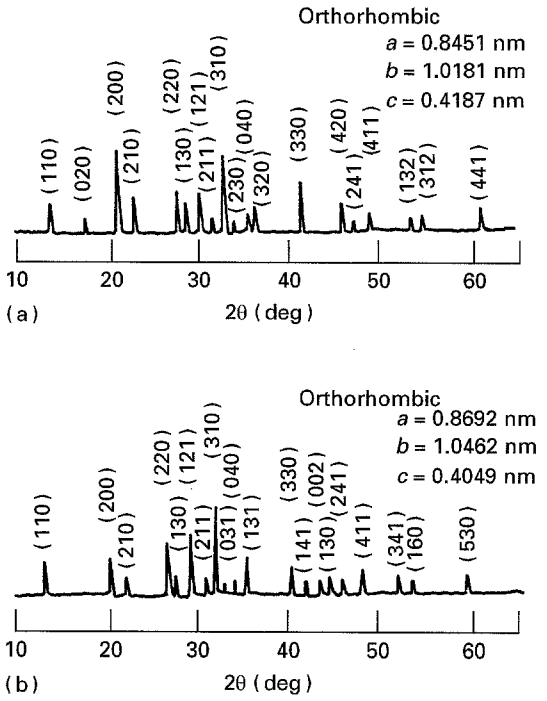


*Figure 1* X-ray diffraction patterns of (a) SbSI:Cr and (b) SbSeI:Cr single crystals.

TABLE I Lattice constants of the chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

| Composition | Lattice constant | Experimental values | |
|---|---|---|---|
| | | Pure (nm) | Cr-doped (nm) |
| SbSI | *a* | 0.8527 | 0.8452 |
| | *b* | 1.0140 | 1.0181 |
| | *c* | 0.4089 | 0.4187 |
| SbSeI | *a* | 0.8698 | 0.8692 |
| | *b* | 1.0412 | 1.0462 |
| | *c* | 0.4127 | 0.4049 |
| BiSI | *a* | 0.8462 | 0.8215 |
| | *b* | 1.0153 | 1.0183 |
| | *c* | 0.4145 | 0.4178 |
| BiSeI | *a* | 0.8713 | 0.8673 |
| | *b* | 1.0542 | 1.0596 |
| | *c* | 0.4193 | 0.4052 |

### 3.2. The optical energy gaps of chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

The optical transmittance spectra of SbSI:Cr and SbSeI:Cr single crystals measured near the band edge region from 10–300 K are shown in Figs 2 and 3, respectively. The transmittance spectra of BiSI:Cr and BiSeI:Cr single crystals were similar. As is known from Figs 2 and 3, the fundamental absorption edge is shifted to the shorter wavelength region with decrease in temperature.

$V^A$–$VI^A$–$VII^A$ type single crystals have an indirect energy-band gap structure [2], so that the optical absorption coefficient, $\alpha$, the incident photon energy, $h\nu$, and the optical energy gap, $E_g$, are related to Equation 1 [4]

$$(\alpha h\nu)^{1/2} \sim (h\nu - E_g) \quad (1)$$

In Figs 4 and 5, the value of $(\alpha h\nu)^{1/2}$ is plotted as a function of the incident photon energy, $h\nu$, for SbSI:Cr and SbSeI:Cr single crystals, respectively. The optical absorption coefficient, $\alpha$, was obtained from the optical transmittance of Figs 2 and 3. From Equation 1, the value of $h\nu$ at $(\alpha h\nu)^{1/2} = 0$ by the extrapolation method is the optical energy gap $E_g$ which is found to be 2.264 eV at 18 K and 1.979 eV at 290 K for SbSI:Cr single crystal, and 1.554 eV at 17 K and 1.458 eV at 290 K for SbSeI:Cr single crystal. Using a similar method, the optical energy gaps of BiSI:Cr and BiSeI:Cr single crystals were found to be 1.613 and 1.201 eV at 290 K, respectively.

The optical energy gaps of the pure and chromium-doped single crystals at 290 K are given in Table II.

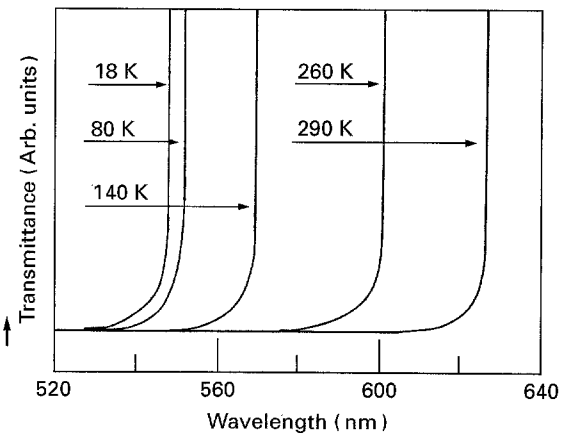


*Figure 2* Optical transmittance spectra of SbSI:Cr single crystal.

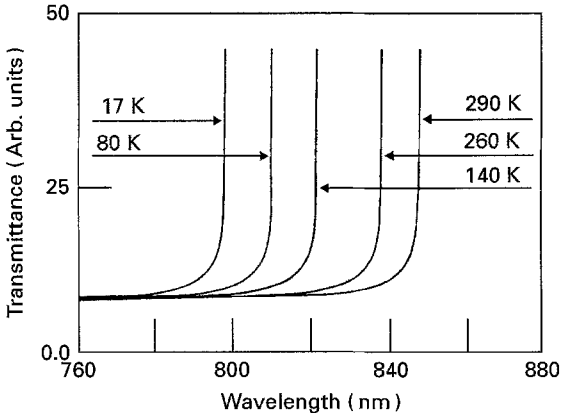


*Figure 3* Optical transmittance spectra of SbSeI:Cr single crystal.

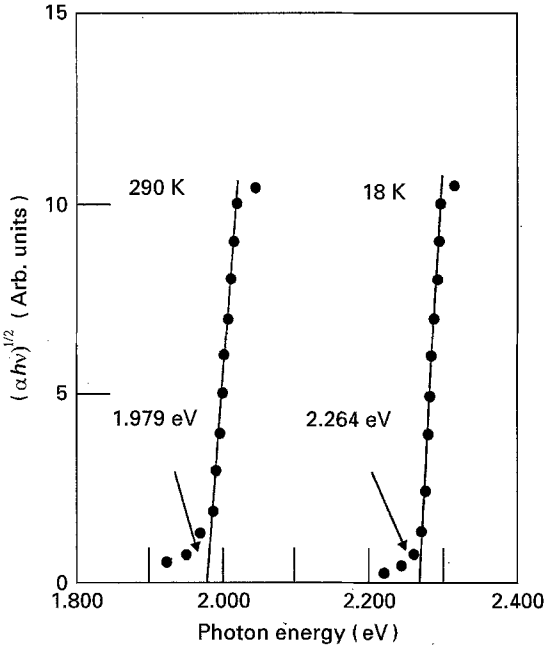


*Figure 4* Relation between the incident photon energy $h\nu$ and $(\alpha h\nu)^{1/2}$ for SbSI:Cr single crystal.

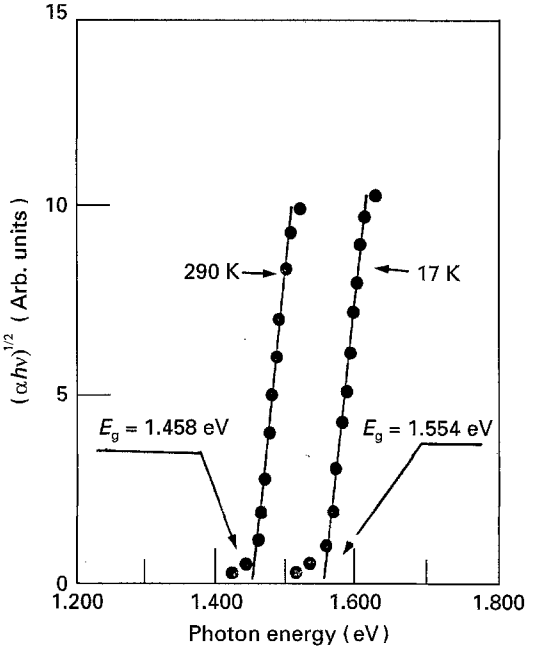


*Figure 5* Relation between the incident photon energy $h\nu$ and $(\alpha h\nu)^{1/2}$ for SbSeI:Cr single crystal.

From Table II it is seen that when chromium is doped in SbSeI, BiSI and BiSeI single crystals, the optical energy gap is decreased in comparison with that of the undoped single crystals. On the other hand, when chromium is doped in SbSI single crystal, the optical energy gap is increased.

When chromium is doped in SbSeI, BiSI and BiSeI single crystals, the doped chromium is substituted for $Sb^{3+}$ or $Bi^{3+}$ ions, and constitutes chromium compounds in SbSeI, BiSI and BiSeI compounds. Then the chromium compounds form solid solutions with SbSeI, BiSI and BiSeI compounds, respectively. Therefore, the energy gaps of SbSeI:Cr, BiSI:Cr and BiSeI:Cr single crystals will be decreased by the effect of the chromium compounds, the energy gap of which is relatively smaller than that of SbSeI, BiSI and BiSeI compounds. However, when chromium is doped in SbSI single crystal, the energy level due to the chromium ion is slightly higher than that of the energy gap of the SbSI single crystal, so that the energy gap of the grown SbSI:Cr single crystal is increased in comparison with that of the undoped SbSI single crystal, which is described by the Burstein–Moss shift ([4] p. 39).

The optical energy gap of the grown single crystals is obtained over the temperature range from 10–300 K, and the temperature dependence for SbSI:Cr and SbSeI:Cr single crystals is plotted in Figs 6 and 7, respectively. As shown in Figs 6 and 7, there are kinks at 158 and 232 K for SbSI:Cr single crystal, and at 144 and 226 K for SbSeI:Cr single crystal. Similar results are obtained for the others, and the kinks are found to be at 160 and 234 K for BiSI:Cr single crystal, and at 135 and 215 K for BiSeI:Cr single crystal. The temperature at which these kinks

TABLE II Optical energy gaps and transition temperature of the chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals at 290 K

| Compounds | Energy gap (eV) | | Transition temp. (K) | | | |
|---|---|---|---|---|---|---|
| | Pure | Cr-doped | Pure | | Cr-doped | |
| | | | I | II | I | II |
| SbSI | 1.963 | 1.979 | 295 | 233 | 158 | 232 |
| SbSeI | 1.674 | 1.458 | – | 223 | 144 | 226 |
| BiSI | 1.592 | 1.613 | 115 | 233 | 160 | 234 |
| BiSeI | 1.285 | 1.201 | – | 133 | 135 | 215 |

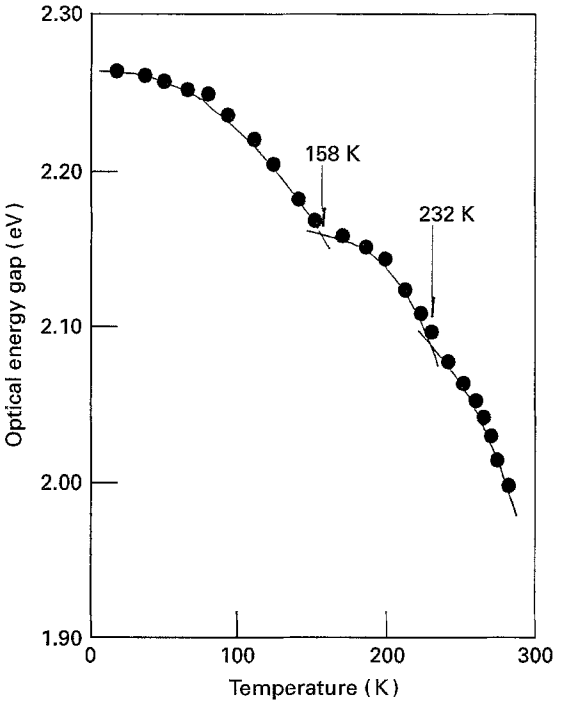


*Figure 6* Temperature dependence of optical energy gap for SbSI:Cr single crystal.

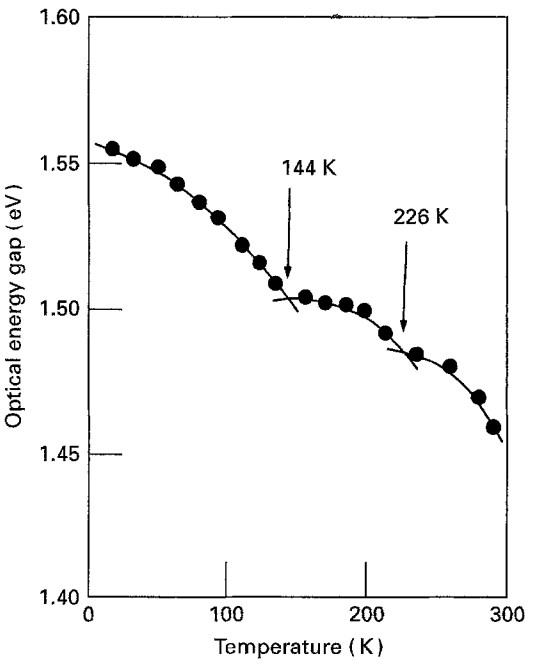


*Figure 7* Temperature dependence of optical energy gap for SbSeI:Cr single crystal.

TABLE III Values of parameters in the Vashini equation for chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

| Compounds | Range of temperature (K) | $E_g(0)$ (eV) | $\alpha$ (eV $K^{-1}$) | $\beta$ (K) |
|---|---|---|---|---|
| SbSI:Cr | 0–158 | 2.264 | $4.25 \times 10^{-3}$ | 881 |
| | 158–232 | 2.162 | $-4.37 \times 10^{-5}$ | −270 |
| | 232–300 | 2.100 | $3.59 \times 10^{-5}$ | −321 |
| SbSeI:Cr | 0–144 | 1.551 | $5.34 \times 10^{-5}$ | −122 |
| | 144–226 | 1.501 | $-8.56 \times 10^{-7}$ | −227 |
| | 226–300 | 1.457 | $-5.23 \times 10^{-7}$ | −307 |
| BiSI:Cr | 0–160 | 1.898 | $3.92 \times 10^{-3}$ | −279 |
| | 160–234 | 1.818 | $-4.52 \times 10^{-5}$ | −245 |
| | 234–300 | 1.758 | $3.76 \times 10^{-5}$ | −315 |
| BiSeI:Cr | 0–135 | 1.296 | $6.63 \times 10^{-5}$ | −132 |
| | 135–215 | 1.243 | $-7.47 \times 10^{-7}$ | −277 |
| | 215–300 | 1.189 | $-6.23 \times 10^{-7}$ | −315 |

occur in the chromium-doped single crystals, and at which the first-order and the second-order phase transitions take place in the undoped SbSI, SbSeI, BiSI and BiSeI single crystals, is listed in Table II. From Table II, we know that the temperatures I and II correspond to the first-order and second-order phase transitions.

As shown in Figs 6 and 7, the curve representing the temperature dependence of the energy gap for SbSI:Cr and SbSeI:Cr single crystals is divided into three parts, one from 10 K to point I, another from point I to point II, and the other from point II to 300 K. In each of the parts, the curve is well fitted in the Varshni equation [5]

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} \quad (2)$$

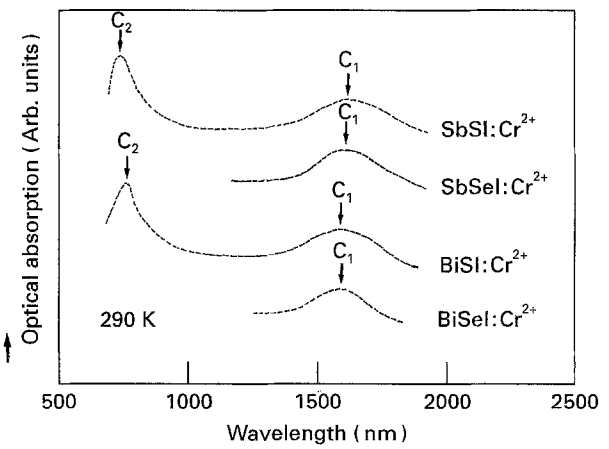


*Figure 8* Impurity optical absorption spectra in SbSI:Cr, SbSeI:Cr, BiSI:Cr, and BiSeI:Cr single crystals.

TABLE IV The optical absorption bands due to the $Cr^{2+}$ ion in chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

| Impurity | | Compound | | | | |
|---|---|---|---|---|---|---|
| | | SbSI | SbSeI | BiSI | BiSeI | Peaks |
| $Cr^{2+}(T_d)$ | $^5T_2(^5D)$ | 1600 nm | 1592 nm | 1584 nm | 1582 nm | $C_1$ |
| | $\rightarrow {}^5E(^5D)$ | 6250 $cm^{-1}$ | 6280 $cm^{-1}$ | 6310 $cm^{-1}$ | 6320 $cm^{-1}$ | |
| | $\rightarrow {}^3T_2(^3H)$ | 715 nm | | 744 nm | | $C_2$ |
| | | 13,986 $cm^{-1}$ | | 13,435 $cm^{-1}$ | | |

$E_g(0)$ is the energy gap at 0 K, and $\alpha$ and $\beta$ are constants. The value deduced from each of the parts for SbSI:Cr, SbSeI:Cr, BiSI:Cr, and BiSeI:Cr single crystals is listed in Table III.

### 3.3. Impurity optical absorption properties of chromium-doped $V^A$–$VI^A$–$VII^A$ single crystals

To obtain the impurity optical absorption spectra due only to the chromium in SbSI:Cr (2 mol %), SbSeI:Cr (2 mol %), BiSI:Cr (2 mol %), and BiSeI:Cr (2 mol %) single crystals, each of the undoped single crystals was located at the reference side, and each of the chromium-doped single crystals at the sample side in the spectrophotometer. The impurity optical absorption spectra are shown in Fig. 8. The impurity optical absorption peaks are found to be at $C_1$ and $C_2$, and the value of the peaks is listed in Table IV.

The impurity optical absorption peaks have the value of 6250 and 13986 $cm^{-1}$ for the SbSI:Cr, 6280 $cm^{-1}$ for the SbSeI:Cr, 6310 and 13435 $cm^{-1}$ for the BiSI:Cr, and 6320 $cm^{-1}$ for the BiSeI:Cr. These values are similar to the impurity optical absorption peak energies in ZnS:$Cr^{2+}$ and ZnSe:$Cr^{2+}$ single crystals [6]. Therefore, the $C_1$ and $C_2$ peaks are assigned to the electron transitions between the energy levels of $Cr^{2+}$ ion, which will be substituted for $Sb^{3+}$ or $Bi^{3+}$ ions having the tetrahedral bonding in the host lattice. Then, the point occupied by the $Cr^{2+}$ ion can be approximately considered as the $T_d$ symmetry site when applying the cubic crystal field theory [3]. Therefore, the impurity optical absorption peaks $C_1$, and $C_2$ peaks are attributed to the electron transitions of the $Cr^{2+}$ ion from the ground state $^5T_2(^5D)$ to the excited states $^5E(^5D)$ and $^3T_2(^3H)$, respectively.

## 4. Conclusions

SbSI:Cr, SbSeI:Cr, BiSI:Cr and BiSeI:Cr single crystals were grown by the vertical Bridgman technique using the ingots synthesized from the mixtures of high-purity elements (99.9999%) with 8.6 mol % excess iodine. The grown single crystals have the orthorhombic structure. The optical energy gap of each of the single crystals is little changed compared with that of each of the respective undoped single crystals. The temperature dependence of the optical energy gap shows kinks at the phase transition points, and is well fitted to the Varshni equation in each of the continuous ranges. When chromium is doped in the pure single crystals, $Cr^{2+}$ ions are substituted for $Sb^{3+}$ or $Bi^{3+}$ ions having the tetrahedral bonding in the host lattice. Then, the impurity optical absorption peaks can be assigned to the electron transitions between the energy levels of $Cr^{2+}$ ions sited at the $T_d$ symmetry of the host lattice.


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