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<th>Title</th>
<th>Preparation, Properties and Crystal Structure of I$_{0.5}$TaSe$_4$ (EXPERIMENTS ON (MX$_4$)$_n$Y COMPOUNDS, International Symposium on NONLINEAR TRANSPORT AND RELATED PHENOMENA IN INORGANIC QUASI ONE DIMENSIONAL CONDUCTORS)</th>
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<tr>
<td>Author(s)</td>
<td>Kikkawa, S.; Uenosono, S.; Koizumi, M.</td>
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Kyoto University
Preparation, Properties and Crystal Structure of $I_{0.5}TaSe_4$

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Abstract

$I_{0.5}TaSe_4$ was obtained by heating the starting mixture having compositional ratio of Se/Ta=4 and I/Ta=1 in 460°C/420°C temperature gradient for 1 week. The compound was tetragonal having lattice parameters $a=9.555\ \AA$ and $c=12.75\ \AA$. The observed density was 5.99 g/cm$^3$. X-ray structural analysis showed that tantalum is coordinated with 4 Se-Se dimers forming $[TaSe_4]$ infinite chain along c-axis. Iodine is located between the chain. There are two kinds of tantalum in the chain. The short distance of $3.24\ \AA$ between Se and I suggests that iodine is partially transferred electrons from every two Ta through Se. The electrical resistivity along c-axis was $1.9 \times 10^3 \ \Omega cm$ at room temperature and the activation energy was 0.06 eV. Magnetic susceptibility showed very weak temperature dependence: $-1.7 \times 10^{-7} \text{ emu/g}$ at room temperature and $-1.7 \times 10^{-8} \text{ emu/g}$ at 77K. The presences of $Ta^{4+}$, $Ta^{5+}$ and $(Se-Se)^2-$ were observed on X-ray photoelectron spectrum comparing with those of $TaSe_2$, $TaSe_3$ and $Ta_2O_5$.

Introduction

Transition metal polychalcogenides are attractive materials as low-dimensional conductors and as possible candidates for secondary battery cathodes (1, 2, 3). There have been extensive investigations on layered dichalcogenides and quasi-one-dimensional trichalcogenides. Especially the compounds of Va group metal are interesting low-dimensional conductors. There are very limited number of polychalcogenides containing more amount of chalcogen.
than trichalcogenides. The mineral patronite, VS₄, has the chain structure (4). Three niobium selenides with approximate composition NbSe₄ were initially reported (5). However, it has recently been shown that two of these are in fact Nb₂Se₉ and I₀.₃NbSe₄ (6, 7). The geometric aspects of their crystal structure show marked one-dimensional character. There have been no report on the presence of tantalum tetraselenide.

In the present manuscript, preparation of TaSe₄ is attempted using iodine as transporting agent below 500°C. New compound, I₀.₅TaSe₄, crystallized in columnar shape. Its preparation, properties and crystal structure are described.

**Experimental**

Mixtures of Ta, Se and I were heated in sealed quartz tubes for 1 week. The products were characterized using X-ray powder diffractometry, fluorescent X-ray spectroscopy, TG-DTA and X-ray photoelectron spectroscopy. Electrical resistivity was measured using two-probe method. Four-circle diffractometer was used for structural determination with MoKα radiation. The crystal structure was refined using the program RFINE on 391 independent reflections.

**Results and Discussion**

The products from a temperature gradient of 700°C/630°C are summarized in Table 1. Equimolar iodine was added to tantalum.

<table>
<thead>
<tr>
<th>Ta:Se:I ratio in starting powder</th>
<th>Products in high temp. region</th>
<th>Products in low temp. region</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:3:1</td>
<td>TaSe₂ + TaSe₃ + phase X</td>
<td>TaSe₃</td>
</tr>
<tr>
<td>1:4:1</td>
<td>TaSe₂ + TaSe₃ + phase X</td>
<td>phase X</td>
</tr>
<tr>
<td>1:5:1</td>
<td>TaSe₂ + TaSe₃ + phase X</td>
<td>phase X + Se</td>
</tr>
</tbody>
</table>

Unknown phase crystallized in the hotter end of the reaction vessel accompanying TaSe₂ and TaSe₃ at all starting compositions. The products in the colder end are TaSe₃ at the starting composition Se/Ta=3, the unknown phase X at Se/Ta=4 and a mixture of the
unknown phase X with selenium at Se/Ta=5. Thus the compositional ratio can be estimated as Se/Ta=4 for the phase X. Then the starting mixture of Se/Ta=4 was reacted with various amount of iodine. The reaction temperature was lowered to the temperature gradient of 560°C/460°C to avoid the formation of TaSe₂. The phase X crystallized with iodine at the colder end and a small amount of TaSe₃ was obtained at the hotter end. With the increase of I/Ta ratio in starting composition from 0.3 to 0.9, the amount of phase X increased and that of TaSe₃ decreased in the product. Monophase of the unknown compound was obtained by heating the starting mixture having ratio Ta:Se:I=1:4:1 in a temperature gradient of 460°C/420°C for 1 week. Excess iodine was removed by washing with acetone. Black single crystals having metallic luster were obtained in columnar shape having maximum dimensions of 0.5 x 0.5 x 3 mm.

Characterization

X-ray diffraction data in Table 2 can be indexed as tetragonal having lattice parameters a=9.555Å, c=12.75Å. Chemical composition was determined as I₀.₅TaSe₄ by fluorescent X-ray spectroscopy using an equimolar mixture of TaSe₂ and KI as standard. The observed density was 5.99 g/cm³ and Z=8. Figure 1 shows the result of thermal analysis. I₀.₅TaSe₄ is gradually oxidized above 230°C and a big exotherm and 60% weight loss were observed at 400°C. Further weight loss was not detected below 1000°C. The sample heated up to 1000°C was Ta₂O₅. Thus the iodine is not simply included as molecular iodine but tightly bound in the compound as selenium. The observed weight loss agrees well with the value expected for the oxidation of I₀.₅TaSe₄ to Ta₂O₅. Electrical resistivity was measured in a temperature range of -80°C to room temperature. It is 1.9 x 10⁻³ Ωcm at room temperature. The compound is a diamagnetic semiconductor with activation energy E₉=0.06 eV, χ₉=-1.7 x 10⁻⁷ emu/g at room temperature and χ₉= -1.7 x 10⁻⁸ emu/g at 77K.

X-ray photoelectron spectra of Ta(4f) and Se(3d) are shown in Figs. 2 and 3. I₀.₅TaSe₄ is compared with Ta₂O₅, TaSe₂ and TaSe₃. The binding energies of 4f⁷/₂ and 4f⁵/₂ are 26.2 eV and 27.8 eV in Ta₂O₅. They are 22.5 eV and 24.5 eV in TaSe₂, and 23.2 eV and 25.0 eV in TaSe₃. A pair of sharp peaks are observed around 23 eV and 25 eV in I₀.₅TaSe₄. The values correspond to those of TaSe₂.
Table 2. X-ray diffraction data for $I_{0.5}$TaSe$_4$

<table>
<thead>
<tr>
<th>$d_{obs.}$</th>
<th>$d_{calc.}$</th>
<th>hkl</th>
<th>$I/I_0$</th>
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<tr>
<td>6.758</td>
<td>6.757</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>4.7780</td>
<td>4.7776</td>
<td>200</td>
<td>59</td>
</tr>
<tr>
<td>4.0566</td>
<td>4.0517</td>
<td>211</td>
<td>18</td>
</tr>
<tr>
<td>3.9002</td>
<td>3.8831</td>
<td>103</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3.3785</td>
<td>3.3783</td>
<td>220</td>
<td>12</td>
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<tr>
<td>3.0129</td>
<td>3.0133</td>
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<td>2.7336</td>
<td>2.7304</td>
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<tr>
<td>2.5938</td>
<td>2.5947</td>
<td>321</td>
<td>6</td>
</tr>
<tr>
<td>2.3891</td>
<td>2.3888</td>
<td>400</td>
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<tr>
<td>2.3220</td>
<td>2.3184</td>
<td>224</td>
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</tr>
<tr>
<td>2.2786</td>
<td>2.2801</td>
<td>411</td>
<td>5</td>
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<td>2.2513</td>
<td>2.2522</td>
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<tr>
<td>2.1961</td>
<td>2.1929</td>
<td>314</td>
<td>15</td>
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<tr>
<td>2.1366</td>
<td>2.1366</td>
<td>420</td>
<td>48</td>
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<tr>
<td>2.0251</td>
<td>2.0259</td>
<td>422</td>
<td>9</td>
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<tr>
<td>1.8898</td>
<td>1.8899</td>
<td>501</td>
<td>2</td>
</tr>
<tr>
<td>1.8733</td>
<td>1.8739</td>
<td>510</td>
<td>12</td>
</tr>
<tr>
<td>1.7570</td>
<td>1.7585</td>
<td>521</td>
<td>5</td>
</tr>
<tr>
<td>1.6879</td>
<td>1.6880</td>
<td>440</td>
<td>5</td>
</tr>
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Fig. 1. TG-DTA curves for $I_{0.5}$TaSe$_4$
Fig. 2. X-ray photoelectron spectra of Ta(4f) and Te(3d) suggesting the presence of Ta\(^{4+}\). Another pair of broad peaks are around 26 eV and 28 eV, which agree well with those of Ta_2O_5. Thus there are two kinds of tantalum in I_{0.5}TaSe_4, formally tetravalent and pentavalent. TaSe_2 has divalent Se and its binding energy of 3d level is 54.2 eV. TaSe_3 has both Se\(^{2-}\) and (Se-Se)\(^{2-}\) (2). It shows an asymmetric peak around 54.2 eV due to the coexistence of two kinds of selenium. The binding energy of 3d electron in (Se-Se)\(^{2-}\) can be expected as ca. 55 eV from the spectrum of TaSe_3. Rijnsdorp showed the spectra having intensity maximum around 54.6 eV for (Se-Se)\(^{2-}\) in NbSe_2Cl_2 and Nb_3Se_9Cl (8). The spectrum of I_{0.5}TaSe_4 has a peak around 55 eV so that the selenium in the compound is probably dimeric and monovalent.
Crystal structure

The systematic extinctions (hkl absent for h+k+l odd) indicate that the space group belongs to I4/mmm, I422, I4mm, I4m2 or I42m. Space group I4/mmm seemed unlikely because the discrepancy factor R was 0.30 even at the end of the anisotropic refinement. Space group I422 was adopted with all atoms in the sites shown in Table 3. Atomic parameters were derived from a Patterson synthesis and refined by a full-matrix least-squares method. The atomic scattering factors were taken from Cromer and Waber (9). At the end of the anisotropic refinement the discrepancy factor R was 0.068 for space group I422. Positional and thermal parameters are summarized in Table 3.

The distance between Se(1) and Se(2) is 2.42 Å as shown in Table 4 expecting the Se covalent radius of 1.16 Å (10). The Se atoms form Se$_2^{2-}$ units and the Ta atoms are coordinated with four Se$_2^{2-}$ as shown in Fig. 4. The shared quadrilateral faces of Ta(Se$_2$)$_4$ unit rotate by 45° each other as depicted in Fig. 5. The I atoms are located between the TaSe$_4$ chains. To simplify the picture, there are no distinctions between Ta(1) and Ta(2) and also between Se(1) and Se(2) in Fig. 5. Fig. 6 illustrates these site differences. The distance between the I atom and the Se(2)
Table 4. Bonding distances (Å) in $I_{0.5}TaSe_4$

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Distance (Å)</th>
</tr>
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<tbody>
<tr>
<td>Ta(1) - Ta(2)</td>
<td>3.188</td>
</tr>
<tr>
<td>Se(1) - Se(1)</td>
<td>3.490</td>
</tr>
<tr>
<td>Se(1) - Se(2)</td>
<td>2.420</td>
</tr>
<tr>
<td>Ta(1) - Se(1)</td>
<td>2.707</td>
</tr>
<tr>
<td>Ta(1) - Se(2)</td>
<td>2.622</td>
</tr>
<tr>
<td>Ta(2) - Se(1)</td>
<td>2.593</td>
</tr>
<tr>
<td>Ta(2) - Se(2)</td>
<td>2.734</td>
</tr>
<tr>
<td>Se(1) - I</td>
<td>4.814</td>
</tr>
<tr>
<td>Se(2) - I</td>
<td>3.239</td>
</tr>
</tbody>
</table>

Fig. 4
Stereoscopic view of $I_{0.5}TaSe_4$. The numbers in the figure respectively, 1:I, 2:Ta(1), 3:Ta(2), 4:Se(1), 5:Se(2).

is 3.24 Å. It is much shorter than the sum of Van der Waals radii of iodine (2.15 Å) and selenium (2.00 Å). A comparable distance, 3.78 Å, is observed between the iodine and the selenium in trimethyl selenonium iodine, $(CH_3)_3SeI$ (11). The compound was assumed as a charge transfer complex, with the iodine ion acting as a donor, and the selenonium ion as acceptor. Much shorter bonding distances of about 2.8 Å are observed on several molecular complexes such as $C_4H_8Se_2IZ_2$ (12). Weak interaction can be expected between the I
Fig. 5. Crystal structure of $I_0.5TaSe_4$ projected on the $xy$ plane

atom and the Se(2) atom in $I_0.5TaSe_4$. The distance between the Ta(1) and the Se(2) atoms is 2.62Å. It is comparable to the Ta-Se distances within the TaSe$_6$ trigonal prism, 2.60-2.65Å, suggesting the relatively strong bonding (2). Thus the Ta(1) atom can be expected to donate its electron to the Se(2) atom through the I atom so that it might be Ta$^{5+}$. On the other hand, the distance between the Ta(2) and the Se(2) is 2.73Å. It corresponds to the distance between Ta and its next nearest neighboring Se belonging to the neighboring TaSe$_6$ units. Thus the interaction between Ta(2) and Se(2) is not so strong. The Ta(2) atom is strongly bound to Se(1) and their bonding distance is 2.59Å.
However, the distance between Se(1) and I is 4.81Å. It is too long for Se(1) and I atoms to make bonding. Thus the Ta(2) atom is tetravalent-like. The Ta(1) and the Ta(2) are alternatively on the TaSe₄ chain and (5d)¹ electrons localize on the Ta(2) atoms. Fig. 7 shows the way how TaSe₄ chains are bonded each other by the charge transfer from the Ta(1) atoms to the I atom through the Se(2) atom. Thus the Ta(1) atoms interact each other in xy planes at level z=0 and at z=0.5 through the bonds to Se(2) and I.

Fig. 7
Cross section of the structure for I₀.₅TaSe₄ at z=0.125

Preparation and crystal structure of niobium analogue, I₀.₃NbSe₄, were reported (7). The compound is formed by the NbSe₄ chains connected each other by charge transfer bond to the interchain iodine. The length of unit cell along c axis is about one and a half times as long as that of I₀.₅TaSe₄. Two kinds of niobium can be distinguishable in the NbSe₄ chains. (4d)¹ electrons localize on Nb⁴⁺. Tetravalent and pentavalent niobiums are in a sequence of Nb⁵⁺ Nb⁴⁺ Nb⁴⁺ Nb⁵⁺ Nb⁴⁺ Nb⁴⁺ Nb⁵⁺. The distance is
3.25 Å between Nb⁴⁺ and Nb⁵⁺. Weak interaction was assumed to be existed between (4d)¹ electrons on Nb⁴⁺ atoms. Such interaction can not be expected in I₂TaSe₄. A careful measurement of magnetic susceptibility showed a weak temperature dependence due to the resulting localizing (5d)¹ electrons on Ta⁴⁺.

In summary, the new compound I₂TaSe₄ was obtained by heating the starting mixture having a compositional ratio of Ta:Se:I=1:4:1 in 460°C/420°C temperature gradient for 1 week. The crystal structure is composed of the infinite chains of TaSe₄ along c-axis. Iodine is located between the chains. Weak charge transfer interaction is observed between the I atoms and the Se atoms. (5d)¹ electrons localize on Ta⁴⁺ in the infinite TaSe₄ chains.

Acknowledgment

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References


* Dr. A. Meershaut informed us on this meeting that he has published the crystal structure of TaSe$_5$ on Acta Cryst. B38, 2877 (1982). He kindly allowed to publish our paper in this proceeding because it contains some chemical merits.