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Synthesis of new compounds of the pseudo-ternary system $SrO–Bi_2O_3–TeO_2$ in air

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The phase equilibria of the pseudo-ternary system $SrO–Bi_2O_3–TeO_2$ at 600° to 850° C were examined in air by solid-state reaction techniques and X-ray powder diffraction. Three pseudo-ternary compounds were found: a hexagonal solid solution $Bi_2O_3 \cdot 2x SrO \cdot 5x TeO_2$ ($x = 0.02$ to 0.20, $a = 0.394(1)$ to $0.399(5)$, $c = 1.89(6)$ to $1.86(7)$ nm), a rhombohedral phase $Bi_4Sr_3Te_5O_{19}$ ($a = 0.405(2)$, $c = 2.71(5)$ nm in hexagonal terms) and a cubic phase Bi_2SrTeO_7 ($a = 1.086(9)$ nm). The Mössbauer spectra of ^{125}Te in the compounds indicated that the tellurium atoms were mostly in the state of Te^{+4} in the former two compounds but were exclusively Te^{+6} in Bi_2SrTeO_7. The electrical conductivity of the first two were about $10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 600° C. However, Bi_2SrTeO_7 was an electrical insulator.

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1. Introduction

As is well known, bismuth-based mixed oxides exhibit excellent ion conduction at comparatively low temperatures. These compounds are classified into two structures, an oxygen deficient fluorite structure which is formed as δ-Bi_2O_3 type solid solutions with some metal oxides such as Ln_2O_3, TeO_2, Ta_2O_5, WO_3 [1–10] and the rhombohedral phases $Bi_{1-x}M_xO_{(3-x)/2}$ (M = Ca, Sr, Ba) [11–14].

The compounds previously reported are limited within binary phases. In the present study, phase research was carried out on the pseudo-ternary system $SrO–Bi_2O_3–TeO_2$. The phase diagram of the $SrO–Bi_2O_3$ system rich in Bi_2O_3 was studied by Levin and Roth [15]. They reported a rhombohedral solid solution which corresponds to the above-mentioned rhombohedral phase $Bi_{1-x}Sr_xO_{(3-x)/2}$. The phase diagram of the system $Bi_2O_3–TeO_2$ rich in Bi_2O_3 was also reported by them. The compounds of the whole system were reported by other investigations [16–19]. A δ-Bi_2O_3 type solid solution exists up to $x = 0.4$ of $(1 - x)Bi_2O_3 \cdot xTeO_2$ in air [19]. However, the phases in this system depend on the oxygen partial pressure (P_{O_2}). Recently, a new compound $Bi_6Te_2O_{15}$, in which all the tellurium atoms were hexavalent, was synthesized in air at temperatures lower than 830° C [19]. This indicates that the existence of Te^{+6} ions in the compounds synthesized in air from the oxides SrO, Bi_2O_3 and TeO_2 is highly possible.

2. Experimental procedure

About 60 polycrystalline specimens of compositions within the $SrO–Bi_2O_3–TeO_2$ system were prepared by solid–solid reactions. The starting materials, $SrCO_3$, Bi_2O_3 and TeO_2, each 99.9% pure, were weighed in the desired proportions and mixed in an agate mortar under ethanol. After drying, the mixtures were heated in a covered platinum crucible in a range from 600° to 850° C for 24 h in air and then cooled rapidly to room temperature. The specimens were examined by X-ray powder diffraction (XRPD) using a conventional diffractometer with Ni-filtered Cu*K*α radiation. When reactions were not complete, the specimen was powdered and reheated at the same or higher temperatures. The final products were in phase equilibrium.

The Mössbauer spectra of ^{125}Te in the pseudo-ternary phases were measured for transmission geometry by cooling a Mössbauer source and each absorber sample at 16 K in a closed cycle helium refrigerator. $Cu^{125}I$ was used as the Mössbauer source for ^{125}Te. The isomer shift of the source was determined to be $-0.13\,mm\,sec^{-1}$ relative to the ZnTe standard absorber [20]. The 35.5 keV Mössbauer γ-ray was detected indirectly by counting the 5.8 keV escaped peak in a $Xe–CO_2$ proportional counter. The ratios of Te^{+6}/Te^{+4} in the samples was estimated by comparing the observed values of the isomer shift with the data reported for α-TeO_2, β-TeO_3 and Ca_3TeO_6 [20–22].

The d.c. conductivity of the compounds in air was measured at equilibrium (i.e. the final constant value conductivity for a set temperature) using a four-probe method.

3. Results and discussion

Compounds stable at 840° C are shown in Fig. 1.

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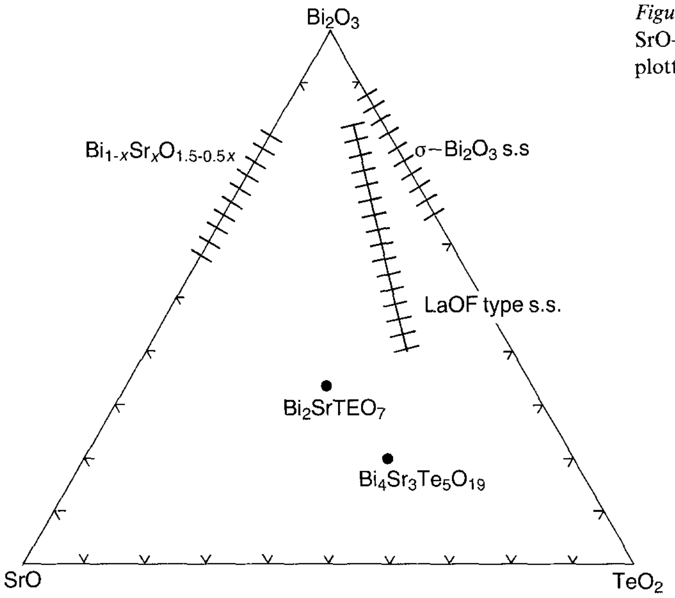

Figure 1 Compounds stable at 840° C in the pseudo-ternary system SrO–Bi_2O_3–TeO_2 in air. The two binary phases reported are also plotted in the diagram.

Incompatible phase relations were not determined since there were some difficulties in identifying phases rich in SrO.

3.1. Hexagonal solid solution

A hexagonal solid solution exists in compositions of $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ (where $x = 0.02$–0.20) at 840° C. XRPD patterns of the phase were indexed by a hexagonal cell with $a = 0.3941$ to 0.3995 ± 0.0002 nm, $c = 1.896$ to 1.867 ± 0.001 nm. For $x < 0.04$, however, possible reflections are limited in the case $-h + k + l = 3n$ ($n = 0, 1, 2, \ldots$ etc.) which is characteristic of a rhombohedral cell. Whereas for $x > 0.04$, weak reflections in the case $0\,0\,l$ ($l \neq 3n$) were detected. The structure of the phase may be isostructural with the rhombohedral form of LaOF which has a superstructure of fluorite [23]; the ions in LaOF are arranged with three-fold symmetry around only one body diagonal of the fluorite cell. The XRPD data of the solid solution are listed in Table I. Variations of the lattice parameters, a and c, and cell volumes, v, with x of $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ are shown in Fig. 2 . The length of the a axis and the cell volume increased with an increase in x, wheras the value c decreased with increasing x. An anomaly in the values a and c was observed at around $x = 0.05$. Such an anomaly has been found in "defect substitutional solid solutions" [24, 25]. In fact, the solid solution seems to consist of oxygen-deficient LaOF-type cells.

The ^{125}Te Mössbauer spectra of the phase $Bi_2O_3 \cdot 0.38SrO \cdot 0.95TeO_2$ (i.e. $x = 0.19$) showed a quadrupole doublet with a small isomer shift (+0.59 mm sec^{-1}) as shown in Fig. 3a. The result indicates that the tellurium atoms exist predominantly as Te^{+4} with a small amount of Te^{+6}; the existence of Te^{+6} is estimated from the unsymmetrical shape of the spectrum. When this sample ($x = 0.19$) was kept at 800° C for 24 h it decomposed to unknown phases, indicating that the phase is not stable at lower temperatures.

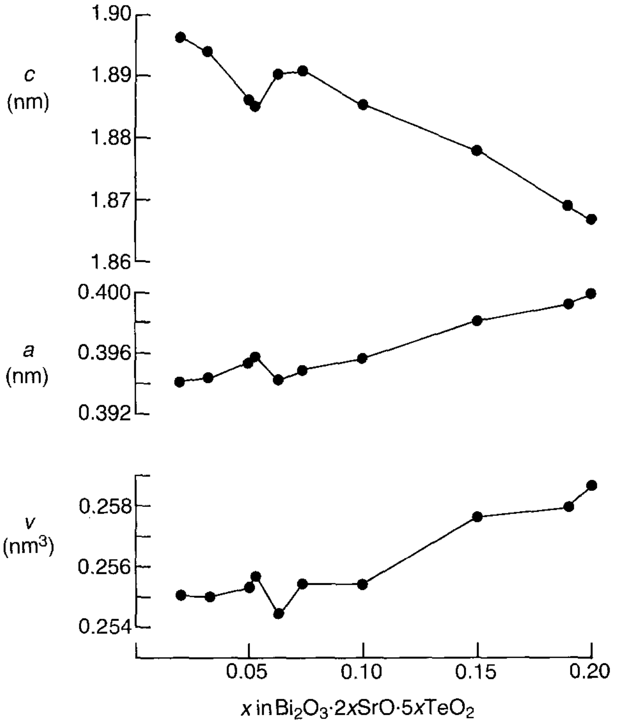

Figure 2 Variation of lattice parameters and cell volumes with x in $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ hexagonal solid solution.

TABLE I XRPD data for the hexagonal phase $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ (Cu$K\alpha$)

$x = 0.07$		$x = 0.15$		hkl
d (nm)	I/I_0	d (nm)	I/I_0	
0.95	< 1	0.938	1	0 0 2*
0.473	1	0.468	3	0 0 4*
0.321	100	0.323	100	0 1 2
0.316	31	0.313	30	0 0 6
0.2770	43	0.2777	72	1 0 4
0.1973	13	0.1988	24	1 1 0
0.1946	14	0.1938	36	0 1 8
–		0.1875	2	0 0 10*
0.1682	9	0.1696	12	2 0 2
0.1672	17	0.1680	23	1 1 6
0.1657	7	0.1648	14	1 0 10
0.1607	6	0.1619	6	0 2 4
0.1576	7	0.1563	4	0 0 12
0.1386	2	0.1390	4	2 0 8

*These reflections are not in the case $-h + k + l = 3n$.

TABLE II XRPD data for the rhombohedral phase $Bi_4Sr_3Te_5O_{19}$ (Cu*Kα*)

d (nm)	I/I_0	*h k l*
0.459	17	0 0 6
0.348	9	1 0 1
0.340	11	0 1 2
0.313	100	1 0 4
0.306	80	0 0 9
0.2962	20	0 1 5
0.2621	2	1 0 7
0.2459	5	0 1 8
0.2169	2	1 0 10
0.2042	3	0 1 11
0.2026	12	1 1 0
0.1839	1	0 0 15
0.1717	5	0 1 14
0.1702	3	0 2 4
0.1691	10	1 1 9
0.1673	2	2 0 5
0.1533	3	0 0 18
0.1473	1	0 1 17

3.2. The phase $Bi_4Si_3Te_5O_{19}$

A discrete compound $Bi_4Sr_3Te_5O_{19}$ was obtained at 850° C and had a rhombohedral cell with $a = 0.4052 \pm 0.0002$, $c = 2.751 \pm 0.001$ nm in terms of a hexagonal cell. The XRPD data indicated that the compound is isostructural with the above-mentioned compound $Bi_{1-x}M_xO_{1.5-x/2}$ (M = Ca, Sr, Ba) which is in the space group $R\bar{3}$ m. The XRPD data are listed in Table II . This specimen when kept at 790° C for 24 h changed to unknown phases, indicating that this phase is also not stable at lower temperatures. The solid solution along the boundary $Bi_{1-x}Sr_xO_{1.5-x/2}$ and $Bi_4Sr_3Te_5O_{19}$ were not observed.

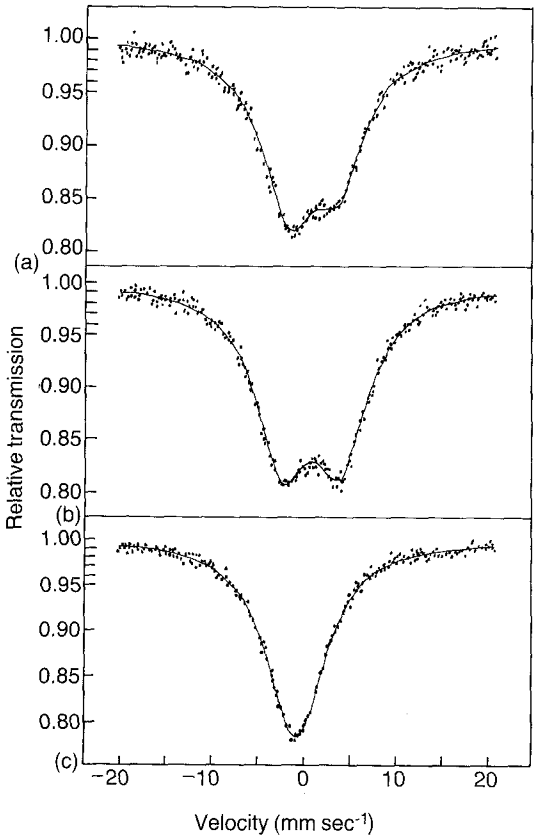

Figure 3 ^{125}Te Mössbauer spectra of $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ (a), $Bi_4Sr_3Te_5O_{19}$ (b) and Bi_2SrTeO_7 (c) with Cu ^{125}I source at 16 K.

TABLE III XRPD data for the cubic phase Bi_2SrTeO_7 (Cu*Kα*)

d (nm)	I/I_0	*h k l*
0.488	8	2 1 0
0.445	3	2 1 1
0.363	1	2 2 1, 3 0 0
0.314	100	2 2 2
0.302	4	3 2 0
0.2913	1	3 2 1
0.2723	43	4 0 0
0.2641	2	3 2 2, 4 1 0
0.2568	2	3 3 0, 4 1 1
0.2436	2	4 2 0
0.2378	8	4 2 1
0.2324	4	3 3 2
0.2137	6	4 3 1, 5 1 0
0.2025	3	4 3 2, 5 2 0
0.1989	1	5 2 1
0.1926	42	4 4 0
0.1791	3	6 1 0
0.1768	3	5 3 1, 6 1 1
0.1702	1	4 4 3, 5 4 0, 6 2 1
0.1681	3	5 4 1
0.1643	32	6 2 2
0.1624	6	2 5 4, 6 3 0
0.1607	4	6 3 1
0.1573	11	4 4 4
0.1557	2	6 3 2, 7 0 0
0.1497	3	6 4 1, 7 2 0
0.1483	2	5 5 2, 6 3 3, 7 2 1
0.1444	1	5 4 4, 7 2 2
0.1395	3	6 4 3, 6 5 0
0.1385	1	6 5 1, 7 3 2
0.1362	3	8 0 0

The ^{125}Te Mössbauer spectra of this phase showed a quadruple splitting as shown in Fig. 3b. The result indicates that the tellurium atoms predominantly exist as Te^{+4}.

3.3. The phase Bi_2SrTeO_7

This compound was formed at temperatures below 900° C. The reflections of XRPD corresponded mostly to those of a fluorite except for some weak reflections. Indexing of the XRPD data was possible with a cubic lattice corresponding to a double *a*-axis of a fluorite cell, $a = 1.0896 \pm 0.0001$ nm. The XRPD data are listed in Table III.

The ^{125}Te Mössbauer spectra of the phase consist of a single peak with a little shift (-1.04 mm sec^{-1}) as shown in Fig. 3c. The result strongly suggests that the tellurium atoms in the phase exist as Te^{6+}, because the observed values of the isomer shift are close to those for β-TeO_3 (-1.11 mm sec^{-1}) and a Ca_3TeO_6 (-1.06 mm sec^{-1}).

3.4. Electrical conductivity measurement

The electrical conductivity of the solid solution $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ ($x = 0.02$–0.20) and of the phase $Bi_4Sr_3Te_5O_{19}$ were measured at temperatures between 200 and 600° C in air. The results are shown in Fig. 4. There is a trend to a decrease of conductivity with increasing x in the phase $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$. The conductivity of the phase $Bi_4Sr_3Te_5O_{19}$ were comparably high, though the content of Bi_2O_3 in this phase is rather low. The change of the slope observed at about 350° C seems to

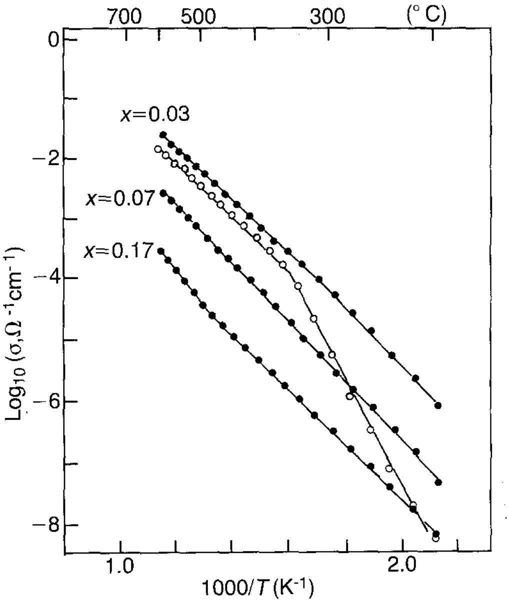

Figure 4 Conductivity of $Bi_2O_3 \cdot 2xSrO \cdot 5xTeO_2$ (●) for various x and of $Bi_4Sr_3Te_5O_{19}$ (○) in air.

be due to a phase transition as found in $Bi_{1-x}Sr_xO_{1.5-x/2}$ [12]. The phase Bi_2SrTeO_2 was an electrical insulator and therefore could not be measured.

In the present study, the attempt to find phases, which are thermodynamically stable at comparatively low temperatures and exhibit high oxide ion conduction, was not successful.

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