

On the crystallochemistry of the binary BiSr_3O_x phase

R. Horyń, M. Wołczyr and R. Andruszkiewicz

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 937, 50-950 Wrocław (Poland)

(Received July 27, 1992)

Abstract

Phase relations prevalent at 850 °C in the Bi_2O_3 – SrO system ($1.5 \leq \text{Sr}:\text{Bi} \leq 5.5$) in air have been reinvestigated in order to clarify the chemical nature of the BiSr_3O_x phase. On the basis of analytical determinations of the average valence of bismuth in samples tested and their densities, it has been found that BiSr_3O_x is a compound which originates from the Bi_2O_5 – SrO system (full chemical formula $\text{BiSr}_3\text{O}_{5.5}$) and is not a real constituent of the binary system with Bi^{3+} . Investigation of the latter under free oxygen access results in unintentional penetration of part of the Bi_2O_3 – SrO – Bi_2O_5 ternary system in which mutual relations between appropriate phases of both Bi binary systems are present and can be identified as three- or two-phase regions of coexistence (e.g. $\text{Bi}^{5+}\text{Sr}_3\text{O}_{5.5} + \text{Bi}^{3+}\text{Sr}_3\text{O}_6$), misleadingly considered until now to occur in the pure Bi_2O_3 – SrO system. The identity of the crystal structures of $\text{BiSr}_3\text{O}_{5.5}$ and $\text{BiNdSr}_2\text{O}_6$ has not been confirmed.

1. Introduction

The binary Bi_2O_3 – SrO system is known to contain at least six phases [1]. Most of them are compounds of fixed composition: Bi_2SrO_4 , $\text{Bi}_3\text{Sr}_4\text{O}_9$ [2], $\text{Bi}_2\text{Sr}_2\text{O}_5$ and $\text{Bi}_2\text{Sr}_3\text{O}_6$. The exception is a rhombohedral phase of maximum bismuth content which has features of a solid solution with a centre near 80 at.% $\text{BiO}_{1.5}$.

There are many controversies concerning the last compound in the system, namely BiSr_3O_x . Until the papers of Abbattista *et al.* [3] and Conflant *et al.* [4], the results of Ikeda *et al.* [5] were commonly and uncritically accepted, especially those concerning the chemical composition, symmetry and lattice parameters of the phase. The investigations of Abbattista *et al.* and Conflant *et al.* have shown that BiSr_3O_x is a phase of very complex crystallographic constitution whose full understanding demands a lot of further work.

Our current interest in the BiSr_3O_x phase results from earlier personal involvement in investigations of phase relations in the Bi_2O_3 – SrO – CuO ternary system. In ref. 2 we described BiSr_3O_x as a solid solution of variable composition (phase x) with a wide range of existence. It is noteworthy that, according to refs. 3 and 4, the BiSr_3O_x phase is formed only at an Sr:Bi ratio equal to 3, and its wider range of existence might possibly be connected with variation in the global oxygen contribution to the structure.

There are also other reasons for our interest in the BiSr_3O_x phase.

(1) There is controversy concerning the problem of the assignment of BiSr_3O_x to the appropriate phase system. Roth *et al.* [1] locate this phase in the Bi_2O_3 – SrO system, whereas Abbattista *et al.* [3] and Conflant *et al.* [4] are of the opinion that its matrix system is Bi_2O_5 – SrO with a global oxygen index equal to 5.5.

(2) There is controversy concerning the basic crystallographic data of BiSr_3O_x . The only unquestionable fact is that the structure is perovskite related. According to Ikeda *et al.* [5], BiSr_3O_x is orthorhombic with lattice parameters $a = 17.147 \text{ \AA}$, $b = 16.758 \text{ \AA}$ and $c = 16.998 \text{ \AA}$. Roth *et al.* [1] propose a rhombohedral unit cell with $a = 6.009 \text{ \AA}$ and $c = 58.633 \text{ \AA}$ (in a hexagonal setting), with possible duplication of the a parameter. Abbattista *et al.* [3] and Conflant *et al.* [4] indicate tetragonal symmetry with lattice parameters $a = 16.993 \text{ \AA}$, $c = 16.648 \text{ \AA}$ and $a = 8.615 \text{ \AA}$, $c = 16.760 \text{ \AA}$ respectively.

(3) Lenz and Müller-Buschbaum [6] report crystallographic data on $\text{BiNdSr}_2\text{O}_6$ (monoclinic unit cell, $a = 5.95 \text{ \AA}$, $b = 6.10 \text{ \AA}$, $c = 8.49 \text{ \AA}$, $\beta = 90.19^\circ$) with a structure closely related to the large family of $\text{BiSr}_2\text{REO}_6$ compositions (RE=rare earth) described in ref. 7. Independently of Lenz and Müller-Buschbaum, we have found this phase in our recent investigations of the Bi_2O_3 – SrO – Nd_2O_3 ternary system. Therefore, we hypothesize that the binary compound discussed here constitutes a matrix for $\text{BiNdSr}_2\text{O}_6$. The very close localization of both these phases in the Bi_2O_3 – SrO – Nd_2O_3 phase diagram and the very high

degree of similarity between their powder diagrams form the basis for such a suggestion.

2. Experimental details

Samples were prepared from Bi_2O_3 and SrCO_3 , each of purity 99.95%. The substrates were mixed (in an agate mortar) in suitable proportions to cover the range of Sr:Bi ratios from 1.5 to 5.5. The pellets obtained (each about 3 g) were fired in air according to the following procedure: 800 °C for 24 h, grinding and re-pelletizing, 900 °C for 48 h, grinding and final homogenization of the powders at 850 °C for 3 days. In all these operations, corundum boats and crucibles were used as containers for the samples. Phase identification was carried out using X-ray powder diffraction (DRON-3, Stoe and Siemens D5000 diffractometers, Cu $K\alpha$ radiation). For each sample the average valence of Bi was determined by the classical iodometric method, while the resultant sample densities were measured by the pycnometric method with CCl_4 as the immersion liquid.

Samples with Sr:Bi > 3 were protected in a desiccator against moisture and CO_2 , but this was not the case for samples subjected to X-ray diffraction. X-ray powder diagrams were taken in air without any protection against the influence of agents destroying SrO.

3. Results and discussion

The phase relations for the series of investigated samples are shown in Fig. 1. It is clearly seen that in the composition range $1.5 \leq \text{Sr:Bi} < 3$ (Figs. 1(a)–1(d)) and with free oxygen access, the substrates form two coexisting phases. According to refs. 3 and 4, the stoichiometries of the boundary compositions are represented by the formulae $\text{Bi}_2\text{Sr}_3\text{O}_6$ and BiSr_3O_x . A somewhat different situation exists in the range $\text{Sr:Bi} \geq 3$ (Figs. 1(e)–1(h)). The absence of the diffraction lines of SrO for all samples in this range may indicate the formation of a solid solution of $\text{Bi}_{1-\Delta}\text{Sr}_{3+\Delta}\text{O}_x$ type as we have suggested in earlier work [2]. The presence of some additional, very weak lines accompanying the main phase (quite new for us at that time) does not necessarily negate this conclusion. However, accepting the last results concerning this region of the Bi–Sr–O system mentioned in Section 1, we have verified our standpoint and performed a more detailed analysis of these additional diffraction lines. We have identified these lines as belonging to $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$, which occurs in the samples as a result of a secondary reaction of SrO with water vapour taking place in the powder material chosen for the X-ray analysis (Fig. 1(h)).

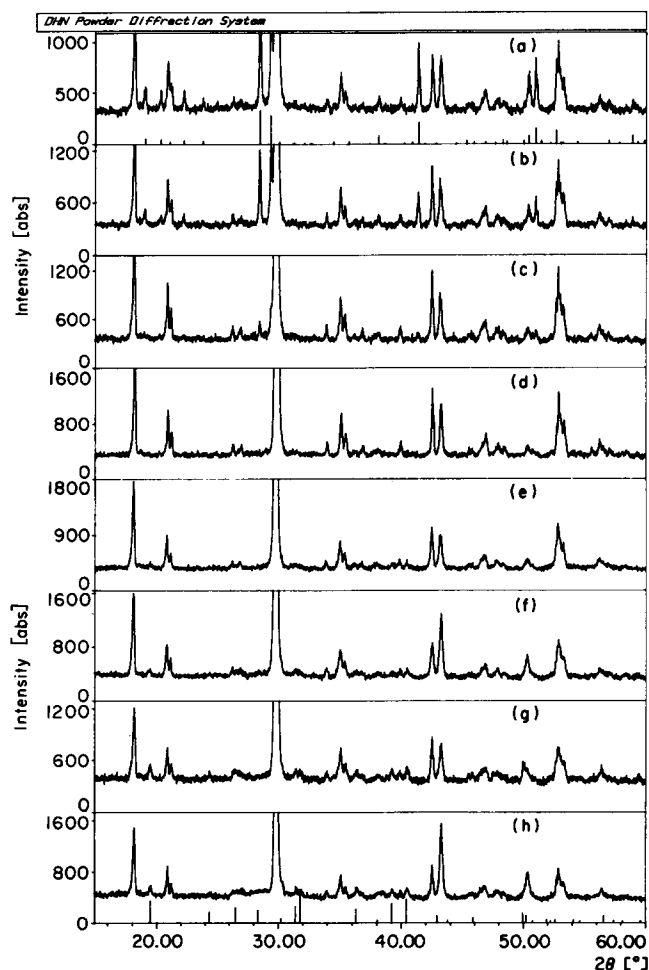


Fig. 1. X-ray powder diffraction diagrams for selected samples from Bi–Sr–O system with Sr:Bi ratio equal to (a) 2.25, (b) 2.5, (c) 2.75, (d) 3.0, (e) 3.5, (f) 4.0, (g) 5.0 and (h) 5.5. For comparison, (a) contains a stick diagram of $\text{Bi}_2\text{Sr}_3\text{O}_6$ and (h) a stick diagram of $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$.

Concerning the average valence of Bi in BiSr_3O_x , we have found that it reaches the value 5+. Consequently, and in agreement with refs. 3 and 4, the full composition of the phase can be expressed as $\text{BiSr}_3\text{O}_{5.5}$. This is based on the results of Bi valence determination performed on samples from the two-phase region of $\text{Bi}_2\text{Sr}_3\text{O}_6$ and BiSr_3O_x coexistence (Fig. 2) as well as on the results of similar determinations for samples with $\text{Sr:Bi} \geq 3$. It is worth mentioning that the solid line of the resultant valence drawn for the $\text{Bi}_2\text{Sr}_3\text{O}_6 + \text{BiSr}_3\text{O}_{5.5}$ range is not a fitted line of experimental data but represents the calculated values, *i.e.* those obtained analytically from the formula holding in this range of compositions, namely

$$\bar{V}_{\text{Bi}} = 3(1-x) + 5x$$

where x is the molar contribution of the $\text{BiSr}_3\text{O}_{5.5}$ phase in the samples of the above two-phase region, with the assumption that for $\text{Bi}_2\text{Sr}_3\text{O}_6$ the bismuth valence is

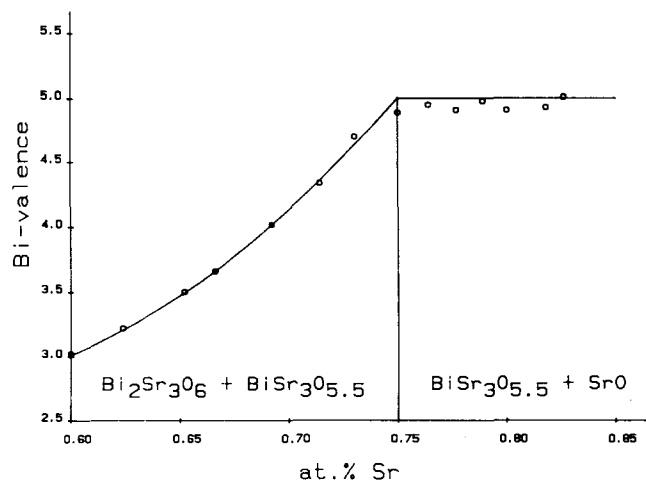


Fig. 2. Plot of bismuth valence *vs.* atomic percentage of Sr for samples from Bi-Sr-O system: circles, experimental data; solid line, calculated values.

3+. Thus for a given Sr:Bi ratio (*n*) the above relation transforms to

$$\text{BiSr}_n = (1-x)\text{BiSr}_{1.5} + x\text{BiSr}_3$$

Then

$$x = \frac{n-1.5}{1.5} \quad \text{and} \quad \bar{V}_{\text{Bi}} = \frac{2n+1.5}{1.5}$$

The very good agreement between experimental data (circles in Fig. 2) and calculated values (full numerical data collected in Table 1) leads to the conclusion that we are dealing with a phenomenon of the coexistence of two stable bismuth-oxygen phases, each exhibiting extremely different bismuth valence. In samples from the range of BiSr₃O_{5.5} + SrO coexistence the bismuth valence is constant and close to 5+.

The density measurements performed on all samples and plotted in Fig. 3 (note that samples were protected against the influence of the destructive components of air) give us an additional argument for regarding BiSr₃O_{5.5} phase as a compound of strict stoichiometry 1:3. There is excellent agreement between the sample densities obtained pycnometrically and the densities calculated assuming that the samples consist of the two phases above, each of specific and constant density but of variable weight contribution (see Table 1). The calculations were based on the following analytical formula [8] determining the resultant density of multiphase samples:

$$\frac{100}{d_{\text{av}}} = \frac{\text{wt.}\%(1)}{d_{(1)}} + \frac{\text{wt.}\%(2)}{d_{(2)}}$$

where *d*₍₁₎ and *d*₍₂₎ are the calculated X-ray densities (*d*_x) of the coexisting phases (here Bi₂Sr₃O₆ + BiSr₃O_{5.5} for 1.5 ≤ Sr:Bi ≤ 3 and BiSr₃O_{5.5} + SrO for Sr:Bi ≥ 3). The *d*_x values were calculated for both Bi binary phases

TABLE 1. Comparison of observed and calculated values of average valence of Bi and sample densities for the Bi-Sr-O series with 1.5 ≤ Sr:Bi ≤ 5.5

Global Sr:Bi ratio	Contribution of BiSr ₃ O _x phase		Resultant density (g cm ⁻³)		Global valence of Bi, (\bar{V}_{Bi})	
	Molar (%)	Weight (%)	Calc.	Obs.	Calc.	Obs.
1.5	0.0	0.0	6.217	6.205	3.000	3.034
1.666	11.111	15.266	6.196	–	3.220	3.230
1.875	25.0	32.453	6.173	–	3.500	3.510
2.0	33.333	41.883	6.160	6.124	3.666	3.670
2.25	50.0	59.040	6.137	6.136, 6.142	4.000	4.026
2.5	66.666	74.245	6.117	6.119	4.333	4.347
2.75	83.333	87.815	6.099	6.154	4.666	4.706
3.0	100.0	100.0	6.083	6.075, 6.108	5.000	4.901
3.25	80.0	95.577	6.030	6.038	^a	4.960
3.5	66.666	91.530	5.982	5.951		4.920
3.75	57.143	87.810	5.938	5.914		4.990
4.0	50.0	84.382	5.900	5.849		4.920
4.25	44.444	81.211	5.863	5.801		–
4.5	40.0	78.270	5.830	5.714		4.940
4.75	36.364	75.534	5.800	–		5.020
5.5	28.571	68.366	5.722	5.606		–

^aConstant value close to 5+ independent of mutual contributions of coexisting phases in tested samples.

Note: Density of BiSr₃O_x phase built only with Bi³⁺, i.e. BiSr₃O_{4.5}, would be equal to 5.388 g cm⁻³, whereas alternative model expressed by formula BiSr₃O₆ (a model with complete anionic sublattice and strontium valence increased to 2.333+) would give 6.431 g cm⁻³ – both distinctly different as compared with experimental data.

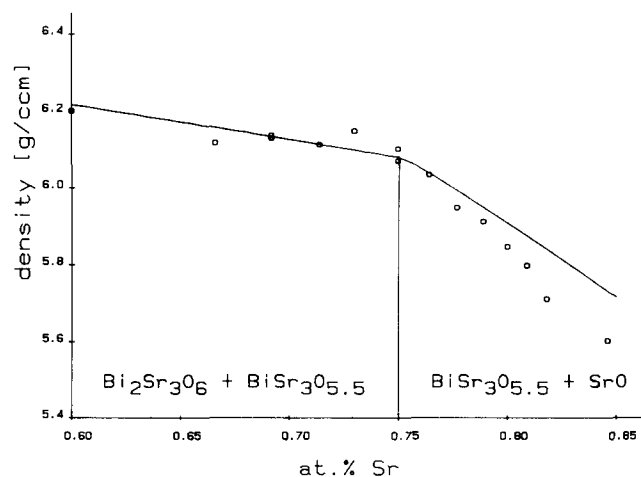


Fig. 3. Plot of resultant density *vs.* atomic percentage of Sr for samples from Bi-Sr-O system: circles, experimental data; solid line, calculated values.

according to the crystallographic data given by Roth *et al.* [1] (see Table 1). The density of SrO (*d*_x = 5.071 g cm⁻³) was calculated from the data of Pearson [9]. A slight deviation of the experimental data from the

calculated ones observed for $\text{Sr}:\text{Bi} > 3$ is probably caused by small amounts of moisture contained in the CCl_4 and reacting with SrO . Another explanation might lie in the crystal structure of SrO , which is known to contain defects (about 6 at.% of vacancies), thus having its molecular weight decreased from 103.6 to 97.4 and its resultant density to about 4.77 g cm^{-3} .

Our supposition on the structural identity of $\text{BiSr}_3\text{O}_{5.5}$ and $\text{BiNdSr}_2\text{O}_6$ [6] has not found confirmation. In spite of the very high degree of similarity between their powder diagrams, the two phases do not form a common solid solution. This is illustrated in Fig. 4, where we compare the powder diagram of a ready-made sample of intermediate composition $\text{BiNd}_{0.5}\text{Sr}_{2.5}\text{O}_{5.75}$ with the powder diagram of an artificial sample prepared as a mechanical mixture of the two phases of the same stoichiometry as the ready-made one.

Summarizing, we can state that, in agreement with Conflant *et al.* [4], the $\text{BiSr}_3\text{O}_{5.5}$ phase should be regarded as an element of the Bi_2O_3 - SrO system. Similarly to the "123"-type phases, $\text{BiSr}_3\text{O}_{5.5}$ exhibits a wide range of existence caused by variations in the global oxygen index in the structure. Depending on the temperature and the partial pressure of oxygen, this phase "partially

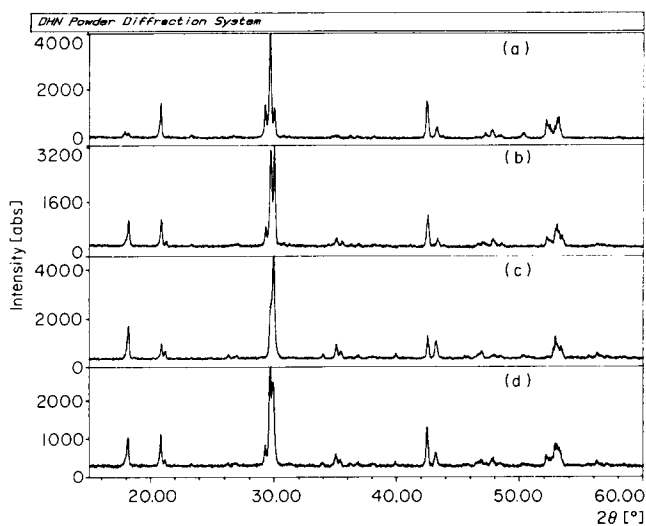


Fig. 4. Comparison of X-ray powder diffraction diagrams of (a) $\text{BiNdSr}_2\text{O}_6$, (b) $\text{BiNd}_{0.5}\text{Sr}_{2.5}\text{O}_{5.75}$, (c) $\text{BiSr}_3\text{O}_{5.5}$ and (d) a mechanical mixture of $\text{BiNdSr}_2\text{O}_6$ and $\text{BiSr}_3\text{O}_{5.5}$ phases of nominal composition $\text{BiNd}_{0.5}\text{Sr}_{2.5}\text{O}_{5.75}$.

penetrates the intersystem space" but never reaches the system with Bi^{3+} . Therefore an investigation of the Bi_2O_3 - SrO system carried out in air requires identification of some phases and compositions existing in part of that intersystem space. This is equivalent to the unintentional investigation of, *de facto*, the real ternary Bi_2O_3 - SrO - Bi_2O_5 system. Generally, the above applies to many two-, three- and multicomponent systems containing CuO and investigated under free oxygen access. Let us take as an example the Bi_2O_3 - SrO - CuO system. In spite of many works on this system [1, 2, 5, 10], the picture of the phase relations is still far from clear. According to us, the picture is complicated mainly by two phases, *i.e.* "232" [2] and "485" [11]. Their behaviour departs significantly from the Gibbs phase rules. These phases, similarly to $\text{BiSr}_3\text{O}_{5.5}$, originate from systems of higher valence of one of their components (in this case copper) disturbing and complicating the picture of the phase relations held in the "pure" Bi_2O_3 - SrO - CuO triangle.

References

- 1 R. S. Roth, C. J. Rawn, B. P. Burton and F. Beech, *J. Res. Natl. Inst. Technol.*, 95 (1990) 291.
- 2 R. Horyń, I. Filatow, J. Ziaja and M. Wołczyr, *Supercond. Sci. Technol.*, 3 (1990) 347.
- 3 F. Abbattista, C. Brisi, D. Mazza and M. Vallino, *Mater. Res. Bull.*, 26 (1991) 107.
- 4 P. Conflant, M. Drache, J. C. Boivin and J. P. Wignacourt, *Proc. EMRS Spring Conf., Strasbourg, 27-31 May, 1991*, *Mater. Res. Bull.*, 26 (1992) 1219.
- 5 Y. Ikeda, H. Ito, S. Shimomura, Y. Oue, K. Inaba, Z. Hiroi and M. Takano, *Physica C*, 159 (1989) 93.
- 6 A. Lenz and Hk. Müller-Buschbaum, *J. Less-common. Met.*, 161 (1990) 141.
- 7 E. T. Shuvaeva and E. G. Fesenko, *Sov. Phys. - Crystallogr.*, 14 (1970) 926.
- 8 R. Horyń, M. Wołczyr and R. Andruszkiewicz, *J. Alloys Comp.*, 184 (1992) L15.
- 9 W. B. Pearson, in G. V. Raynor (ed.), *International Series of Monographs on Metal Physics and Physical Metallurgy*, Vol. 4, *A Handbook of Lattice Spacings and Structure of Metals and Alloys*, Pergamon, Oxford, 1964, p. 243.
- 10 K. Schulze, P. Majewski, B. Hettich and G. Petzow, *Z. Metallk.*, 81 (1990) 836.
- 11 A. Fuertes, C. Miravittles, J. Gonzales-Calbert, M. Vallet-Regi, X. Obradors and J. Rodriguez-Carvajal, *Physica C*, 157 (1989) 525.