

# Synthesis and Crystallochemical Characterization of the $Tb_{1-x}Bi_xSrO_3$ -Type Solid Solution

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Solid solution of the  $Tb_{1-x}Bi_xSrO_3$  type was investigated under oxidizing sintering conditions. The domain of homogeneity was determined to be within the range  $0 \leq x \leq 0.33$ . Variations of lattice parameters as well as sample densities vs. the substitution parameter  $x$  are given. The effective valency of Bi and Tb ions,  $\bar{V}_{(Tb,Bi)}$ , remains invariant and is close to +4 through the whole domain of homogeneity. The present data do not permit the exact variation of valencies of Bi and Tb ions to be separately recognized. However, the solubility limit found directly indicates a nearly +5 valency of Bi ions and a variable valency of Tb ions, the latter decreasing vs.  $x$  to the level of +3.5 characteristic for  $Tb_4O_7$ —the most stable terbium oxide in air. The possibility of a successful synthesis of the hypothetical  $Tb^{+3}Bi^{+5}Sr_2O_6$  is explored. © 1996 Academic Press, Inc.

## INTRODUCTION

There are several reports in literature concerning crystal structure and magnetic properties of  $REMeO_3$ -type binary systems ( $RE = Ce, Pr, Tb; Me = Sr, Ba$ ) (1–6). The compounds crystallize in a rhombohedrally ( $TbBaO_3$ ) or orthorhombically ( $PrBaO_3, CeBaO_3, and TbSrO_3$ ) distorted perovskite structure. Their unit cells contain four molecules of  $REMeO_3$  with  $RE$  and  $Me$  ions distributed within two independent sets of atomic positions (6, 7). A report on the isotypical  $NdBiSr_2O_6$  (8) proves that the structure distortion may be even monoclinic. Our extended studies on the crystallochemistry of the remaining  $RE$  representatives of the  $REBiSr_2O_6$ -type family (9) fully confirm this feature.

In Ref. (9) we have also shown that, in air, the  $REBiSr_2O_6$  ternaries are created only by those  $REs$  whose oxidation state does not exceed +3. In other words, a characteristic feature of the Bi-substituted derivatives of the  $REMeO_3$ -type parent compounds is the coexistence of Bi ions in the +5 and of  $RE$  ions in the +3 oxidation states. As a result, the effective valency  $\bar{V}_{(RE,Bi)} = (\bar{V}_{RE} + \bar{V}_{Bi})/2$  remains equal to +4. This is a reason for which the

$REBiSr_2O_6$  series does not contain tetravalent  $REs$ , such as Ce, Pr, and Tb. These elements form, however, with alkaline-earths stable in air binary oxides  $REMeO_3$  of the same structure type.

The aim of this work was to check on the extent to which tetravalent terbium in  $TbSrO_3$  can be replaced by bismuth along the line between two phases, the  $TbSrO_3$  and the hypothetical  $TbBiSr_2O_6$ , and how this would affect the valencies of the Tb and Bi ions. Our preliminary considerations indicate the possibility that in air one can reach a solubility of ca. 16.67 at% of bismuth, with its valency remaining at a constant level +5, whereas the valency of Tb ions decreases on average from +4 to +3.5, i.e., to the level which exists in  $Tb_4O_7$ . Such behavior is in a full agreement with the requirement of invariability of the effective valency of the Tb and Bi component,  $\bar{V}_{(Tb,Bi)}$ , as expressed by  $\bar{V}_{(Tb,Bi)} = (1 - x) \cdot \bar{V}_{Tb} + x \cdot \bar{V}_{Bi} = +4$ .

## EXPERIMENTAL

Samples of nominal compositions corresponding to the general formula  $Tb_{1-x}Bi_xSrO_3$  have been prepared using Johnson Mathey 3N purity chemical reagents ( $Bi_2O_3, Tb_4O_7, and SrCO_3$ ) as starting components. The preparation conditions were

- (i) calcination of the appropriate mixtures in air at 800°C for 24 h,
- (ii) regrinding, pelletization, and sintering in air at 900°C for 48 h, and
- (iii) repetition of the procedure (ii) at 850°C.

In all these operations alumina boats served as sample holders.

The resulting products, brown colored pellets, were subjected to X-ray diffraction to check on their phase composition and to determine the lattice parameters. For this purpose, a DRON-3 diffractometer ( $CuK\alpha$  radiation) was used with silicon as a standard for peaks position calibrations. The X-ray data reported in Ref. (6) for the  $TbSrO_3$  matrix served as a reference for indexing the X-ray patterns and for computing the lattice parameters.

For each single-phase sample the effective valency of

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Tb- and Bi-structure components, denoted as  $\bar{V}_{(\text{Tb,Bi})} = (1 - x) \cdot \bar{V}_{\text{Tb}} + x \cdot \bar{V}_{\text{Bi}}$ , was determined iodometrically. These data served to determine the overall oxygen index  $y = [(1 - x) \cdot \bar{V}_{\text{Tb}} + x \cdot \bar{V}_{\text{Bi}}]/2 + 1$  for each composition within the homogeneity domain of the series. Finally, the X-ray densities ( $d_{\text{calc}}$ ) were calculated for some chosen models, to serve as the basis for comparison with the experimental values ( $d_{\text{exp}}$ ), the latter having been determined pycnometrically at  $25 \pm 0.1^\circ\text{C}$  using  $\text{CCl}_4$  as the immersion liquid. The measuring accuracy of the lattice parameters, densities, and valency factors was  $\sim 0.1\%$  of the appropriate values.

### Description of the Analytical Methods

**Titration.** Free iodine, released from KI during reaction of the latter with  $6n$  HCl solutions of  $\text{Tb}_{1-x}\text{Bi}_x\text{SrO}_3$  samples, was titrated against  $\sim 0.01n$  sodium thiosulfate, using a starch as indicator (pH of the solution being titrated was kept within 4–5). Prior to titration, the thiosulfate was carefully calibrated with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution of known concentration. Three analyses were usually performed for each composition and the final results were taken as an average.

**Pycnometry.** A pycnometer, of well-defined weight and volume, was filled with a powdered sample (typical amount used  $\sim 2$  g), weighed, and outgassed up to  $\sim 10^{-4}$  Torr. The sample was then cut off from the vacuum line and subjected to a stream of  $\text{CCl}_4$  vapor, the latter as being released from a container of liquid  $\text{CCl}_4$  through a special valve and a fine capillary. This part of the system was intimately connected to the vacuum line. The  $\text{CCl}_4$  vapor saturated the powder; due to a small temperature gradient, intentionally created between the container of liquid  $\text{CCl}_4$  and the pycnometer, it condensed on the sample until the powder became entirely immersed in liquid  $\text{CCl}_4$ . The pycnometer was then transferred out from the vacuum system and immersed in distilled  $\text{CCl}_4$ , which was kept in a temperature-controlled special weighing system (a Sartorius balance comprised with a kit for density measurements). The density of  $\text{CCl}_4$ , as well as the volume of the pycnometer, were well calibrated for different temperatures at which the measurements were being done.

## RESULTS AND DISCUSSION

According to the X-ray phase analysis, samples of the  $\text{Tb}_{1-x}\text{Bi}_x\text{SrO}_3$  stoichiometry represent the solid solution of the  $\text{TbSrO}_3$  whose structure type (6) extends along the tested line up to  $x = 0.33$ . Within the domain of homogeneity, the variation of the  $b$  and  $c$  lattice parameters is linear, while the  $a$  parameter remains practically independent of  $x$  (Fig. 1). Surprisingly, the  $c$  parameter of our starting  $\text{TbSrO}_3$  sample is higher ( $8.371 \text{ \AA}$ ) than the value ( $8.345$

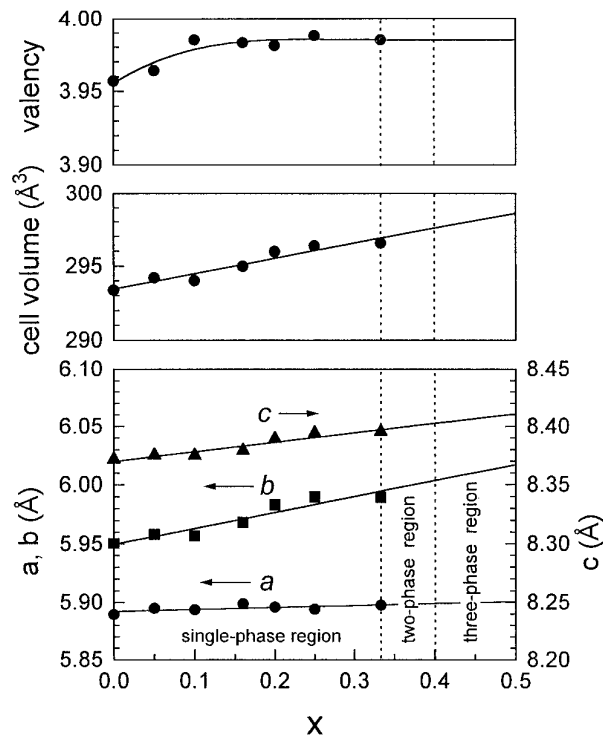


FIG. 1. Lattice parameters ( $a$ ,  $b$ , and  $c$ ), unit cell volume, and the effective valency  $\bar{V}_{(\text{Tb,Bi})}$  as a function of substitution parameter  $x$  within the  $\text{Tb}_{1-x}\text{Bi}_x\text{SrO}_3$  solid solution. Lines fitting the experimental data are extrapolated outside the domain of homogeneity ( $0 \leq x \leq 0.33$ ).

$\text{\AA}$ ) reported in (6) for this phase. In the multiphase regions we have found that the secondary phases that remain in equilibrium with the solid solution are  $\text{Tb}_4\text{O}_7$  (in the two-phase region) and  $\text{Tb}_4\text{O}_7 + \text{Sr}$ -intercalated ternary phase of the  $\text{Tb}_5\text{Bi}_3\text{O}_{12}$ -structure type (in the three-phase region). Such phase relations arise due to deviation of the solid solution domain from its original direction, i.e.,  $\text{Tb}_{1-x}\text{Bi}_x\text{SrO}_3$ , toward the  $\text{Bi}_2\text{Sr}_3\text{O}_6$  phase, that starts beginning at  $x \approx 1/3$ .

As expected, the effective valency  $\bar{V}_{(\text{Tb,Bi})}$  is independent of  $x$ , reaching a value close to +4, at least for the compositions of  $x > 0.05$  (Fig. 1). A slight deviation from +4 is encountered in samples of  $x < 0.05$ ; this shows that within the series presented, the valency of Tb ions never reaches +4. We conclude that oxygen deficiency has to be present in these low bismuth-content compositions, and we suspect that this is the reason for the somewhat larger  $c$ -lattice parameter of the  $x = 0$  sample as compared with the deficiency-free one (6). With increasing concentration of pentavalent Bi ions, however, this deficiency disappears quickly, as seen through a sudden increase of  $\bar{V}_{(\text{Tb,Bi})}$  to the expected constant level of +4.

The experimental densities are presented in Fig. 2. Comparison with those calculated for the deficiency-free structure model reveals a small but noticeable discrepancy that suggests the existence of vacancies in both the anionic

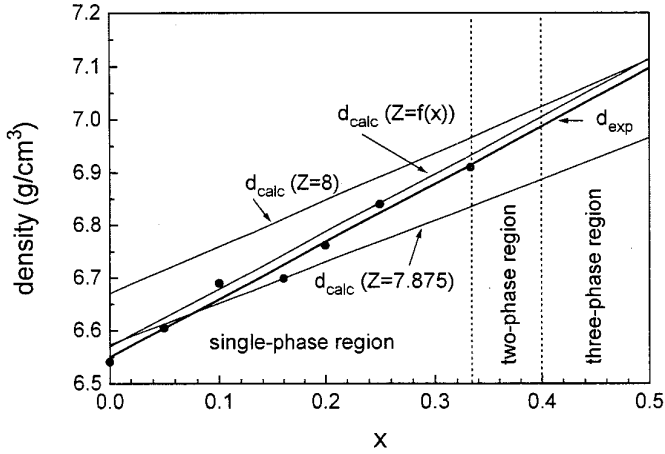


FIG. 2. Experimental densities  $-d_{\text{exp}}$  (full circles and bold, solid line) vs. substitution parameter  $x$  compared to those resulting from the several models considered: (i) vacancy free structure model  $-d_{\text{calc}}(Z = 8)$ , (ii) constant vacancy model  $-d_{\text{calc}}(Z = 7.875)$ , and (iii) variable vacancy model  $-d_{\text{calc}}(Z = f(x))$ .

and the cationic sublattices of the crystal structure. The calculations were based on the formula  $d_{\text{calc}} = Z \cdot A_{\text{MeO}_{1.5}} / (0.602 \cdot abc)$ , in which  $a, b, c$  are the lattice parameters in Å and  $A_{\text{MeO}_{1.5}}$  represents molecular weight of a given Tb<sub>1-x</sub>Bi<sub>x</sub>SrO<sub>3</sub> sample expressed in a reduced form as MeO<sub>1.5</sub>. In this notation  $Z = 8$  for the deficiency-free model.

As seen, the deficiency appears to be  $x$ -dependent, decreasing to 0 at  $x = 0.5$ . Within our uncertainty, we express this decrease in terms of a variable atomic occupancy of the unit cell as  $Z_{\text{real}} = Z_0 + x/4$ , with  $Z_0 = 7.875$  instead of 8.

A steady shift of the experimental densities from the deficient model with  $Z = 7.875$  toward the model of the ideal occupancy with  $Z = 8$  confirms the continuous structure densification that takes place in real samples of the Tb<sub>1-x</sub>Bi<sub>x</sub>SrO<sub>3</sub> type. Since the deficiency equally affects, through  $Z$ , both the anionic and cationic sublattices of the crystal structure, its occurrence seems to originate from inappropriate sintering conditions and not to be a natural feature of the matrix. It is interesting to note the terminal value of  $d_{\text{exp}} = 7.09 \text{ g/cm}^3$ , which arises from the extrapolation of densities to  $x = 0.5$ . This value corresponds exactly to what has been predicted in our previous paper (9) for the hypothetical Tb<sup>+3</sup>Bi<sup>+5</sup>Sr<sub>2</sub>O<sub>6</sub>. Admittedly, the bismuth concentration corresponding to  $x = 0.5$  is far above the upper limit of its solubility in the TbSrO<sub>3</sub> matrix found in air. Nevertheless, it may indicate that under somewhat different sintering conditions, this limit can be shifted up to  $x = 0.5$ . As a result, the Tb representative of the RE<sup>+3</sup>Bi<sup>+5</sup>Sr<sub>2</sub>O<sub>6</sub>-type series (9) may be accessible as deficiency-free material, with probable average valencies of Tb and Bi corresponding to +3.5 and +4.5, respectively.

Considering the constant effective valency  $\bar{V}_{(\text{Tb,Bi})}$ , equal to +4 within the series, we can state that this is a direct consequence of the substitution process that occurs between the two terminal compositions: Tb<sup>+4</sup>SrO<sub>3</sub> and the hypothetical Tb<sup>+3</sup>Bi<sup>+5</sup>Sr<sub>2</sub>O<sub>6</sub>. In real samples such state can be realized in several ways. The main ones are

(i) through the constant valency of Bi ions,

$$\bar{V}_{\text{Bi}} = +5 \text{ then } \bar{V}_{\text{Tb}} = \frac{4 - 5x}{1 - x};$$

(ii) through the constant valency of Tb ions,

$$\bar{V}_{\text{Tb}} = +4 \text{ then, independently on } x, \bar{V}_{\text{Bi}} = +4.$$

Between these two basic possibilities an infinite number of intermediate states exist, each characteristic of a constant average valency of Bi ions and accompanied by a variable average valency of terbium ions. However, we also have to consider the case of variable valencies of both components.

The analytical expressions describing such cases are  
 (iii)  $\bar{V}_{\text{Bi}} = 5 - x$  and  $\bar{V}_{\text{Tb}} = 4 - x$ ; which leads to  $\bar{V}_{(\text{Tb,Bi})} = (1 - x) \cdot \bar{V}_{\text{Tb}} + x \cdot \bar{V}_{\text{Bi}} = +4$ ,  
 (iv)  $\bar{V}_{\text{Bi}} = 4 + 2x$  and  $\bar{V}_{\text{Tb}} = 4 - 2x^2/(1 - x)$ ; which also ensures that  $\bar{V}_{(\text{Tb,Bi})} = +4$ .

To determine which of the possibilities given above takes place in real samples of the series we plan to perform magnetic susceptibility measurements. The idea is to evaluate variation of the effective moment ( $\mu_{\text{eff}}$ ) vs.  $x$  in order to determine the percentage contributions of Tb<sup>+3</sup> and Tb<sup>+4</sup>. Note that magnetic moments of Tb<sup>+4</sup> (7.94  $\mu_{\text{B}}$ ) and Tb<sup>+3</sup> (9.72  $\mu_{\text{B}}$ ) are quite well separated from each other, whereas both Bi<sup>+5</sup> and Bi<sup>+3</sup> are nonmagnetic. The results will be presented separately (10).

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