

# On the Existence of PrSrO<sub>3</sub>-Type Phase and Its Bi/Pr-Substituted Solid Solution

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Solid solution of the Pr<sub>1.1(1-x)</sub>Bi<sub>0.8x</sub>Sr<sub>0.9+0.3x</sub>O<sub>2.932+0.094x</sub>-type has been obtained and characterized through X-ray diffraction, effective valency of Bi and Pr, and through the density measurements. At 900°C in air this solid solution begins from the Pr<sub>1.1</sub>Sr<sub>0.9</sub>O<sub>2.932</sub>-terminus and extends toward Bi<sub>2</sub>Sr<sub>3</sub>O<sub>6</sub> up to  $x \cong 0.5$  (20 at % Bi). Its crystal structure represents monoclinically distorted perovskite-type atomic arrangement, identical to that occurring in the Tb<sub>1-x</sub>Bi<sub>x</sub>SrO<sub>3</sub> analog, several Tb-, and/or Pr-alkaline-earth binaries of the RE<sup>+4</sup>MeO<sub>3</sub>-type ( $Me = Sr$  or  $Ba$ ), and to a large group of RE<sup>+3</sup>Bi<sup>+5</sup>Sr<sub>2</sub>O<sub>6</sub>-type ternaries. Characteristic features of this solid solution are (i) independent on  $x$ , constant oxidation states of Pr and Bi, equal to +3.694 and +4.565, respectively, resulting in  $x$ -dependent increase of the average effective valency of these components ( $\bar{V}$ ); (ii)  $x$ -dependent deficiency of the overall oxygen index, decreasing to 0 far above the solubility limit of Bi; and (iii)  $x$ -dependent deficiency of the cationic sublattice, increasing with the factor proportional to  $0.2x/(0.9 + 0.3x)$ , i.e. to the atomic fraction of total Sr ions located on Pr sites. © 1996 Academic Press, Inc.

## INTRODUCTION

Since 1972, several papers have been published (1–7) concerning existence, crystal structure, and magnetic properties of RE $MeO_3$ -type phases ( $RE = Ce, Pr, Tb$  and  $Me = Sr, Ba$ ). Characteristic feature of these phases is that they are created by those RE's only, whose oxidation states may approach +4. All remaining RE's need pentavalent bismuth as copartner to create the structure type typical for RE $MeO_3$  (1). As the result, a large group of compounds of the exact stoichiometry REBiSr<sub>2</sub>O<sub>6</sub> has been found (8) to possess crystal structure that was first characterized for the Nd-representative of the series (9). This strict stoichiometry is a direct consequence of the perovskite atomic arrangement which requires its oxygen sublattice to be complete. The latter means also that effective valency of the average  $Me$  ion in these compounds ( $Me = (Bi +$

RE)/2) is constant and equal to +4, as in binary counterparts.

The compositional interval between these two groups of isostructural materials has not been studied yet, apart from our recent effort (10) centered on the extension of TbSrO<sub>3</sub> into the ternary system with bismuth oxide. Thanks to this, a terminal solid solution of the Tb<sub>1-x</sub>Bi<sub>x</sub>SrO<sub>3</sub>-type ( $x = \frac{1}{3}$ ) has been described in which effective valency of the average  $Me$  ions ( $Me = Tb_{1-x}Bi_x$ ) occurs to be constant indeed and equal to +4.

In this light, investigation of the Bi–Pr–Sr–O system, at least of that part which is situated in close vicinity of PrSrO<sub>3</sub>, may represent certain scientific interest, namely a unique opportunity to stabilize the +4 oxidation state of Pr and to determine its possible variation vs content of bismuth. This is especially important if we consider that of the binary Pr–alkaline-earth phases of Pr $MeO_3$ -type, only PrBaO<sub>3</sub> has been reported in the literature up to now. PrSrO<sub>3</sub> seems to be difficult to synthesize and so does its Bi-containing solid solution.

## EXPERIMENTAL

Samples were prepared using Johnson-Matthey 3N purity Bi<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, and SrCO<sub>3</sub>. Appropriate mixtures of these reagents were calcinated in air at 800°C for 24 h. Then they were reground, pelletized, and sintered at 900°C for 48 h. Final heat treatment was performed in air at 900°C for 72 h. Alumina boats served as sample holders. Within the binary system Pr<sub>6</sub>O<sub>11</sub>–SrO, chemical compositions of these samples covered a certain interval centered around 1 : 1 stoichiometry (Pr<sub>1±x</sub>Sr<sub>1∓x</sub>O<sub>3</sub> with  $0 \leq x \leq 0.2$ ). The three-component samples were arranged as series, changing their compositions along some chosen directions. Of them, the most important were series

- (i) along the Pr<sub>1±x</sub>Sr<sub>1∓x</sub>O<sub>3</sub>–Bi<sub>2</sub>Sr<sub>2</sub>O<sub>5</sub> line and
- (ii) along the Pr<sub>1±x</sub>Sr<sub>1∓x</sub>O<sub>3</sub>–Bi<sub>2</sub>Sr<sub>3</sub>O<sub>6</sub> line.

Phase composition of the resulting products was determined by a X-ray powder diffraction method (DRON-3 diffractometer with CuK $\alpha$  radiation). The lattice param-

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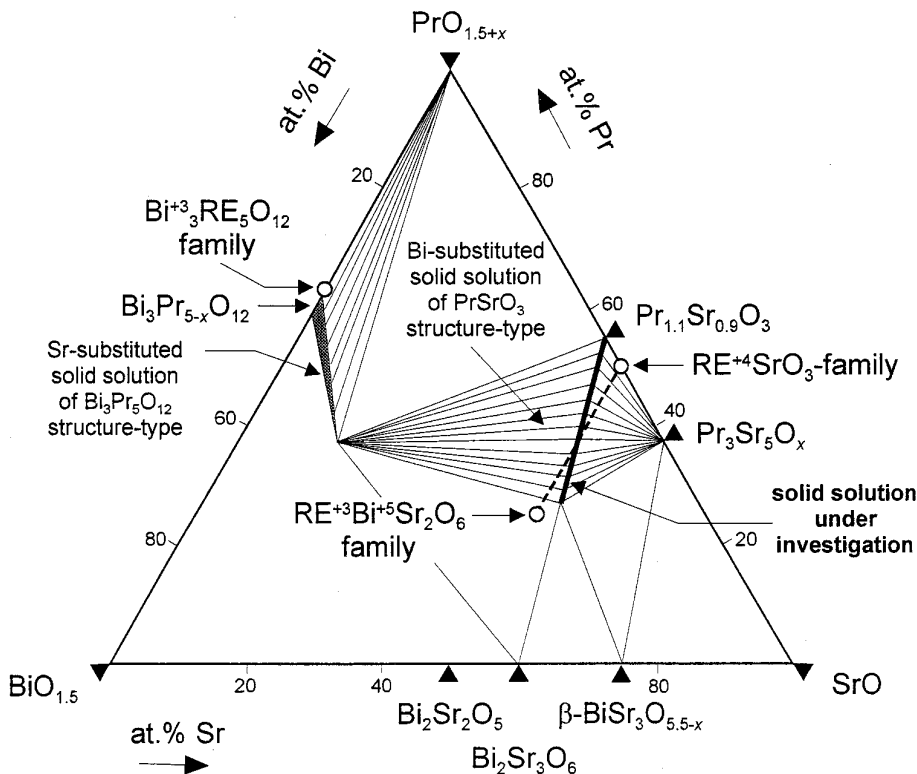


FIG. 1. Phase relations in the Bi-Pr-Sr-O system at 900°C in air. Details on crystallochemical nature of  $RE^{+3}Bi^{+5}Sr_2O_6$  and of  $Bi_3^{+3}RE_5O_{12}$ -type compounds are available in Refs. (8) and (11), respectively.

ters were calculated with the data calibrated according to silicon standard. All single phase samples were subjected for density measurements performed as described in (10). The effective valency of the Bi- and Pr-structure components ( $\bar{V}$ ) taken as effective valency of the average *Me* ion was determined iodometrically according to the procedure also given in (10).

## RESULTS AND DISCUSSION

### Domain of Existence

In contrast to  $TbSrO_3$  (10), domain of existence of the Pr-based analog of the  $REMeO_3$ -type family occurs to be slightly shifted from the 1:1 stoichiometry. The exact composition found for this binary compound corresponds to 55 at% of Pr. This gives the formula  $Pr_{1.1}Sr_{0.9}O_3$  and proves occupation of Sr sites by Pr ions as acceptable by the crystal structure. Moreover, it also proves that the inverse occupation of the sites mentioned above is forbidden, otherwise domain of the binary  $PrSrO_3$  phase would cover as well some Sr-rich compositions beyond 1:1 stoichiometry. As a consequence, the Bi/Pr-substituted solid solution found to originate from the  $Pr_{1.1}Sr_{0.9}O_3$  terminal occurs to be also shifted as compared to that of  $Tb_{1-x}Bi_xSrO_3$  (10). In addition, direction of its extension into the

ternary system does not coincide at all with the hypothetical  $PrBiSr_2O_6$ . Instead, it develops toward the binary compound of trivalent bismuth, i.e.,  $Bi_2Sr_3O_6 \equiv Bi_{0.8}Sr_{1.2}O_{2.4}$  (Fig. 1).

### General Analytical Formulas

Taking into account the chemical composition of the terminals  $Pr_{1.1}Sr_{0.9}O_3$  and  $Bi_{0.8}Sr_{1.2}O_{2.4}$  as constituents of the solid solution found, as well as the oxidizing conditions of its synthesis, an analytical expression describing this solid solution can be deduced, namely

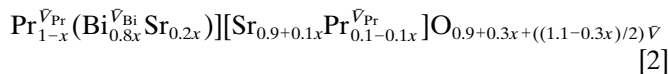
$$Pr_{1.1(1-x)}^{V_{Pr}} Bi_{0.8x}^{V_{Bi}} Sr_{0.9+0.3x}^{+2} O_{0.9+0.3x+(1.1-0.3x)/2} \bar{V}, \quad [1]$$

where  $x$  is the fraction of Bi entering the  $Pr_{1.1}Sr_{0.9}O_3$  matrix,  $\bar{V}_{Pr}$  and  $\bar{V}_{Bi}$  are the average valencies of Pr and Bi, respectively, and

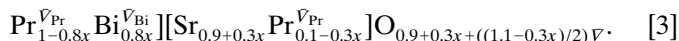
$$\bar{V} = \frac{1.1 \cdot (1-x) \cdot \bar{V}_{Pr} + 0.8x \cdot \bar{V}_{Bi}}{1.1 - 0.3x} \quad [1a]$$

is the effective valency of the average *Me* ion. According to X-ray analysis, the coefficient  $x$  was found to cover the interval  $0 \leq x \leq 0.5$ . Within the given interval, lattice parameters change as shown in Table 1.

Having in mind, as for each derivative of the  $REMeO_3$ -type, that crystal structure of this solid solution should be characteristic of two sets of atomic positions for metallic components (1), we can express formula [1] in two different ways, namely as



or



Of these two formulas, [3] looks more promising as it does not allow Sr ions to share the coordination polyhedra typical for Pr ions. The inverse occupation seems to be acceptable by the structure, as proved by the terminal sample of  $x = 0$ .

On the other hand, the type of occupation reflected by the formula [3] cannot be maintained further than up to  $x = \frac{1}{3}$ . Higher concentration of bismuth must cause a situation when a certain amount of Sr ions is located on Pr sites, similar to what arises from the formula [2], in which Sr ions persist on Pr sites through the whole interval of  $x$  available.

Assuming that the occupation of Pr sites by Sr ions is highly limited, if not entirely forbidden, two deficient structure models, easily distinguishable of each other through the density measurements, can be deduced from the formulas given above, namely:

(I) a model in which contribution of cation-type vacancies would occur through the whole interval of  $x$ , increasing vs  $x$  with the factor proportional to  $0.2x/(0.9 + 0.3x)$ —consequence of formula [2];

(II) a model in which cation-type vacancies would occur beginning from  $x > \frac{1}{3}$  with their contribution increasing by a factor proportional to  $0.3(x - \frac{1}{3})/(0.9 + 0.3x)$ —consequence of formula [3].

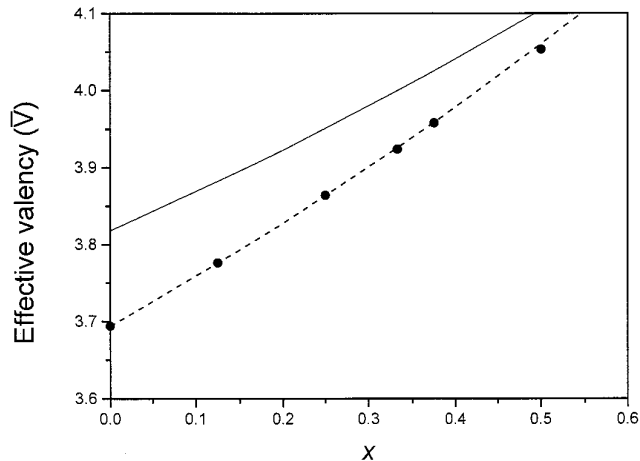


FIG. 2. Experimental effective valency  $\bar{V}$  (circles) and its calculated values for the model with  $y = 3$  (formula [4], solid line) and for the model of optimized valencies of Bi and Pr ions (formula [5], dashed line).

In both cases, the proportionality factors represent contribution of Sr ions to Pr sites (forbidden) related to the concentration of total strontium present in crystal structure. Physical sense of these factors is the driving force creating vacancies in the crystal structure.

#### Effective Valencies of Bi and Pr Ions

In order to verify the type of deficiency (if any) created within the solid solution prepared, an analytical expression describing variation of the overall oxygen index ( $y$ ) should be known. By applying the iodometric titration data found for the effective valency  $\bar{V}_{\text{exp}}$  (cp. Table 1) to formula [1], it is easy to notice that in real samples this index is far away from being constant and equal to +3, as expected for perovskite-type matrix. In our recent paper on  $\text{Tb}_{1-x}\text{Bi}_x\text{SrO}_3$  solid solution (10), the invariable character of  $\bar{V}$  has been entirely confirmed.

In Fig. 2 we present variation of the  $\bar{V}$  factor calculated

TABLE 1  
Results of X-Ray Analysis, Iodometric Titration, and Density Measurements for the  $\text{Pr}_{1.1(1-x)}\text{Bi}_{0.8x}\text{Sr}_{0.9+0.3x}\text{O}_{2.932+0.094x}$ -Type Solid Solution

$x$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta$ (deg)	$\nu$ ( $\text{\AA}^3$ )	$A_{MeO_{y/2}}$	$\bar{V}_{\text{exp}}$	$\bar{V}_{\text{calc}}$	$d_{\text{exp}}$ ( $\text{g/cm}^3$ )	$d_{\text{calc}}(Z = f(x))$ ( $\text{g/cm}^3$ )	$d_{\text{calc}}(Z = 8)$ ( $\text{g/cm}^3$ )
0.000	5.9797	6.1297	8.5617	90.073	313.819	140.383	3.69	3.694	5.93	5.944	5.944
0.125	5.9792	6.1276	8.5545	90.114	313.420	142.880	3.78	3.776	6.00	6.037	6.058
0.250	5.9756	6.1187	8.5432	90.162	312.368	145.379	3.86	3.864	6.11	6.145	6.184
0.333	5.9709	6.1176	8.5417	90.097	312.004	147.045	3.92	3.926	6.21	6.210	6.263
0.375	5.9616	6.1081	8.5307	90.134	310.636	147.878	3.96	3.958	6.23	6.267	6.326
0.500	5.9563	6.1021	8.5233	90.127	309.787	150.377	4.05	4.060	6.35	6.374	6.450

Note. The measuring accuracy of the lattice parameters corresponds to 0.1%, and densities and valencies to 1% of the appropriate values.  $\bar{V}_{\text{calc}}$  is calculated according to formula [5].  $d_{\text{calc}}(Z = f(x))$  is calculated with  $Z_{\text{eff}} = 8 - (0.2x/(0.9 + 0.3x))$ .  $A_{MeO_{y/2}}$  is calculated to formula [7].

for the case of constant, equal to 3, overall oxygen index (solid line) as compared with the experimental data (circles). The analytical expression used for calculations was evaluated from formula [1] by applying

$$y = 0.9 + 0.3x + \frac{1.1 - 0.3x}{2} \cdot \bar{V} = 3; \quad \text{hence} \quad [4]$$

$$\bar{V} = \frac{2 \cdot (2.1 - 0.3x)}{1.1 - 0.3x}.$$

As seen, all the experimental values of the  $\bar{V}$  factor are smaller in comparison with those calculated and although they show a much faster increase with  $x$  than those calculated, the oxygen sublattice in real samples is persistently deficient in the whole domain of homogeneity. It reaches 3 but far above ( $x = 0.724$ ) the upper limit of Bi solubility found.

By applying to Eq. [1a] the average valencies of Bi and Pr ions as constant through the whole domain of homogeneity, namely  $\bar{V}_{\text{Bi}} = 4.565$   $\bar{V}_{\text{Pr}} = 3.694$  (the latter as corresponding to the valency of Pr ions found in terminal sample with  $x = 0$ ), the dependence manifested by the experimental values of the  $\bar{V}$  factor (circles in Fig. 2) becomes analytically describable with the following equation:

$$\bar{V} = \frac{1.1 \cdot (1 - x) \cdot 3.694 + 0.8x \cdot 4.565}{1.1 - 0.3x} \quad [5]$$

$$= \frac{2 \cdot (2.032 - 0.206x)}{1.1 - 0.3x}.$$

The dashed line passing through the circles in Fig. 2 reflects a degree of fitting. Several other contributions of  $\bar{V}_{\text{Bi}}$  and  $\bar{V}_{\text{Pr}}$  values (including some  $x$ -dependent ones) have been also tested but a fit of comparable quality could not be obtained.

The result obtained looks somewhat unexpactive when compared with the appropriate one found for the effective valency  $\bar{V}$  in the Tb<sub>1-x</sub>Bi<sub>x</sub>SrO<sub>3</sub>-type solid solution (10). Note, that according to (10), invariability of the  $\bar{V}$  factor occurs therein as a result of  $x$ -dependent decrease of the Tb valency, no matter the valency of Bi ions. In contrast to that, the  $\bar{V}$  factor in Bi/Pr-substituted Pr<sub>1.1</sub>Sr<sub>0.9</sub>O<sub>3</sub>-matrix presented herein exhibits an  $x$ -dependent increase in spite of the constant valencies of Pr and Bi ions. In our opinion, the peculiarity mentioned above is nothing else but a direct consequence of the specific stoichiometry according to which the solid solution is constructed (cp. formula [1]). As seen in Fig. 2, this stoichiometry makes the  $\bar{V}$  factor always  $x$ -dependent, no matter if the oxygen sublattice of the matrix is complete or deficient. The problem, why the increase of the  $\bar{V}$  factor is insufficiently strong to preserve full occupation of the oxygen sublattice, we may explain

with chemical nature of Pr, whose oxidation above the level which exists in Pr<sub>6</sub>O<sub>11</sub> evidently does not proceed in air. In this situation, the only source of an extra oxygen that could be incorporated to suppress the deficiency in the oxygen sublattice would stay in a higher than +4.565 oxidation state of Bi ions. The reason, however, why Bi ions cannot reach a +5 oxidation state may originate from inappropriate sintering conditions applied (air instead oxygen). The fact that the solid solution under discussion preserves its existence in spite of the evident oxygen deficiency, one can also interpret with a high stability of the perovskite matrix, even if somewhat deficient (12).

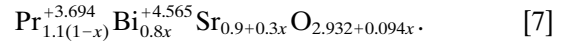
### Deficiency and Its Characterization through the Density Measurements

Having the  $\bar{V}$  factor analytically determined, variation of the overall oxygen index ( $y$ ) in solid solution reported can now be precisely described, namely as

$$y = 0.9 + 0.3x + \left( \frac{1.1 - 0.3x}{2} \right) \cdot \frac{2 \cdot (2.032 - 0.206x)}{1.1 - 0.3x} \quad [6]$$

$$= 2.932 + 0.094x,$$

which transforms formula [1] to the final form



Note that even for the case of full occupation of the cationic sites, the oxygen sublattice of the solid solution exhibits persistent  $x$  - dependent deficiency. For this reason we can classify the solid solution as belonging to a large family of oxygen-deficient perovskites described by Galasso (12).

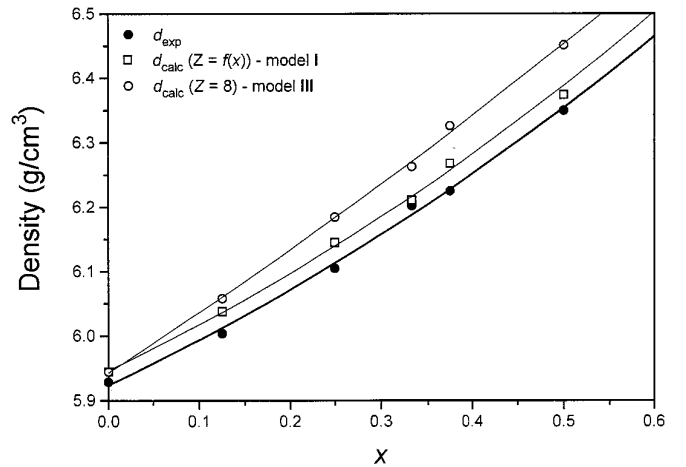


FIG. 3. Experimental density (full circles and bold line) compared with its calculated values resulting from model I (squares) and from model III (open circles).

TABLE 2  
Collected Crystallochemical Data on the Solid Solution under Investigation

General formula	$\text{Pr}_{1.1(1-x)}^{+3.694} \text{Bi}_{0.8x}^{+4.565} \text{Sr}_{0.9+0.3x} \text{O}_{2.932+0.094x}$	$[\text{Pr}_{2.875} \text{Bi}_{1.057} \square_{0.066}][\text{Sr}_{3.966} \text{Pr}_{0.033}][\text{O}_{11.754} \square_{0.245}]$
Domain of existence	$0 \leq x \leq 0.5$	$x = 0.333$
Number of $\text{MeO}_{y/2}$ -type molecules in unit cell	$Z_{\text{eff}} = 8 - \frac{0.2x}{0.9 + 0.3x}$	$Z_{\text{eff}} = 7.933$
Unit cell content		
Bi ions	$\frac{0.8x}{2} \cdot Z_{\text{eff}}$	1.057
total Pr ions	$\frac{1.1 \cdot (1-x)}{2} \cdot Z_{\text{eff}}$	2.909
Pr ions on Pr sites	$\frac{2 - 0.8x}{2} \cdot Z_{\text{eff}} - 4$	2.875
Pr ions on Sr sites	$4 - \frac{0.9 + 0.3x}{2} \cdot Z_{\text{eff}}$	0.033
Sr ions	$\frac{0.9 + 0.3x}{2} \cdot Z_{\text{eff}}$	3.966
O ions	$\frac{2.932 + 0.094x}{2} \cdot Z_{\text{eff}}$	11.754
Vacancies in cationic sublattice presumably located on Pr-sites	$\frac{0.2x}{0.9 + 0.3x}$	0.066
Vacancies in oxygen sublattice	$12 - \frac{2.932 + 0.094x}{2} \cdot Z_{\text{eff}}$	0.245

Note. The last column contains distribution of the appropriate structure components and vacancies in sublattices calculated for  $x = \frac{1}{3}$ .

With the above estimation, a recognition of real occupancy of all the atomic sites in the crystal structure of the solid solution presented can be made through density and its dependency vs  $x$ . The calculations were performed for the structure models of different cation-type deficiency, described above as I and II, as well as for the cation deficiency-free one denoted as III.

The analytical expression for density used was

$$d_x = Z_{\text{eff}} \cdot \frac{A_{\text{MeO}_{y/2}}}{0.602 \cdot \nu},$$

in which  $A_{\text{MeO}_{y/2}}$  is  $\frac{1}{2}$  of the molecular weight arising from [7],  $\nu$  is the unit cell volume in  $\text{\AA}^3$ , and  $Z_{\text{eff}}$  is the vacancy-dependent number of  $\text{MeO}_{y/2}$ -type molecules in unit cell, expressed as follows:

(i) for model I,

$$Z_{\text{eff}} = 8 - \frac{0.2x}{0.9 + 0.3x} \quad \text{for } 0 \leq x \leq 1;$$

(ii) for model II,

$$Z_{\text{eff}} = 8 - \frac{0.3 \cdot (x - \frac{1}{3})}{0.9 + 0.3x} \quad \text{for } \frac{1}{3} \leq x \leq 1;$$

(within the interval  $0 \leq x < \frac{1}{3}$  the structure would be free

of any cation-type deficiency, as in the case of the model III, below).

(iii) for model III,

$$Z_{\text{eff}} = 8 \quad \text{for } 0 \leq x \leq 1.$$

The results of fitting are presented in Fig. 3. As seen, atomic occupancy of the unit cell in solid solution tested exhibits the  $x$ -dependent deficiency identical to that predicted for the model I. Indeed, contribution of cation-type vacancies in real samples of this solid solution (presumably located within the set of atomic positions for Pr ions) undergoes an increase which is proportional to the atomic fraction of total Sr ions on Pr sites given by the formula [2]. There is no need to admit that according to the growing contribution of cation-type vacancies, also the deficiency in oxygen sublattice becomes proportionally deeper (cp. formula [7]). This we can express analytically as

$$\left[ \text{Pr}_{\left(\frac{2-0.8x}{2}\right) \cdot Z_{\text{eff}} - 4}^{+3.694} \text{Bi}_{\left(\frac{0.8x}{2}\right) \cdot Z_{\text{eff}}}^{+4.565} \square_{0.2x/(0.9+0.3x)} \right] \left[ \text{Sr}_{\left(\frac{0.9+0.3x}{2}\right) \cdot Z_{\text{eff}}} \text{Pr}_{4 - \left(\frac{0.9+0.3x}{2}\right) \cdot Z_{\text{eff}}}^{+3.694} \right] \left[ \text{O}_{\left(\frac{2.932+0.094x}{2}\right) \cdot Z_{\text{eff}}} \square_{12 - \left(\frac{2.932+0.094x}{2}\right) \cdot Z_{\text{eff}}} \right],$$

which, with

$$Z_{\text{eff}} = 8 - \frac{0.2x}{0.9 + 0.3x},$$

reflects distribution of atoms and vacancies through atomic positions available in the unit cell.

In this way, the crystallochemical nature of the Bi-containing Pr<sub>1.1</sub>Sr<sub>0.9</sub>O<sub>3</sub> matrix has been clarified satisfactorily and can serve as a basis for further confirmation with other methods. Final results are collected in Table 2. A separate work on crystal structure refinement by neutron diffraction is in progress.

#### ACKNOWLEDGMENT

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#### REFERENCES

1. A. J. Jacobson, B. C. Tofield, and B. E. F. Fender, *Acta Crystallogr. Sect. B* **28**, 956 (1972).
2. B. C. Tofield, A. J. Jacobson, and B. E. F. Fender, *J. Phys. C* **5**, 2887 (1972).
3. J. B. Bulman, M. V. Kuric, R. P. Guertin, S. Foner, E. J. McNiff Jr., G. Cao, J. O'Riely, J. E. Crow, P. P. Wise, and Tan Yuen, *J. Appl. Phys.* **69**, 4874 (1991).
4. G. Cao, Tan Yuen, P. P. Wise, J. E. Crow, J. W. O'Reilly, M. V. Kuric, R. P. Guertin, A. Rosov, and J. W. Lynn, *J. Appl. Phys.* **70**, 6332 (1991).
5. I. Felner, Y. Yeshurun, G. Hilscher, T. Holubar, G. Schaudy, U. Yaron, O. Cohen, Y. Wolfus, E. R. Yacoby, L. Klein, F. H. Potter, C. S. Rastomjee, and R. G. Egdell, *Phys. Rev. B* **46**, 9132 (1992).
6. N. Rosov, J. W. Lynn, Q. Lin, G. Cao, J. W. O'Reilly, P. Pernambuco-Wise, and J. E. Crow, *Phys. Rev. B* **45**, 982 (1992).
7. Y. Hinatsu, *J. Solid State Chem.* **100**, 136 (1992).
8. R. Horyń, M. Wołczyr, A. Wojakowski, and A. J. Zaleski, *J. Alloys Comp.* in press.
9. A. Lenz and Hk. Müller-Buschbaum, *J. Less Comm. Met.* **161**, 141 (1989).
10. R. Horyń, Z. Bukowski, and M. Wołczyr, *J. Solid State Chem.* **122**, 321 (1996).
11. R. Horyń, M. Wołczyr, and A. Wojakowski, *J. Solid State Chem.* **116**, 68 (1995).
12. F. S. Galasso, "Structure, Properties and Preparation of Perovskite-Type Compounds." Pergamon Press, Oxford, 1969.