

# Synthesis and Crystallochemical Characterization of the $\text{Bi}_3\text{RE}_5\text{O}_{12}$ -Type Phases

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A series of  $\text{Bi}_3^{3+}\text{RE}_5\text{O}_{12}$ -type phases ( $\text{RE} = \text{Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu}$ ) has been prepared in air at 950°C and characterized by X-ray powder diffraction and density and valence measurements performed on single-phase samples. With the exception of the Er, Yb, and Lu varieties, the characteristic feature of the series is rhombohedral symmetry. The lattice parameters of the individual phases depend on the RE element and are within the intervals  $a = 3.755\text{--}3.959 \text{ \AA}$  and  $c = 9.482\text{--}9.964 \text{ \AA}$  (hexagonal setting). Traces of very weak superstructure peaks indicate a possible unit cell multiplication. The series is stable in air and exhibits a comparatively wide compositional interval centered around the  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  stoichiometry. © 1995 Academic Press, Inc.

## INTRODUCTION

In recent studies of phase relations along the  $\text{BiSr}_{3-x}\text{La}_x\text{O}_{5.5-y}$  section of the Bi-Sr-La-O system in air at 850°C (1) we observed a new phase with a rather simple X-ray pattern, the quantity of which increased for samples with  $x \geq 1$ . This minority phase has been identified as belonging to a new series of binary (Bi, RE) oxides formed by most REs. The characteristic feature of this series is a comparatively large compositional domain centered around the  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  stoichiometry.

Many binary systems of the  $\text{Bi}_2\text{O}_3\text{--RE}_2\text{O}_3$  type have been studied. The majority of these studies have been restricted to the Bi-rich region of the appropriate  $\text{Bi}_2\text{O}_3\text{--RE}_2\text{O}_3$  systems because the fluorite-type oxygen-deficient  $\delta$ -form of  $\text{Bi}_2\text{O}_3$  and numerous metal-oxide containing solid-solutions of  $\delta^*$ -type are ionic conductors (2, 3). Considering somewhat RE-richer compositions, a large group of rhombohedral phases composed of most of the REs ( $\text{Bi}_{0.7}\text{La}_{0.3}\text{O}_{1.5}$  (4), as an example) has been found to exist and these phases have relatively wide compositional ranges. With the exception of the  $\text{La}_2\text{O}_3\text{--Bi}_2\text{O}_3$  system, the RE-rich side of the appropriate binary systems have not been explored. In the  $\text{La}_2\text{O}_3\text{--Bi}_2\text{O}_3$  system, an

orthorhombic compound of exact  $\text{Bi}_8\text{La}_{10}\text{O}_{27}$  composition has recently been characterized (5).

In this work we present a preliminary crystallochemical characterization of the new  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  phases. Crystal structure analysis and electron diffraction studies, centered on details of the  $\text{Bi}_3\text{RE}_5\text{O}_{12}$ -type structure, are described in a separate paper (6). The high concentration of REs leads us to expect that these phases exhibit various types of magnetic ordering at low temperatures.

## EXPERIMENTAL

Johnson Mathey's RE and Bi oxides, all of 4N purity, served as starting components for the preparation of appropriate samples. The preparation consisted of heating the mixtures of the oxides in air at 800°C for 24 hr, then regrinding, pelletizing, and subsequently heating at 900°C for 48 hr. Final sintering of the products was performed at 950°C for 3 days. The samples were then characterized through X-ray powder diffraction (Siemens D 5000 diffractometer,  $\text{CuK}\alpha$  radiation, Ni-filtered), iodometric titration to determine the average power factor for redox, denoted as:

$$\bar{V}_{\text{Mc}} = \frac{\text{at.}\%_{\text{Bi}} \cdot \bar{V}_{\text{Bi}} + \text{at.}\%_{\text{RE}} \cdot \bar{V}_{\text{RE}}}{100},$$

where  $\bar{V}_{\text{Bi}}$  and  $\bar{V}_{\text{RE}}$  are the averaged valences of Bi- and RE-structure components, respectively, and pycnometric measurements of the densities of samples ( $d_{\text{exp}}$ ) of these new chemical individuals. The latter was especially important for the recognition of possible crystal structure deficiencies.

## RESULTS AND DISCUSSION

Of all the RE oxides available and tested herein, 10, namely, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho, have yielded a series of  $\text{Bi}_3\text{RE}_5\text{O}_{12}$ -type phases of the same structure type. To a very good approximation, their

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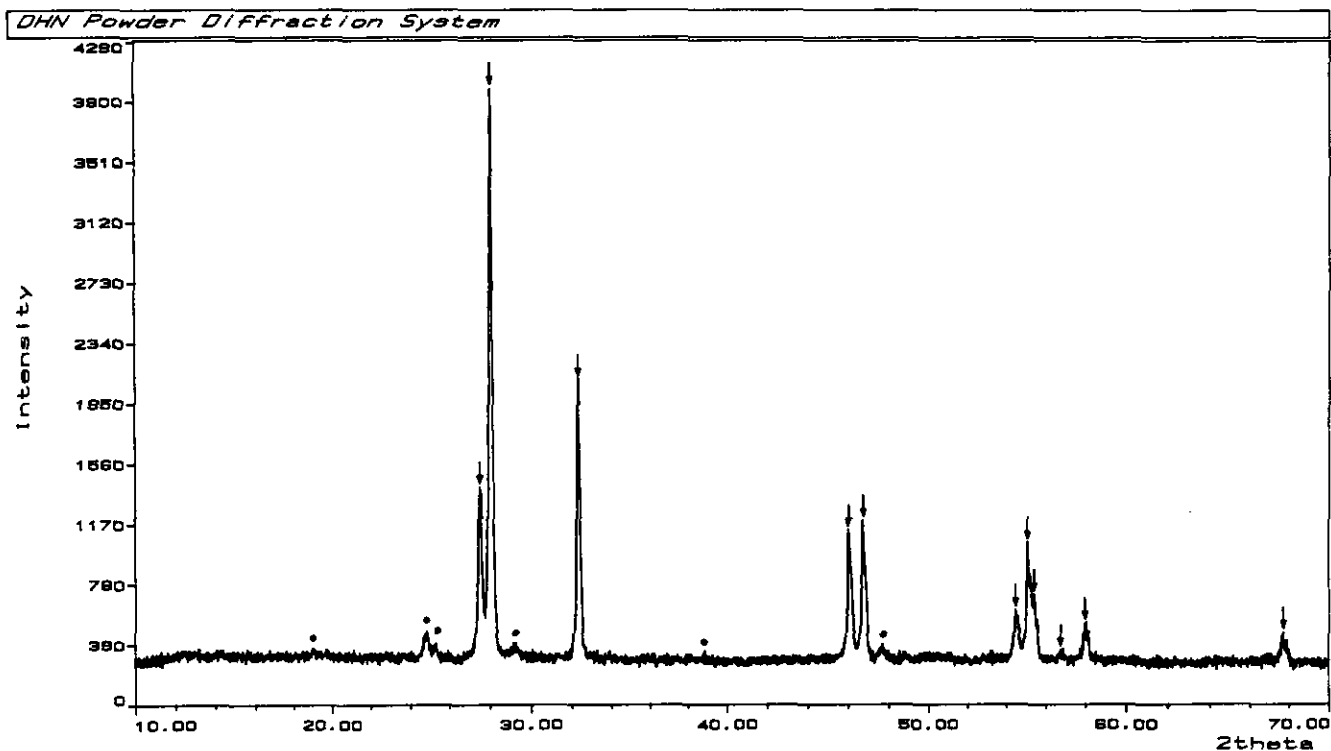


FIG. 1. X-ray powder diffraction diagram of  $\text{Bi}_3\text{Nd}_5\text{O}_{12}$  typical for all the  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  phases tested in this work. Arrows denote peaks indexed in the rhombohedral subcell and shaded circles represent the superstructure peaks.

X-ray powder diffraction diagrams (e.g., Fig. 1 and Table 1) can be indexed with a rhombohedral unit cell and the lattice parameters given in Table 2. The diffraction patterns overlap those known for  $\text{BiO}$  (7) and  $\text{La}_3\text{Sb}_3\text{O}_{11}$  (8), justifying a simple rhombohedral prototype structure. However, a few very weak peaks that remain unindexed indicate a superstructure. For simplicity, in this paper we will refer the series to the rhombohedral subcell, whereas details concerning the superstructure are given in (6).

Based on the experimental results presented in Table 2, several important conclusions can be drawn:

(i) The series is characterized by comparatively wide composition domains of existence centered around the  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  stoichiometry. This compositional flexibility is illustrated by some chosen RE representatives, intentionally prepared as off- $\text{Bi}_3\text{RE}_5\text{O}_{12}$  stoichiometry (cf. Pr, Tb, and Eu in Table 2).

(ii) The series is characterized by a  $\bar{V}_{\text{Mc}}$ -factor equal to 3. Exceptions are the Pr- and Tb-representatives, i.e., phases based on REs which are known to exhibit higher than +3 oxidation states in an oxidizing environment. This means that:

(a) the oxidation state of Bi ions is +3 within the series, with the  $\bar{V}_{\text{Mc}}$ -values providing direct measures of the average valence of REs ( $\bar{V}_{\text{RE}}$ ).

TABLE 1  
Observed Interplanar Spacings ( $d_{\text{obs}}$ ), Bragg Angles ( $2\Theta_{\text{obs}}$ ), and Relative Intensities ( $I_{\text{rel}}$ ) for  $\text{Bi}_3\text{Nd}_5\text{O}_{12}$  Sample (shown in Fig. 1) Compared with the Calculated Values for the Refined Subcell ( $a = 3.883 \text{ \AA}$ ,  $c = 9.723 \text{ \AA}$ )

$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$2\Theta_{\text{obs}}$ (°)	$2\Theta_{\text{calc}}$ (°)	$hkl$	$I_{\text{rel}}$ (%)
4.675		18.97		<i>s</i>	1.1
3.586		24.81		<i>s</i>	4.8
3.518		25.29		<i>s</i>	2.5
3.241	3.241	27.50	27.50	003	30.4
3.178	3.179	28.05	28.05	101	100.0
3.058		29.10		<i>s</i>	2.5
2.766	2.766	32.34	32.34	102	48.9
2.316		38.85		<i>s</i>	0.7
1.970	1.970	46.04	46.03	104	22.6
1.941	1.942	46.75	46.74	110	23.8
1.906		47.68		<i>s</i>	2.5
1.683	1.683	54.46	54.46	105	8.0
1.666	1.666	55.09	55.09	113	19.6
1.657	1.657	55.42	55.40	201	11.3
1.620	1.620	56.77	56.77	006	1.7
1.589	1.589	57.99	57.98	202	5.9
1.383	1.383	67.68	67.69	204	4.0

Note. Miller indices  $hkl$  are given for the subcell only. Superstructure peaks are denoted by *s*.

TABLE 2  
Lattice Parameters ( $a$ ,  $c$ ), Average Valence ( $\bar{V}_{Me}$ ), Densities ( $d_{exp}$ ,  $d_{calc}$ ), and Crystallographic Formulas of  $Bi_3RE_5O_{12}$ -Type Phases

Starting composition	$a$ (Å)	$c$ (Å)	$\bar{V}_{Me}$	$d_{exp}$ (g/cm <sup>3</sup> )	Crystallographic formula	$d_{calc}$ (g/cm <sup>3</sup> )
$Bi_3Y_5O_{12}$	3.755	9.515	3.00	6.74	$Bi[Y_{1.875}Bi_{0.125}]O_{4.50}$	6.77
$BiLa_2O_{4.5}$	3.959	9.964	3.00	6.83	$BiLa_2O_{4.50}$	6.86
$Bi_3Pr_{5-x}O_{12}$ $x = 0.211$	3.895	9.773	3.08	7.41	$Bi[Pr_{1.845}Bi_{0.155}]O_{4.62}$	7.44
$Bi_3Pr_{5-x}O_{12}$ $x = 0.500$	3.899	9.784	3.08	7.44	$Bi[Pr_{1.800}Bi_{0.200}]O_{4.62}$	7.46
$Bi_3Pr_{5-x}O_{12}$ $x = 0.700$	3.899	9.784	3.08	7.47	$Bi[Pr_{1.767}Bi_{0.239}]O_{4.62}$	7.49
$Bi_3Nd_5O_{12}$	3.883	9.723	3.00	7.51	$Bi[Nd_{1.875}Bi_{0.125}]O_{4.50}$	7.56
$Bi_3Sm_5O_{12}$	3.850	9.569	3.00	7.91	$Bi[Sm_{1.875}Bi_{0.125}]O_{4.50}$	7.97
$Bi_3Eu_{5+x}O_{12}$ $x = 0.240$	3.836	9.509	3.00	7.97	$Bi[Eu_{1.908}Bi_{0.091}]O_{4.50}$	8.09
$Bi_3Gd_5O_{12}$	3.824	9.484	3.00	8.24	$Bi[Gd_{1.875}Bi_{0.125}]O_{4.50}$	8.32
$Bi_3Tb_{5-x}O_{12}$ $x = 0.197$	3.784	9.517	3.07	8.48	$Bi[Tb_{1.846}Bi_{0.154}]O_{4.61}$	8.56
$Bi_3Tb_{5-x}O_{12}$ $x = 0.714$	3.781	9.584	3.08	8.53	$Bi[Tb_{1.765}Bi_{0.235}]O_{4.62}$	8.57
$Bi_3Dy_5O_{12}$	3.774	9.482	3.00	8.60	$Bi[Dy_{1.875}Bi_{0.125}]O_{4.50}$	8.69
$Bi_3Ho_5O_{12}$	3.758	9.508	3.00	8.74	$Bi[Ho_{1.875}Bi_{0.125}]O_{4.50}$	8.80

(b) The oxygen sublattices for the series contain deficiencies which can easily be eliminated under preferable conditions such as presence of oxidable  $RE$  element, e.g., Pr or Tb (manifested by higher  $\bar{V}_{Me}$ -factors, seen in these phases in spite of the variable concentration of the  $RE$ s).

(iii) No more than three  $MeO_{1.5}$ -type molecules ( $Me = (\text{at.}\%_{Bi} + \text{at.}\%_{RE})/100$ ) within the elementary subcell are consistent with the comparisons of the experimental and calculated densities for the  $Bi_3RE_5O_{12}$  formula.

(iv) A direct consequence of (iii) is the 1 : 2-type crystallographic formula of the series, unexpectedly realized with the 3 : 5 stoichiometry. Analytically this feature can be expressed as

$$\begin{aligned} Bi_3RE_5O_{12} &= Bi_{9/8}RE_{15/8}O_{36/8} = Bi(RE_{15/8}Bi_{1/8})O_{4.5} \\ &= Bi(RE_{2-x}Bi_x)O_{4.5}, \end{aligned}$$

where  $x = \frac{1}{8}$ ; or generally, to obey the case of Pr-, Tb-, and Eu-based samples tested in this work and including the case where  $\bar{V}_{Me} > 3$ ,

$$\begin{aligned} Bi_3RE_{5+x}O_{(8+x)\frac{\bar{V}_{Me}}{2}} &= Bi\left(\frac{RE_{15+3x}Bi_{1+x}}{8+x}\right)O_{3\frac{\bar{V}_{Me}}{2}} \\ &= Bi\left[\frac{RE_{(16+2x)-(1+x)}Bi_{1+x}}{8+x}\right]O_{3\frac{\bar{V}_{Me}}{2}} \end{aligned}$$

for  $0 \leq x \leq 1$ . This result can be further simplified to

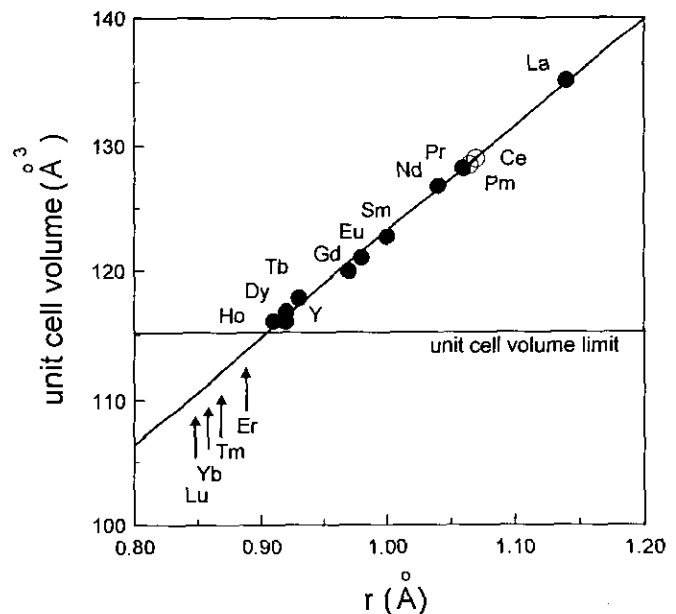


FIG. 2. Cell volume vs Ahren's (9)  $RE^{+3}$  ionic radii dependence for the  $Bi_3RE_5O_{12}$ -type phases. Open circles represent hypothetical positions of Ce and Pm phases not synthesized in this work. Arrows denote  $RE$ s which do not form the  $Bi_3RE_5O_{12}$ -type phases.

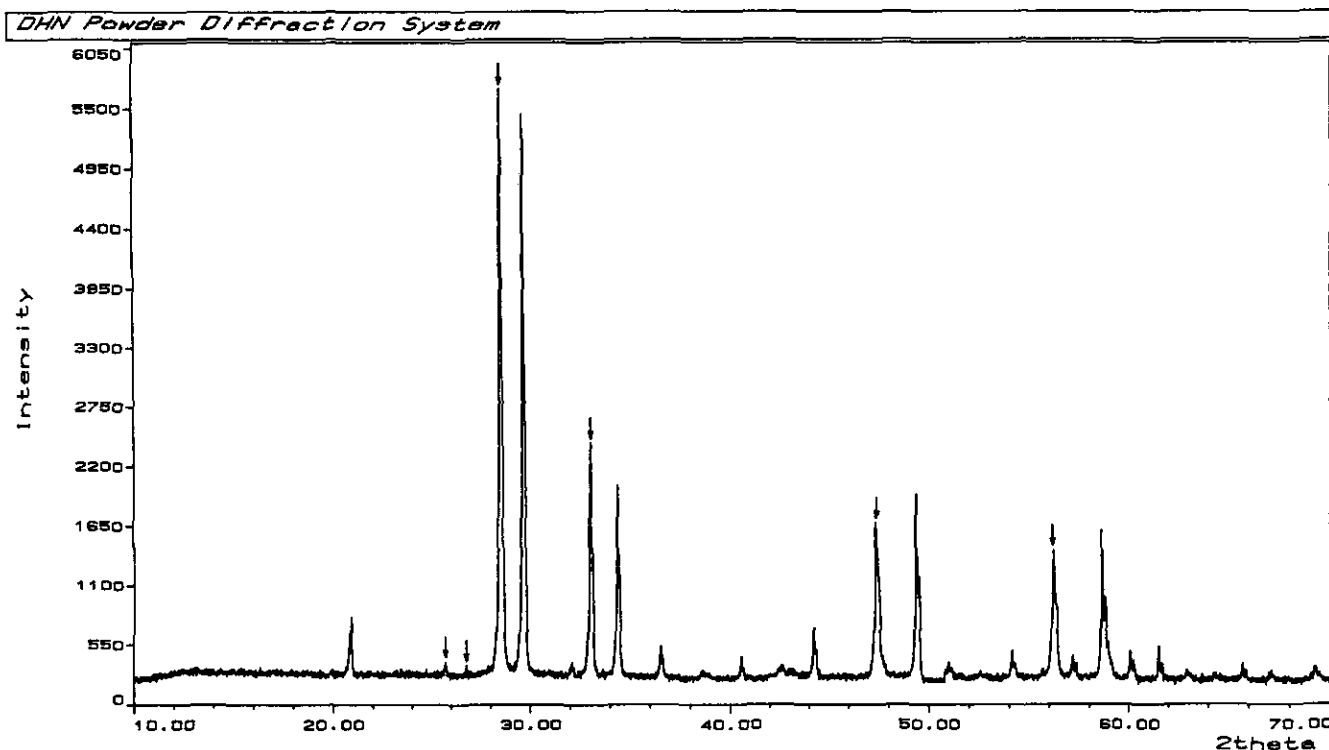
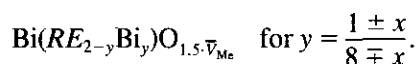


FIG. 3. X-ray powder diffraction diagram of  $\text{Bi}_2\text{YbO}_{4.5}$  (peaks indicated by arrows) typical also for the Er and Lu members of the  $\delta^*$ - $\text{Bi}_2\text{O}_3$  structure type. A secondary phase is  $\text{Yb}_2\text{O}_3$ .



In this light, it is interesting to note that the position of the La representative of the series (cf. Table 2) seems quite logical and should be considered as reflecting the case of a pure occupation of appropriate Bi and RE positions within the  $\text{AB}_2\text{O}_{4.5}$ -type unit cell, common for the whole series. The unique position of  $\text{BiLa}_2\text{O}_{4.5}$  comes from the fact that within the  $\text{Bi}_2\text{O}_3$ - $\text{La}_2\text{O}_3$  binary system, very close to the 3:5 stoichiometry, there is a neighboring  $\text{Bi}_8\text{La}_{10}\text{O}_{27}$  phase (5). Accordingly, the chemical composition of the La representative of our series is shifted from 3:5 to 1:2.

As stated above, three REs tested in this work (Er, Yb, and Lu; cf. Fig. 2) do not form appropriate  $\text{Bi}_3\text{RE}_5\text{O}_{12}$  phases. This means that there is a certain limit of the RE-atomic radii, close to 0.9 Å, below which no representative of the series can exist. Therefore, samples of the 3:5 stoichiometry containing these lanthanides have occurred as two-phase mixtures, composed of considerable amounts of  $\text{RE}_2\text{O}_3$  in equilibrium with other phases of quite different structure type. According to our X-ray powder diffraction (Fig. 3) and chemical analyses, these phases have overall stoichiometries close to 2:1 and be-

long to a cubic system with lattice parameters equal to 5.403, 5.418, and 5.441 Å for Er, Yb, and Lu, respectively. They represent a structure-type of fluorite-like  $\delta^*$ - $\text{Bi}_2\text{O}_3$  (2, 3).

High concentration of REs, wide domains of homogeneity, variable deficiency of the oxygen sublattice efficiently compensated by variable valence of appropriate RE ions; all these features make these phases attractive subjects for fundamental studies of physical properties, particularly magnetics.

#### REFERENCES

1. M. Wolcyrz and R. Horyń, *J. Alloys Compounds* **202**, 143 (1993).
2. K. Koto, H. Mori, and Y. Ito, *Solid State Ionics* **18**, 720 (1986).
3. D. Mercurio, M. El Farissi, B. Frit, J. M. Reau, and J. Senegas, *Solid State Ionics* **39**, 297 (1990).
4. D. Mercurio, M. El Farissi, J. C. Champarnaud-Mesjard, B. Frit, P. Conflant, and G. Rault, *J. Solid State Chem.* **80**, 133 (1989).
5. C. Michel, V. Caignaert, and B. Raveau, *J. Solid State Chem.* **90**, 296 (1991).
6. M. Wolcyrz, L. Kępiński, and R. Horyń, *J. Solid State Chem.* **116**, 72 (1995).
7. A. A. Zavyalova, R. M. Imamov, and Z. G. Pinsker, *Kristallografiya* **10**, 480 (1965).
8. T. A. Toporenska and M. B. Warfolumev, *Russ. J. Inorg. Chem. Engl. Transl.* **27**, 1388 (1982).
9. L. H. Ahrens, *Geochim. Cosmochim. Acta* **2**, 155 (1952).