

# Stability, Thermal Behavior, and Crystal Structure of Ion Ordered $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$ Phases ( $\text{Ln} = \text{Sm–Dy}$ )

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This paper deals with the bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  phases recently isolated in the composition range  $0.275 \leq x \leq 0.40$  depending on the lanthanide substituent ( $\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy}$ ). These phases are slowly obtained by long time annealing ( $\cong 1500$  hr) of the corresponding fcc  $\delta\text{-Bi}_2\text{O}_3$  type phase at about  $800^\circ\text{C}$ , and exhibit a cell parameter almost twice the fcc parameter. X-ray diffraction investigations of the stability and crystal structure properties of the phases during thermal treatments have clearly shown that they are stable only in the temperature range  $800\text{--}1000^\circ\text{C}$ , depending on the lanthanide substituent. Below  $800^\circ\text{C}$ , they are metastable, but an annealing treatment or a slow dynamic thermal treatment between  $600$  and  $800^\circ\text{C}$  leads to a partial transformation into the true low temperature stable phases of the systems. Above  $1000^\circ\text{C}$  the fast transformation bcc to fcc  $\delta\text{-Bi}_2\text{O}_3$  type occurs systematically. The crystal structure of bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  has been refined with  $a = 11.0488(1)$  Å,  $I2_13$  space group ( $Z = 32$ ), using the Rietveld method. Starting from a  $\delta\text{-Bi}_2\text{O}_3$  type phase, the formation of this bcc phase can be explained on the basis of a structural disorder–order transformation as a result of a long time annealing process at high temperature. © 1977 Academic Press

## INTRODUCTION

The  $\delta\text{-Bi}_2\text{O}_3$  variety is well known for its attractive ionic conductivity properties in its stability temperature range,  $730\text{--}825^\circ\text{C}$  (1). Numerous partial cationic substitutions for  $\text{Bi}^{3+}$  have been investigated, aiming at preserving the face centered cubic (fcc hereafter)  $\delta\text{-Bi}_2\text{O}_3$  structure down to

room temperature. In particular, this has been achieved using trivalent cations such as  $\text{Y}^{3+}$  or lanthanides (2–7). Different sources suggest the existence of an anionic or/and cationic order in the fcc phase obtained at room temperature (8–10). It seems that the  $\delta$ -type structure cannot be effectively stabilized at room temperature, and that the reported phases are in fact metastable (11). A recent investigation of the  $\delta$  phase belonging to different  $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$  systems ( $\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy}$ ) confirms this assumption (12, 13).

A process of annealing (at about  $800^\circ\text{C}$ ) of  $\delta$  phases belonging to these systems, within the composition range  $0.275 \leq \text{Ln}/(\text{Ln} + \text{Bi}) \leq 0.40$  (depending on  $\text{Ln}$ ), and conducted for a long period of time, i.e., up to 1500 hr, yields a structural modification. As a result, new diffraction lines grow out of the original fcc pattern and characterize a true body centered cubic (bcc hereafter) cell with  $a_{\text{bcc}} \cong 2 \cdot a_{\text{fcc}}$ . The fcc  $\rightarrow$  bcc transformation is very slow, in contrast with the opposite transformation (bcc  $\rightarrow$  fcc), which is quickly observed at a temperature above  $900\text{--}1000^\circ\text{C}$ , depending on the material composition. The preliminary formation of the  $\delta$  type phase seems to be necessary to obtain the bcc new phase; this was also observed, e.g., in the  $\text{Bi}_2\text{O}_3\text{--Gd}_2\text{O}_3$  system during a synthesis process based on a starting mixture of a rhombohedral  $\text{Bi}_{0.765}\text{Sr}_{0.235}\text{O}_{1.383}$  type solid solution and a rhombohedral LaOF type phase. This led us to consider that the bcc phase formation was resulting from an ordering of the fcc phase formation.

This paper deals with the thermal behavior (stability and crystallographic data) of various samples of bcc  $\text{Bi–Ln–O}$  phases. As the composition  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  is the most easily obtained under these conditions, its structure has been refined from precise powder X-ray diffraction data, using the Rietveld method.

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## EXPERIMENTAL

## THERMAL EVOLUTION

Polycrystalline samples of bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  phases were prepared by repeated 1-week treatments at about  $800^\circ\text{C}$  in platinum crucibles, with a total duration as long as 2 mo. At the end of each treatment, the materials were air quenched and were analyzed by X-ray powder diffraction (XRPD) using  $\text{CuK}\alpha$  radiation. Pure bcc phases were obtained for  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  phases with  $\text{Ln} = \text{Sm}$  ( $x = 0.38$ ),  $\text{Eu}$  ( $x = 0.375$ ),  $\text{Gd}$  ( $x = 0.275\text{--}0.40$ ),  $\text{Tb}$  ( $x = 0.275\text{--}0.35$ ),  $\text{Dy}$  ( $x = 0.30\text{--}0.35$ ), and  $\text{Y}$  ( $x = 0.315\text{--}0.35$ ) (14). In order to check that no composition evolution occurred during these particularly long thermal treatments, two experiments were made: First, a Bi chemical analysis, using chelatometric titration with EDTA, was realized on  $\text{Bi}_{0.625}\text{Eu}_{0.375}\text{O}_{1.5}$  and  $\text{Bi}_{0.62}\text{Sm}_{0.38}\text{O}_{1.5}$ , and the results confirmed the bismuth nominal values. Second, a synthesis of the bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  phase was conducted in parallel in platinum and gold crucibles. Both resulting pure bcc phases allowed us to exclude any platinum incorporation in the sample.

The thermal behavior of different samples was investigated through various complementary techniques:

- Differential thermal analyses were realized in gold (below  $1000^\circ\text{C}$ ) or in alumina (up to  $1100^\circ\text{C}$ ) crucibles using a heating-cooling rate of  $300^\circ\text{C}\cdot\text{h}^{-1}$  (DuPont Instruments)

- X-ray thermodiffractometry studies were carried out using either a Guinier Lenné camera (gold grid sample holder; heating rate  $20^\circ\text{C}\cdot\text{h}^{-1}$ ) or a Siemens D5000 X-ray diffractometer equipped with a Siemens HTK10 high temperature device (platinum sample holder; average heating-cooling rate  $300^\circ\text{C}\cdot\text{h}^{-1}$ ; air gas flow). In both cases, the materials were deposited on the sample holders using an ethanol slurry which yields, upon evaporation, a regular layer of the powdered sample.

- The thermal behavior of the bcc phase, during isothermal treatments at various temperatures, was also investigated through room temperature XRPD patterns of annealed samples.

The structure of the bcc phase has been investigated for the  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  term. Its powder X-ray diffraction data were recorded at room temperature on a Siemens D5000 diffractometer using a Bragg-Brentano geometry with a back monochromatized  $\text{CuK}\alpha$  radiation. The diffraction pattern was scanned by steps of  $0.03^\circ$  ( $2\theta$ ) over the angle range  $10^\circ\text{--}120^\circ$ , with a counting time of 50 s per step. In order to minimize the orientation effects which occur when powdered samples are pressed, we have used a side loading method and the sample was rotated at  $3.14\text{ rad}\cdot\text{sec}^{-1}$  during the data recording. The precise positions of the peaks were determined by means of the fitting program FIT available in the PC software package DIFFRAC-AT from SOCRIM.

Most of the DTA thermograms exhibit a broad endothermic effect in the temperature range  $900\text{--}1050^\circ\text{C}$ , with a maximum near  $975^\circ\text{C}$ . No thermal effect is observed on the cooling runs. In all cases, for DTA investigations conducted in gold crucibles, only the typical reflections of  $\delta\text{-Bi}_2\text{O}_3$  type phases are noted on the XRPD patterns of the final residues. In a preliminary interpretation, these DTA results were taken as a proof that this bcc phase was a true low temperature stable phase in the investigated  $\text{Bi}_2\text{O}_3\text{--Ln}_2\text{O}_3$  systems; as a result, the  $\text{fcc} \rightarrow \text{bcc}$  transformation was considered to be extraordinarily slow on cooling. On the basis of previously published refined cell parameters of the bcc phases, Fig. 1a presents the composition to parameter relations. Surprisingly enough, whatever the lanthanide, the variations of  $a$  versus  $x$  are very small in contrast to the related expansion of the  $\text{fcc } \delta$  type cell parameter (4). Figure 1b shows a linear dependence of the bcc cell parameter on the  $\text{Ln}^{3+}$  radius (15,16), estimated for  $\text{Bi}_{0.625}\text{Ln}_{0.375}\text{O}_{1.5}$ .

X-ray thermodiffractometry was used to elucidate the high temperature behavior of these phases, on a D5000 diffractometer, between room temperature and  $1100^\circ\text{C}$  during a heating-cooling cycle for various samples. The X-ray reflections have been indexed in the bcc phase ( $a \cong 11.0 \text{ \AA}$ ) and in the  $\text{fcc } \delta$  type phase ( $a \cong 5.5 \text{ \AA}$ ) for the heating and for the cooling run, respectively; the cell parameters have been refined for all the investigated temperatures.

A linear domain represents the dependence of the lattice constant  $a$  on the temperature and characterizes the bcc phase, except for  $\text{Bi}_{0.725}\text{Gd}_{0.275}\text{O}_{1.5}$ , which is partly decomposed above  $600^\circ\text{C}$ . In the temperature range  $1000\text{--}1100^\circ\text{C}$ , the extinction of many reflections characterizes the  $\delta$ -type phase formation. Two linear domains of  $a_{\text{fcc}}$  lattice parameter evolution vs temperature are observed on cooling; they are also observed during a heating-cooling cycle of  $\delta$ -type phase previously prepared and quenched. Figure 2 presents, for the  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  material, the evolutions of the cell parameters vs temperature for the bcc phase during a heating process (a) and for the  $\delta$ -type phase upon heating (b) and upon cooling (c). Figure 3 shows the temperature-cell parameter dependence of some examples of the bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  phase ( $\text{Ln} = \text{Gd}$  and  $\text{Tb}$ ).

It is probable that the presence of two domains of evolution of the  $\text{fcc}$  cell parameter characterizes the existence of at least two levels of order of elements. Down to  $450^\circ\text{C}$  the disordered high temperature form is preserved under dynamic cooling conditions ( $300^\circ\text{C}\cdot\text{hr}^{-1}$ ). Below this temperature ordering occurs slowly; it disappears on heating in similar dynamic conditions nearly  $600^\circ\text{C}$ . The fast data recording conditions do not make it possible to notice any reflection characteristic of such an ordering, which is quite difficult to investigate.

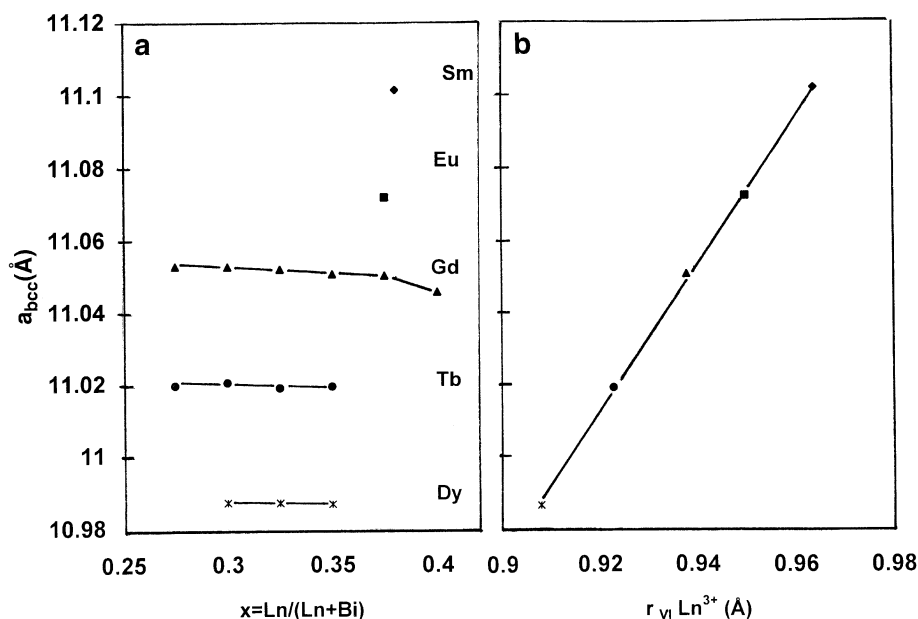


FIG. 1. Variations of bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  cell parameter versus (a)  $x = \text{Ln}/(\text{Bi} + \text{Ln})$  ratio; (b)  $\text{Ln}^{3+}$  radius ( $a$  estimated for  $x = 0.375$ ).

When heated above  $600^\circ\text{C}$ ,  $\text{Bi}_{0.725}\text{Gd}_{0.275}\text{O}_{1.5}$  is partly decomposed, and this is unambiguously proved by the appearance of the principal X-ray reflections of the rhombohedral  $\text{Bi}_{0.765}\text{Sr}_{0.235}\text{O}_{1.383}$  type phase; these lines are particularly intense near  $750^\circ\text{C}$  (Fig. 4). This observation led us to undertake an isothermal annealing, at  $700^\circ\text{C}$ , of the  $\text{Bi}_{1-x}\text{Gd}_x\text{O}_{1.5}$  materials of bcc structure ( $x = 0.275$ – $0.35$ – $0.375$ ) and fcc  $\delta$ -type structure ( $x = 0.35$ ). For all samples, the characteristic reflections of the rhombohedral

$\text{Bi}_{0.765}\text{Sr}_{0.235}\text{O}_{1.383}$  type phase were clearly identified after one week treatment. Furthermore similar decomposition was observed during a thermodiffraction investigation of  $\text{Bi}_{0.675}\text{Tb}_{0.325}\text{O}_{1.5}$  ( $670$ – $755^\circ\text{C}$ ) using a Guinier Lenné camera, as well as during isothermal annealing at  $700^\circ\text{C}$  for other samples. This clearly indicates that each bcc phase is in fact metastable between room temperature and  $700^\circ\text{C}$ . Its decomposition during isothermal annealing treatments is perceptible for temperature above  $600^\circ\text{C}$ . The bcc phase is a true stable phase in the temperature range  $800$ – $1000^\circ\text{C}$ . Decomposition at higher temperatures leads to the corresponding fcc phase.

From these experimental observations it becomes evident that the  $\text{Bi}_2\text{O}_3$ – $\text{Sm}_2\text{O}_3$  phase diagram, which was previously proposed (7), has to be somehow corrected near the composition  $\text{Bi}_{0.62}\text{Sm}_{0.38}\text{O}_{1.5}$  and should display the bcc phase in the temperature range  $800$ – $900^\circ\text{C}$ ; the compositional narrowness of its domain makes it impossible to propose any sure modification of the phase diagram.

### STRUCTURAL INVESTIGATION

In a previous work (13) it was shown that the XPRD pattern of  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  is in good agreement with a pure C-type rare-earth oxide model (space group  $Ia\bar{3}$  (17)) provided the  $hk0$  reflections ( $h, k$  odd) are removed from the list.

The crystal structure refinement was first considered on the basis of the structure of the C-type rare-earth oxide

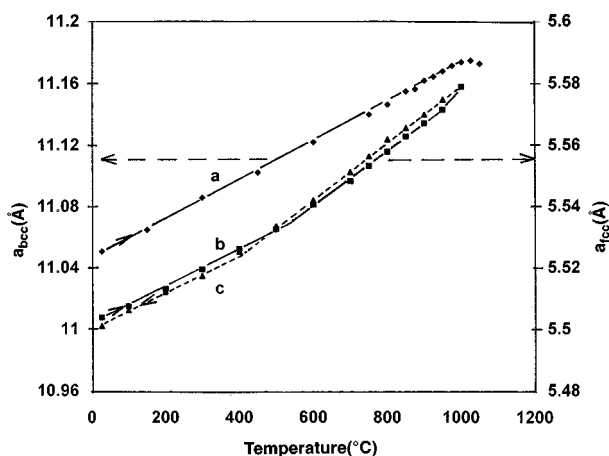
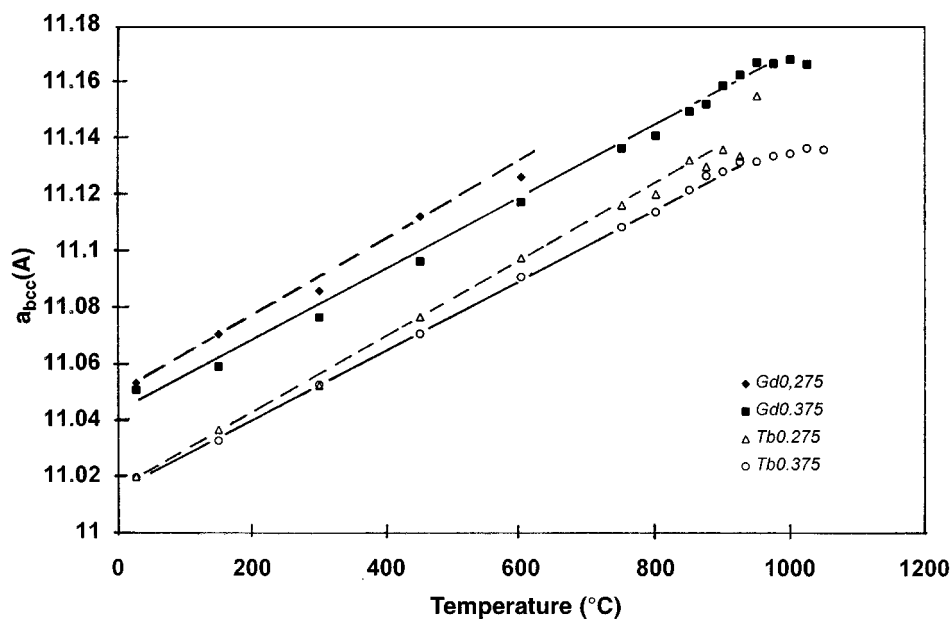
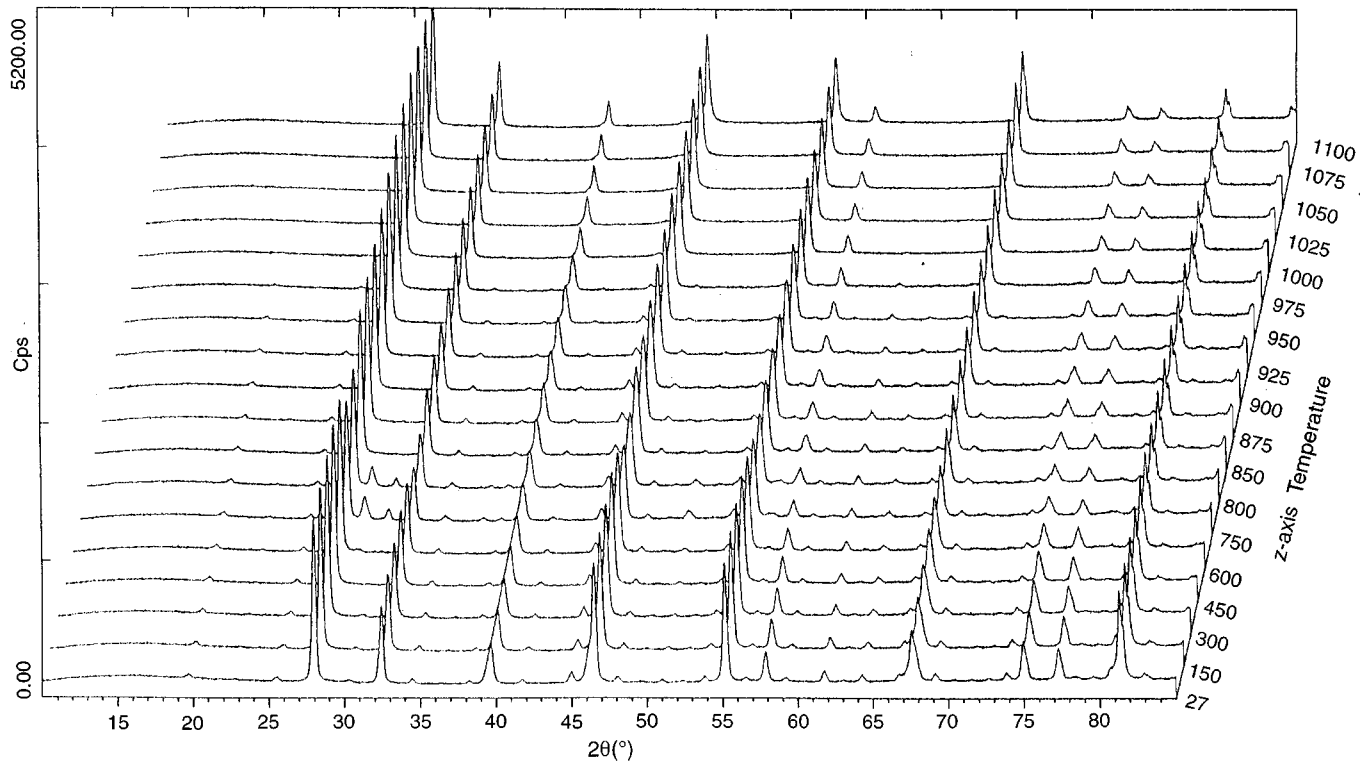


FIG. 2.  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  lattice parameters evolution versus temperature for bcc ordered phase during a heating process (a) and for fcc  $\delta$  type phase upon heating (b) or upon cooling (c).


 FIG. 3. Typical temperature dependence of bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  cell parameter.

family (18). The accurate cell parameter  $a = 11.0488(1) \text{ \AA}$  has been refined from precise peak positions determined using the typical conditions described in Experimental; the density value,  $d_m = 8.44(1) \text{ g cm}^{-3}$  and the lattice constant

agree with the presence of  $32 \text{ Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  formulae per unit cell ( $d_x = 8.46$ ). This implies 48 oxygen atoms in the unit cell. The six space groups which are potential candidates would be  $Im3m$ ,  $I432$ ,  $I43m$ ,  $Im3$ ,  $I23$ , and  $I2_13$ ; they


 FIG. 4. Evolution of the X-ray diffraction pattern versus temperature for bcc  $\text{Bi}_{0.725}\text{Gd}_{0.275}\text{O}_{1.5}$ .

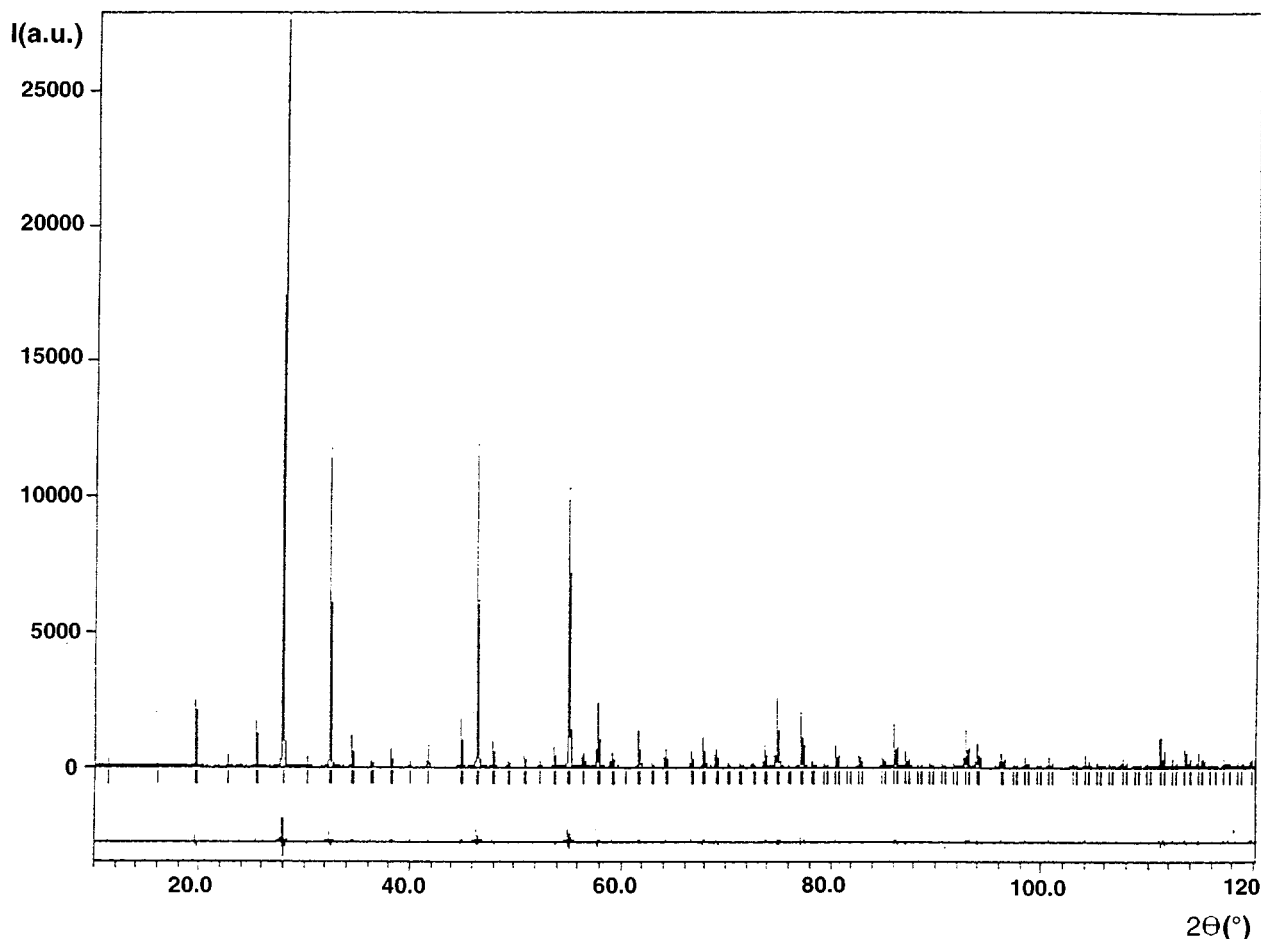
**TABLE 1**  
**Atomic Coordinates and Isotropic Thermal Parameters for bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  ( $I2_13$  Space Group,  $Z = 32$ )**

Atom	Site	Occup. factor	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$
Bi(1)	8a	1	0.2702(2)	0.2702(2)	0.2702(2)	1.8(1)
Bi(2)	12b	1	-0.0163(4)	0.0	0.25	0.29(4)
Bi(3)	12b	0.066	0.4979(6)	0.0	0.25	1.9(8)
Gd	12b	0.934	0.4979(6)	0.0	0.25	1.9(8)
O(1)	24c	1	0.373(3)	0.079(5)	0.388(4)	2.4(6)
O(2)	24c	1	0.127(4)	0.349(3)	0.139(4)	2.4(6)

were examined from the point of view of the spatial arrangement of the oxygen atoms.  $I2_13$  seemed to be the only space group giving a reasonable atomic arrangement. Then the cations' positions were examined on the basis of this space group hypothesis. Structural refinements led us to exclude some possibilities upon trial, and one solution has been selected: the special positions (8a) and (12b) are occupied by 20 Bi atoms. The other 12 cations, i.e., 0.8 Bi and 11.2 Gd atoms, are statistically distributed in another set of (12b)

special positions; their occupancy factors were fixed to fit the nominal composition. All oxygen atoms are located in two sets of general (24c) sites (Table 1).

At the end of the refinement process, the agreement between observed and calculated data was indicated by the reliability factors  $R_{\text{Bragg}} = \sum_k |I_k - I_k^{\text{calc}}| / \sum_k I_k = 8.9\%$  and  $R_F = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}| = 9.9\%$  and by the representation of the observed and calculated patterns for  $10^\circ < 2\theta < 120^\circ$  (Fig. 5). The refinement converged at



**FIG. 5.** Observed (points) and calculated (continuous line) powder X-ray diffraction patterns of bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$ ; the difference between the observed and calculated patterns appears in the lower part.

$\chi^2 = (R_{\text{wp}}/R_{\text{exp}})^2 = 4.2$  for 404 observations and 32 variables. Selected interatomic distances are reported in Table 2. The cations are represented in the unit cell cross sections at  $z = 0, 1/4, 1/2, 3/4$  (Fig. 6), while O atoms are located near  $z = 1/8, 3/8, 5/8, 7/8$  sections.

An interesting feature of this bcc structure is its close relationship with its parent fcc fluorite type structure: we

can consider that the bcc unit cell of  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  ( $Z = 32$ ) can be decomposed into 8 cubes, their centers defining the fcc unit cell.

In the  $\delta\text{-Bi}_2\text{O}_3$  fluorite type structure, the lattice is built from  $\text{Bi}^{3+}$  cations in the fcc sites, where the  $\text{O}^{2-}$  anions are randomly distributed in six out of the eight tetrahedral crystallographic sites, thus leaving two vacant sites. In

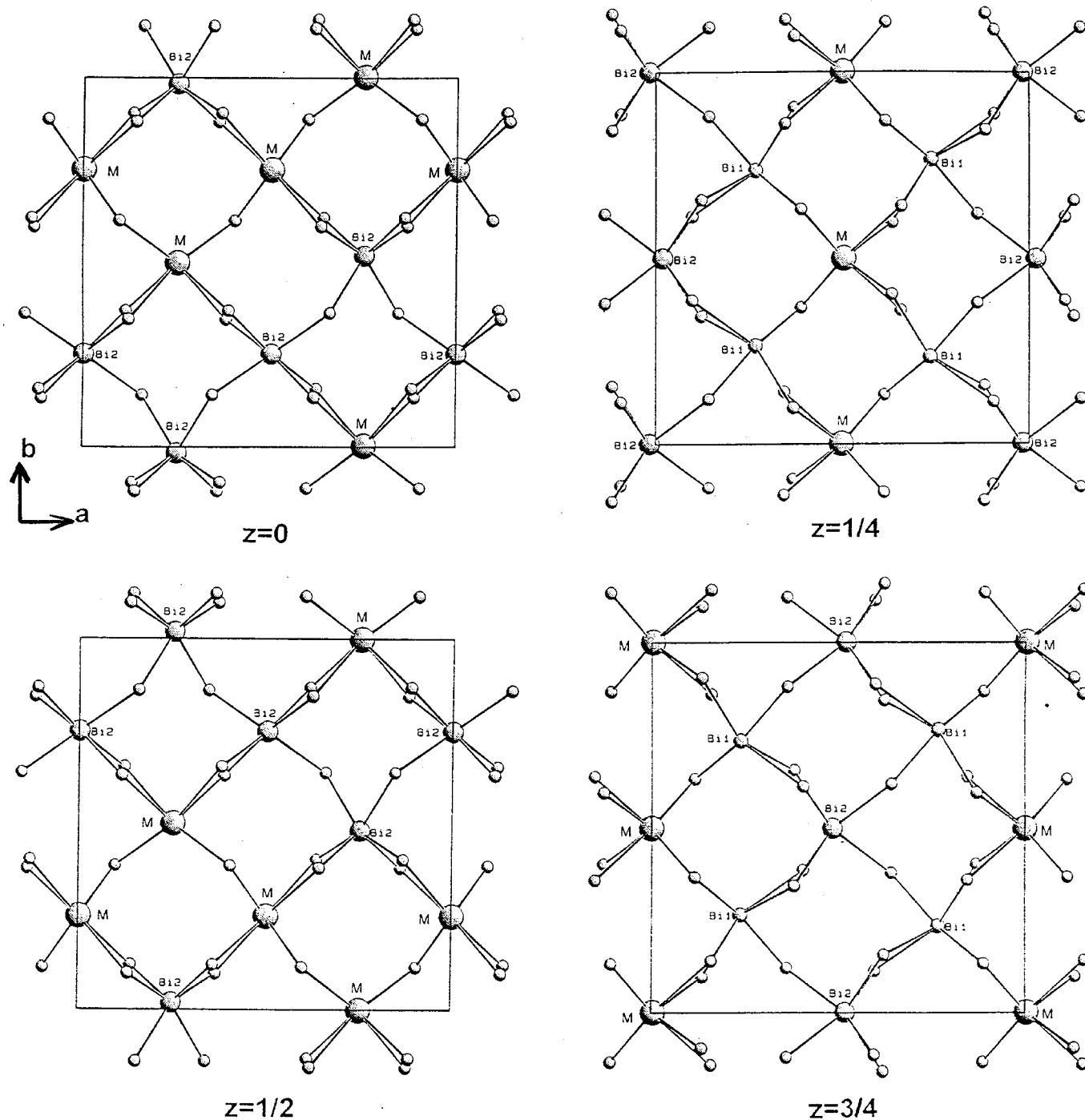


FIG. 6. Cross sections at  $z = 0, 1/4, 1/2, 3/4$ , of the bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  cell ( $M = \text{Gd-Bi}(3)$  mixed site; oxygen atoms are not labeled).

**TABLE 2**  
Selected Interatomic Distances (Å) for bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$

$\text{Bi}(1)\text{-O}(1)_i$	2.73(4)	$\text{O}(1)\text{-O}(2)_{ii}$	2.67(5)
$\text{Bi}(1)\text{-O}(2)_i$	2.31(4)	$\text{O}(1)\text{-O}(2)_{iii}$	2.97(6)
$\text{Bi}(2)\text{-O}(1)_{viii(0\bar{1}0)}$	1.96(4)	$\text{O}(1)\text{-O}(2)_v$	2.43(6)
$\text{Bi}(2)\text{-O}(2)_{ii}$	2.48(4)	$\text{O}(1)\text{-O}(2)_{ix(001)}$	2.95(6)
$\text{Bi}(2)\text{-O}(2)_{vi(0\bar{1}0)}$	2.40(4)		
$\text{Bi}(3)/\text{Gd}\text{-O}(1)_i$	2.24(4)		
$\text{Bi}(3)/\text{Gd}\text{-O}(1)_{vii(1\bar{1}0)}$	2.67(4)		
$\text{Bi}(3)/\text{Gd}\text{-O}(2)_{iii}$	2.63(4)		

Note.  $A(n)_{i(pqr)}$  represents atom  $A(n)$  to which the symmetry  $i$  has been applied followed by a translation  $pa + qb + rc$ . Symmetry code (i)  $x, y, z$ ; (ii)  $z, x, y$ ; (iii)  $y, z, x$ ; (v)  $y, \bar{z}, \bar{x}$ ; (vi)  $\bar{x}, 1/2 + y, 1/2 - z$ ; (vii)  $\bar{z}, 1/2 + x, 1/2 - y$ ; (viii),  $\bar{y}, 1/2 + z, 1/2 - x$ ; (ix)  $1/2 - z, x, \bar{y}$ .

For example,  $\text{O}(2)_{ix(001)}$ : atom position O(2), symmetry card (ix), and translation (001).

$\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$ , the refined structural model is an fcc related sublattice, built from Bi(1) atoms defining the summits of the unit cell, with the face centered positions occupied half by Bi(2) and half by ( $\text{Gd}_{0.934}\text{Bi}(3)_{0.066}$ ) mixed cations; both of these cations are in a pseudo-cubic coordination made of six oxygen atoms and two vacancies. As a result, these sublattice cations positions are slightly shifted from their theoretical fcc positions, thus imposing the overall bcc lattice type for the investigated  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  composition.

In the bcc lattice, we observe an ordered distribution of the  $\text{O}^{2-}$  anions altogether with the “vacant” sites, which are located at regular distances ( $a_{\text{bcc}}\sqrt{3}/4$ ) in four crystallographic directions,  $[1\ 1\ 1]$ ,  $[1\ 1\ \bar{1}]$ ,  $[1, \bar{1}, 1]$ , and  $[1, \bar{1}, \bar{1}]$ , running respectively through the origin and the centers of the (010), (100), and (001) faces.

In the  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  bcc unit cell (space group  $I2_13$ ) the cations are located in two sets of 12b sites. The first is fully occupied by  $\text{Bi}^{3+}$ ; the second is statistically occupied by 11.2  $\text{Gd}^{3+}$  and 0.8  $\text{Bi}^{3+}$ , according to the starting composition. Obviously, the composition resulting from a  $\text{Gd}^{3+}$  full occupancy of the second set would be formulated as  $\text{Bi}_{0.625}\text{Gd}_{0.375}\text{O}_{1.5}$ , thus corresponding to a cation ordered structure. This theoretical model is corroborated by the results previously described:

- The material  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  belongs to a solid solution domain with  $0.275 \leq \text{Gd}/(\text{Bi} + \text{Gd}) \leq 0.40$ , thus covering the particular 0.375 model. Apparently, two different types of lattice parameter evolution exist on the two sides of  $x = 0.375$  (Fig. 1a).

- With  $\text{Ln} = \text{Sm}$  and  $\text{Eu}$ , a bcc single phase material has been obtained only for  $\text{Bi}_{0.625}\text{Ln}_{0.375}\text{O}_{1.5}$ . For  $\text{Ln} = \text{Tb}$ ,  $\text{Dy}$ ,  $\text{Y}$ , solid solutions domains of bcc phases have been identified for  $\text{Ln}/(\text{Bi} + \text{Ln}) \leq 0.35$ . Considering these results, clearly relating the width of the solid solution domains to the  $\text{Ln}$  element, it seems reasonable to expect the syn-

thesis of the totally ordered 0.375 phase by a modification of the temperature treatment.

## CONCLUSION

This investigation has revealed significant information on the bcc  $\text{Bi}_{1-x}\text{Ln}_x\text{O}_{1.5}$  phases:

- The thermal behavior of these phases depends on the sample composition as well as on the experimental scan speed. For most samples decomposition of the bcc phase has been evidenced after long treatment in the temperature range 600–800°C. Therefore the bcc phase has to be considered as a high temperature stable phase above 800°C. An annealing or a slow dynamic thermal treatment below this temperature can lead to its transformation into the low temperature stable phase of the system.

- When heated at a significant dynamic heating rate ( $300^\circ\text{C}\cdot\text{hr}^{-1}$ ), no decomposition of the bcc phase occurs from room temperature up to 1000°C. Above this temperature the set of bcc diffraction lines disappears and the fcc lines are restored.

- The structure of bcc  $\text{Bi}_{0.65}\text{Gd}_{0.35}\text{O}_{1.5}$  has been refined using the Rietveld method. It can be interpreted on the basis of a structural disorder  $\rightarrow$  order transformation, obtained from the corresponding fluorite type phase, after a long annealing process at high temperature.

The fully ordered cation structure corresponds to the composition  $\text{Bi}_{0.625}\text{Gd}_{0.375}\text{O}_{1.5}$ .

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