

BRIEF COMMUNICATION

Structural Disorder and Ionic Conduction: The Case of Bi_2O_3

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The structural aspects of the ionic conduction properties of Bi_2O_3 are analyzed with a model based on the search of the common features in the X-ray diffraction pattern of the Bi_2O_3 phases. Within this model, which allows one to point out similarities in the metal sublattice distributions, static disorder effects are introduced and the α to β and β to δ phase transitions are described in terms of order–disorder transformations in the cation and anion sublattices, respectively. This finding makes it possible to outline, in parallel with previous results on ZrO_2 , possible conditions for obtaining high-temperature oxygen-ion conductors. © 1996 Academic Press, Inc.

Due to their physical properties, Bi_2O_3 polymorphs have raised much interest for industrial applications in the field of fuel cells and catalysis. Indeed, the high temperature δ - Bi_2O_3 phase is the best known ionic conductor oxide (1). New electrolytes based on bismuth oxide for fuel applications at moderate temperatures have recently been developed (2) while leaving some problems unresolved (3, 4). The physical properties of the α -, β -, and δ - Bi_2O_3 phases can be usefully discussed on a structural basis provided that structural models which reveal analogies and differences among these phases are derived. This modeling could also allow a comparison with other ionic conductors such as the stabilized zirconias. In this letter, the structural study of the Bi_2O_3 phases is proposed on the basis of a model recently developed for the Mo–Bi–O mixed oxides (5). The model is based on the search of the common features detectable in the metal sublattice distributions. Thus it is possible to describe the α - to β -phase transition as an order–disorder transformation in the metal sublattice. As for the β - to δ -phase transition, following the idea that the high-temperature phase can be derived by introducing a structural (static) disorder into the phase which is stable at the lowest temperature—this assumption being supported by the observed stabilization by impurities of the Bi_2O_3 (6), ZrO_2 (7), and WO_3 (8) high-temperature phases—the model allows one to describe the β - to δ -

phase transition as mainly due to an order–disorder transformation in the anion sublattice.

The Bi_2O_3 α and β phases are usually described as layer structures, while the δ phase is modeled as a defective fluorite structure, similar to that of the cubic zirconia phase. As results from a close inspection of Fig. 1, the two phases show remarkable differences. Bi ions have two different coordinations in the α phase (threefold and fourfold) while they have only a threefold coordination in the β phase. A straightforward relation between the two structures cannot be found. Therefore, a different viewpoint is needed to contrast and compare the structures. As shown below, this new viewpoint will be individuated through an analysis of the single crystal diffraction patterns and will allow a description of the Bi_2O_3 phases in terms of Bi layers.

The simulated X-ray diffraction patterns of Bi_2O_3 single crystals belonging to α , β , and δ phases show strong analogies. As can be observed in Fig. 2, even though the crystal structures of the phases are different, the XRD patterns are quite similar, all showing the same hexagonal symmetry. Further simulations show that these patterns do not change when the contribution of the oxygen ions is neglected; therefore, the character of the pattern can be ascribed to the Bi ion contribution and the similarities must depend on the metal distribution in the structures. Indeed, in this view all the considered phases can be described as formed by layers of metal atoms stacked with the periodicity defined by the d value of the most intense peak of the XRD powder pattern (Fig. 3). In the β and δ phases these layers have hexagonal symmetry, while the metal layer of the α phase has a distorted hexagonal geometry. In this approach, the metal atoms in the layer of the β - Bi_2O_3 phase are distributed about the average position of the α - Bi_2O_3 metal sites. The phase transition from α - to β - Bi_2O_3 can be described as an increase in symmetry in the arrangement of the metal atoms in the layer. This fact can also explain the higher entropy of the β phase compared to that of α - Bi_2O_3 (9). This is the first time that such relationship among

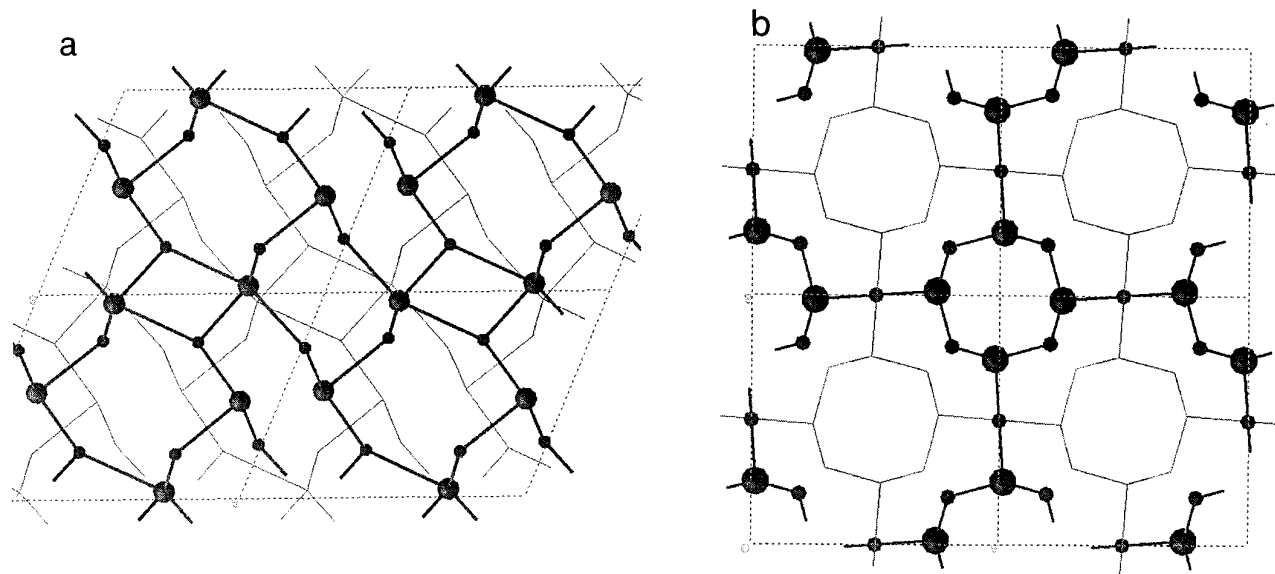


FIG. 1. Projection along the c axis of the α - Bi_2O_3 (a) and β - Bi_2O_3 (b) crystal structures. The single layers formed by oxygen and bismuth ions are indicated by a stick-and-ball representation. Bi ions (larger spheres) and O ions (smaller spheres) belonging to a single layer are connected by sticks. The coordination pattern of the underlying layer is represented by thin lines. Dotted lines represent the unit cell borders.

the metal distributions is identified in inorganic polymorphs. It is possible that the metal to metal interaction plays a fundamental role in the building of these structures. Actually, even in the BiO phase (10) the distribution of the metal atoms can be described by hexagonal layers. This observation may explain the fact that bismuth-oxide-based electrolytes are easily reduced when the partial pressure of oxygen is low (11). Indeed, the metal distribution in the layers is the same in the BiO and Bi_2O_3 phases and the reduction of Bi can be obtained only by a migration of oxygen between the metal layers. Moreover, similar layers

of metal atoms have been found in the Mo-Bi-O , W-Bi-O , and V-Bi-O systems (5). In the layers of these mixed oxides the cation in the higher oxidation state generates structural vacancies in the metal sites of the layer, that anyhow keeps its hexagonal geometry. Also, the γ - Bi_2O_3 type of structure can be described as formed by layers of metal atoms. However the hexagonal geometry is almost completely lost. This fact can be attributed to the presence in the structure of some cation, such as Si^{4+} , Ge^{4+} , or Bi^{5+} , with tetrahedral coordination (10).

In the δ - Bi_2O_3 phase perfectly hexagonal layers are

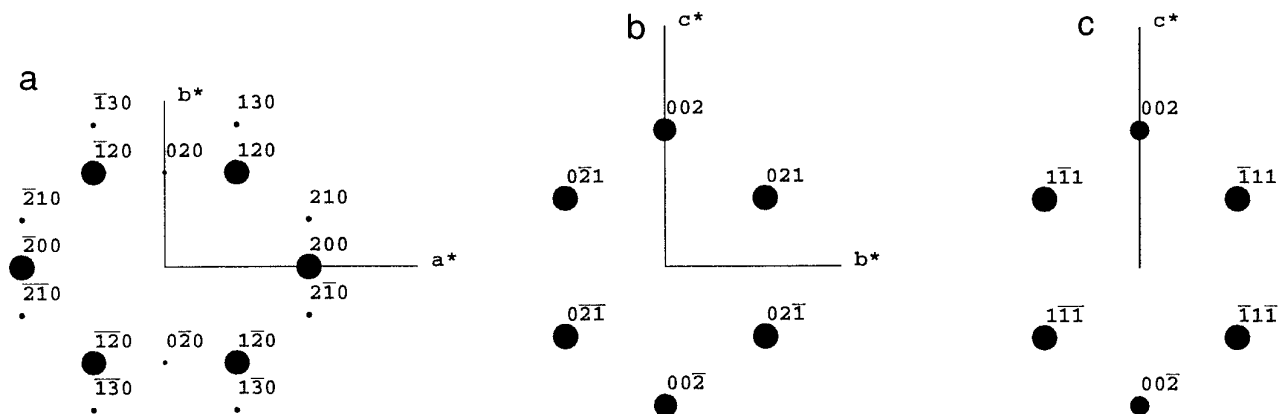


FIG. 2. Simulation of the single crystal X-ray diffraction patterns of α - Bi_2O_3 phase with the $[001]$ zone axis (a), β - Bi_2O_3 phase with the $[110]$ zone axis (b), and δ - Bi_2O_3 phase with the $[110]$ zone axis (c). The simulations have been performed on the basis of the results reported in the ICSD single crystal database. In all simulations an X-ray wavelength $\lambda = 1.5418 \text{ \AA}$ and a 2θ diffraction angle ranging from 0° to 40° were chosen. These results were generated using the program CERIU2, developed by Molecular Simulations Incorporated.

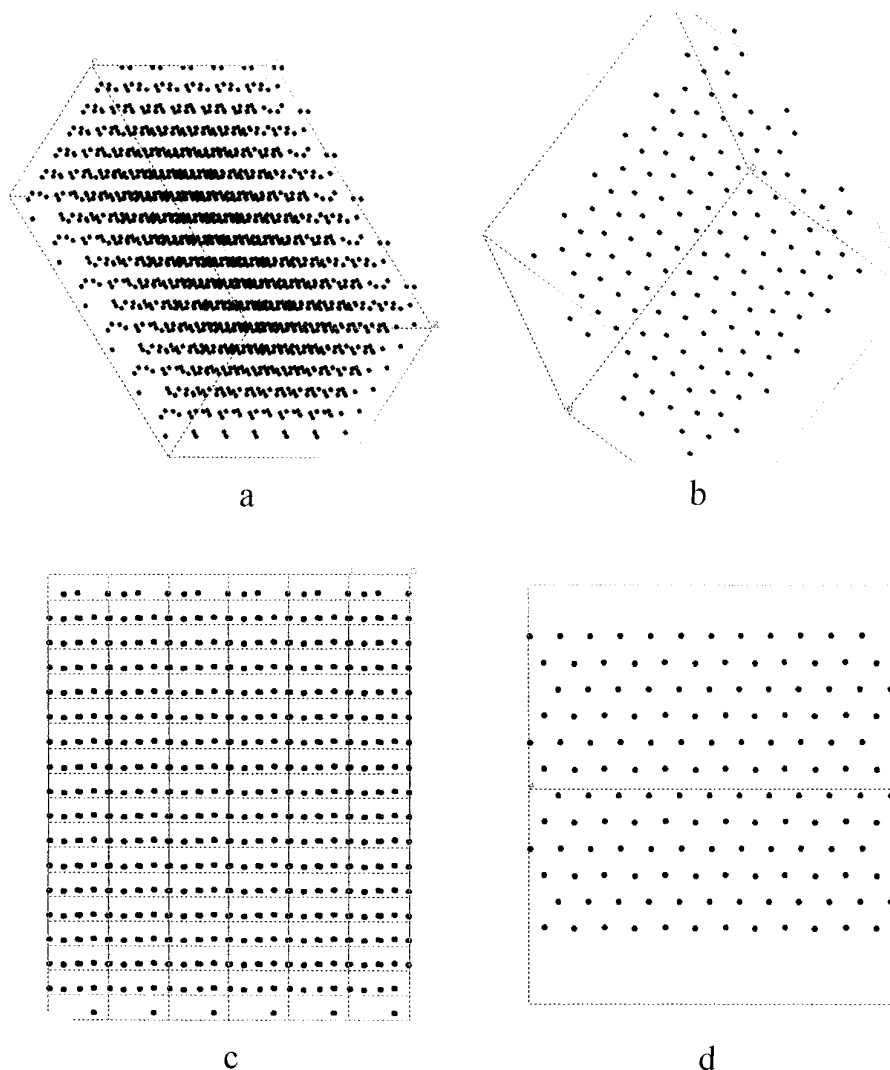


FIG. 3. (a) Projection perpendicular to the (021) plane of the metal sublattice of the α - Bi_2O_3 phase. The structure can be described as a sequence of parallel Bi layers stacking along the [021] direction. Oxygen ions, not reported, lay between the Bi layers. The layer is composed of Bi ions spreaded above and below the ideal (021) plane. (b) View of one of the Bi layers of the α phase. (c) Projection perpendicular to the (021) plane of the metal sublattice of β - Bi_2O_3 . The spread of Bi atoms belonging to a single layer is remarkably smaller with respect to case (a). (d) View of one of the Bi layers of the β phase. In the β - Bi_2O_3 phase the Bi layers have a hexagonal symmetry, while in the α - Bi_2O_3 phase the metal layers have a distorted hexagonal symmetry.

stacked to form a face centered cubic cation sublattice (12). The metal atom distribution in the β and δ structures is very similar, provided that the distortion in the β phase is not considered. Indeed, in the transition from the β to the δ phase, differences in the structure must be attributed only to the oxygen sublattice. A disordered model can be obtained from the β phase by applying the symmetry operations of the $P23$ space group (Fig. 4). The same approach was already used to justify the stability of the cubic ZrO_2 phase in nanopowders (13) and the presence of cubic WO_3 phase in thin film samples (14).

As shown in Fig. 4, the obtained structural model slightly differs from that resulting by fitting of a powder neutron diffraction pattern obtained at high temperature (15). In the latter model the oxide ions are statistically distributed in the $32f$ (Wyckoff) sites of the $Fm\bar{3}m$ space group and displaced from the tetrahedral site to the center of a triangular face of the tetrahedron. The occupancy of the two oxides are 0.43 and 0.08, respectively. In contrast, in the disordered model proposed here, the local structure is that of the β phase, which has already been related to the α phase, and only the long range ordering is lost. That makes

the symmetry increase. Therefore, at least in the case when the δ phase is stabilized at low temperature by impurities, it seems to be necessary to start from an ordered model in which the coordination of the metal, in this case Bi, should be similar to that found in the ordered low-temperature phases, in this case the β phase. In this frame, the

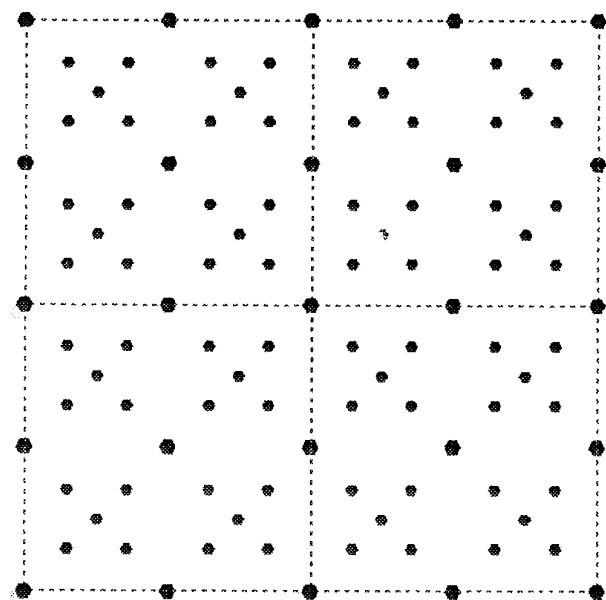
phase transition from the β to the δ phase can be seen with diffraction experiments, i.e., on a long-range scale, as an order-disorder transformation.

The present model is based on the hypothesis of a similar cation coordination for all the considered phases. Indeed, structural studies on the pure δ - Bi_2O_3 phase suggest that short-range ordering, possibly characteristic of α - Bi_2O_3 , does persist at temperatures closer to the α to δ transition temperature (Ref. 16 and references therein). However, a lack of diffuse scattering seen in δ - Bi_2O_3 seems to suggest, within the experimental sensitivity, a lack of local order (16).

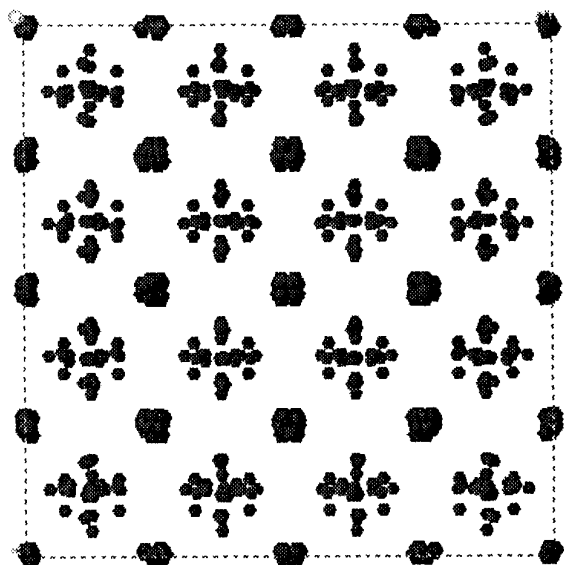
It is important to note that recent EXAFS results do not agree with the model proposed on the basis of a neutron diffraction experiment (17) and the Bi-O distances found in this work could be better justified by the model proposed here. Moreover this model can justify the conductivity behavior that is predominantly electronic in the α phase and mainly ionic in β - and δ - Bi_2O_3 (18).

If the present reasoning is correct, a cubic phase in Bi_2O_3 nanopowders as it is the case in ZrO_2 is expected. Since electrolytes based on stabilized bismuth oxide show no evidence of a grain boundary contribution to their conductivity (19) and since the effect of the dopants is to lower the conductivity (20), the possible use of pure Bi_2O_3 nanopowders in electrolytes must be explored.

In conclusion, it was shown that, as in the case of ZrO_2 , the disorder in the high-temperature phase of Bi_2O_3 can be structurally derived from the corresponding low-temperature phases. In both compounds the coordination in the room-temperature phase has a low symmetry and, as a consequence of the disorder, the oxygen sublattice has a liquid-like behavior (18). Therefore, the low symmetry and the low coordination number, as those observed for the room-temperature phases of ZrO_2 and Bi_2O_3 , may be necessary conditions for obtaining high-temperature oxygen-ion conductors. Moreover, in this frame some differences between ZrO_2 and Bi_2O_3 can be appreciated. In fact, as was already shown (5), a smaller number of oxygen ions is present between the cation layers in Bi_2O_3 than in ZrO_2 , which may promote a higher ion diffusion in the Bi_2O_3 lattice.



a



b

FIG. 4. (a) Disordered model proposed in Ref. (15) for the δ - Bi_2O_3 phase. The projection along the $[100]$ axis is shown. The Bi atoms are distributed over the ccp sites. O atoms are distributed over two positions: $1/4, 1/4, 1/4$ with an occupancy of 0.43, and 0.354, 0.354, 0.354 with an occupancy of 0.08. (b) Disordered model for the δ - Bi_2O_3 phase as proposed in the present work. The projection along the $[100]$ axis is shown. For both Bi and O the occupancy is normalized to 1. Bi atoms can be found again in a ccp sublattice. While Bi atoms are slightly spread over each cubic site, the effect of disorder, simulated by symmetry in the unit cell of the β phase, is dramatic in the case of oxygen ions.

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