

The Cation Array in the Bixbyite-Type Structures

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The structures of the bixbyite-type sesquioxides, M_2O_3 ($M = \text{In, Tl, Sc, Y, Ln}$) are analyzed in terms of their cation arrays. In all cases, with the exception of Yb_2O_3 , the M - M distances in the oxides are comparable to those of their parent metal. Topologically, the cation aggregates present in the oxides are fragments of the hcp, fcc, bcc, or bct elemental structures. © 1995 Academic Press, Inc.

in rutile (TiO_2) can be derived from the hcp-Ti structure instead of that of β -Hg as proposed in (1), and the above mentioned β - CsBeF_3 , KClO_3 , and CrB can be derived from the bcc structures of Cs, K, and Cr, respectively (3).

The aim of this work is to apply these principles to M_2O_3 compounds ($M = \text{Sc, Y, In, Tl, Ln}$), all of which crystallize in the bixbyite-type structure, also known as the C-type structure of the rare earth sesquioxides.

INTRODUCTION

It has been reported that in many cases the cations in oxides and fluorides adopt the structure of either simple alloys or elements. Examples are presented by the structures of β - CsBeF_3 and KClO_3 , whose cationic arrays are those of the CrB-type alloy, and TiO_2 (rutile), where the Ti array is that of β -Hg (1). The interest of this model is that it correlates compounds as different as β - CsBeF_3 , KClO_3 , and CrB and that it allows for a better understanding of some structures considering the anion-centering cation polyhedra instead of the classical cation-centering anion polyhedra (2). However, objections could be raised in the sense that the structure type itself remains unrelated to any other parent structure.

One of the most significant observations (1) is that in some isolated cases the cation arrangements in the oxides are identical to those of the constituent elements, i.e., Ca_2Si in β - Ca_2SiO_4 , Y_5Si_3 in $\text{Y}_5(\text{SiO}_4)_3\text{N}$, Ca in CaF_2 , etc. Furthermore, the unit cell dimensions of the oxide (fluoride) are almost identical to those of the alloy (element). This suggests the following question to us: Why is a cation array, for example, Mg_2Si in Mg_2SiO_4 (forsterite), related to the Ni_2In structure and not to the Mg_2Si alloy itself? We think that a model which relates a given structure with that of its constituent atoms has a more physical meaning. For this reason we propose a different model which considers the structures of oxides as fragments or deformations of the parent metal structure by the inclusion of other atoms (3–6). In this way, Mg_2SiO_4 is described as a derivative of hcp-Mg with SiO_4 groups inserted between Mg fragments. Similarly, the Ti subarray

DISCUSSION

References to this structure can be found in (7–9). It is cubic, $Ia\bar{3}$, with the metal atoms at two different sites, $M(1)$ at $8b$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and $M(2)$ at $24d$ ($x, 0, \frac{1}{4}$). The structure has been described as derived from that of CaF_2 in which $\frac{1}{4}$ of the anions are missing and the MX_8 cubes of the fluorite structure become MX_6 distorted octahedra in the C-type structure. Distortion of the anion packing would also induce a distortion of the cationic fcc array, observed in the CaF_2 -type structure, which is not present in the sesquioxides (8).

The cation array is represented in Fig. 1 for In_2O_3 (4). As seen there, all metal atoms appear six-coordinated, forming In_7 centered hexagons. Those centered by $\text{In}(1)$ atoms are slightly puckered and are rather regular in dimensions, i.e., $\text{In}(1)$ – $\text{In}(2)$ distances of $6 \times 3.348 \text{ \AA}$ and $\text{In}(2)$ – $\text{In}(2)$ distances of $6 \times 3.365 \text{ \AA}$. The hexagons are parallel to (111) planes and are interconnected by common $\text{In}(2)$ atoms forming a 3D network (see Fig. 1). The $\text{In}(2)$ atoms are also 6-coordinated by four $\text{In}(2)$ and two $\text{In}(1)$ atoms, but in this case the hexagons are rather difficult to define because two of the $\text{In}(2)$ – $\text{In}(2)$ distances are lengthened up to 3.837 \AA . The result would be very distorted puckered hexagon which is not drawn in Fig. 1. As seen in Table 1, this In array can be related in topology and distances to the structure of tetragonal indium ($I4/mmm$; $a = 3.253$, $c = 4.945 \text{ \AA}$, and $d_{c-v} = 8 \times 3.377 \text{ \AA}$). The topological relationship can be clearly observed in Figs. 2 and 3. The In-array in $\text{C-In}_2\text{O}_3$ also allows for the definition of two kinds of distorted body-centered prisms. One of them is centered by $\text{In}(1)$ atoms and has dimensions of 2×3.365 and $2 \times 3.837 \text{ \AA}$ (in the bases), and 2×5.05

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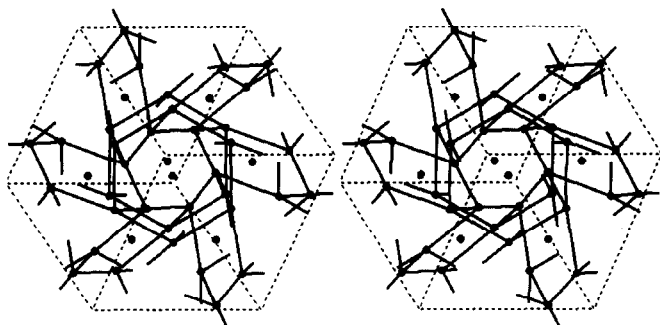


FIG. 1. Stereopair of a unit cell of $C\text{-In}_2\text{O}_3$ viewed along (111), showing the In substructure. Bonds are drawn between In(2) atoms to represent the hexagons described in the text. The hexagons are centered by In(1) atoms.

and $2 \times 5.10 \text{ \AA}$ (in the heights). The other one is centered by In(2) atoms and is represented in Fig. 2. It has the same dimensions as the former but differs from it in the space distribution of the In–In distances. The differences also extend to the eight d_{c-v} distances. In the former, the values are 4×3.348 and $4 \times 3.822 \text{ \AA}$. In the latter, these distances are slightly longer, 4×3.365 and $4 \times 3.867 \text{ \AA}$ (s and m distances of Fig. 2b, respectively). Compare all these values with the In–In distances of metallic indium which are collected in Table 1. It is also worth mentioning

TABLE 1

Selected $M\text{-}M$ Distances (\AA) in $C\text{-}M_2\text{O}_3$ Compounds and in Their Parent Metals

	a Parameter	$M(1)\text{-}M(2)$ $M(2)\text{-}M(2)$, s	Distances between hexagons, m	c Axes of the deformed bct cell
In_2O_3	10.117	6×3.348 6×3.365	3.822, 3.837	5.059, 5.103
Tl_2O_3	10.543	6×3.518 6×3.531	3.950, 3.961	5.272, 5.307
Sc_2O_3	9.845	6×3.240 6×3.260	3.739, 3.756	4.922, 4.973
Y_2O_3	10.607	6×3.516 6×3.533	4.000, 4.015	5.304, 5.348
	In	Tl	Sc	Y
	$I4/mmm$	$Im\bar{3}m$	$Fm\bar{3}m$	$Im\bar{3}m$
	$a = 3.253$	$a = 3.882$	$a = 4.541$	$a = 4.11$
	$c = 4.945$			
d_{M-M}	8×3.377	8×3.360	12×3.211	8×3.56
		$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
		$a = 3.456$	$a = 3.309$	$a = 3.647$
		$c = 5.525$	$c = 5.273$	$c = 5.731$

Note. The hexagons are those drawn in Figs. 1 and 2. The deformed bct cell is represented in Fig. 2 and s and m are the distances represented in Fig. 2b.

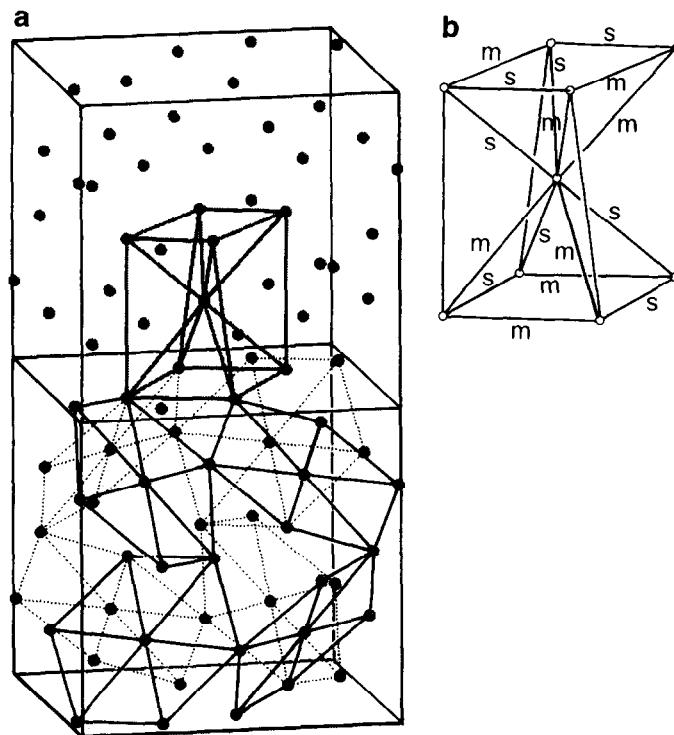


FIG. 2. (a) Perspective view of the In subarray in $C\text{-In}_2\text{O}_3$. Two unit cells are represented. At the bottom, the In(1)In(6)₆ centered hexagons are drawn. At the top, the deformed bct cell is depicted. (b) The distorted body-centered tetragonal prism, centered by In(2) atoms, s and m denote shortest and medium distances of Table 1.

that the heights of the prisms are also very close to the value of the c axis in elemental indium.

From the above discussion, we can conclude that the In_7 hexagons in $C\text{-In}_2\text{O}_3$ (Figs. 1 and 2) can be regarded as fragments of (101) planes of elemental In. Figure 3 shows its I tetragonal net, which has been decomposed into hexagons, such as those appearing in the sesquioxide. The conversion of one structure into the other can be thought of as the result of a lengthening of six (one-half) of the shortest In–In distances in the metal ($d_{cv} = 3.377$, $a = 3.253 \text{ \AA}$) up to the values close to 3.8 \AA in the oxide, but maintaining almost constant the other six distances. This results in an opening of the structure of elemental In, involving a volume increase of 19% ($26.14 \text{ \AA}^3/\text{at}$ and $32.25 \text{ \AA}^3/\text{at}$, respectively).

Y_2O_3 and Tl_2O_3 cation arrays can be related to the bcc nets of their parent Y and Tl, respectively (10, 11). The $M\text{-}M$ distances are collected in Table 1. One could think in a similar decomposition based on fragments of the $(110)_{\text{bcc}}$ planes of the parent metal. If this were so, the M_7 hexagons would be irregular, having distances of $4 \times a$ and $8 \times a \sqrt{3}/2$, and one must think of another rearrangement of the atoms to give the almost regular hexa-

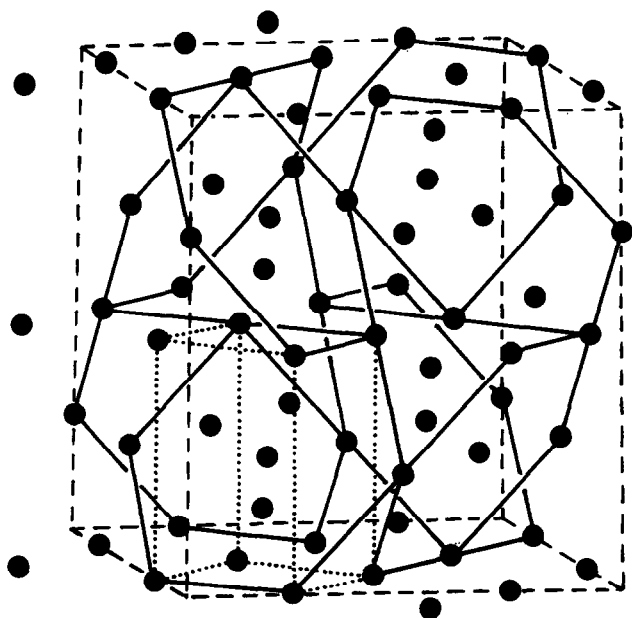


FIG. 3. The structure of elemental In decomposed in centered In_7 hexagons like those appearing in $\text{C-In}_2\text{O}_3$. Its bcc unit cell is represented by dotted lines. Discontinuous lines represent a unit cell equivalent to that of the sesquioxide.

gons which appear in the oxides. In the case of Y_2O_3 , the arrangement reproduces the shortest Y–Y distances in bcc-Y (see Table 1). However, if the mean distances of the (110) plane are taken into account, a disagreement of 5% is obtained. It should be outlined that the distances between hexagons (4.00 \AA) are almost coincident with the a axis of bcc-Y (4.11 \AA).

In the case of Tl_2O_3 , the Tl–Tl distances correspond to mean value of the distances involved in the $(110)_{\text{bcc}}$ planes (3.524 and 3.534 \AA , respectively), and, in addition, the shortest distances between hexagons are about 3.95 \AA , a value which is also close to the value of the a axis (3.88 \AA) of elemental bcc-Tl. Note also how the M – M distances in the oxides are close to the values in the hcp phases.

Sc presents four crystalline phases, i.e., hcp, fcc, In-type, and Np-type (10). The unit cell dimensions of hcp and fcc phases are collected in Table 1. The In-type structure has not been collected because its unit cell dimen-

sions ($a = 3.758$, $c = 4.761 \text{ \AA}$) and the shortest Sc–Sc distances ($d = 3.56 \text{ \AA}$) do not agree with the values observed in Sc_2O_3 (see Table 1) even if, from a topological point of view, this phase would be the most appropriate to describe the Sc arrangement in the oxide. As seen in Table 1, the Sc_7 hexagons are in fact fragments of both the fcc-Sc and hcp-Sc structures, although topologically, the Sc subarray can be better described as a distortion of the fcc phase.

It should be added that the same feature is observed in all $\text{C-Ln}_2\text{O}_3$ compounds, which can be described as fragments of their corresponding bcc or fcc phases (10, 11), preserving the M – M distances of the pure elements. The only exception is Yb_2O_3 , whose shortest Yb–Yb distances (3.45 \AA) are 10% shorter than in the metal (3.84 \AA).

The compounds just discussed are additional examples of how the structure of the metal remains as fragments in their compounds, which in this case are far from being considered as metal-rich compounds.

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