JOURNAL OF SOLID STATE CHEMISTRY 55, 101–105 (1984)

BRIEF COMMUNICATIONS

A Homologous Series of Recurrent Intergrowth Structures of the Type $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ Formed by Oxides of the Aurivillius Family

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Received March 21, 1984; in revised form May 28, 1984

Introduction

Polytypism wherein solids such as ZnS, CdI_2, and perovskite oxides exhibit unit cells where one of the parameters falls anywhere between a few and a few thousand Ångstroms is well documented in the literature (*1, 2*). Long periodicities are found in alloys such as CuAu (*3*) and in shear plane structures (*4*) as well, but the origin of the long periodicity in these two systems is different. What is of concern to us in this communication is the formation of long-period structures entailing coherent recurrent intergrowth of two chemically distinct but structurally related units possessing a nearly identical crystallographic plane. Across such a plane, the crystal can pass from one structure to another without significant strain, but with a change in composition. Recurrent intergrowth can accordingly generate a homologous series of compounds with a progressive increase in unit cell dimensions. An example of such recurrent intergrowth is provided by hexagonal barium ferrites, M_pY_q, where M = $BaFe_{12}O_{19}$ and Y = $Ba_2Me_2Fe_{12}O_{22}$ (*5*); in these ferrites, magnetic interactions seem to be important since the long-period structures are not formed when Fe^{3+} is replaced by Al^{3+}. We have investigated new recurrent intergrowth structures formed by oxides of the general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, first described by Aurivil-

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0022-4596/84 $3.00

lius (*6*). We have employed high-resolution electron microscopy (HREM) as well as diffraction methods for the present study, the use of HREM being specially crucial for a proper identification of recurrent intergrowth, which in turn depends entirely on the presence of local order in the arrangement of the lamellae of the two parent units. X-Ray diffraction can only give structural data averaged over a large number of unit cells and is not sensitive to disorder at the level of the local structure. The present study does indeed establish the occurrence of the homologous series of recurrent intergrowth structures of the general formula $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ where A = Ba or Bi. These oxides probably constitute a family of intergrowth structures where elastic interactions alone (*7*) seem to be responsible for the long periodicity.

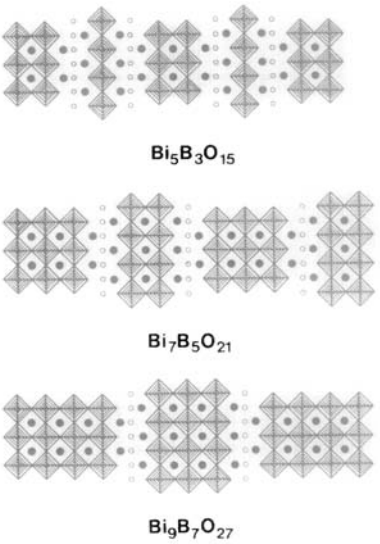

FIG. 1. Schematic illustration of the first three members of a homologous series of structures with general formula $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$ (A and Bi ions are shown as filled circles, with O^{2-} as open circles. BO_6 groups are represented in polyhedral form). The three compositions shown correspond to n = 2, 3, and 4 members of the homologous series. Note that n in the homologous series is equal to m + 1 of the Aurivillius family.

Experimental

Various oxide compositions were prepared by the reaction of the component oxides around 1300 K. The intergrowth structures examined by us are $Bi_5Nb_3O_{15}$, $Bi_7Ti_{4.5}W_{0.5}O_{21}$, $Bi_9Ti_6CrO_{27}$, $Bi_9Ti_6FeO_{27}$, and $BaBi_8Ti_7O_{27}$, all having been prepared and characterized for the first time (*4*). X-Ray diffraction patterns showed that the unit cells of all these oxides have similar a and b parameters (5.41–5.46 and 5.40–5.46 Å, respectively), but the c parameter varied depending on the composition (oxygen/metal ratio). Details of the local variation in the c parameter were revealed in the HREM examination at both 200 kV (interpretable point resolution of ca. 2.5 Å) and 500 kV (resolution of 2.0 Å). A JEOL-200CX electron microscope and the Cambridge University high-resolution electron microscope were employed for this purpose. Images were recorded at magnifications in the range 300,000–600,000×, after correction for both astigmatism and beam inclination. Computer simulation of model HREM images using the multislice method (*8*) was employed to confirm the intergrowth nature of the structures observed.

Results and Discussion

The homologous series of oxides formed by the recurrent intergrowth of two adjacent members of the Aurivillius family of compounds can be visualized as in Fig. 1. Accordingly, $Bi_5B_3O_{15}$ would be formed by the intergrowth of the m = 1 and m = 2 members of the Aurivillius family, $(Bi_2O_2)(A_{m-1}B_mO_{3m+1})$, while $Bi_9B_7O_{27}$ would be formed by the m = 3 and m = 4 members; $Bi_7B_5O_{21}$ would be formed by the m = 2 and m = 3 members. We have investigated all the three types of intergrowths.

$Bi_5Nb_3O_{15}$ gave an X-ray pattern with $c \simeq$ 21 Å which is about half the sum of the c-

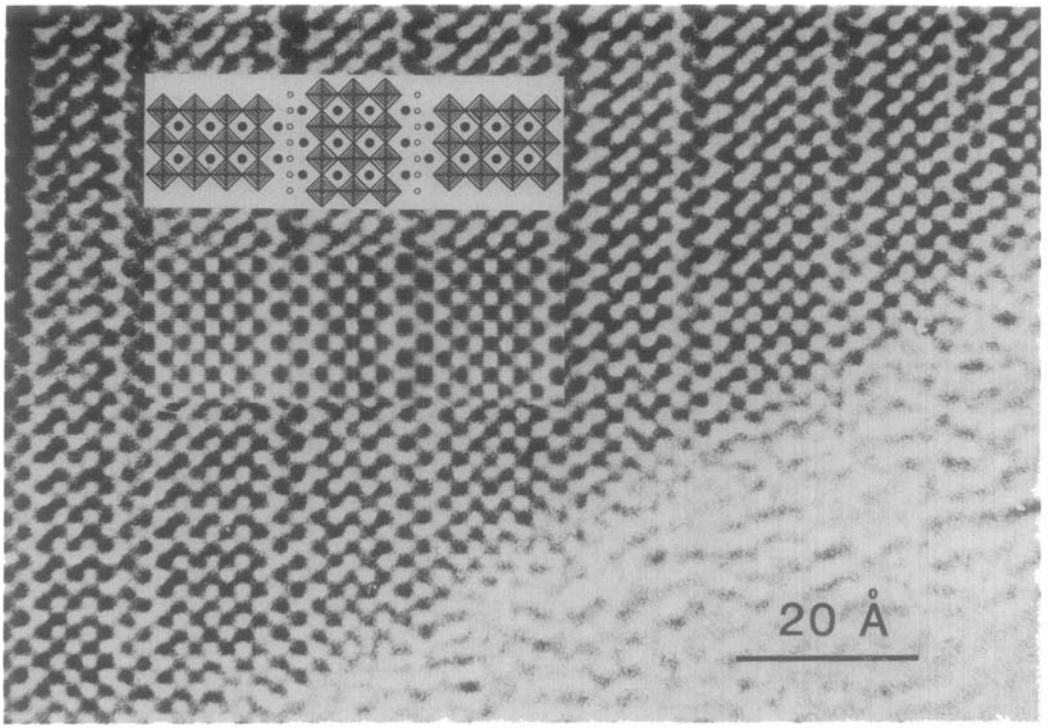

FIG. 2. High-resolution image of $Bi_9Ti_6CrO_{27}$, recorded at 500 kV. The regular nature of the intergrowth structure is clearly evident. The computer-simulated image (inset) corresponds to a specimen thickness of 30 Å and an underfocus of ca. 750 Å.

parameters of the $m = 1$ and $m = 2$ Aurivillius compounds. The electron micrograph showed the expected ordered arrangement of the $m = 1$ and $m = 2$ units, the observed image showing good agreement with the computed image. This sample was somewhat beam-sensitive.

$Bi_7Ti_{4.5}W_{0.5}O_{21}$ had a c parameter of ~29 Å expected of an alternate ordered arrangement of the $m = 2$ ($Bi_3Ti_{1.5}W_{0.5}O_9$) and $m = 3$ ($Bi_4Ti_3O_{12}$) members of the Aurivillius family. This intergrowth structure is different from the 1,2 intergrowth structure $Bi_5Nb_3O_{15}$ in that the component units involved in the recurrent intergrowth have independent existence. In $Bi_5Nb_3O_{15}$, the component units (Bi_2NbO_6 and $Bi_3Nb_2O_9$) are oppositely charged and recurrent intergrowth would be favored due to electrostatic considerations. The HREM image of $Bi_7Ti_{4.5}W_{0.5}O_{21}$ clearly showed that lamellae of $m = 2$ and $m = 3$ members of the Aurivillius family were present alternately over extended regions just as in $Bi_7Ti_4NbO_{21}$ examined by Horiuchi *et al.* (*9*). Furthermore, the computed image based on the model shown in Fig. 1 agreed well with the observed images.

We have examined three intergrowth structures of compositions $Bi_9Ti_6CrO_{27}$, $Bi_9Ti_6FeO_{27}$, and $BaBi_8Ti_7O_{27}$, all formed by $m = 3$ and $m = 4$ members of the Aurivillius family. All the three systems exhibit remarkable order extending over large distances (1000 Å or more) in the HREM images and all of them have a c parameter of ~37 Å. The ordered arrangement of the $m = 3$ and $m = 4$ lamellae can be seen in the 500 kV HREM image of $Bi_9Ti_6CrO_{27}$ in Fig. 2 where we have also shown the computed

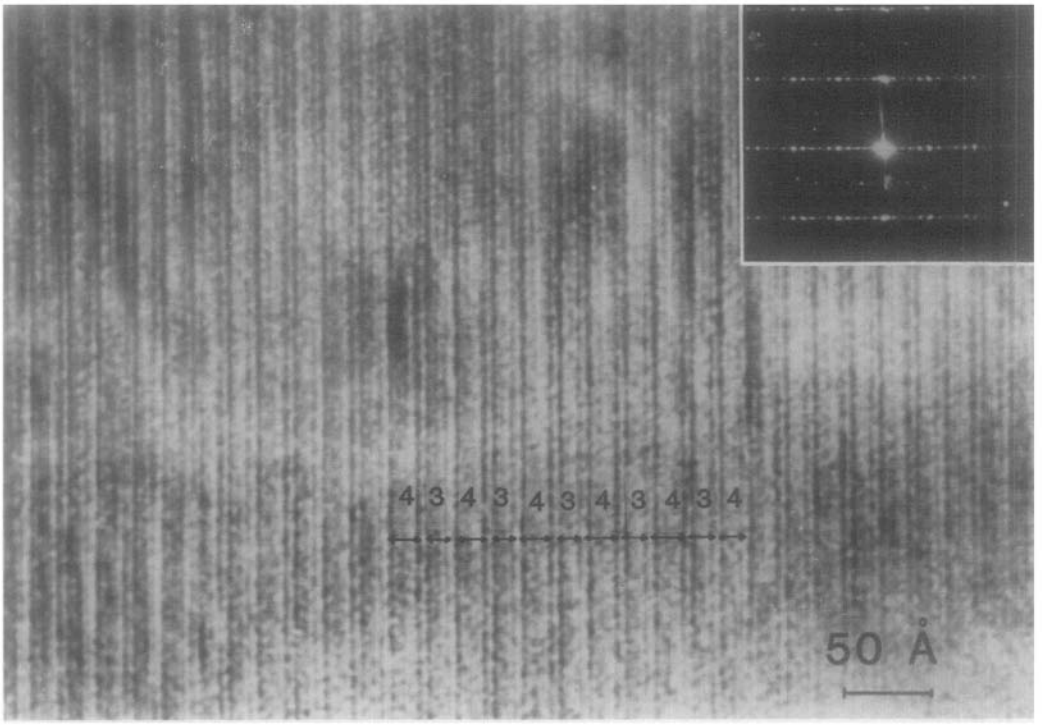

FIG. 3. Image of $BaBi_8Ti_7O_{27}$, recorded at 200 kV and lower resolution, but indicating the regularity of $m = 3$, $m = 4$ alternation.

image. The agreement between the computed and observed images is excellent as is the structural detail revealed by the high-resolution image. $Bi_9Ti_6FeO_{27}$ also gives similar images exhibiting long-range order. We have obtained images of such perfectly ordered intergrowth in the case of $BaBi_8Ti_7O_{27}$ as well (Fig. 3) indicating that magnetic interactions are of no consequence in giving rise to the long periodicity observed in this system. In the case of $Bi_9Ti_6FeO_{27}$, we have been able to refine the powder X-ray diffraction intensities ($R \simeq 7\%$) on the space group *Ibam*.

Following Kikuchi (*10*), we are able to express the elastic strain energy accompanying the formation of the intergrowth structure in terms of the volume change $\Delta V'$

$$\Delta V' = 2V'_B\left(\frac{1 - a^2}{a'^2_B}\right)^2 + mk_mV'_p\left(\frac{1 - a^2}{a'^2_p}\right)^2 + (m + 1)k_{m+1}V''_p\left(\frac{1 - a^2}{a''^2_p}\right)^2$$

where k is related to the bulk modulus of the oxide, a'' is the lattice parameter of the unconstrained perovskite slab of $(m + 1)$ dimension, V'_p and V''_p are the volumes of the unconstrained perovskite slabs of m and $m + 1$ dimensions, and V'_B represents the volume of the unconstrained Bi_2O_2 layer; the other terms are as in the paper of Kikuchi (*10*). We find that $\Delta V'$ so calculated (for the three intergrowth structures studied by us) is slightly smaller than the sum of the ΔV

values of the corresponding Aurivillius oxides (obtained by Kikuchi's procedure). For example, the $\Delta V'$ values of the three intergrowths formed by $m = 3$ and $m = 4$ members are between 0.24 and 0.31 while the sum of ΔV values are in the range 0.33–0.40. The $\Delta V'$ for $BaBi_{12}Ti_{10}O_{39}$ which corresponds to the intergrowth of two $m = 3$ members along with one $m = 4$ member of the Aurivillius family is close to the sum of the ΔV values of 3 and 4 members. Lattice images of this composition only occasionally showed the presence of 3,3,4 sequences over short stretches.

We are continuing our studies on these intergrowth structures and plan to publish a detailed paper in due course.

Acknowledgments

The authors thank the University Grants Commission and the Department of Science and Technology, Government of India, for support of this research. Electron microscopic facilities were provided by the Science Research Council, to whom one of us (DJS) is grateful for financial support.

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