

Structure and Dielectric Properties of Recurrent Intergrowth Structures Formed by the Aurivillius Family of Bismuth Oxides of the Formula $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$

G. N. SUBBANNA, T. N. GURURAO, AND C. N. R. RAO¹

*Materials Research Centre and Solid State & Structural Chemistry Unit,
Indian Institute of Science, Bangalore 560 012, India*

Received October 2, 1989

Crystal structures and dielectric properties of three recurrent intergrowth structures $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$, $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$, and $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$ formed by the Aurivillius family of bismuth oxides of the formula $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$ are reported. The intergrowths exhibit ferroelectricity and accordingly belong to the noncentrosymmetric space group *Cmm2*. The ferroelectric curie temperatures of the intergrowths are in the 630–1070 K range. © 1990 Academic Press, Inc.

Introduction

Structure and properties of the Aurivillius family of bismuth oxides of the general formula $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ containing perovskite layers have been investigated fairly extensively (1, 2). Many members of this family of oxides exhibit ferroelectricity with relatively high T_{CS} . A fascinating property of these oxides is the propensity with which they form long-period structures arising from the recurrent intergrowth of two different members of the family (3, 4). Thus, $\text{Bi}_9\text{Ti}_6\text{Cr}(\text{Fe})\text{O}_{27}$ and $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$ are formed by the recurring intergrowth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$ member of the Aurivillius family) along with the $n = 4$ member, $\text{Bi}_5\text{Ti}_3\text{Cr}(\text{Fe})\text{O}_{15}$ or $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. An idealized projection of such an 3,4 intergrowth structure is shown in Fig. 1. Although these intergrowths have been examined by high resolution electron

microscopy (4, 5), their crystal structures have not been investigated. Furthermore, dielectric properties of these intergrowth structures have not been investigated with a view to find out whether they exhibit ferroelectricity, just as the component members of the Aurivillius family. In this paper, we report the crystal structure and the dielectric behavior of the 3,4 intergrowth structures.

Experimental

The $n = 3$ and $n = 4$ members of the Aurivillius family of oxides and the corresponding 3,4 intergrowths $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$, $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$, and $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$ were prepared by heating the appropriate mixtures of Bi_2O_3 , TiO_2 , Fe_2O_3 , Cr_2O_3 , and BaCO_3 in the temperature range of 1200–1300 K. X-ray powder diffraction ($\text{CuK}\alpha$ radiation), electron diffraction, and high resolution electron microscopy (HREM) using a JEOL JEM 200 CX electron microscope

¹ To whom all correspondence should be addressed.

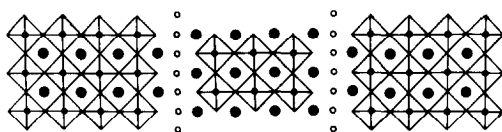


FIG. 1. Idealized schematic structure of a 3,4 intergrowth formed by the Aurivillius oxides.

were carried out to confirm the formation of respective intergrowths. Pressed discs of 13 mm diameter and 2–3 mm thickness of the intergrowth structures as well as the parent oxides were used in the study of dielectric properties. The frequency and temperature dependence of the dielectric constant were measured using an automatic HP LCR bridge. Ferroelectric hysteresis was measured at 50 Hz using a Sawyer–Tower circuit.

Results and Discussion

In Fig. 2, X-ray powder diffractograms of the three 3,4 intergrowth structures studied are shown. The patterns clearly indicate the formation of the phase and not simple mixtures of the parent oxides. The patterns could be indexed on the basis of an orthorhombic cell with $a \approx 5.4 \text{ \AA}$, $b \approx 5.46 \text{ \AA}$, and $c \approx 37 \text{ \AA}$. The value of the c -parameter is close to half the sum of the c -parameters of the $n = 3$ and 4 members. In Table I, we list the structural parameters of all the relevant oxides studied by us. Electron diffraction patterns of the 3,4 intergrowth structures support the orthorhombic symmetry with $a \approx 5.4 \text{ \AA}$, $b \approx 5.46 \text{ \AA}$, and $c \approx 37 \text{ \AA}$. A typical selected area diffraction pattern recorded along (110) direction is shown in Fig. 3. HREM studies on the three intergrowth phases confirm the regular stacking of 3 and 4 perovskite layers alternatively (Fig. 4). In a preliminary X-ray analysis carried out in the case of $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$ (4, 6), the space group $Ibam$ was assigned by taking $c \approx 74 \text{ \AA}$. On a careful examination of the X-ray and electron dif-

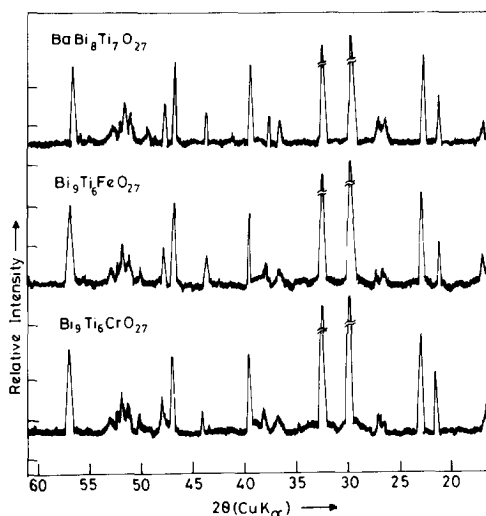


FIG. 2. X-ray powder diffractograms of the three 3,4 intergrowth structures.

fraction patterns, we find that doubling of the c -parameter is not necessary. In the present study, we assign a value of $\sim 37 \text{ \AA}$ for the c -parameter. Furthermore, from the systematic absences observed in the X-ray powder patterns (hkl ; $h + k = 2n$, $0kl$; $k = 2n$, $h0l$; $h = 2n$ and $00l$; no conditions), we find that the space group of the 3,4 intergrowths can be either $Cmm2$ or $Cmmm$.

The dielectric constant, ϵ_r , versus temperature plots of the parent Aurivillius oxides as well as of the 3,4 intergrowths are

TABLE I

UNIT CELL PARAMETERS AND FERROELECTRIC CURIE TEMPERATURES OF THE LAYERED BISMUTH OXIDES

Compound	No. of perovskite layers	Unit cell parameters ($\text{\AA}$)			$T_c(\text{K})$
		a	b	c	
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	3	5.410	5.448	32.84	925
$\text{Bi}_3\text{Ti}_3\text{CrO}_{15}$	4	5.460	5.460	40.75	470
$\text{Bi}_3\text{Ti}_3\text{FeO}_{15}$	4	5.468	5.464	41.23	1060
$\text{BaBi}_4\text{Ti}_4\text{O}_{15}$	4	5.461	5.461	41.85	690
$\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$	3,4	5.437	5.437	36.95	630
$\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$	3,4	5.464	5.474	37.08	1070
$\text{BaBi}_8\text{Ti}_7\text{O}_{27}$	3,4	5.444	5.444	37.45	750

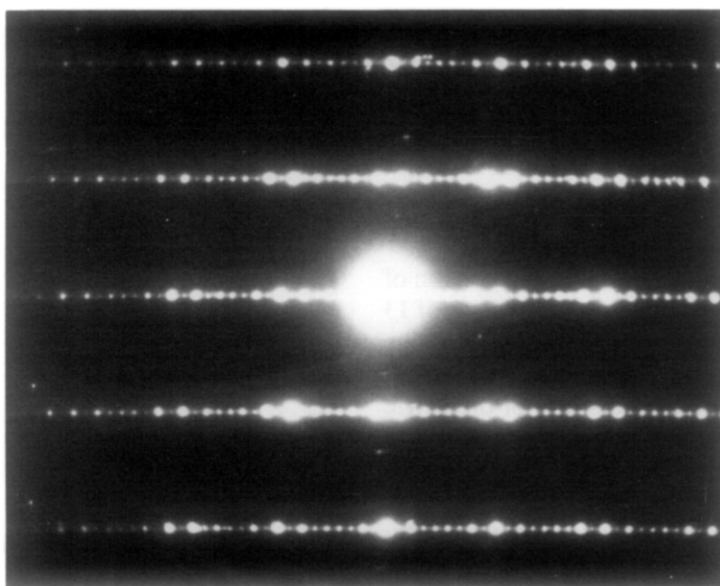


FIG. 3. Selected area diffraction pattern of $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$ along the (110) direction.

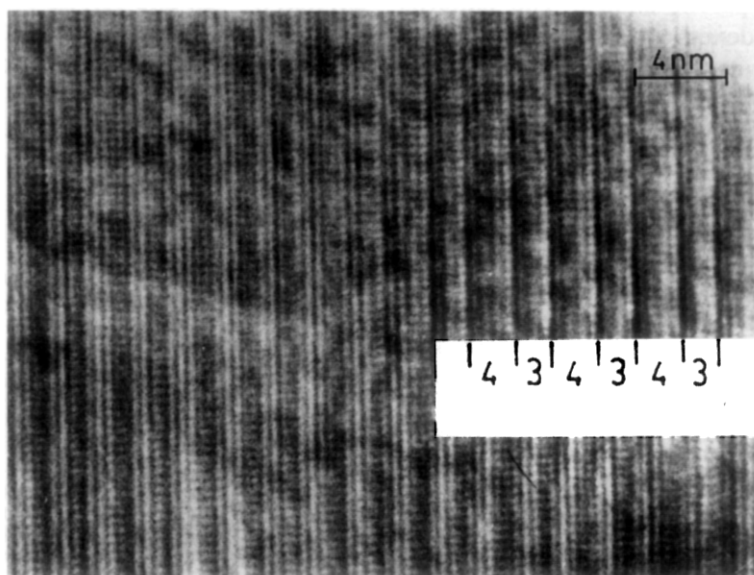


FIG. 4. A high-resolution electron microscope image showing recurrent intergrowth of 3 and 4 perovskite layers in $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$.

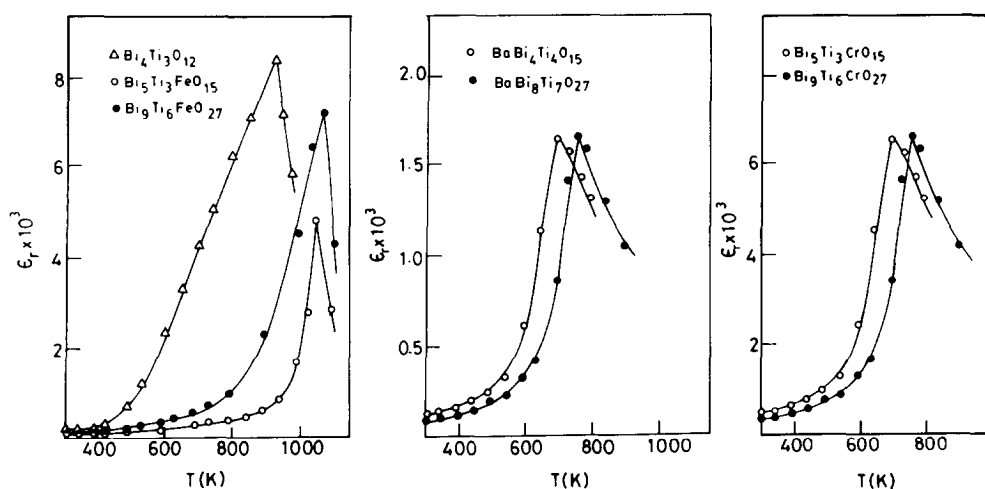


FIG. 5. Dielectric constant versus temperature plots for the 3,4 intergrowth structures along with those for the corresponding parent oxides.

shown in Fig. 5. All of them show good maxima with characteristic curie temperatures. The curie temperature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$) is 925 K; the T_c value of the $n = 4$ members $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, $\text{Bi}_5\text{Ti}_3\text{CrO}_{15}$, and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ are 1060, 470, and 690 K, respec-

tively. The dielectric constant maxima corresponding to the T_c in the case of the 3,4 intergrowth $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$ was found to be 1070 K, which is close to that of the parent

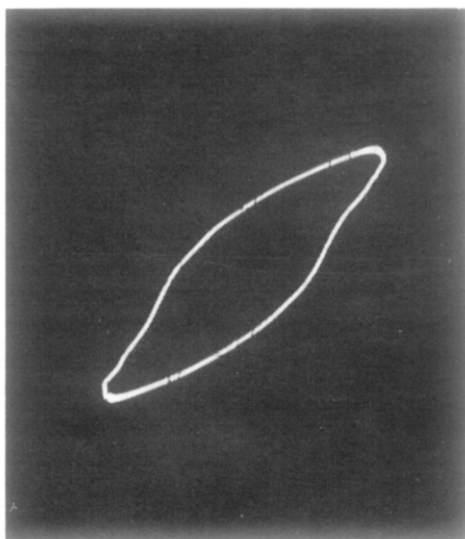


FIG. 6. Dielectric hysteresis loop shown by $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$.

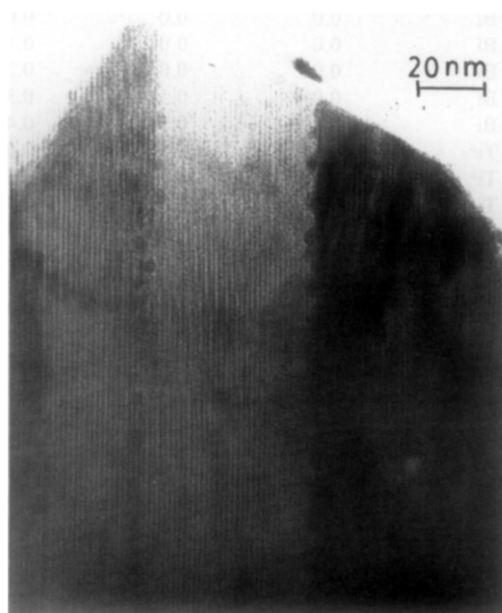


FIG. 7. Ferroelectric-type domains along the c -direction in $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$.

Aurivillius oxide $n = 4$. In the other two 3,4 intergrowths, $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$ and $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$, the T_c s are 630 and 750 K, respectively, which are higher than those of the corresponding $n = 4$ member. Thus, the curie temperatures of the 3,4 intergrowths are either higher or nearly equal to that of the component $n = 4$ member. Only in the case of $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$, the T_c is higher than that of the $n = 3$ member. We also find that the dielectric constant at any given temperature is much higher in $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$ and $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$ than that of $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$. The dielectric constant decreases exponentially with the increase in frequency in all the systems studied.

All the three 3,4 intergrowth structures show polarization–electric field hysteresis

TABLE II
ATOMIC COORDINATES OF $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$, SPACE
GROUP $Cmm2$ ($Z = 2$)^a

Atom	x	y	z
Bi	0.0	0.0	0.0
Bi	0.0	0.0	0.12
Bi	0.0	0.0	0.24
Bi	0.0	0.5	0.32
Bi	0.0	0.5	0.45
Ti ^b	0.0	0.5	0.05
Ti ^b	0.0	0.5	0.19
Ti	0.0	0.0	0.38
Fe ^c	0.0	0.0	0.38
Fe ^c	0.0	0.5	0.19
Ti	0.0	0.0	0.50
O	0.25	0.25	0.0
O	0.25	0.25	0.12
O	0.25	0.25	0.24
O	0.25	0.25	0.38
O	0.25	0.25	0.50
O	0.5	0.5	0.32
O	0.5	0.5	0.45
O	0.5	0.5	0.19
O	0.5	0.5	0.05
O ^b	0.0	0.0	0.28
O ^b	0.0	0.5	0.28

^a Molecule 2 is generated as $x, y, \frac{1}{2} + z$.

^b Occupancy, 75%.

^c Occupancy, 25%.

TABLE III
OBSERVED AND CALCULATED INTERPLANAR
SPACINGS AND INTENSITIES OF $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$

$h\ k\ l$	$d_{\text{obsd}}\ \text{\AA}$	$d_{\text{calcd}}\ \text{\AA}$	I_{obsd}	I_{calcd}
0 0 5	7.375	7.416	3	3
0 0 7	5.215	5.297	7	3
0 0 9	4.152	4.120	14	23
1 1 0		3.839		
1 1 1	3.833	3.819	38	35
1 1 6	3.254	3.261	3	8
1 1 8	2.980	2.957	100	100
2 0 0		2.730		
0 2 0	2.732	2.700	50	50
2 0 7		2.427		
0 2 7		2.407	6	3
1 1 12	2.435	2.406		
0 0 16	2.362	2.318	8	11
2 0 9		2.276		
0 2 9	2.281	2.258	23	18
0 0 18	2.070	2.060	5	2
2 2 0	1.933	1.920	23	28
1 1 17		1.897		
0 2 14	1.905	1.891	8	17
2 0 16		1.767		
0 2 16	1.790	1.759	20	20
2 2 9		1.740		
3 1 1		1.723		
1 3 1	1.727	1.708	7	8
0 2 18		1.644	2	2
2 0 18	1.638	1.638		
3 1 8		1.616		
1 3 8	1.618	1.604	25	34

loops when examined with a Sawyer–Tower circuit. A typical hysteresis loop recorded in the case of $\text{Bi}_9\text{Ti}_6\text{CrO}_{27}$ is shown in Fig. 6. The loop disappears as the temperature approaches the T_c . The hysteresis behavior confirms the presence of ferroelectricity in the intergrowth structures. Bright field electron microscopic images of the intergrowth structures show ferroelectric type domains as illustrated in Fig. 7. Domains were observed in the a – b -plane as well as along the c -direction.

The ferroelectric behavior of the 3,4 intergrowth structures demands the space group to be noncentrosymmetric. We

TABLE IV
OBSERVED AND CALCULATED INTERPLANAR
SPACINGS AND INTENSITIES OF $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$

$h\ k\ l$	$d_{\text{obsd}}\ \text{\AA}$	$d_{\text{calcd}}\ \text{\AA}$	I_{obsd}	I_{calcd}
0 0 5	7.465	7.416	6	3
0 0 7	5.160	5.297	3	2
0 0 9	4.162	4.120	13	22
1 1 0	3.867	3.839	25	37
1 1 1		3.819		
1 1 6	3.226	3.260	10	8
1 1 8	2.975	2.957	100	100
2 0 0	2.734	2.73		
0 2 0		2.70	55	50
2 0 7	2.410	2.427		
1 1 12		2.407	4	3
0 2 7		2.406		
0 0 16	2.350	2.318	10	11
2 0 9	2.180	2.276		
0 2 9		2.258	3	17
0 0 18	2.070	2.060	5	2
2 2 0	1.940	1.919	31	29
1 1 17	1.882	1.897		
0 2 14		1.890	5	17
2 0 16		1.767		
0 2 16	1.775	1.759	20	21
2 2 9		1.740		
3 1 1	1.713	1.723		
1 3 1		1.708	6	8
0 2 18	1.653	1.644		
2 0 18		1.639	4	2
3 1 8	1.620	1.616		
1 3 8		1.604	19	34

therefore assign the *Cmm2* space group in preference to *Cmmm*. We could fix the positional coordinates of the 3,4 intergrowths based on packing considerations and keeping in view the earlier model (5, 6) based on HREM image simulations and also consistent with a *c*-parameter of 37 Å. Several models were tested using a locally developed program based on the interatomic distance criterion and the X-ray diffraction

patterns were simulated with the help of the LAZY-PULVERIX program. The final coordinates derived are shown in Table II. In Table III, we show a comparison of the observed and calculated interplanar spacings and intensities for $\text{Bi}_9\text{Ti}_6\text{FeO}_{27}$. The agreement is quite satisfactory. In Table IV, we show the observed and calculated X-ray diffraction pattern of $\text{BaBi}_8\text{Ti}_7\text{O}_{27}$; the agreement is good in this intergrowth structure as well. The average computed Bi–O and Ti–O bond distance in the perovskite layers is 1.92 Å while the Bi–O distance in the Bi_2O_2 layers is 1.5 Å. When compared to the bond distance observed in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (7), the Bi_2O_2 layer is compressed by about 0.7 Å. This compression of Bi_2O_2 layers in the 3,4 intergrowths found by us in the present study is in concurrence with the HREM observations and image simulations on these intergrowths (5).

Acknowledgments

The authors thank the Department of Science & Technology and the Universities Grants Commission for the support of this research.

References

1. B. AURIVILLIUS, *Ark. Kemi* **2**, 519 (1950).
2. J. L. HUTCHISON, J. S. ANDERSON, AND C. N. R. RAO, *Proc. R. Soc. London A* **355**, 301 (1977).
3. C. N. R. RAO AND J. M. THOMAS, *Acc. Chem. Res.* **18**, 113 (1985).
4. J. GOPALAKRISHNAN, A. RAMANAN, C. N. R. RAO, D. A. JEFFERSON, AND D. J. SMITH, *J. Solid State Chem.* **55**, 101 (1984).
5. D. A. JEFFERSON, M. K. UPPAL, C. N. R. RAO, AND D. J. SMITH, *Mater. Res. Bull.* **19**, 1403 (1984).
6. A. RAMANAN, Ph.D. thesis, Indian Institute of Science (1984).
7. R. E. NEWNHAM, R. W. WOLFE, AND J. F. DORRAN, *Mater. Res. Bull.* **6**, 1029 (1971).