Structural Studies of the Ferroelectric Phase Transition in $Bi_4Ti_3O_{12}$

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Received July 3, 2003. Revised Manuscript Received October 20, 2003

A variable-temperature synchrotron X-ray diffraction study of the phase transitions in the ferroelectric $n = 3$ Aurivillius oxide $Bi_4Ti_3O_{12}$ is described. At room temperature the structure of $Bi_4Ti_3O_{12}$ is orthorhombic in space group *B*2*eb* and this continuously transforms to the high-temperature tetragonal *I*4/*mmm* structure via an intermediate orthorhombic phase. The possible space groups of this intermediate orthorhombic phase have been identified by using group theory.

Introduction

The Aurivillius oxides are represented by the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ where B is a diamagnetic transition metal such as Ti^{4+} or Nb^{5+} and A is an alkali or alkaline earth cation.[1] The structure of the Aurivillius oxides consists of arrays of Bi_2O_2 and perovskite-like $A_{n-1}B_nO_{3n+1}$ layers. The ferroelectric properties of such oxides have been known for around 50 years,[2,3] yet the structural origins of their ferroelectricity have only recently been established.[4,5]

Following the pioneering work of Scott and co-workers,[6] the possibility of employing these Aurivillius oxides in ferroelectric memory devices has been extensively studied. A serious barrier to their practical utilization is their poor thermal stability.[7−10] Formation of thin-film ferroelectric devices involves a sintering step at high temperatures and this invariably degrades the performance of the simpler Aurivillius oxides. Consequently, a number of studies of the high-temperature behavior and structures of Aurivillius oxides have been reported.[11−14] In comparison to the $n = 2$ oxides based on $SrBi_2Ta_2O_9$ very little is known about the high-temperature properties of the $n = 3$ oxides such as $Bi_4Ti_3O_{12}$, yet such oxides are reported to have ferroelectric properties superior to those of the better-studied $n = 2$ oxides.[15]

Although it has been reported[5] that $Bi_4Ti_3O_{12}$ is monoclinic at room temperature, very-high-resolution powder diffraction data suggest that powder samples of $Bi_4Ti_3O_{12}$ are actually orthorhombic at room temperature.[16] Heating $Bi_4Ti_3O_{12}$ above 670 °C is reported to result in an apparently first-order phase transition to a paraelectric tetragonal phase.[16,17] A significant volume change between the high-temperature and low-temperature phases is likely to be detrimental to the stability of any thin films annealed or sintered above the Curie temperature. Conversely, continuous transitions are less likely to adversely influence the properties of the thin films. Hervoches and Lightfoot have demonstrated, using powder neutron diffraction methods, that for $Bi_4Ti_3O_{12}$ the high-temperature paraelectric phase is in space group *I*4/*mmm* and that the room-temperature orthorhombic phase is in *B*2*eb*.[16]

The main structural basis for the ferroelectricity in $Bi_4Ti_3O_{12}$ is the displacement of the Bi atoms within the perovskite-like layers, along the crystallographic *a*-axis with respect to the chains of corner-sharing TiO_6 octahedra. This corresponds to a [110] displacement referred to the parent *I*4/*mmm*. The TiO_6 octahedra are tilted relative to each other and the tilt system can be

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(1) Aurivillius, B. *Arkiv Kemi* **1949**, *1*, 463.

(2) Subbarao, E. C. *J. Phys. Chem. Solids* **1962**, *23*, 665.

(3) Smolenskii, G. A.; Isupov, V. A.; Agranovskaya, A. I. *Sov. Phys. Solid State* **1961**, *3*, 651.

(4) Rae, A. D.; Thompson, J. G.; Withers, R. *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, *48*, 418.

(5) Rae, A. D.; Thompson, J. G.; Withers, R.; Willis, A. C. *Acta Crystallogr., Sect. B: Struct. Sci.* **1990**, *46*, 474.

(6) Paz de Araujo, C. A.; Cuchlaro, J. D.; McMillan, L. D.; Scott, M.; Scott, J. F. *Nature (London)* **1995**, *374*, 627.

(7) Shimakawa, Y.; Kubo, Y.; Tauchi, Y.; Kamiyama, T.; Asano, H.; Izumi, F. *Appl. Phys. Lett.* **2000**, *77*, 2749.

(8) Shimakawa, Y.; Kubo, Y.; Tauchi, Y.; Asano, H.; Kamiyama, T.; Izumi, F.; Hiroi, Z. *Appl. Phys. Lett.* **2001**, *79*, 2791.

(9) Boulle, A.; Legrand, C.; Guinebretière, R.; Mercurio, J. P.; Dauger, A. *Thin Solid Films* **2002**, *391*, 42.

(10) Aizawa, K.; Tokumitsu, E.; Okamoto, K.; Ishiwara, H. *Appl. Phys. Lett.* **2000**, *79*, 2791.

(11) Macquart, R.; Kennedy, B. J.; Hunter, B. A.; Howard, C. J.; Shimakawa, Y. *Integr. Ferroelectr.* **2002**, *44*, 101−112.

(12) Hervoches, C. H.; Irvine, J. T. S.; Lightfoot, P. *Phys. Rev. B* **2002**, *64*, 100102(R).

(13) Liu, J.; Zou, G.; Yang, H.; Cui, Q. *Solid State Commun.* **1994**, *90*, 365.

(14) Macquart, R.; Kennedy, B. J.; Vogt, T.; Howard, C. J. *Phys. Rev B* **2002**, *66*, 212102.

(15) Park, B. H.; Kang, B. S.; Bu, S. D.; Noh, T. W.; Lee, J.; Jo, W. *Nature* (*London*) **1999**, *401*, 682.

(16) Hervoches, C. H.; Lightfoot, P. *Chem. Mater.* **1999**, *11*, 3359.

(17) Hirata, T.; Yokokawa, T. *Solid State Commun.* **1997**, *104*, 673.

10.1021/cm034580l CCC: $25.00

described as $a^-a^-c^0$ in Glazer's notation.[18] These two structural features act in concert to lower the symmetry from tetragonal to orthorhombic, however, they are not linked, and there is no reason to suppose that both modes will condense at precisely the same temperature. Rather, it is probable that these modes will condense successively and the two end member phases will be linked by an intermediate phase. Using powder neutron diffraction methods, Macquart and Lightfoot have independently shown that the $A2_1am$ to $I4/mmm$ transition in the $n = 2$ Aurivillius phases $SrBi_2Ta_2O_9$ [11] and $Sr_{0.85}Bi_{2.1}Ta_2O_9$ [12] proceeds via an intermediate paraelectric $Amam$ phase in each case. This $Amam$ phase is also seen in $PbBi_2M_2O_9$ (M = Nb, Ta).[19] That is, upon cooling from the $I4/mmm$ phase, the tilting of the octahedra occurs before the cation displacement. The same sequence is reported to occur in the $n = 4$ Aurivillius oxide $SrBi_4Ti_4O_{15}$.[20]

The aim of the present work is to establish whether the $B2eb$ to $I4/mmm$ transition in $Bi_4Ti_3O_{12}$ is first order as proposed by Hirata and Yokakowa[17] or if it actually occurs continuously via an intermediate phase as seen in $SrBi_2Ta_2O_9$.[11] To establish this we have investigated the temperature dependence of the structure of $Bi_4Ti_3O_{12}$ from room temperature to 800 °C using high-resolution synchrotron radiation. Near the Curie temperature fine temperature intervals have been used to detect the intermediate phase which exists over a very limited temperature range.

Experimental Section

The crystalline sample of $Bi_4Ti_3O_{12}$ was prepared by the solid-state reaction of stoichiometric quantities of Bi_2O_3 (99.999%, Aldrich) and TiO_2 (99.9%, Aldrich). The heating sequence used was 700 °C/24 h and 850 °C/48 h, with intermediate regrinding. The sample was slowly cooled to room temperature in the furnace.

The sample purity was established by powder X-ray diffraction measurements using Cu Kα radiation on a Shimadzu D-6000 Diffractometer. Room- and variable-temperature synchrotron X-ray powder diffraction patterns were collected on a high-resolution Debye Scherrer diffractometer at beamline 20B, the Australian National Beamline Facility, at the Photon Factory, Japan.[21] The sample was finely ground and loaded into a 0.3-mm quartz capillary that was rotated during the measurements. All measurements were performed under vacuum to minimize air scatter. Data were recorded using two Fuji image plates. Each image plate was 20 × 40 cm and each covered 40° in 2θ. A thin strip (ca. 0.5 cm wide) was used to record each diffraction pattern so that up to 30 patterns could be recorded before reading the image plates. The data were collected at a wavelength of 0.75 Å (calibrated with a NIST Si 640c standard) over the 2θ range of 5−75° with step size of 0.01°. The patterns were collected in the temperature range of 100−800 °C in 25 °C steps or 600−803 °C in 7 °C steps, and with 30-min counting time at each temperature. Structures were refined by the Rietveld method using the program Rietica.[22] The positions of the cations were well described in these analyses, however the estimated standard deviations (esds) of the Ti−O bond distances (typically around 0.02 Å) preclude any detailed discussion of the temperature dependence of the bond distances.

Results and Discussion

The published room-temperature structure for $Bi_4Ti_3O_{12}$ was used as a starting model in our Rietveld refinements, and the structural refinement proceeded without event. The temperature dependence of the lattice parameters and volumes are illustrated in Figure 1. All the lattice parameters show a smooth increase due to thermal expansion as the sample is heated to ca. 500 °C. Above this temperature the cell continues to expand along both the *b*- and *c*- directions, however the *a*-parameter is essentially constant. This behavior is very similar to that displayed by a number of simpler ABO_3 perovskites[23−25] and is apparently related to the gradual reduction in distortion resulting from a reduction in the magnitude of the tilting of the BO_6 octahedra as the temperature is increased. Near 675 °C there is a rapid decrease in the *a*-parameter although as is clearly evident from Figure 1 this is not a discontinuous decrease but rather a rapid progressive drop. At the same temperature the *c*-axis expands rapidly, Figure 1.

The transition to the tetragonal phase is clearly evident in the 200/020 and 317/137 reflections (near $2\theta \approx 15.8$ and 26.7°, respectively, where $\lambda = 0.75$ Å). As illustrated in Figure 2 the diffraction pattern recorded at 670 °C shows obvious splitting of the 200/020 and 317/137 reflections that is clearly indicative of orthorhombic symmetry. This splitting remains clearly visible to the eye until 677 °C and can be discerned by profile analysis at 684 °C. At 691 °C no splitting or diagnostic asymmetry of these or other peaks is apparent and it is concluded that the structure is tetragonal. That is, the transition to the tetragonal structure occurs near 690 °C, which is around 15° above the reported ferroelectric Curie temperature for $Bi_4Ti_3O_{12}$. (Some care is required when comparing the transition temperatures reported in various studies because of both sample variation (induced by the different heating regimes used) and possible variations in the high-temperature thermometry.)

Above 691 °C the structure has been refined in the tetragonal space group $I4/mmm$ and is as described by Hervoches and Lightfoot.[16] That the paraelectric phase is tetragonal in $I4/mmm$ well above the ferroelectric Curie temperature was confirmed from the high-resolution powder neutron diffraction data by Hervoches and Lightfoot from both the cell metric and the absence of any superlattice reflections indicative of TiO_6 tilting.

The thermal expansion of the *c*-axis both above and below the T_c is relatively linear and can be well-fitted to a simple linear equation $c = 5.277 \times 10^{-4}T + 32.725$ for $T < 677$ °C, and $c = 5.116 \times 10^{-4}T + 32.725$ for $T > 691$ °C. Examining the temperature dependence of the long *c*-axis we observed a large difference between the

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(18) Glazer, A. M. *Acta Crystallogr. B* **1972**, *28*, 3384.

(19) Macquart, R.; Kennedy, B. J.; Hunter, B. A.; Howard, C. J. *J. Phys.: Condens. Matter* **2002**, *14*, 7955.

(20) Hervoches, C. H.; Snedden, A.; Riggs, R.; Kilcoyne, S. H.; Manuel, P.; Lightfoot, P. *J. Solid State Chem.* **2002**, *164*, 280.

(21) Sabine, T. M.; Kennedy, B. J.; Garrett, R. F.; Foran, G. J.; Cookson, D. J. *J. Appl. Crystallogr.* **1995**, *28*, 513.

(22) Howard C. J.; Hunter, B. A. *A Computer Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns*; Lucas Heights Research Laboratories: New South Wales, Australia, 1998; pp 1−27.

(23) Howard, C. J.; Knight, K. S.; Kisi, E. H.; Kennedy, B. J. *J. Phys.: Condens. Matter* **2000**, *12*, L677.

(24) Kennedy, B. J.; Howard, C. J.; Thorogood, G. J.; Hester, J. R. *J. Solid State Chem.* **2001**, *161*, 106.

(25) Kennedy, B. J.; Howard, C. J.; Chakoumakos, B. C. *J. Phys. C: Condens. Matter* **1999**, *11*, 1479.

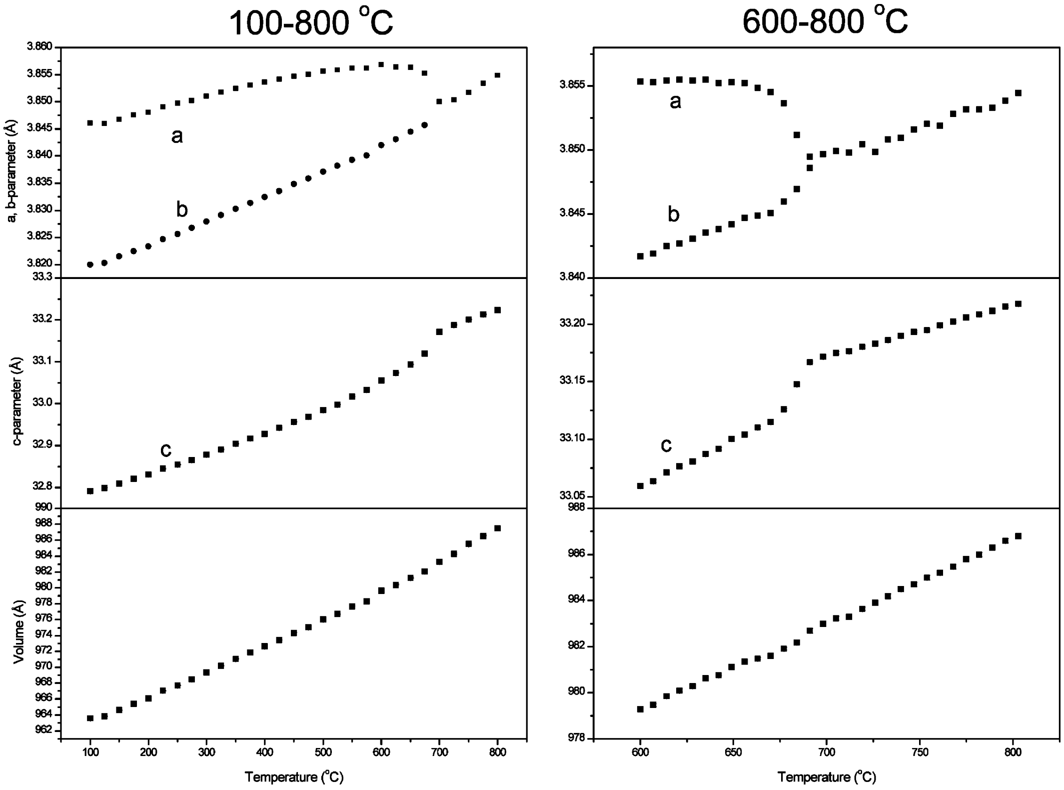

Figure 1. Temperature dependence of the lattice parameters and volume for $Bi_4Ti_3O_{12}$ obtained from Rietveld analysis of variable-temperature synchrotron diffraction data. For ease of comparison the values in the $\sqrt{2} \times \sqrt{2} \times 1$ orthorhombic cells have been reduced to the equivalent tetragonal values.

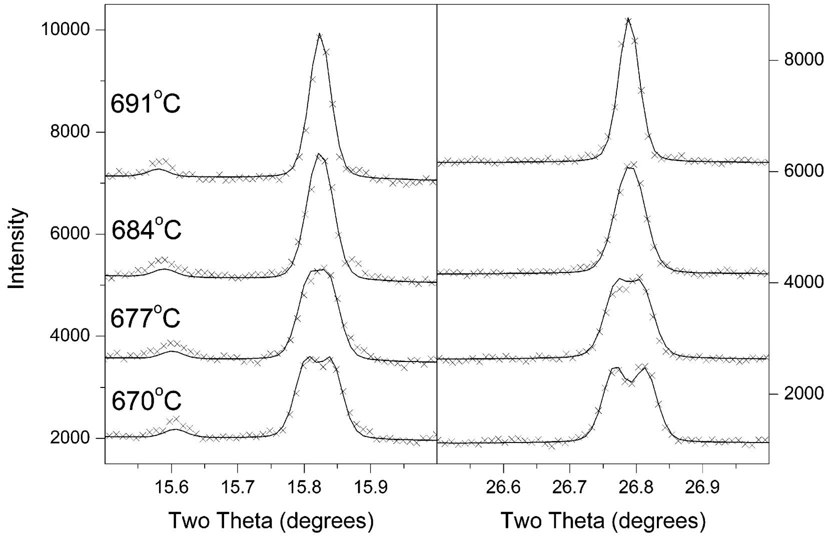

Figure 2. Portions of the Rietveld fits for $Bi_4Ti_3O_{12}$ showing the temperature dependence of the splitting of the tetragonal 110 reflection into the orthorhombic 200/020 pair near $2\theta = 15.8°$ and of the 127 reflection into the 317/137 pair near $2\theta = 26.8°$. The 0012 reflection is apparent near $2\theta = 15.6°$.

values of the low-temperature orthorhombic, ferroelectric phase and those for the high-temperature tetragonal and paraelectric phase. Clearly the value for the *c*-parameter at 684 °C does not fall into either series. A similar conclusion can be made for both the *a*- and *b*-parameters. These temperature-dependent changes in the lattice parameters are more reminiscent of the continuous-phase transitions observed in oxides such as $Bi_2PbNb_2O_9$ [19] than of the more subtle changes observed in the high-temperature second-order incommensurate-to-commensurate phase transition observed in Bi_2MoO_6.[26] A feature of many first-order phase transitions is the coexistence of a two phase region. Attempts to fit the pattern at 684 °C to a two-phase orthorhombic/tetragonal model with lattice parameters obtained by appropriate linear extrapolation were unsuccessful. It was concluded that a single phase was present at this temperature and this was neither the orthorhombic in *B*2*eb* nor the tetragonal *I*4/*mmm*.

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(26) Buttrey, D. J.; Vogt, T.; White, B. D. *J. Solid State Chem.* **2000**, *155*, 206.

(27) www.physics.byu.edu/~stokesh/isotropy.html.

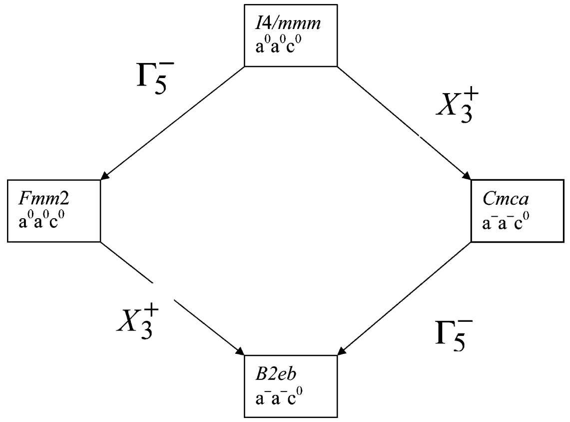

Figure 3. Schematic diagram showing the group−subgroup relationships for the $n = 3$ Aurivillius oxides. The solid lines show the transitions that are allowed to be continuous. The tilt system for the intermediate phases is given.

In summary, we observe an orthorhombic structure at 684 °C whose lattice parameter clearly distinguishes it from the low-temperature orthorhombic and high-temperature tetragonal phases. (In fact, even if we could not distinguish this as a separate phase, the observed continuity of transition, together with the group theoretical arguments to follow, would indicate that such an intermediate orthorhombic phase is involved in the transition.) If we assume that all three phases have commensurate structures then it should be possible to identify the space group of the intermediate phase from a group theoretical analysis. To do this we used the program ISOTROPY.[27] This analysis confirmed that a direct *B*2*eb* to *I*4/*mmm* transition could not be continuous. The two modes responsible for the transition were identified as Γ_5^- describing the cation displacement and X_3^+ associated with the tilting of the TiO_6 octahedra.[28] Whichever of these modes condenses first, an intermediate orthorhombic structure based on a $\sqrt{2} \times \sqrt{2} \times 1$ superstructure of the parent *I*4/*mmm* structure is involved, as illustrated in Figure 3, and the successive phase transitions through either of these intermediates are allowed to be continuous. If the initial distortion is cation displacement via the Γ_5^- mode then a ferroelectric orthorhombic structure that lacks any tilting of the TiO_6 octahedra is expected. The resulting structure in *Fmm*2 can continuously transform to the observed room-temperature orthorhombic *B*2*eb* phase through tilting of the TiO_6 octahedra via the X_3^+ mode. (This description refers still to the parent structure in *I*4/*mmm*.) Alternatively, the initial distortion may be the introduction of tilting of the TiO_6 octahedra resulting in a *Cmca* phase followed by cation displacement. The available synchrotron diffraction data do not allow us to unequivocally distinguish between these two possibilities; however, by analogy with $SrBi_2Ta_2O_9$, we favor the latter possibility.[11] The confirmation of this will require a high-resolution neutron diffraction study.

It is illuminating to compare our results with those of Hirata and Yokokawa.[17] First, Figure 2 of their report suggests they recorded very little data in the ferroelectric phase with only four temperature points obvious. A somewhat greater number of temperatures were examined (nine) in the paraelectric phase, apparently at 20 °C intervals. Crucially, no data appear to have been collected between 475 and 675 °C, the latter corresponding to the reported ferroelectric Curie temperature for $Bi_4Ti_3O_{12}$. There is then a relatively large jump in the temperatures used by Hirata and Yokokawa to above 695 °C. In our present study we have used relatively coarse temperature increments (25 °C) to monitor the general form of the phase transition, but then we have used much finer intervals (7 °C) to probe the nature (first order or continuous) of the ferroelectric to paraelectric transition. We conclude that as a result of the relatively coarse temperature intervals used by Hirata and Yokokawa it was not possible for those authors to establish whether the ferroelectric to paraelectric transition in $Bi_4Ti_3O_{12}$ was first order or continuous. The temperature dependence of the lattice parameters established using powder neutron diffraction data described by Lightfoot and Hervoches[16,29] is very similar to that observed here for the data collected in 25 °C intervals. On the basis of a similar density of data, Lightfoot and Hervoches[29] concluded that the transition is first order. In comparison, our data collected in 7 °C intervals using high-resolution synchrotron X-ray methods strongly suggests the transition is continuous, albeit involving an intermediate phase.

In conclusion we have identified the existence of an intermediate orthorhombic phase in the solid-state phase transition of the ferroelectric $n = 3$ Aurivillius phases $Bi_4Ti_3O_{12}$. Two possible orthorhombic phases were identified using group theory, *Fmm*2 and *Cmca*, depending on the sequence in which the two modes responsible for the lowering of symmetry condense. By analogy with the $n = 2$ oxide $SrBi_2Ta_2O_9$, the most likely sequence of transitions is $B2cb \xrightarrow{670\,°C} Cmca \xrightarrow{695\,°C} I4/mmm$. Clearly confirming the existence of and establishing the precise structure of the proposed intermediate phase is of considerable interest, and efforts aimed at this are in progress.

Acknowledgment. This work performed at the Australian National Beamline Facility was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities program. B.J.K. acknowledges the support of the Australian Research Council. The assistance of Dr. James Hester at the ANBF is gratefully acknowledged. We thank Dr. P. Lightfoot for bringing ref 29 to our attention while this manuscript was under review.

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(28) Miller, S. C.; Love, W. F. *Tables of Irreducible Representations of Space Groups and Co-representations of Magnetic Space Groups*; Pruett Press: Boulder, CO, 1967.

(29) Hervoches, C. H.; Lightfoot, P. *Proceedings of CIMTEC, 10th International Ceramics Congress*, Florence, Italy, July 2002.