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Effect of Synthesis Conditions on Cation Ordering in Barium Bismuth Oxide (Ba/Bi = 2)

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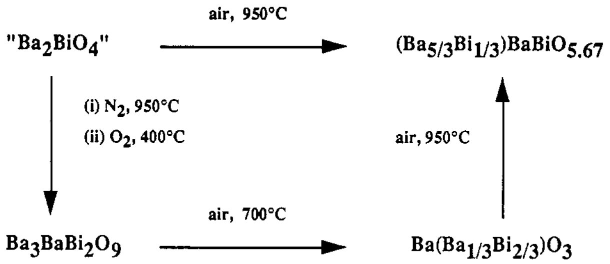
Recent studies of superconducting oxides containing bismuth or copper show that changes in metal oxidation states and in oxygen stoichiometry typically occur during normal syntheses. Reaction of the component oxides at high temperature to form a specific structure in oxygen-deficient form, followed by low-temperature oxidation, exemplified by the preparation of $YBa_2Cu_3O_7$, is a commonly used technique.[1] In other cases, for example $Ba_{0.7}K_{0.3}BiO_3$,[2] specific compositions can only be synthesized by control of the oxygen partial pressure during the entire synthesis. The dependence of cation distributions on sample history with respect to oxygen partial pressure in addition to temperature is a similar though more subtle effect. For example, in $YBa_2(Cu_{1-x}Fe_x)_3O_7$, an increased occupancy of the CuO_2 planes by iron is obtained when reducing conditions are used to convert Fe^{3+} to Fe^{2+} cations in the initial synthesis.[3] We have been investigating the effect of thermal history and oxygen partial pressure on the B cation distribution in the Ba–Bi–O system. Attempts to synthesize "Ba_2BiO_4" with the La_2CuO_4 structure type by changing the reaction conditions always result in compounds with the perovskite structure.[4–7] The specific cation distribution, however, depends markedly on the sequence of temperatures and oxygen partial pressures that is used in a particular synthesis. In this communication, we report the preliminary results of our study.

In perovskite oxides containing two B cations with the general composition $A_2BB'O_6$ ordered or disordered arrangements can occur. Large size and/or charge differences lead to B site cation order. In Sr_2BiNdO_6 (Bi(V) 0.76 Å, Nd(III) 0.983 Å) the Bi and Nd ions order on the B,B′ sites,[8] whereas the B cations in La_2CoMnO_6 (Co(III) 0.545 Å, Mn(III) 0.58 Å are disordered.[9] In compositions $A_3BB'_2O_9$, 1:2 B site ordering has been observed in several compounds, for example, $Ba_3TaZn_2O_9$.[10,11] A theoretical calculation of lattice energies for $Ba_3TaZn_2O_9$ showed that the ordered model is favorable over the disordered model.[12]

Scheme I



In substituted barium bismuth oxide phases, examples of both ordered and disordered structures are known. The superconducting phases $BaPb_{1-x}Bi_xO_3$[13] and $Ba_{1-x}K_xBiO_3$[2] are examples of disordered cation distributions, whereas the parent composition $BaBiO_3$ has a 1:1 ordered arrangement of Bi^{3+} and Bi^{5+} ions on the B sites. All of the bismuth-containing perovskite phases are easily reduced to oxygen deficient structures containing Bi^{3+} cations, often in unusual coordination environments.[14,15] In the structure of $BaBiO_{2.5}$,[16] the Bi^{3+} cations are 3-fold coordinated by oxygen atoms and in $Ca_4Bi_6O_{13}$ the bismuth atom coordination ranges from three to six.[17] Reduction of Bi^{5+} to Bi^{3+} cations in $Ba_2La_xBi_{1-x}O_6$ has previously been shown to provide a reaction pathway for converting the stable B cation ordered structure to a metastable phase with a disordered cation distribution.[18] The same approach is applied in the present work to the barium bismuth oxide system.

The reaction pathways that lead to significant differences in B cation distributions are summarized in Scheme I. Starting with the nominal composition "Ba_2BiO_{4+x}", three distinct cation ordering schemes have been obtained. Synthesis in air/oxygen at 950 °C leads to a 1:1 ordered perovskite, $A_2BB'O_6$.[4–7,19] Synthesis in nitrogen at 950 °C followed by annealing in oxygen at lower temperature (400 °C) leads to a 1:2 ordered perovskite, $A_3BB'_2O_9$. The same reaction sequence followed by a higher temperature anneal in oxygen (700 °C) gives a disordered distribution of the cations, $Ba(Ba_{1/3}Bi_{2/3})O_3$. The 1:2 ordered $Ba_3BaBi_2O_9$ phase converts to the disordered structure at approximately 700 °C. The disordered compound converts to the 1:1 ordered structure on heating at 950 °C for 24 h in air/oxygen. The 1:1 ordered compound cannot be con-

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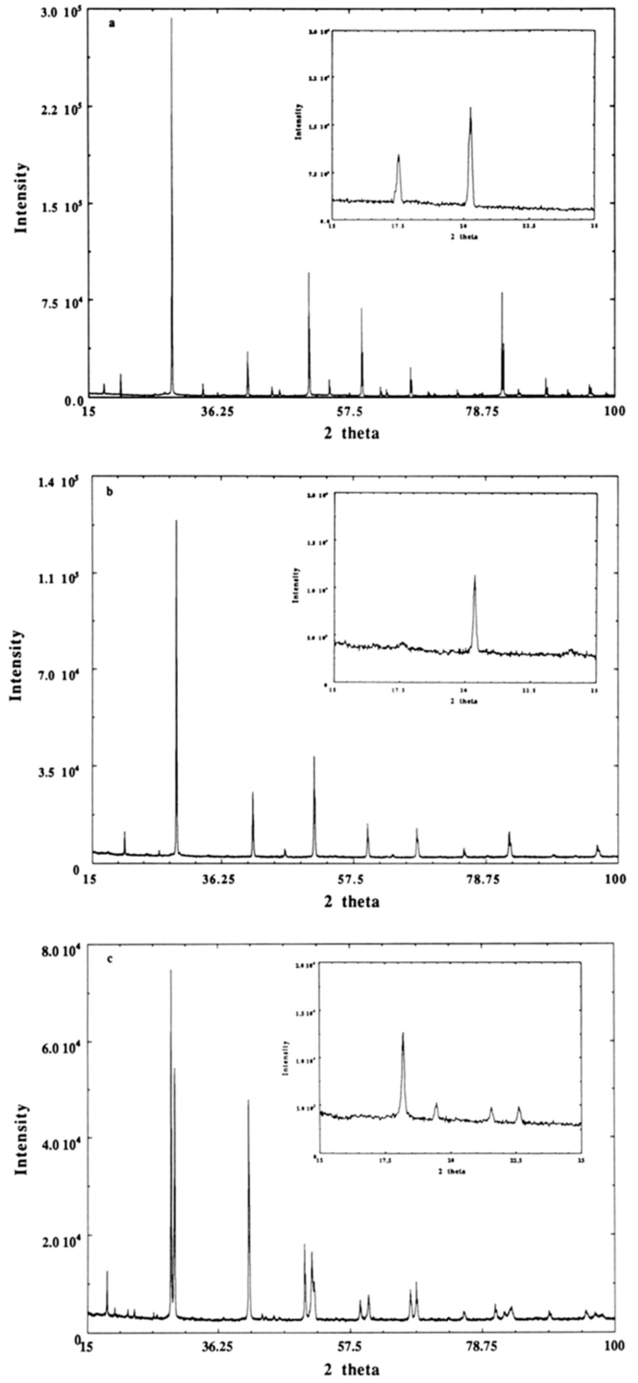

Figure 1. X-ray powder diffraction patterns of (a) (Ba$_{5/3}$Bi$_{1/3}$)BiBaO$_{5.67}$, 1:1 ordered face-centered doubled-cubic cell, (b) Ba(Bi$_{2/3}$,Ba$_{1/3}$)O$_3$, disordered primitive cubic cell, (c) Ba$_3$Bi$_2$BaO$_9$, 2:1 ordered rhombohedral cell. In each case, the region from 15° to 25° is shown on an expanded scale in the insert.

verted to the other structures by heating in nitrogen. The 1:1 compound decomposes at 950 °C in nitrogen.

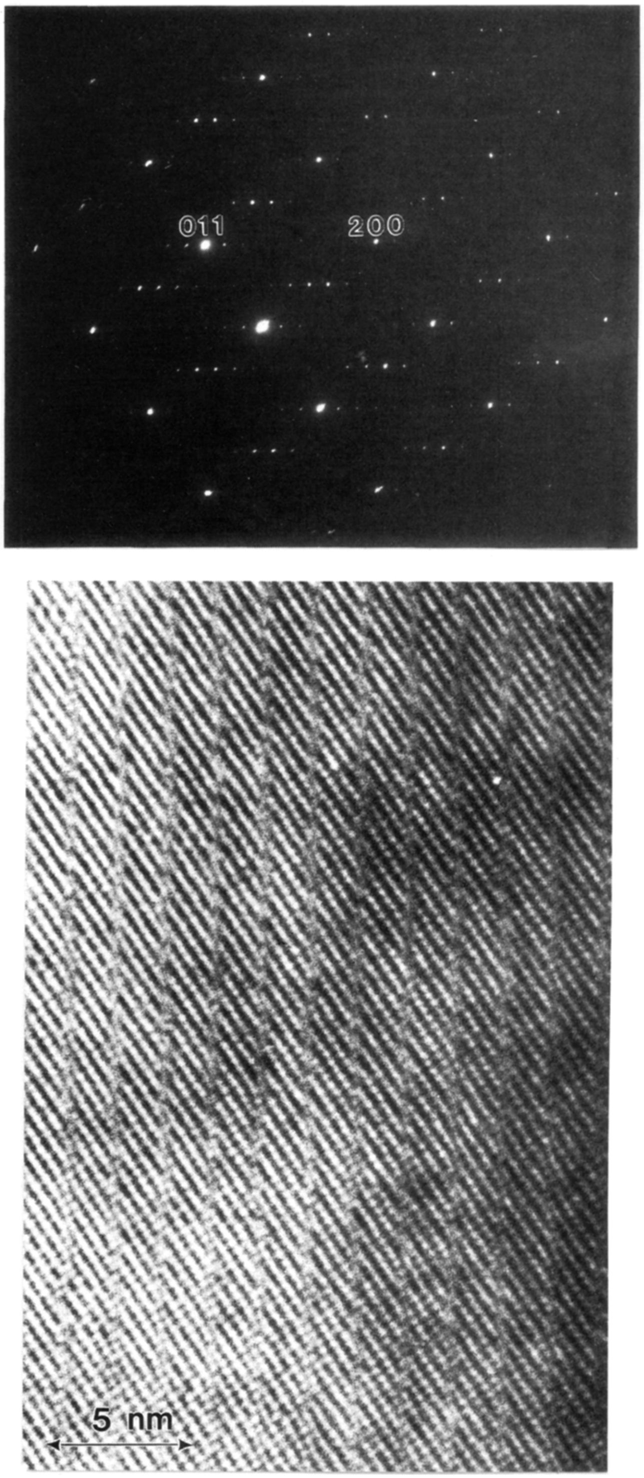

Figure 2. Electron diffraction pattern (a) and corresponding lattice image (b) for Ba$_3$Bi$_2$BaO$_9$ showing the commensurate superlattice and the periodic antiphase boundaries. The Ba/Bi order is not apparent in the lattice image. However, lattice image simulations show that for most imaging conditions, the contrast arising from the cation ordering is expected to be weak.

Figure 1 shows the X-ray powder patterns of the products obtained by high-temperature synthesis in air/oxygen and by heating in a nitrogen atmosphere followed by annealing in oxygen either at 400 °C or at 700 °C.[20] The X-ray pattern of the product (Figure 1a) synthesized in air/oxygen can be indexed on a face-centered cubic cell with $a = 8.799(4)$ Å. The unit cell is doubled relative to perovskite because of the ordering of Ba^{2+} and Bi^{5+} cations on the B sites as evidenced by the appearance of the superlattice lines (111, 311, etc.). A previous powder neutron diffraction study has shown that the cation distribution of this compound is best represented by Ba$_{5/3}$Bi$_{1/3}$[BaBi]O$_{5.67}$.[7] The X-ray powder pattern of the product obtained at 700 °C in oxygen (Figure 1b) was indexed with a primitive perovskite cell; $a = 4.3769(1)$ Å.

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[20] X-ray powder diffraction data were collected using a Scintag XDS2000 automated powder diffractometer and Cu Kα radiation. Data points were collected in 0.02° steps in the angular range $15 \leq 2\theta \leq 120$ with counting times of 5 s/point. The data were analyzed using the GSAS programs.

The X-ray powder diffraction data were fitted by the Rietveld method using the GSAS programs.[21] The results indicated a disordered distribution of $1Ba^{2+}$ and $2Bi^{5+}$ cations over the B sites. The X-ray pattern (Figure 1c) obtained from the compound prepared by heating first in nitrogen at 950 °C followed by annealing in oxygen at 400 °C is clearly different from both the 1:1 ordered and the disordered phases. The X-ray pattern contains two types of reflections. One set is obtained from a rhombohedral distortion of the primitive cubic perovskite cell and corresponds to the condition that $h + k + l = 2n$ (where the Miller indices refer to the primitive perovskite cell). The second set are not indexable on the rhombohedral cell but are observed in the vicinity of the perovskite primitive cell reflections corresponding to $h + k + l = 2n + 1$ (see insert in Figure 1c which shows four reflections in the vicinity of (100); note that the (100) primitive cubic reflection is absent in Figure 1c though clearly observed in Figure 1a,b). The origin of these superlattice peaks is discussed in more detail below. The intensities of the subcell reflections were fitted to a R-hexagonal cell with $a = 6.104(4)$ Å, $c = 7.7508(8)$ Å (the corresponding rhombohedral cell has $a = 6.258(3)$ Å, $\alpha = 58.80(1))^\circ$ and atom positions corresponding to a 1:2 ordered arrangement, $Ba_3BaBi_2O_9$. The reflections corresponding to a 1:1 order of the B cations are clearly absent from the pattern.

Thermogravimetric reduction in hydrogen confirmed that the disordered and 1:2 ordered compounds are stoichiometric with respect to the oxygen lattice in contrast to the 1:1 phase which is significantly oxygen deficient.

The origin of the superlattice reflections was further investigated by transmission electron microscopy.[22] Electron diffraction data are consistent with the presence of periodic antiphase boundaries in $Ba_3BaBi_2O_9$ (see Figure 2). As mentioned above, all reflections with $h + k + l = 2n$ based on the parent perovskite structure are present while reflections with $h + k + l = 2n + 1$ are absent. For a given odd reciprocal lattice vector $\mathbf{g}_{\text{odd}}$, reflections are present at $\mathbf{g}_{\text{odd}} \pm n\mathbf{q}$ where the modulation vector $\mathbf{q}$ is equal to $^1/_{18}\mathbf{g}_{211}$ (i.e., $^1/_{18}$ of the 211 reciprocal lattice vector) and the integer n is odd. Furthermore, all even reflections $\mathbf{g}_{\text{even}}$ are accompanied by satellite reflections at $\mathbf{g}_{\text{even}} \pm m\mathbf{q}$, where m is even. A periodic antiphasing model in which perovskite A and B sites are interchanged across an antiphase boundary explains the absence of perovskite reflections with $h + k + l = 2n + 1$ and the presence of reflections at $\mathbf{g}_{\text{odd}} \pm n\mathbf{q}$. The satellite reflections around the even perovskite reflections can be explained by a displacive relaxation of the structure due to the antiphasing. The shift vector for the antiphasing is $^1/_2[111]$ (perovskite) and is perpendicular to the boundary; i.e., with this shift vector, $\mathbf{q}$ can be parallel to $[\bar{2}11]$, $[1\bar{2}1]$, or $[11\bar{2}]$ (disregarding, for the moment, the inequivalence of the various {211} perovskite planes once the parent structure is distorted to give the rhombohedral subcell). A similar modulated structure was recently reported for the compound $Ba_2La_2Cu_2Sn_2O_{11}$.[23] In this compound the B cations adopt an unusual arrangement of $-CuO_2-SnO_2-SnO_2-CuO_2-$ layers perpendicular to (001). The modulation in the structure was attributed to the mismatched Cu–O and Sn–O bond lengths. A similar situation exists for $Ba_3BaBi_2O_9$ with B cation layers perpendicular to the (111) direction in the sequence $-Ba-O_3-Bi-O_3-Bi-O_3-$. The difference between the Ba–O and Bi–O bond distances causes a severe mismatch at the interface between the two types of layers. The resulting strain is released by the insertion of periodic antiphase boundaries.

In conclusion, the "Ba_2BiO_4" system is an unusual example of a mixed-metal oxide perovskite where the three most commonly observed B site cation distributions can be synthesized with the same cation stoichiometry by variation of both the thermal and redox pathways used during synthesis. A more detailed account of this work will be published elsewhere.

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