Single-phase perovskites were formed in the (1−x)Ba-(Zn_{1/3}Nb_{2/3})O_3−xLa(Zn_{2/3}Nb_{1/3})O_3 system for compositions with 0.0 ≤ x ≤ 0.6. Although the stability of the trigonal “1:2” ordered structure of the Ba(Zn_{1/3}Nb_{2/3})O_3 end member is very limited (0.0 ≤ x ≤ 0.05), low levels of lanthanum induce a transformation to a cubic, “1:1” ordered structure that has a broad range of homogeneity (0.05 ≤ x ≤ 0.6). Samples with x > 0.6 were comprised of La_2O_3, ZnO, and a perovskite with x = 0.6. The cubic 1:1 phases were fully ordered and no evidence was found for a compositionally segregated microstructure. These observations could not be reconciled in terms of a “space-charge” model; rather, they supported a charge-balanced, “random-site” structure for the 1:1 cation-ordered Ba(B^{1+}_2B^{5+}_2)O_4 phases.

I. Introduction

Barium-based, Ba(B^{1+}_2B^{5+}_2)O_4-type perovskites that contain a 1:2 mixture of divalent and pentavalent ions on the octahedral sites adopt a structure in which the two cations order onto individual (111) crystallographic planes of the cubic subcell.1–3 The long-range ordering and associated displacements of the oxygen anions between the cation planes yields a trigonal “1:2” structure with a \{B^{2+}B^{5+}\} layer repeat.1–3 It has been shown that the symmetry of the B-site ordering in these systems can be altered by low-level substitutions of appropriate cations on either the A-site (e.g., La^{3+}) or B-site (e.g., Zr^{4+}) sublattice.4,5 In both cases, the cation substitutions promote a transformation to a cubic (Fm\overline{3}m) “1:1” ordered structure with a doubled perovskite repeat and a NaCl-type arrangement of the 1:1 cation-ordered domains.8,9 For all the lanthanum-substituted 1:2 perovskites, the stabilization of a 1:1 ordered cation arrangement has been interpreted in terms of the so-called “space-charge” model.8–11 In this model, the β′ and β″ positions in the 1:1 phases are claimed to be occupied exclusively by the B^{2+} and B^{5+} cations, respectively, and the composition of the ordered regions is represented by \{A^{3+}_{0.5}La^{3+}_{0.5}\}B^{2+}_{1/2}B^{5+}_{1/2}O_3{0.5-x}. To conserve electroneutrality, it has been assumed that the charge imbalance in the 1:1 structure is compensated by an equal and oppositely charged, B^{4+}-rich disordered matrix that surrounds the regions of 1:1 order. Support for the space-charge model has come from the increase in the stability and size of the 1:1 ordered domains with increasing x, which is thought to result from the reduction of the charge imbalance by the lanthanum donor dopants.8,9

For the B-site (e.g., Zr^{4+})-substituted 1:2 perovskites, a different crystal chemical model has been used to interpret the transformation to 1:1 order. The most-extensive studies of this type of substitution have been reported for solid solutions of BaZrO_3 with Ba(Mg_{1/3}Ta_{2/3})O_3, Ba(Zn_{1/3}Ta_{2/3})O_3, and Ba(Mg_{1/3}Nb_{2/3})O_3.4,6,7 In each case, a 1:1 ordered supercell is stabilized for compositions with ~4–25 mol% BaZrO_3.4,6,7 Rietveld refinements and transmission electron microscopy (TEM) studies revealed that the 1:1 ordering in these systems could be understood in terms of a “random-site” model for the Ba^{1+}_{B/2}Ba^{5+}_{B/2}O_3 structure.4,5,7 In this model, the β′ sites are occupied by B^{4+} (tantalum or niobium), and the β″ positions contain a random distribution of the B^{2+}, Zr^{4+}, and remaining B^{5+} cations. For the random-site model, the Ba^{1−x}_{B/2}Ba^{x}_{B/2}O_3 phase is charge balanced, and the 1:1 ordered (1−x)Ba^{1+}_{B/2}Ba^{5+}_{B/2}O_3−xLaZrO_3 solid solutions can be represented by Ba^{1−x}_{B/2}Ba^{x}_{B/2}O_3−xLa(Zn_{1/3}Ta_{2/3})O_3, where −0.04 ≤ x ≤ 0.25.

In this communication, we report on our investigations of the effect of lanthanum doping on the cation ordering in Ba-(Zn_{1/3}Nb_{2/3})O_3. According to the currently accepted space-charge model, 1:1 order in the Ba_{1−x}La_{x}Zn_{1/3}Nb_{2/3}O_3 system should produce a phase-separated, charge-imbalanced microstructure for lanthanum concentrations up to x = 0.5. To ascertain whether this model is correct, we have examined the phase stability and microstructure of compositions across the entire Ba(Zn_{1/3}Nb_{2/3})O_3−La(Zn_{2/3}Nb_{1/3})O_3 pseudo-binary system using X-ray and TEM techniques.

II. Experimental Methods

The BLZN ceramics were batched according to the chemical formula, Ba_{1−x}La_{x}Zn_{1/3}Nb_{2/3}O_3, with x = 0.0, 0.05, 0.15, 0.35, 0.5, 0.6, 0.75, 0.9, and 1. Stoichiometric quantities of high-purity (99.9%) precursors were mixed with BaO, ZnO, La_{2}O_{3}, and BaCO_3 in an agate mortar for 10 min and then calcined at 1100°C for 12 h. The resultant powder was ball milled for 10 h, and rods 8–10 mm long and 10 mm in diameter were isostatically pressed at 600 MPa.

Sintering of the BLZN pellets was conducted at 1350°C for 3 h with a heating and cooling rate of 300°C/h. To inhibit any...
possible loss of ZnO during sintering, the pellets were immersed in a powder of the same composition and covered with an inverted platinum crucible. The success of this method was gauged by the lack of any weight loss during sintering and the absence of any significant impurity peaks in the X-ray patterns. The final density of the fired ceramics was >95% of the theoretical value.

The phase content of the samples was monitored by using X-ray diffractometry (XRD) (Model Geigerflex, D-Max-B, Rigaku Co., Tokyo, Japan; CuKα radiation, produced at 45 kV and 30 mA), and the microstructure of the sintered pellets was characterized by TEM (Model 400EM (Philips Electronic Instruments, Mahwah, NJ) operated at 120 kV or Model 4000EX (JEOL, Tokyo, Japan) operated at 400 kV). The TEM samples were prepared by grinding the ceramic pellets to a thickness of ~30 μm and polishing both sides with 5, 3, 1, and 0.25 μm Al₂O₃ powder. Copper support grids were then placed on the thin sections, and the final thinning to perforation was conducted by using ion milling (Model 600 Dual Ion Mill, Gatan, Pleasanton, CA) (Ar⁺ ions, produced at 5.5 kV and 6 mA). The thin foils were carbon coated to prevent charging.

III. Results and Discussion

After sintering at 1350°C for 3 h, the X-ray patterns of pure BZN contained very weak and diffuse superlattice reflections from a 1:2 ordered structure. By quenching the samples from higher temperatures, evidence was found for a transition from 1:2 to a fully disordered perovskite. During the course of this work, additional support for this transformation appeared in the literature. Fully 1:2 ordered samples of BZN with stronger and sharper supercell reflections could be stabilized by annealing at 1350°C for 12 h (see Fig. 1).

The effect of the substitution of lanthanum on the cation order is readily observed through the changes in the position and intensity of the superlattice reflections in the X-ray patterns of BLZN samples with x > 0. For 0.05 ≤ x ≤ 0.6, all the X-ray patterns could be indexed in terms of a single-phase 1:1 ordered, cubic (Fm3m) supercell with a = 2a_{perovskite}. Further additions of lanthanum resulted in the formation of secondary phases, and, for 0.6 < x < 1, the X-ray patterns contained reflections from a perovskite with x = 0.6, La₆NbO₁₂, and ZnO (Fig. 1). Reaction of the lanthanum end-member composition, LaZn₃/2Nb₁/3O₉, failed to produce any evidence for a perovskite phase, and the sample was comprised of a two-phase mixture of La₆NbO₁₂ and ZnO. This phase assemblage is consistent with its position on the La₆NbO₁₂–ZnO tie line in the ZnO–La₆NbO₁₂–Nb₂O₅ ternary system. Interestingly, the phase stability of LaZn₃/2Nb₁/3O₉ is quite different to its lanthanum magnesium zinc niobate counterpart, which has been reported to form a stable single-phase perovskite.

The microstructures of the 1:1 ordered BLZN phases were investigated by centered dark-field TEM techniques using the (3/2,3/2,3/2) supercell reflection. Figure 2 shows an image collected from a sample of BLZN with x = 0.05 after a heat treatment at 1350°C for 12 h. This micrograph shows no evidence for any regions of a disordered perovskite phase, and the sample is fully 1:1 ordered with domain sizes that approach 1–2 μm. The lack of any type of phase separation and the observation of complete 1:1 ordering cannot be reconciled in terms of the space-charge model.

It is our opinion that the results for the BLZN system are more readily explained in terms of a charge-balanced, random-site model for the 1:1 cation order. In this ordering scheme, the B⁺

positions in the 1:1 ordered Ba₁₋ₓLaₓ[Zn₁₋ₓ/₃(Nb₂−ₓ₋₁/₃)O₃]

phases are occupied by Nb⁵⁺ cations, and the B sites contain a random distribution of Zn²⁺ cations and the remaining Nb³⁺ cations with a stoichiometry [Zn₂₋ₓ/₃(Nb₁₋ₓ/₃)O₃]. For this model, the composition of the 1:1 ordered Ba₁₋ₓLaₓ[Zn₁₋ₓ/₃(Nb₂−ₓ₋₁/₃)O₃] phases can be represented as Ba₁₋ₓLaₓ[Zn₂₋ₓ/₃(Nb₁₋ₓ/₃)O₃] for an x value of 0.5. Because the structure is charge balanced for this model, the microstructures of equilibrated 1:1 ordered ceramics should not exhibit any regions of disorder; this is in agreement with the TEM results. Additional support for the random-site model comes from the change in the relative intensities of the supercell reflections across the region of stability of the 1:1 ordering. From the X-ray patterns in Fig. 1, it is apparent that the intensity of these reflections increases systematically from x = 0.05 to x = 0.5. This observation is consistent with the enrichment of the B’ sites in Zn, which, at x = 0.5, is the sole occupant of this cation position. At x = 0.6, there seems to be a reversal of this trend and the supercell reflections are somewhat broader and weaker; this will be discussed below.

IV. Discussion

Compositions in the Ba₁₋ₓLaₓ[Zn₁₋ₓ/₃(Nb₂−ₓ₋₁/₃)O₃] system form a single-phase perovskite for 0.0 ≤ x ≤ 0.6. The 1:2 ordered structure of the BZN end member has a very limited range of stability (0 ≤ x < 0.05), and low levels of lanthanum promote a transformation to a 1:1 ordered structure that has a broad range of homogeneity (0.05 ≤ x ≤ 0.6). Equilibrated samples of the 1:1 ordered phases show no evidence for any type of chemical segregation or residual disorder and are comprised of large, ordered domains. We begin this discussion by considering the unfavorable effect of this substitution on the energetics of the 1:2 ordering in BZN. The primary stabilizing feature of the 1:2 ordering in Ba(B⁵⁺O₃/₂)O₃ mixed-metal perovskites is the accommodation of the different B³⁺–O and B⁵⁺–O bond lengths through a concerted displacement of the (111) anion layers toward the smaller B³⁺ cations. It is unlikely that very small concentrations of lanthanum on the A-sublattice would, on their own, produce a large reduction in stability; it is...
more probable that the loss of 1:2 order can be attributed to the accompanying increase in the concentration of zinc on the B-sublattice. Because of the mismatch in the size of the Zn$^{2+}$ (0.72 Å (0.072 nm)) and Nb$^{5+}$ cations (0.64 Å (0.064 nm)), the introduction of small levels of zinc onto the niobium layers is very effective in impeding the long-range anion displacements and significantly reduces the thermodynamic stability of the 1:2 ordered phase.

The formation of a 1:1 ordered structure as an alternative to 1:2 order, or to a completely disordered perovskite, is identical to the behavior observed in the BaZrO$_3$-substituted 1:2 perovskites. Because the results for the microstructures of 1:1 ordered BLZN are entirely inconsistent with a space-charge model, we propose that the structures of these phases also exist. Using this model, the changes in the stability of the 1:1 phase from 0.05 $\leq x \leq 0.5$ can be understood in terms of the stoichiometry, (Zn$_{(2+2x)/3}$Nb$_{(1-2x)/3}$)$_{(1/2)}$O$_3$, of the randomly distributed cations on the $\beta'$ sites of the Ba$_{1-x}$La$_x$(Zn$_{(1/2)}$Pb$_{(1/2)}$)$_x$O$_3$ structure. For low levels of lanthanum, the $\beta'$ position contains an $\approx 2:1$ distribution of Zn:Nb; for $x = 0.5$, it is exclusively populated by zinc and the structure is represented by Ba$_{1-x}$La$_x$(Zn$_{1/2}$}$\beta'$$\beta''$O$_3$. Because the enrichment of zinc on the $\beta'$ site increases the difference in the charge and size of the $\beta'$ and $\beta''$ cation positions, a corresponding enhancement in the stability of the 1:1 phase is to be expected.

Although the stability and structures of the 1:1 phases can be successfully interpreted up to $x = 0.5$ using a model with a random distribution of cations on the $\beta'$ sites, our studies indicate that the region of 1:1 order can be extended up to $x$ values as large as 0.6. We propose that the lanthanum-rich phases also adopt a random-site structure; however, in this case, the mixing of the cations occurs on the $\beta'$ positions. Specifically, for $0.5 \leq x \leq 1.0$, we suggest that it is possible to form $\beta'$ random-site 1:1 ordered phases with Ba$_{1-x}$La$_x$[(Zn)$_{1/2}$]$\beta'$$\beta''$[Nb$_{(1-2x)/3}$Zn$_{(2-1.5x)/3}$]$1/2$O$_3$. For the zinc-based system, this phase only extends up to $x = 0.6$ and the perovskite end member, La[(Zn)$_{1/2}$]$\beta'$$\beta''$[Nb$_{(1/2)}$Zn$_{(1/3)}$]$1/2$O$_3$, does not exist. However, as noted earlier, this phase does form in the corresponding magnesium-based system, and, in a future communication, the properties of Ba(Mg$_{(1/3)}$Nb$_{(2/3)}$)$_{1−x}$La(Mg$_{(2/3)}$Nb$_{(1/3)}$)$_{x}$O$_3$ solid solutions will be described. The reduction in the intensity of the 1:1 supercell reflections at $x = 0.6$ and the lack of stability of higher $x$ values in BLZN can also be interpreted in terms of the reduction in difference in the scattering cross section, charge, and size of the $\beta'$ and $\beta''$ positions for $x > 0.5$.

V. Conclusions

The 1:2 ordered structure of Ba(Zn$_{(1/2)}$Nb$_{(2/3)}$)$_x$O$_3$ has a limited stability in the Ba$_{1-x}$La$_x$(Zn$_{(1/2)}$)$\beta'$$\beta''$O$_3$ system. For lanthanum compositions with $0.05 \leq x \leq 0.6$, the solid solutions form a cubic 1:1 ordered phase with a doubled perovskite repeat. The fully ordered microstructure of the 1:1 ordered samples is not consistent with a space-charge-type model for the cation order; instead, these phases are best interpreted by a random-site structure. In this model, the ordered solid solutions can be represented as Ba$_{1-x}$La$_x$[(Mg$_{(1/3)}$Nb$_{(2/3)}$)$_{(1-2x)/3}$]$\beta'$$\beta''$[Nb$_{(1/2)}$]$1/2$O$_3$. The change in the stability of the 1:1 structure results from the increase in the size and charge difference of the two cation sites with increasing $x$.

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References


