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Phase segregation in mixed Nb–Sb double perovskites $Ba_2LnNb_{1-x}Sb_xO_6$

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Abstract

The phase composition of two series of mixed Nb^{5+}–Sb^{5+} double perovskites formed between the pairs Ba_2EuNbO_6–Ba_2PrSbO_6 and Ba_2NdSbO_6–Ba_2NdNbO_6 have been studied using synchrotron X-ray powder diffraction methods. In both series extensive phase segregation is observed demonstrating limited solubility of Sb^{5+} in these Nb^{5+} perovskites, irrespective of the precise structures of the double perovskite. Evidence for a monoclinic $I2/m$ phase in the series formed between tetragonal $I4/m$ Ba_2EuNbO_6 and rhombohedral $R\bar{3}$ Ba_2EuNbO_6 is presented. It is postulated that this phase segregation is a consequence of competing bonding requirements of the Nb^{5+} and Sb^{5+} cations associated with their electronic configurations.

Keywords: Perovskite; Phase segregation; Rietveld refinement

1. Introduction

Metal oxides with the double perovskite structure continue to attract attention due to the diverse range of properties exhibited by these materials including colossal magneto-resistance, ionic conductivity, ferro- and piezo-electricity and ferromagnetism [1]. Such properties are known to be strongly influenced by the precise structure of the oxides, as exemplified by the recent illustration of switching from ferromagentism to antiferromagnetism in A_2CrSbO_6 by Retuerto et al. [2]. Consequently structural studies of such perovskites are pivotal in understanding these important physical properties. In particular, properties such as colossal magneto-resistance and ferroelectricity tend to be most prominent in compounds close to a structural instability that may take the form of a phase transition or a solubility limit [3]. This is extremely well documented for ferroelectrics based on Pb–Zr–Ti perovskites (PZT) where optimal performance occurs near the morphotropic phase boundary [4,5]. The diverse range of structures adopted by perovskites and the presence of structural, electronic and magnetic phase transitions between these demonstrates a greater complexity in the structure and chemistry of these oxides than may be naively expected from the relatively simple structure of the parent primitive cubic perovskite.

The chemistry and structures of perovskites containing Nb^{5+} and Sb^{5+} provide a number of examples of unexpected structural complexity [6–9]. The similar charge and ionic radii of Sb^{5+} (0.60 Å) and Nb^{5+} (0.64 Å) [10] lead to the assumption that antimonate and niobate compounds should adopt similar perovskite structures. There are, however, numerous examples in the perovskite family where the niobate and antimonate compounds adopt different structures or where the antimonate but not the corresponding niobate, or vice versa, forms. Examples where the antimonate but not the corresponding niobate exists include Ba_2BiSbO_6 [11] and $Ba_4NaSb_3O_{12}$ [12] while the Aurivillius phase $BaBi_2Nb_2O_9$ [13] is known to exist but $BaBi_2Sb_2O_9$ is unknown. The series $Ba_2LnB'O_6$ (Ln = lanthanide and $B' = Nb^{5+}$ or Sb^{5+}) provides an unusual example of perovskite-type oxides where both the antimonate and niobate form, but these adopt different structures. Both series undergo a sequence of phase transitions with decreasing average ionic radii of the

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B-site cations from $I2/m$ monoclinic (Glazer tilt system $a^-a^-c^0$ [14,15]) to an intermediate structure and then ultimately to $Fm\bar{3}m$ cubic ($a^0a^0a^0$) symmetry [7]. The intermediate structure adopted by the two series is, however, different with the antimonates having a $R\bar{3}$ rhombohedral ($a^-a^-a^-$) intermediate while the majority of niobates adopt an $I4/m$ tetragonal ($a^0a^0c^-$) structure [6,7]. The differences in the physio-chemistry and structure of antimonate and niobate perovskites indicates that factors other than ionic radii and valency play an important role in the formation and stability of the resulting perovskites.

Understanding of the chemical basis for the differences between Nb^{5+} and Sb^{5+} containing perovskites is clearly needed. Although superficially similar and having near identical tolerance factors the two oxides Ba_2PrSbO_6 and Ba_2EuNbO_6 (tolerance factors of 0.795 and 0.794, respectively [1]) adopt alternate intermediate structures, $R\bar{3}$ and $I4/m$, respectively, at room temperature. Structural studies of solid solutions of the type $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ are, therefore, expected to shed light on the chemical differences between Nb^{5+} and Sb^{5+} while also providing further insight into the complex phase transition behaviour in $Ba_2LnB'O_6$ oxides. A related study by Mitchell and co-workers [16] on the series $Sr_{1-2x}Na_xLa_xTiO_3$ (solid solution between $SrTiO_3$ and $Na_{0.5}La_{0.5}TiO_3$) concluded that the transition from $I4/mcm$ to $R\bar{3}c$ occurs directly via a discontinuous phase transition [17]. The $I4/mcm$ to $R\bar{3}c$ transition in these ABO_3 perovskites involves the same two Glazer tilt systems, $a^0a^0c^-$ and $a^-a^-a^-$, as an $I4/m$ to $R\bar{3}$ transition that may occur in the $A_2BB'O_6$ double perovskite series $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$. The difference in symmetry between the two series is a consequence of the ordering of the two different *B*-site cations in $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$. Interestingly the $I4/mcm$ phase is not observed in the series $La_{1-x}Sr_xCr_{1-x}Ti_xO_3$ where a first-order transition from $Pnma$ to $R\bar{3}c$ occurs [18].

The tetragonal to rhombohedral phase transition in $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ may be first order, as seen for $Sr_{1-x}Na_xLa_xTiO_3$, or it may involve an intermediate phase. This would most likely be either $I2/m$ monoclinic ($a^-a^-c^0$) or $Fm\bar{3}m$ cubic ($a^0a^0a^0$), both of which are observed in the two $Ba_2LnB'O_6$, $B' = Nb^{5+}$ or Sb^{5+}, series. Alternatively, the different structures observed for Ba_2PrSbO_6 and Ba_2EuNbO_6 may indicate that Nb^{5+} and Sb^{5+} are incompatible in the same perovskite structure. Such incompatibility could manifest itself as a solubility gap that would lead to segregation and the formation of two or more phases with different chemical compositions. Such segregation would be consistent with the apparent chemical incompatibility of niobium and antimony perovskites mentioned previously.

In order to determine which of these three possibilities (direct first-order phase transition, presence of an intermediate phase or phase segregation) occurs we have synthesized two series of oxides, namely $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ and $Ba_2NdNb_{1-x}Sb_xO_6$ and structurally characterized these using synchrotron X-ray diffraction and, as required, analytical electron microscopy. These oxides were chosen to minimize the changes in volume and tolerance factor across the series. That is, the only significant difference across each series will be the exchange of Sb^{5+} for Nb^{5+}. The resolution and high intensity offered by synchrotron X-ray powder diffraction makes it easier to resolve the splitting of peaks in perovskites, particularly those that appear to be pseudo-cubic, allowing the symmetry of compounds to be determined. High resolution is also important in determining whether the samples consist of single or multiple perovskite phases.

2. Experimental

All starting materials were obtained from Sigma-Aldrich Chemicals. The lanthanide oxides and barium carbonate were dried prior to use by heating at 1000 and 100 °C overnight. Samples of $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ and $Ba_2NdNb_{1-x}Sb_xO_6$ ($x = 0, 0.1, 0.2, \ldots, 1$) were prepared from stoichiometric mixtures of $BaCO_3$, Nb_2O_5, Sb_2O_3 and the appropriate lanthanide oxides; Pr_6O_{11}, Nd_2O_3 and Eu_2O_3. The appropriate starting mixtures were finely ground as an acetone slurry and, after drying, were heated for a period of 24 h at 800 °C followed by heating at 1000, 1100 and 1200 °C for periods of 24 h. The samples were then pressed into pellets and heated at 1300 °C for 24 h followed by heating, in pelleted form, for a maximum of 48 h at 1350 °C and 24 h at 1400 °C in order to yield samples with the maximum purity. In all cases samples were reground and, if required, repelleted after each heating period.

The reactions were monitored by powder X-ray diffraction using Cu-$K\alpha$ radiation on a Shimadzu X-6000 Diffractometer. Synchrotron X-ray diffraction data were recorded on the Debye Scherrer diffractometer at the Australian National Beamline Facility, Beamline 20B at the Photon Factory, Tsukuba, Japan [19]. The samples were housed in 0.3 mm capillaries that were continuously rotated during measurement to reduce the effects of preferred orientation. Data were collected using three image plates as detectors covering the range of $5 < 2\theta < 125°$ with a step size of 0.01° and a wavelength of 0.80073 or 0.80286 Å. Variable temperature measurements, at temperatures of up to 500 °C, were carried out using a custom built furnace over a range of $5 < 2\theta < 85°$.

Refinements of the crystal structures were performed with the program RIETICA [20]. The diffraction peaks were described by a pseudo-Voight function using a Howard asymmetry correction where necessary [20]. The background was estimated from interpolation between up to 40 selected points.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were conducted for selected samples using a Phillips XL 30 SEM with a tungsten filament operating at 25 keV and a spot size of 5 μm. The EDX operation and data analysis was performed using the DX-4eDX ZAF operating system.