The Connection Between B-Cation Site Disorder and Oxygen Non-stoicheiometry in the Perovskite $Ba_2Bi_{2-x}La_xO_{6-y}$

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The extent of B-cation disorder in the perovskite $Ba_2Bi_{2-x}La_xO_{6-y}$ is strongly connected to the oxygen non-stoicheiometry and consequently depends on the redox history of the sample.

Compounds of composition $A_2BB'O_6$ with the perovskite structure show B-cation order especially for large differences in charges and radii of B and B'.[1] The ordered structure consists of alternate layers of B and B' cations, normal to a cubic [111] direction, and results in a doubling of the simple cubic unit cell. The relation between the superlattice intensities and cation order has been established by detailed structural studies of, for example, Ba_2BiSbO_6[2] and Ba_2LaBiO_6.[3,4] In this paper, we show that the extent of Bi, La order in the perovskite series $Ba_2Bi_{2-x}La_xO_{6-y}$ is strongly connected to the oxygen non-stoicheiometry and consequently depends on both the redox and thermal history of the material.

A fully oxidized ordered perovskite of composition $Ba_2Bi_{1.5}La_{0.5}O_6$ was prepared by heating, with intermediate regrinds, a stoicheiometric mixture of $Ba(NO_3)_2$, $Bi(NO_3)_3{\cdot}5H_2O$, and La_2O_3 in air at 400 °C (2 h), 800 °C (1 h), 800 °C (60 h), and finally in oxygen at 950 °C (16 h). The product was a single phase ordered pseudo-cubic perovskite with a doubled unit cell [a = 8.737(5) Å] and a (111) reflection indicative of B-cation order. The oxidized phase was then reduced to $Ba_2Bi_{1.5}La_{0.5}O_5$ at 950 °C in an argon–oxygen mixture with $p(O_2) = 10^{-4}$ atm, and finally it was completely reoxidized at 600 °C in pure oxygen. The reaction conditions were determined in ancillary thermogravimetric experiments.

The X-ray powder diffraction data for the final product show that the (111) reflection observed in the ordered starting material is absent, indicating that the B cations are completely disordered. This was confirmed quantitatively by least-squares fitting the X-ray intensities. The perovskite cell is distorted to rhombohedral symmetry [a = 6.174 Å, α = 60.4° derived from the splitting of the (444) pseudo-cubic reflection] and refinement of the disordered structure in space group $R\bar{3}c$ ($LaAlO_3$ type)[5] gave excellent agreement with the observed data. The results indicate that during reduction at 950 °C, Bi and La cation interdiffusion has occurred to produce a disordered material in which all B cation layers are equivalent. The B-site interdiffusion occurs in synergy with the creation of anion vacancies and metal valence defects upon reduction of $Ba_2Bi_{1.5}La_{0.5}O_6$ to $Ba_2Ba_{1.5}La_{0.5}O_5$. Reoxidation at 600 °C restores the oxygen to the lattice but traps the B cation configuration of the reduced state.

The pseudo-cubic cell constant of the disordered phase [8.755(5) Å] is significantly larger than the value (8.737 Å) observed for the ordered material indicating that the disordered compound is metastable. Consequently, when the disordered phase is heated at high temperatures without changing the composition (oxygen, 900 °C, 48 h), reordering occurs to give a phase with a lattice constant identical to that of the starting material and a clearly observable (111) intensity. The diffraction intensities for the reordered phase were calculated assuming the monoclinic Ba_2LaBiO_6 structure.[4] The observed and calculated ratios for $I(111)/I(200)$, 0.17 and 0.19, respectively, are in good agreement and confirm reordering of the B cations.

Cation disorder, associated with reduction at high temperatures, is also observed at other compositions in the series $Ba_2Bi_{2-x}La_xO_6$. In general, more severe reducing conditions are required to reduce the Bi^{5+} cations completely as the lanthanum content, x, ($0 \leqslant x \leqslant 1$) increases. At 1000 °C and $p(O_2) = 3 \times 10^{-6}$ atm, complete reduction could not be obtained for compounds with lanthanum contents greater than $x = 0.67$ and no reduction is observed at $x = 1.0$. The strong dependence of the reducibility on the lanthanum content indicates that the underlying reason for the coupling of the B site disorder to the oxygen non-stoicheiometry lies in the relative ease of removal of oxygen from Bi^{V}–O–La^{III} and Bi^{V}–O–Bi^{III} structural units. It is probable that the energy of formation of an oxygen vacancy and two five-co-ordinate Bi^{3+} cations is much lower than that for the alternative arrangement which would result in a very unusual five-co-ordinate La^{3+} cation. In the ordered structure, the number of Bi^{V}–O–La^{III} linkages is proportional to the lanthanum content. At a particular lanthanum content, cation disorder increases the probability of occurrence of Bi^{V}–O–Bi^{III} linkages which can accommodate the oxygen vacancies introduced on reduction of Bi^{5+} to Bi^{3+}. Consequently, the reduced composition $Ba_2Bi_{2-x}La_xO_5$ is more stable in the B cation disordered form.

The kinetics of reduction of the ordered phases are determined by B cation interdiffusion and not by oxide ion mobility which is known to be high.[6] Thus, the reduced disordered phases can all be reoxidized in oxygen at 600 °C without cation reordering. The disordered oxidized compounds have larger unit cell volumes as noted above for $x = 0.5$ and the difference increases as x increases, for example, at $x = 0.67$, values of 8.747(5) and 8.775(5) Å were observed. The increase indicates that the ordering energy increases with increasing lanthanum content. Finally, we note that the coupling of the redox chemistry to the cation order has consequences for the use of these materials in hydrocarbon oxidation.[7,8]

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References

1 L. Katz and R. Ward, *Inorg. Chem.*, 1964, **3**, 205.
2 G. Thornton and A. J. Jacobson, *Acta Crystallogr., Sect. B.*, 1978, **34**, 351.
3 Van R. Scholder, K. W. Ganterr, H. Gläser, and G. Merz, *Z. Anorg. Allg. Chem.*, 1963, **319**, 375.
4 R. A. Beyerlein, J. M. Newsam, K. R. Poeppelmeier, and A. J. Jacobson, in preparation.
5 A. M. Glazer, *Acta Crystallogr., Sect. B*, 1972, **28**, 3384.
6 R. A. Beyerlein, A. J. Jacobson, and L. N. Yacullo, *Mater. Res. Bull.*, 1985, **20**, 877.
7 R. A. Beyerlein, A. J. Jacobson, and K. R. Poeppelmeier, U.S. Pat., 1984, No. 4 482 644.
8 R. A. Beyerlein, K. R. Poeppelmeier, and A. J. Jacobson, U.S. Pat., 1985, No. 4 503 166.