JOURNAL OF SOLID STATE CHEMISTRY 84, 82–87 (1990)

The Perovskite $Ba(Bi_{1-x}Li_x)O_{3-y}$: A New Type of Cation Order for $x = 0.25$, $Ba_4Bi_3LiO_{11}$

C. GREAVES AND S. M. A. KATIB

School of Chemistry, Superconductivity Research Group, University of Birmingham, Birmingham B15 2TT, England

Received May 18, 1989; in revised form August 31, 1989

The structural properties of the perovskite system $Ba(Bi_{1-x}Li_x)O_{3-y}$ have been investigated for $0.0 < x < 0.25$. Over this composition range, the nominal Bi oxidation state varies between +4 and +4.33 and no superconducting propeties were observed. The Li-rich end member of this series, $Ba_4Bi_3LiO_{11}$, exhibits a new type of superstructure due to cation order in the octahedral sites—tetragonal $P4/mmm$, $Z = 1$, $a = 6.101(1)$, $b = 8.628(2)$ Å. The ordered structure is different from that observed for the analogous $Ba_4M_3LiO_{12}$ phases where M = Sb, Nb, Ta, and possible reasons for this are discussed. In particular, the structures of the Sb and Bi phases are compared in detail using Madelung energy calculations.

Introduction

Superconducting behavior can be induced in the perovskite $BaBiO_3$ by appropriate cation substitutions to lower the Fermi energy in the nominally half-full Bi 6*s* band. Substitution at the passive Ba site would appear to be the preferred substitution route, and recent substitutions of K for Ba (*1, 2*) have resulted in T_c values of around 30 K. However, the earliest report of superconductivity (*3*) related to Pb substitutions on the Bi site, for which $T_c = 13$ K. The similar ionic radii of Bi^{5+} and Li^+ (both 0.76 Å in octahedral coordination (*4*)) suggested that substitution of Li for Bi in $BaBiO_3$ may be possible, with a consequential increase in the Bi oxidation state. The structural chemistry of $Ba(Bi_{1-x}Li_x)O_3$, $0 < x < 0.25$, has therefore been examined, since this range would span nominal Bi oxidation states of 4+ to 5+ if full oxygen stoichiometry were retained. Low-temperature magnetic measurements have been made and examined for indications of superconductivity.

The structural properties of Sb^{5+}, Nb^{5+}, Ta^{5+}, and Bi^{5+} are generally quite similar (ionic radii for octahedral coordination 0.60, 0.64, 0.64, and 0.76 Å, respectively (*4*)), but whereas perovskite-related phases of the type $Ba(M_{0.75}Li_{0.25})O_3$ have been reported for M = Sb, Nb, Ta (*5, 6*), no similar data relate to M = Bi. Synthesis of the Nb and Ta phases at temperatures below 1000°C results in cubic structures with disorder on the octahedral sites whereas for prolonged heating or treatments at higher temperatures, mixed stacking (ccch) of the BaO_3 layers occurs with the Li atoms preferentially located in the face-shared octahedral positions (*5*). In $Ba(Sb_{0.75}Li_{0.25})O_3$, 1 : 3 long-range cationic order is found, but the simple cubic perovskite subcell is now

0022-4596/90 $3.00

maintained: Li atoms are at the corners and body-center of a doubled unit cell, space group $Im3m$, $a = 8.224(1)$ Å (6). Due to the different ordering effects observed for the Sb, Nb, and Ta analogs, particular attention was given to the possibility of cation ordering for the composition $Ba(Bi_{0.75}Li_{0.25})O_3$.

Sample Preparation and Characterization

$Ba(Bi_{1-x}Li_x)O_3$ samples ($x = 0.05$, 0.10, 0.15, 0.20, and 0.25) were prepared from high purity, dry $BaCO_3$, α-Bi_2O_3, and Li_2CO_3. Appropriate stoichiometric mixtures were intimately ground together and heated in air at 680°C for 24 hr; the products were reground and reheated at 780°C in air for 24 hr. Some samples were given an additional heat treatment for 16 hr at 750°C in oxygen to maximize the bismuth oxidation state. Powder X-ray diffraction (Philips PW 1050/70 diffractometer, Cu$K\alpha$ radiation) indicated that all samples, which were black or very dark brown, were single phase with a simple cubic perovskite structure. At higher values of x, additional phases were observed, in particular $LiBiO_2$. The perovskite unit cell dimension and instrumental zero-point error were determined for each composition using a standard least-squares minimization program operating on observed and calculated $\sin^2(\theta)$. Weak additional peaks were observed in some samples with $x = 0.25$, and these were the subject of a more detailed examination, as discussed below.

The bismuth oxidation state was estimated by iodometric titrations, using a method similar to that described for Cu-containing materials (7). Bismuth oxidation states were always less than those required to balance the effects of the Li substitution, and suggested a significant oxygen deficiency in all samples, $BaBi_{1-x}Li_xO_{3-y}$: $x = 0.05$, $y = 0.04$ ($Bi^{4.07+}$); $x = 0.10$, $y = 0.10$ ($Bi^{4.11+}$); $x = 0.15$, $y = 0.16$ ($Bi^{4.16+}$); $x = 0.20$, $y = 0.20$ ($Bi^{4.25}$); $x = 0.25$, $y = 0.25$ ($Bi^{4.33+}$). No significant differences were observed between samples heated in air and in oxygen. Alternating current susceptibility measurements revealed no detectable Meissner effect down to 4 K in any sample.

Structural Investigations

The variation of the unit cell dimension with x for $Ba(Bi_{1-x}Li_x)O_{3-y}$ samples is shown in Fig. 1. The gradual contraction resulting from Li substitution can be correlated with ionic radii effects. If we regard $BaBiO_3$ as $Ba_2Bi^{3+}Bi^{5+}O_6$, the substitution can be regarded as the partial replacement of Bi^{3+} (ionic radius 1.03 Å) with Li^+ and Bi^{5+} (both ionic radii 0.76 Å), with the creation of oxygen vacancies.

Weak superstructure peaks, which were observed in some samples of composition $Ba(Bi_{0.75}Li_{0.25})O_3$, were surprisingly found to be incompatible with the body-centered cubic superstructure reported for $Ba(Sb_{0.75}Li_{0.25})O_3$ (6). The additional peaks were always weak but varied in intensity from sample to sample, and were frequently unobservable. Various synthetic parameters, temperature (up to 800°C,

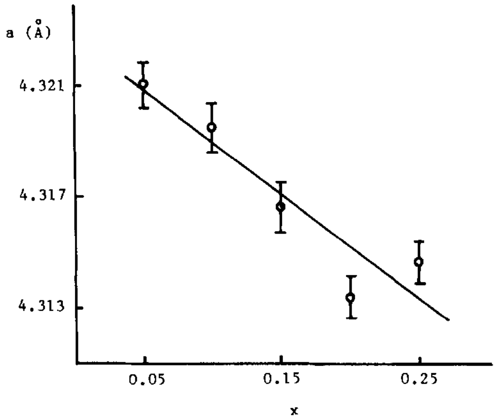

FIG. 1. The variation of perovskite unit cell length, a, for $Ba(Bi_{1-x}Li_x)O_{2.75}$; error bars represent one standard deviation.

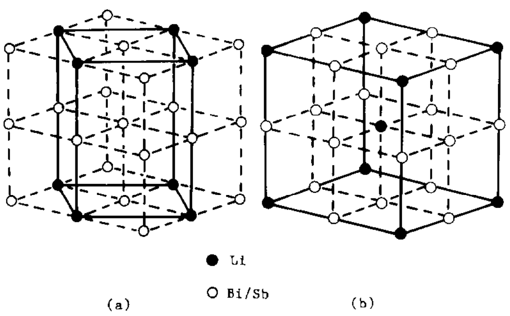

FIG. 2. The proposed structure for $Ba(Bi_{0.75}Li_{0.25})O_{2.75}$ (a), compared with that of $Ba(Sb_{0.75}Li_{0.25})O_3$ (b). Only Bi/Sb and Li cations are shown, which are at the corners of perovskite subcells.

when problems with melting were encountered), atmosphere (air, oxygen, and evacuated, sealed quartz tubes), and cool rate, were therefore examined in order to optimize the ordering conditions, but no procedure was found which consistently gave highly ordered products. The sample with the most pronounced superstructure peaks was chosen for further detailed structural investigation.

All peaks in the diffraction pattern could be indexed on a tetragonal cell with $a = \sqrt{a}_{\mathrm{c}}$, $c = 2a_{\mathrm{c}}$, where a_{c} is the simple perovskite subcell edge length. The implied Bi and Li order is compatible with space group *P4/mmm* and is compared with that for $Ba(Sb_{0.75}Li_{0.25})O_3$ in Fig. 2. Integrated intensities and positions were measured for X-ray diffraction peaks with $2\theta < 70°$, and structural parameters were refined using a least-squares program (*8*); cell dimensions were determined separately from the peak positions. Due to the small number and weak intensities of the superstructure reflections, the refinement was restricted to six parameters (five atomic parameters and a scale factor) by introducing a number of constraints. Due to the low Li and O scattering factors, Li atoms were excluded from the refinement, and O atom order could not be investigated. O atoms were confined to idealized perovskite positions with occupation numbers in accordance with the chemical analysis. In addition, a single isotropic thermal parameter was assigned to all atoms of a given type. The refinement confirmed the structure shown in Fig. 2a, but implied partial occupancy of the Li site, (0, 0, 0), by Bi; this was interpreted as partial disorder involving the Bi and Li cations. In the final structural model used, the Li atoms removed from the origin were assumed to be randomly distributed on the other three octahedral positions. The observed and calculated X-ray diffraction data are shown in Table I, and the resultant refined atomic parameters are in Table II.

The X-ray profile of the proposed ordered structure was simulated by computer (*9*) in order to examine the calculated intensities of superstructure reflections which were not observed, and therefore not included in the refinement. No significant discrepancies between observed and calculated data were observed for these very weak peaks, and good agreement existed between the observed and calculated complete profiles.

Discussion of Structure

The Ba and O temperature factors appear unrealistically high, but are considered to be consistent with the nature of the structure and the constraints applied during the refinement. Ordering of the Li and Bi cations in the octahedral interstices results in a displacement of the Ba atom along ⟨001⟩ away from the ideal perovskite subcell position at (0.5, 0.0, 0.25). However, since such ordering is clearly incomplete, the refined z parameter (0.229) represents an average position, and this would be reflected in a high amplitude of thermal vibration. A similar effect would result from ignoring the possibility of oxygen atom ordering and constraining the O atoms to their ideal sub-

TABLE I

X-RAY DIFFRACTION DATA FOR $Ba(Bi_{0.75}Li_{0.25})O_{2.75}$

$h\ k\ l$	d_{calc} (Å)	d_{obs} (Å)	I_{calc}	I_{obs}	σI_{obs}
0 1 0	6.101	6.103	2.8	3.0	1.0
0 1 1	4.981	4.985	3.5	2.5	1.0
0 0 2 1 1 0	4.314	4.313	3.0	4.4[a]	1.0
1 1 1	3.859	3.865	4.4	3.5	1.0
0 1 2	3.522	3.521	1.5	1.6	0.5
0 2 0 1 1 2	3.051	3.049	102.0	100.0[a]	5.0
0 0 3 0 2 1	—	—	1.6	1.6	0.5
2 1 0	—	—	0.8	1.2	1.0
0 1 3 1 2 1	—	—	2.1	2.0	1.0
0 2 2	—	—	0.1	1.0	1.0
1 1 3	—	—	0.1	0.1	0.1
1 2 2	—	—	1.0	2.0	1.0
2 2 0 0 0 4	2.157	2.156	23.2	25.0[a]	2.0
0 2 3 2 2 1	—	—	2.0	2.5	1.0
0 1 4 0 3 0	—	—	0.5	0.6	0.5
1 2 3 0 3 1	—	—	1.0	1.3	1.0
1 1 4 2 2 2 3 1 0	1.930	1.930	3.7	4.6[a]	1.1
1 3 1	—	—	1.1	1.3	1.0
0 3 2	—	—	0.3	0.3	0.2
0 2 4 1 3 2	1.761	1.761	35.2	36.3[a]	3.0
0 0 5 2 2 3	—	—	1.0	1.3	1.0
1 2 4 3 2 0	—	—	0.6	1.3	1.0
0 1 5 0 3 3 2 3 1	—	—	0.7	1.0	0.4
1 1 5 1 3 3	—	—	1.2	1.0	0.4
2 3 2	—	—	0.3	0.7	0.5
2 2 4 0 4 0	1.525	1.525	11.8	10.2[a]	1.4
0 2 5 0 4 1	—	—	0.1	0.3	0.2
0 3 4 4 1 0	—	—	0.3	0.4	0.2
1 2 5 2 3 3 1 4 1	—	—	0.7	1.2	0.5
0 0 6 1 3 4 0 4 2 3 3 0	—	—	3.0	2.7[a]	0.5
3 3 1	—	—	0.2	0.2	0.2
0 1 6 1 4 2	—	—	0.3	0.3	0.2
1 1 6 3 3 2 4 2 0	1.364	1.364	13.1	13.8[a]	2.0

Note. $a = 6.101(1)$ Å, $c = 8.628(2)$ Å. $R_I = 7.8\%$.

[a] Intensities corresponding to the perovskite subcell reflections.

cell positions, which are probably inappropriate for links between Li and Bi. It is relevant to note that the latter parameters are, of course, of limited reliability in such an X-ray diffraction study involving the heavy Ba and Bi atoms, and therefore have very high standard deviations.

The difference between the structural chemistry of the ordered phases $Ba(Sb_{0.75}Li_{0.25})O_3$ (cubic) and $Ba(Nb_{0.75}Li_{0.25})O_3$ and $Ba(Ta_{0.75}Li_{0.25})O_3$ (hexagonal) has been attributed to the noble gas electron configurations of Nb^{5+} and Ta^{5+} (*10*). However, the present study has clearly shown that the preferred cation order in $Ba(Bi_{0.75}Li_{0.25})O_{3-y}$ is different from $Ba(Sb_{0.75}Li_{0.25})O_3$, although both are based on cubic packing. The presence of oxygen vacancies in the bismuth compound could clearly be an important factor in this respect, and to gain

TABLE II

REFINED ATOMIC PARAMETERS FOR $Ba(Bi_{0.75}Li_{0.25})O_{2.75}$

	x/a	y/b	z/c	$B(\text{Å}^2)$	Cell occupancy
Bi(1)	0.0	0.0	0.0	0.1(3)	0.27(2)[a]
Bi(2)	0.5	0.5	0.0	0.1(3)	0.91(1)[a]
Bi(3)	0.0	0.0	0.5	0.1(3)	0.91(1)[a]
Bi(4)	0.5	0.5	0.5	0.1(3)	0.91(1)[a]
Ba	0.5	0.0	0.229(2)	4.1(5)	4.0
O(1)	0.0	0.0	0.25	9.3(4.3)	1.83
O(2)	0.25	0.25	0.0	9.3(4.3)	3.67
O(3)	0.25	0.25	0.5	9.3(4.3)	3.67
O(4)	0.5	0.5	0.25	9.3(4.3)	1.83

[a] Occupancy of all Bi sites is completed by Li.

insight into this possibility, the thermodynamics of the two latter ordering schemes for complete anion sublattices (assuming complete oxidation to Bi^{5+}) was investigated using lattice energy considerations. Simple Madelung energy calculations were therefore performed using a computer program which also allows estimates of polarization energies *(11)*.

For ions constrained to the idealized perovskite-related positions, the body-centered cubic structure, Fig. 2b, was found to be electrostatically more stable than the tetragonal order determined in this study, Fig. 2a, by about 45 kJ $mole^{-1}$. However, for the cubic order, any given perovskite subcell can be seen to have two Li^+ ions at the extremities of a body diagonal, whereas the tetragonal superstructure results in Li^+ ions on opposite corners of one of its faces. Relaxation of Ba^{2+} ions toward these faces should consequently be anticipated for the tetragonal order, as was indeed found in the refinement, Table II, and this should increase the stability of the structure. In the $Ba(Sb_{0.75}Li_{0.25})O_3$ structure, on the other hand, the Ba ions retain their central location. Oxygen ion displacements from their ideal location midway along perovskite edges might also occur, but such shifts would be expected to provide comparable stabilization for both structural arrangements. The Madelung energy and polarization energy (resulting from O^{2-} polarization only; O^{2-} polarizability 2.4 Å^3) were therefore calculated for the tetragonal order as a function of the parameter z_{Ba} and compared with values for the cubic order. Although the repulsive energies in $Ba(Bi_{0.75}Li_{0.25})O_3$ will be somewhat different from those in $Ba(Sb_{0.75}Li_{0.25})O_3$ due to ionic radii considerations, it is not possible to account for such effects directly. The influence of ionic radii on unit cell size was, however, included, and for both ordering schemes calculations were performed using cell parameters appropriate to $Ba(Bi_{0.75}Li_{0.25})O_3$ and $Ba(Sb_{0.75}Li_{0.25})O_3$. The results of these calculations are shown in Fig. 3, where it is seen that the larger ionic radius of Bi^{5+} results in a pronounced difference in the

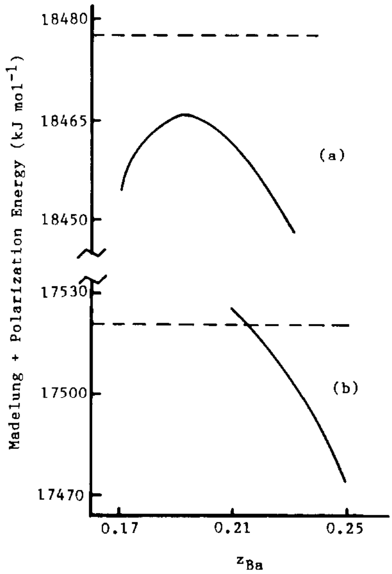

FIG. 3. Comparison of the total attractive (Madelung plus polarization) energies of the body-centered cubic structure (Fig. 2b, broken lines) and tetragonal structure (Fig. 2a, continuous lines) for perovskite subcell sizes appropriate to (a) $Ba(Sb_{0.75}Li_{0.25})O_3$ and (b) $Ba(Bi_{0.75}Li_{0.25})O_3$.

relative stabilities of the two structures under consideration. Whereas for the Bi-containing system the tetragonal superstructure appears more stable for $z_{Ba} < 0.215$, the cubic arrangement is of lower energy for the Sb phase for all realistic values of z_{Ba}. The refined value of this parameter for $Ba(Bi_{0.75}Li_{0.25})O_3$, 0.229, is in reasonable agreement with the energy predictions of Fig. 3, particularly when it is recalled that the unit cell origin, the Li site, is partially occupied by Bi ions. This would result in a higher z_{Ba} parameter than would be applicable for the ideal structure with no such disorder.

The energy calculations account for the different cation ordering patterns without consideration of the added influence of anion vacancies in $Ba(Bi_{0.75}Li_{0.25})O_{3-y}$, although vacancy ordering could obviously play an additional significant role. The calculations may also provide a plausible explanation for the problems encountered in obtaining ordered samples of $Ba(Bi_{0.75}Li_{0.25})O_{3-y}$. There appears to be only a small energy difference between the two possible ordering schemes, and some samples might contain short-range order only, or possibly small domains of both structure types. An alternative possibility is that small domains of only the tetragonal structure exist, but the domain size is small and twinning results in a random distribution of the unique tetragonal c-axis along all equivalent cubic subcell axes. Microstructure of these types would produce X-ray diffraction patterns compatible with an average unit cell containing a random cation distribution.

Acknowledgments

We thank the Science and Engineering Research Council for financial support, and Um-AlQura University, Saudi Arabia, for the provision of a scholarship to S.M.A.K.

References

1. R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp, Jr., A. E. White, K. Short, W. F. Peck, and T. Kometani, *Nature (London)* **332,** 814 (1988).
2. D. G. Binks, B. Dabrowski, J. D. Jorgensen, A. W. Mitchell, D. R. Richards, Shiyou Pei, and Donglu Shi, *Nature (London)* **333,** 836 (1988).
3. A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, *Solid State Commun.* **17,** 27 (1975).
4. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
5. B. M. Collins, A. J. Jacobson, and B. E. F. Fender, *J. Solid State Chem.* **10,** 29 (1974).
6. J. A. Alonso, E. Mzayek, and I. Rasines, *Mater. Res. Bull.* **22,** 69 (1987).
7. A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura, and J. B. Torrance, *Physica C* **153–155,** 1367 (1988).
8. P. J. Wiseman, D. Phil. thesis, Oxford University (1974).
9. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).
10. G. Blasse, *J. Inorg. Nucl. Chem.* **27,** 993 (1965).
11. J. W. Weenk and H. A. Harwig, *J. Phys. Chem. Solids* **38,** 1047 (1977).