JOURNAL OF SOLID STATE CHEMISTRY 106, 511–513 (1993)

BRIEF COMMUNICATIONS

Synthesis and Characterization of a New Bi(V) Containing Perovskite $BaBi_{2/3}Zn_{1/3}O_3$

M. A. SUBRAMANIAN

Central Research and Development Department, E.I. du Pont de Nemours and Company, P.O. Box 80328, Experimental Station, Wilmington, Delaware 19880-0328

Received May 14, 1993; accepted May 24, 1993

A new Bi(V) containing cubic perovskite, $BaBi_{2/3}Zn_{1/3}O_3$ has been prepared under high oxygen pressure in a tetrahedral anvil press. The lattice parameter calculated from powder X-ray diffraction data is $a = 4.208 \pm 0.001$ Å (space group, $Pm3m$), implying a disorder of Bi and Zn atoms at the B-site of the ABO_3 perovskite structure. The compound is an insulator and has a relatively high dielectric constant. No dielectric anomaly is observed between liquid nitrogen and room temperature.

Introduction

The perovskite structure, having the general composition ABO_3, where A is a twelvefold coordinated cation, and B is an octahedral ion, is adopted by a large group of oxides (*1*). To date, no simple oxide of the type $ABi^{V}O_3$ (A, monovalent cation) with perovskite structure is known. The compound $KBi^{V}O_3$ is well established, but adopts the cubic $KSbO_3$ structure which involves an edge-shared octahedral network (*2*). However, the perovskite structure exists for compositions such as Ba(Bi, Pb)O_3 (*3*) and (Ba, K)BiO_3 (*4*), with Bi in mixed valent state (III and V) and is known to exhibit superconducting properties. The compound $BaBi^{V}_{1/2}Bi^{III}_{1/2}O_3$ has been described as monoclinic and an electrical insulator. The insulating behavior of $BaBiO_3$ might be considered surprising because the presence of Bi^{IV} would involve a half-filled 6s band which should give rise to metallic properties. Neutron diffraction studies showed, however, an ordering of Bi^{III} and Bi^{V} in the B-site of the perovskite structure; disproportionation of Bi^{IV} ($6s^1$) into Bi^{III} ($6s^0$) and Bi^{V} ($6s^2$) makes this compound an insulator (*5*). Similarly, ordered perovskite-type oxides containing Bi(V), $BaBi_{1/2}M_{1/2}O_3$ (M, lanthinide, Y) with cubic symmetry have been reported (*1*, *6*, *7*). Recently, Demazeau and co-workers have synthesized the cubic perovskite $Ba(Bi_{1/2}Fe_{1/2})O_3$ and shown it to contain an ordered Bi^{V} and Fe^{III} arrangement (*8*). In this paper, we report on the synthesis and characterization of $Ba(Bi^{V}_{2/3}Zn^{II}_{1/3})O_3$ with a perovskite-related structure.

Experimental

$Ba(Bi^{V}_{2/3}Zn_{1/3})O_3$ was synthesized by heating an intimate mixture of stoichiometric quantities of BaO_2 (>99% pure), Bi_2O_3 (99.9%), and ZnO (electronics grade) in a platinum capsule at 800°C under 58 kbar, using an tetrahedral anvil apparatus. The BaO_2 also served as a source for excess oxygen required during the synthesis. X-ray diffraction data were recorded on a SCINTAG diffractometer with Cu$K\alpha$ radiation, using Si as an internal standard. Unit cell parameters were refined by a least squares method.

0022-4596/93 $5.00

TABLE I

POWDER X-RAY DATA FOR $Ba(Bi_{2/3}Zn_{1/3})O_3$

h k l	d_{obs} (Å)	d_{cal} (Å)	I/I_0
1 0 0	4.195	4.209	1
1 1 0	2.971	2.976	100
1 1 1	2.430	2.430	2
2 0 0	2.1041	2.1045	30
2 1 0	1.8823	1.8821	<1
2 1 1	1.7184	1.7183	41
2 2 0	1.4880	1.4881	18
3 0 0	1.4034	1.4030	5
3 1 0	1.3310	1.3312	9
3 1 1	1.2692	1.2691	10
2 2 2	1.2154	1.2150	14

TABLE II

LATTICE PARAMETER AND CALCULATED TOLERANCE FACTOR FOR VARIOUS Ba[Bi(V), M]O_3 PEROVSKITES

Compound	a (Å)	Δr^a (Å) $(r_{Bi(V)} - r_M)$	t	Ref.
$BaBi_{1/2}La_{1/2}O_3$	8.759	−0.27	0.93	(6)
$BaBi_{1/2}Dy_{1/2}O_3$	8.5831	−0.15	0.95	(7)
$BaBi_{1/2}Y_{1/2}O_3$	8.5681	−0.14	0.96	(7)
$BaBi_{1/2}In_{1/2}O_3$	4.248	−0.04	0.98	(1)
$BaBi_{2/3}Zn_{1/3}O_3$	4.208	+0.02	0.99	This work
$BaBi_{1/2}Fe_{1/2}O_3$	8.279	+0.11	1.01	(8)

[a] Octahedral coordination. Ionic radius values are taken from Ref. (9).

The dielectric constant and loss factors were measured on a dense sintered sample at frequencies ranging from 10^3 to 10^6 Hz, using a Hewlett Packard (4284A) automating LCR bridge.

Results and Discussion

The powder X-ray diffraction of $Ba(Bi^V_{2/3}Zn_{1/3})O_3$ has been indexed on the basis of a cubic unit cell. No superstructure reflections were observed in X-ray diffraction patterns, indicating a disordering of Bi and Zn cations in the B-site of the perovskite structure. The disordering is due to the fact that Zn(II) and Bi(V) are nearly identical in size ($r_{Bi(V)} = 0.76$ Å, $r_{Zn(II)} = 0.74$ Å) (9). The observed and calculated powder pattern for $Ba(Bi^V_{2/3}Zn_{1/3})O_3$ is given in Table I. The pattern is indexed on the basis of a primitive cubic unit cell (space group, $Pm3m$) with $a = 4.208 \pm 0.002$ Å.

Goldschmidt tolerance factors (10), defined as $t = (r_A + r_O)/[\sqrt{2}(r_{B(ave)} + r_O)]$, where r represent the respective ionic radii (9) in $A(BB')O_3$, have been calculated for several Ba[Bi(V), M]O_3 oxides and are given in Table II. The t value for $Ba(Bi^V_{2/3}Zn_{1/3})O_3$ is 0.99, which is very close to the ideal value ($t = 1$) for the stabilization of simple cubic perovskite structure.

A plot of the pseudocubic unit-cell parameter a_c defined as the cube root of the volume of the perovskite unit cell ($a_c = \sqrt[3]{Vp/Z}$, where Vp is the volume of the perovskite cell and Z is number of molecules per unit cell) versus mean ionic radius r_{ave} [$(r_{Bi(V)} + r_{M(III)})/2$ or $(2/3r_{Bi(V)} + 1/3r_{Zn(II)})/2$] is shown in Fig. 1. The a_c value versus r_{ave} follows a linear relationship and in the case of $Ba(Bi_{2/3}Zn_{1/3})O_3$ the average ionic radius corresponding to 2/3Bi(V) and 1/3Zn(II) fits very well with the observed unit cell parameter.

$Ba(Bi_{2/3}Zn_{1/3})O_3$ is a dark brown solid. DC electrical resistivity measurements showed no appreciable electronic conductivity at room temperature. The insulating behavior is easily explained on the basis of the elec-

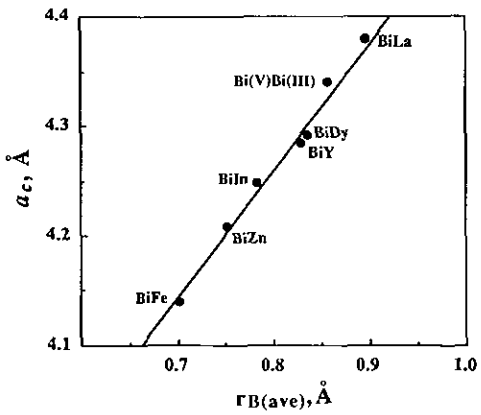

FIG. 1. The linear relationship between cube root of cell volume and average ionic radius of [Bi(V), M] for Ba(Bi, M)O_3.

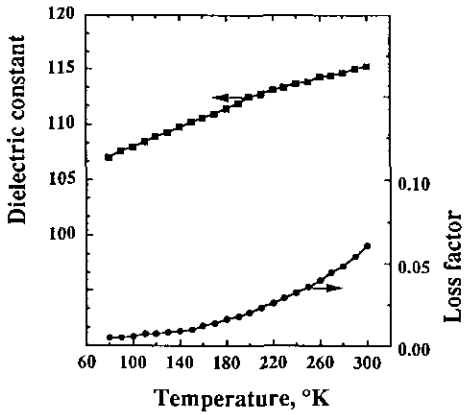

FIG. 2. Temperature dependence of dielectric constant (ε) and loss factor ($\tan\delta$) for $Ba(Bi_{2/3}Zn_{1/3})O_3$.

tronic configuration of Bi^V (empty, $6s^0$) and Zn^{II} (filled, $3d^{10}$). The compound had a dielectric constant (ε) of 115 at room temperature when measured at 1 kHz. This value is relatively high in general, which renders it worth examining further. Since $Ba(Bi_{2/3}Zn_{1/3})O_3$ is cubic and has a centric space group, the dielectric constant measurements were carried out in the temperature range 80 to 300 K. Figure 2 shows the temperature dependence of ε and $\tan\delta$ (loss factor) for $Ba(Bi_{2/3}Zn_{1/3})O_3$. No dielectric anomaly was observed: both ε and $\tan\delta$ increased monotonically with temperature; the compound is considered paraelectric in this temperature range. The increase in dielectric constant and dielectric loss are probably associated with the mobility of defects (such as oxygen vacancies), which increases with rising temperature.

In summary, we can state that the new compound, $Ba(Bi_{2/3}Zn_{1/3})O_3$ is another addition to the ever expanding list of simple cubic perovskite compounds.

References

1. S. NOMURA, "Landolt-Börnstein," Group III, Vol. 12a, Springer-Verlag, New York/Berlin (1978).
2. S. KODIALAM, V. C. KORTHIU, R.-D. HOFFMANN, AND A. W. SLEIGHT, *Mater. Res. Bull.* **27,** 1379 (1992).
3. A. W. SLEIGHT, J. L. GILSON, AND P. E. BIERSTEDT, *Solid State Commun.* **17,** 27 (1975).
4. L. F. MATTHEISS, E. M. GYORGY, AND D. W. JOHNSON, JR., *Phys. Rev. B* **37,** 3745 (1988); R. J. CAVA *et al.*, *Nature* **332,** 814 (1988).
5. D. E. COX AND A. W. SLEIGHT, *Acta Crystallogr. Sect. B* **35,** 1 (1979).
6. R. SCHOLDER, K. W. GANTER, H. GLASER, AND G. MERZER, *Z. Anorg. Allg. Chem.* **319,** 375 (1963).
7. A. LENZ AND H. MÜLLER-BUSCHBAUM, *J. Less-Common Met.* **161,** L15 (1990).
8. S. BYEON, G. DEMAZEAU, J. CHOY, AND L. FOURNES, *Mater. Lett.* **12,** 163 (1991).
9. R. D. SHANNON, *Acta Crystallogr Sect. A* **32,** 751 (1976).
10. V. M. GOLDSCHMIDT, "Geochemische Verteilungsgesetze der Elemente," VII, VIII (1927/1928).