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Ordered Perovskites Containing Pentavalent Bismuth: $Ba(Bi_{0.75}M_{0.25})O_3$ and $Ba(Bi_{0.67}M_{0.33})O_3$

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

New Bi^{5+}-containing perovskites of the types $Ba(Bi^{5+}_{0.75}M^{1+}_{0.25})O_3$ (M = Li or Na) and $Ba(Bi^{5+}_{0.67}M^{2+}_{0.33})O_3$ (M = Mg, Ca, Sr, Ba, Cd, or Cu) have been synthesized under high oxygen pressure by using thermal decomposition of peroxides of Ba, Li, Na, or Sr in sealed platinum capsules. The compounds have been characterized by X-ray diffraction, chemical analysis, and infrared spectroscopy. X-ray diffraction studies showed that all the compounds have cubic perovskite-related structures. Superlattice reflections due to the ordering of Bi^{5+} and M cations can be seen for all the compounds, except for $BaBi_{0.66}Cu_{0.33}O_3$. The powder X-ray diffraction patterns of $Ba(Bi_{0.67}M_{0.33})O_3$ phases were indexed in the space group *Fm3m* [$(NH4)_3FeF_6$ type], indicating a 1:1 ordering between $\frac{1}{2}Bi^{5+}$ and $(\frac{1}{3}M + \frac{1}{6}Bi^{5+})$, while the superlattice reflections seen in the X-ray data for $Ba(Bi_{0.75}Na_{0.25})O_3$ and $Ba(Bi_{0.75}Li_{0.25})O_3$ were indexed in the space group *Im3m*, indicating a 1:3 long-range order of M^{1+} and Bi^{5+} ions at the B site of the ABO_3 perovskite structure. Such an ordering requires the structure to contain linear 180° Bi–O–Bi bonds along the a, b, and c axes, which is not a common feature among the perovskite family of compounds. All the compounds, except $Ba(Bi_{0.67}Cu_{0.33})O_3$, are electrical insulators with relatively high dielectric constants. The high electrical conductivity in the copper compound has been attributed to the presence of Bi in mixed valence states. © 1994 Academic Press, Inc.

INTRODUCTION

The perovskite structure, having the general composition ABO_3, where A is a 12-fold coordinated cation, and B is an octahedral ion, is known for a large group of oxides (1). If the criteria of electrical charge neutrality and ionic tolerance factor are satisfied, complex oxides of the general formula $A(B_xB'y)O_3$ with perovskite-related structure can occur, and in fact, many compounds with (x, y) = (0.5 0.5), (0.67, 0.33), and (0.75, 0.25) have been synthesized and reported in the literature (2). It is now well known that if more than one cation is present in the B position it is most probable that these B ions are ordered when a large difference exists in the size or charge of the ions. Many compounds with 1 : 1 ordering of B site cations have been reported for $A(B_{0.5}B'_{0.5})O_3$. For perovskites of the general formula $A(B_{0.67}B'_{0.33})O_3$, two types of ordering are well known. Some compounds adopt a 1 : 1 ordered structure where $\frac{1}{4}$ of the B ions are randomly arranged with B' ions in one position which is ordered with reference to the position occupied by the remaining B ions. While this arrangement allows partial ordering, complete ordering of B and B' (1 : 2) has been observed for few compounds which results in a hexagonal unit cell containing three close-packed BaO_3 layers with B and B' ions in an ordered arrangement in the octahedral sites (3). In the case of $A(B_{0.75}B'_{0.25})O_3$ perovskites, the most common arrangement is either a completely disordered structure (*Pm3m*) or a 1 : 1 ordered structure (*Fm3m*) (4). A 1 : 3 ordered structure is very rare among $A(B_{0.75}B'_{0.25})O_3$ perovskites and has been reported only in the case where B = Li or Na and B' = Sb^{5+} (5). Such an ordering results in a body-centered cubic unit cell (*Im3m*) with octahedra of alkali ion occupying the center and the vertices of the unit cell and SbO_6 octahedra located at the center of the faces and edges.

Ordered perovskite-type oxides containing Bi^{5+}, $BaBi_{0.5}M_{0.5}O_3$ (M = rare earth, Y, Fe) with cubic symmetry have been reported (1, 6–8). In all of the above compounds, each oxygen has only one Bi^{5+} near neighbor and hence they contain no 180° Bi–O–Bi continuous bonds. In this paper we report on the high-pressure stabilization of new Bi^{5+}-containing oxides of the type $Ba(Bi^{5+}_{0.75}M^{1+}_{0.25})O_3$ (M = Li or Na) and $Ba(Bi^{5+}_{0.67}M^{2+}_{0.33})O_3$ (M = Ba, Sr, Ca, Mg, Cd, or Cu) with 1 : 3 and 1 : 1 ordering of the B-site cations, respectively. A 1 : 3 ordered structure of $Ba(Bi_{0.75}M_{0.25})O_3$ should contain BiO_6 octahedra connected in linear chains along the a, b, and c axes with continuous 180° Bi–O–Bi bonds. Use of the formal-valence nomenclature such as Bi^{5+} merely indicates that the oxygen $2p$ are completely filled.

EXPERIMENTAL PROCEDURE

High-Pressure Synthesis

$Ba(Bi_{0.75}M_{0.25})O_3$ (M = Li or Na) compounds were synthesized by heating an intimate mixture of stoichiometric

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quantities of BaO_2 (>99%), Bi_2O_3 (99.9%), along with peroxides or simple oxides of M metal. The peroxides used were Na_2O_2 99%), Li_2O_2 (>95% pure), BaO_2 (99%), SrO_2, or CaO_2 (Technical Grade). The other oxides used were high-purity CuO, CdO, and MgO. The starting mixture in the form of pellets was sealed in platinum tubes (3/8 in. diameter and 3 in. length). All the weighting mixing, and loading of the platinum tubes were done in a dry box. The tubes were heated in an autoclave at 700 to 800°C for 6 hr under an external pressure of 3 kbar. In some cases the starting mixtures were subjected to 58 kbar pressure in platinum capsules in a tetrahedral anvil press. The oxidation of Bi(III) to Bi(V) was accomplished by the use of peroxides and the reaction schemes can be represented as

$$BaO_2 + \tfrac{3}{8}\,Bi_2O_3 + \tfrac{1}{8}\,M_2O_2 \rightarrow Ba(Bi_{3/4}M_{1/4})O_3 + \tfrac{3}{8}\,O \quad (M = \text{Li or Na})$$

$$BaO_2 + \tfrac{1}{3}\,Bi_2O_3 + \tfrac{2}{3}\,MO_2 \rightarrow Ba(Bi_{2/3}M_{1/3})O_3 + \tfrac{4}{3}\,O \quad (M = \text{Ba, Sr, or Ca})$$

$$BaO_2 + \tfrac{1}{3}\,Bi_2O_3 + \tfrac{2}{3}\,MO \rightarrow Ba(Bi_{2/3}M_{1/3})O_3 + \tfrac{2}{3}\,O \quad (M = \text{Mg, Cd, or Cu}).$$

Characterization of Samples

X-ray diffraction data were recorded on a SCINTAG (Pad IV) diffractometer with CuK_α radiation. Unit cell parameters were refined by least squares using Si as internal standard. Density measurements were performed on powders using 1330 Micrometritics helium pycnometer. The infrared spectra were recorded at room temperature on a Nicolet 60 SX FTIR spectrometer (down to 400 cm^{-1}, KBr pellets; down to 200 cm^{-1}, CsCl pellets).

The formal valence state of bismuth was determined by volumetric titrations based on the bismuthate method used in the determination of Mn^{2+} (9). For this purpose, a weighed specimen was added to a solution containing 25% nitric acid and a known excess of manganese(II) salt. The Mn(II) should reduce Bi^{5+} to Bi^{3+} according to the equation

$$2Mn^{2+} + 5\,BiO_{3^-} + 14\,H^+ \rightarrow 5Bi^{3+} + 2MnO_{4^-} + 7H_2O.$$

The mixture was stirred vigorously under nitrogen atmosphere until the solid was completely dissolved. A crimson color solution was obtained. To determine the quantity of permanganic acid formed, and hence the equivalent quantity of bismuth(V), a known excess of 0.01 N ferrous sulfate solution was added to reduce the permanganic acid. The excess of ferrous sulfate solution was back-tritrated with 0.01 N $KMnO_4$ solution. A blank experiment was carried out simultaneously. The compounds containing Li and Na were washed with deionized water and the washings were analyzed for Li or Na by ICP. No detectable amounts of Li or Na were found in any of the filtrate. As all the preparations were performed in an enclosed system under high pressure and at relatively low temperatures, no elemental analysis were performed.

Electrical resistivity measurements were performed on high-density sintered pellets with gold sputtered electrodes by the standard two-probe method using a Keithly 617 electrometer or a Hewlett–Packard 4339A high-resistance meter. The dielectric constant and loss factors were measured on the same samples at frequencies ranging from 10^3 to 10^6 Hz using a Hewlett–Packard (4284A) LCR bridge.

RESULTS AND DISCUSSION

$Ba(Bi_{0.75}M_{0.25})O_3$ (M = Li or Na) Perovskites

Recently Alonso *et al.* (5) reported the formation of $Ba(Sb_{0.75}M_{0.25})O_3$ (M = Li or Na) with a 1:3 ordered cubic perovskite structure. Subsequently, Greaves and Katib (10) attempted the synthesis of isostructural $Ba(Bi_{0.75}Li_{0.25})O_3$ by reacting carbonates under atmospheric conditions and succeeded only in the formation of oxygen-defective perovskite of the type $Ba(Bi_{0.75}Li_{0.25})O_{2.75}$ with a tetragonal structure with a formal oxidation state of Bi close to +4.33. This is probably due to the difficulty in stabilizing the pentavalent Bi under normal synthetic conditions. The observed structural distortion was attributed to the presence of oxygen vacancies.

$Ba(Bi_{0.75}M_{0.25})O_3$ (M = Li or Na) phases obtained in this study, under high-oxygen-pressure conditions, were dark brown in color and their X-ray diffraction patterns were very sharp and characteristic of perovskites (Fig. 1). The diffraction pattern contained additional reflections to those of an ideal perovskite cell. These additional reflections could be satisfactorily accounted for by doubling the perovskite unit cell and indexing the entire powder X-ray diffraction pattern in the space group $Im3m$. The lattice parameters are listed in Table 1. Table 2 lists the observed and calculated powder diffraction pattern for $Ba(Bi_{0.75}Na_{0.25})O_3$. The calculated intensities listed in Table 2 are derived by assuming a 1:3 ordering of M and Bi cations at the B site of the perovskite as shown in Fig. 2a and are in good agreement with the observed intensities. In this structure, the alkali ions occupy the bodycenter and corners of the cubic unit cell, while those of Bi ions are located at the center of the faces and the middle point of the edges. The atomic coordinates used in the intensity calculation are similar to the one given for $Ba(Sb_{0.75}M_{0.25})O_3$ (5).

Although the ordering of Na^{1+} and Bi^{5+} at the B site of the perovskite structure is anticipated due to their large

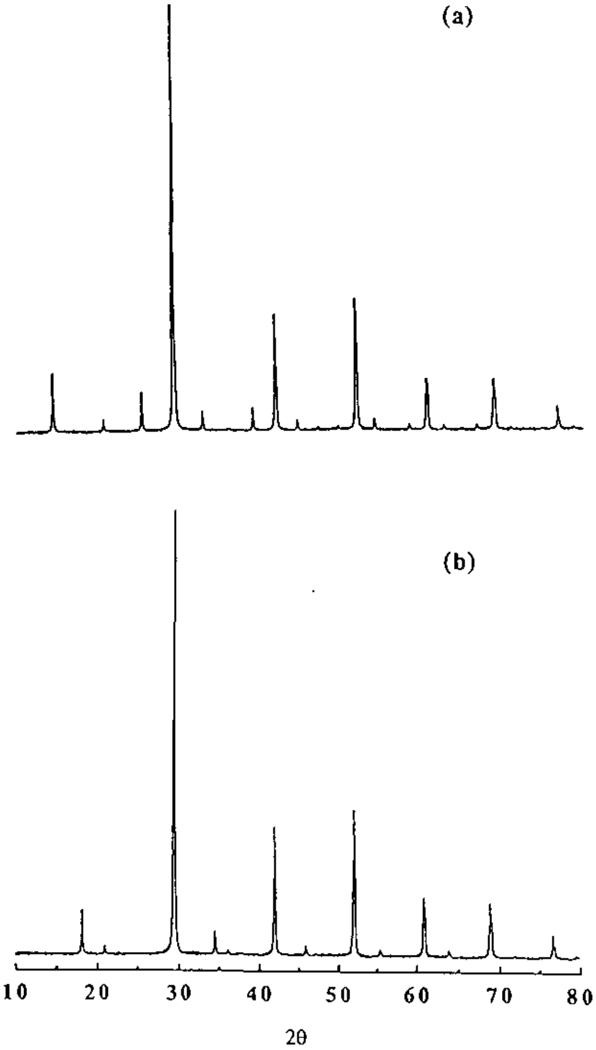
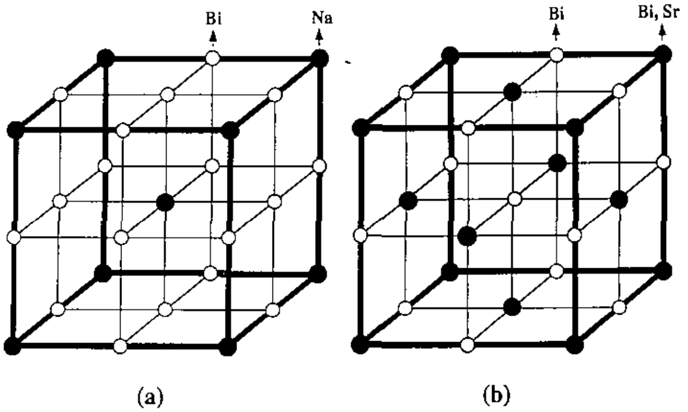


FIG. 1. X-ray diffraction patterns for (a) $Ba(Bi_{0.75}Na_{0.25})O_3$ and (b) Ba $(Bi_{0.67}Ca_{0.33})O_3$. The 2θ values are in degrees.

size and charge difference, the observed ordering of Li^{1+} and Bi^{5+}, where both cations are identical in size (0.76 Å, octahedral coordination), is somewhat surprising. The ordering is probably due to the large difference in the covalent character of Bi^{5+}–O and Li^{+}–O bonds.



(a) (b)

FIG. 2. Cation arrangement in perovskites: (a) 1:3 ordered Ba $(Bi_{0.75}M_{0.25})O_3$ (M = Li or Na) and (b) 1:1 ordered $Ba(Bi_{0.67}M_{0.33})O_3$ (M = Mg, Ca, Sr, Ba, or Cd). If we consider a small 1/8 cube, Ba ions are at the centers and O ions are at the edge centers.

Table 1 shows oxygen content derived from the estimation of Bi^{5+} from chemical analysis. The results indicate that both $Ba(Bi_{0.75}Na_{0.25})O_3$ and $Ba(Bi_{0.75}Li_{0.25})O_3$ contain almost all the bismuth in the 5+ oxidation state. We have recorded the infrared spectra of both the perovskite phases to provide further support for the presence of Bi in the pentavalent state in $Ba(Bi_{0.75}Na_{0.25})O_3$ and $Ba(Bi_{0.75}Li_{0.25})O_3$. It is known that the infrared spectra of ordered perovskites show two regions of strong absorption and these have been assigned to two IR active vibrational T_{1u} modes of the BO_6 octahedron, viz. $\nu 3$, the higher frequency stretching vibration, and $\nu 4$, the lower frequency bending vibration (11). Earlier studies of the infrared spectra of the perovskite $Ba_2Bi^{3+}Bi^{5+}O_6$ showed in addition to the low-frequency band ($\nu 4$) two other bands in the regions 540 and 440 cm^{-1} (Table 3) and were assigned to the stretching vibrations of Bi^{5+} and Bi^{3+} ions in oxygen octahedra, respectively (12, 13). Further, the IR spectra of the ordered perovskite $Ba_2La^{3+}Bi^{5+}O_6$

TABLE 1

Lattice Parameter and Oxygen Content for Various Ba(Bi, M)O_3 Perovskites

Compound	a (Å) (±0.002)	Space group	B-site ordering	Oxygen content	Color
$BaBi_{0.75}Li_{0.25}O_3$	8.461	$Im3m$	1:3	2.98	Dark brown
$BaBi_{0.75}Na_{0.25}O_3$	8.578	$Im3m$	1:3	3.00	Dark brown
$BaBi_{0.67}Cd_{0.33}O_3$	8.542	$Fm3m$	1:1	2.90	Black
$BaBi_{0.67}Mg_{0.33}O_3$	8.390	$Fm3m$	1:1	2.93	Black
$BaBi_{0.67}Ca_{0.33}O_3$	8.597	$Fm3m$	1:1	2.99	Dark brown
$BaBi_{0.67}Sr_{0.33}O_3$	8.699	$Fm3m$	1:1	3.02	Dark brown
$BaBi_{0.67}Ba_{0.33}O_3$	8.836	$Fm3m$	1:1	2.98	Dark brown
$BaBi_{0.67}Cu_{0.33}O_3$	4.267	$Pm3m$	Disordered	—	Black

TABLE 2
X-Ray Powder Diffraction Data for $Ba(Bi_{0.75}Na_{0.25})O_3$

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}[a]
1 1 0	6.0489	6.0656	11.5	13.1
2 0 0	4.2788	4.2890	2.0	2.3
2 1 1	3.5005	3.5020	6.1	7.2
2 2 0	3.0285	3.0328	100.0	100.0
3 1 0	2.7118	2.7126	3.0	3.7
2 2 2	2.4758	2.4763	<1.0	0.5
3 2 1	2.2930	2.2926	3.7	4.5
4 0 0	2.1448	2.1445	31.0	28.4
3 3 0	2.0231	2.0220	<1.0	0.8
4 1 1	2.0196	2.0220	1.0	1.5
4 2 0	1.9174	1.9181	<1.0	0.9
3 3 2	1.8291	1.8288	<1.0	1.1
4 2 2	1.7598	1.7600	36.5	39.1
4 3 1	1.6831	1.6823	2.0	1.7
5 2 1	1.5662	1.5661	1.0	1.3
4 4 0	1.5166	1.5164	19.8	17.0
5 3 2	1.3920	1.3915	<1.0	0.9
6 2 0	1.3558	1.3563	18.0	16.1
5 4 1	1.3226	1.3236	<1.0	0.7
6 3 1	1.2641	1.2648	<1.0	0.6
4 4 4	1.2382	1.2381	6.3	5.4

[a] Relative peak height intensities are calculated on the basis of an ideal 1:3 ordered perovskite cell with *Im*3*m* symmetry. Atomic positions used are Ba at 8(*c*), $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$; Bi at 6(*b*), 0 $\frac{1}{2}\ \frac{1}{2}$; Na at 2(*a*), 0 0 0; O1 and O2 atoms at 12(*d*), $\frac{1}{4}$ 0 $\frac{1}{2}$, and 12(*e*), $\frac{1}{4}$ 0 0, respectively.

showed a single $\nu 3$ stretching band with a maximum at around 550 cm^{-1} and no other band near 440 cm^{-1} (12). The fact that infrared spectra (Fig. 3 and Table 3) of both $Ba(Bi_{0.75}Na_{0.25})O_3$ and $Ba(Bi_{0.75}Li_{0.25})O_3$ showed only bands with maxima around 550 cm^{-1} and no bands near 440 cm^{-1} confirms the absence of Bi in the lower oxidation state in these materials.

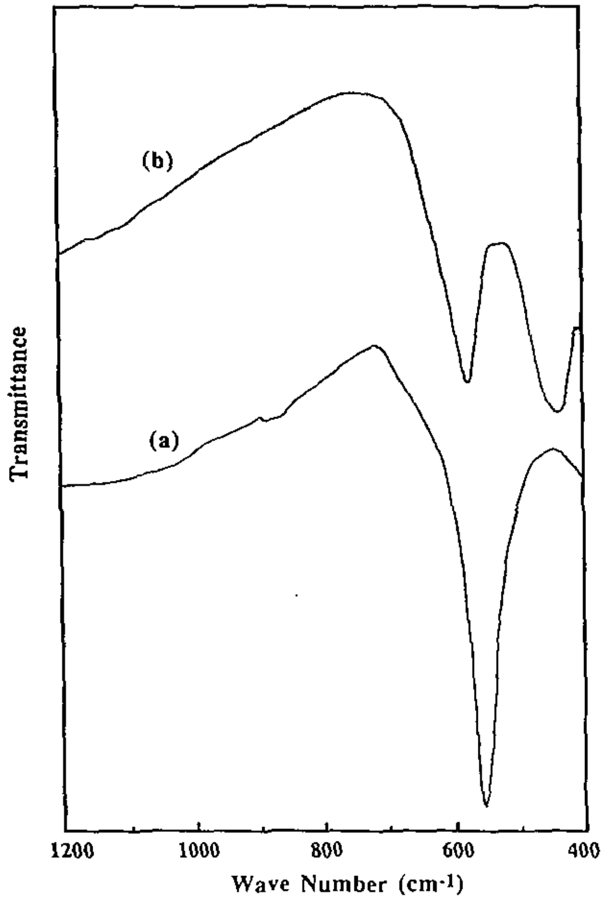


FIG. 3. Infrared spectra for (a) $Ba(Bi_{0.75}Na_{0.25})O_3$ and (b) $Ba\ Bi_{0.67}Cu_{0.33})O_3$.

Electrical measurements on highly dense pellets (>90% theoretical) showed that both compounds are insulators and have relatively high dielectric constants (ε) and low dielectric losses (tan δ) (Table 4). This is anticipated from the fact that both $Ba(Bi_{0.75}Na_{0.25})O_3$ and $Ba(Bi_{0.75}Li_{0.25})O_3$ synthesized here are stoichiometric phases with all the Bi in the pentavalent state with no detectable oxygen deficiency.

TABLE 3
Position of the Infrared Absorption Band Maxima for $Ba(Bi, M)O_3$ Perovskites

Compound	$\nu 3$ (cm^{-1})	$\nu 4$ (cm^{-1})	Ref.
$BaBiO_3$	440; 540	265	(13)
$BaBi_{0.5}La_{0.5}O_3$	540	300	(12)
$BaBi_{0.67}Pb_{0.33}O_3$	500 (v. b)	260	(12)
$BaBi_{0.75}Li_{0.25}O_3$	550	300	This work
$BaBi_{0.75}Na_{0.25}O_3$	555	290	This work
$BaBi_{0.67}Ca_{0.33}O_3$	545	275	This work
$BaBi_{0.67}Sr0.33O_3$	550	280	This work
$BaBi_{0.67}Ba_{0.33}O_3$	560	285	This work
$BaBi_{0.67}Cu_{0.33}O_3$	445; 565	260	This work

TABLE 4
Electrical Data for $Ba(Bi, M)O_3$ Perovskites

Compound	$\rho_{300\,K}$ (Ω cm)	E_a (eV)[a]	$\varepsilon_{300\,K}$	Tan δ
$BaBi_{0.75}Li_{0.25}O_3$	1×10^9	0.90	85	0.0010
$BaBi_{0.75}Na_{0.25}O_3$	$>10^{10}$	0.96	95	0.0005
$BaBi_{0.67}Mg_{0.33}O_3$	1×10^7	0.74	67	0.0150
$BaBi_{0.67}Ca_{0.33}O_3$	5×10^7	0.76	81	0.0050
$BaBi_{0.67}Sr_{0.33}O_3$	4×10^8	0.85	76	0.0050
$BaBi_{0.67}Ba_{0.33}O_3$	6×10^9	0.91	105	0.0025
$BaBi_{0.67}Cd_{0.33}O_3$	8×10^6	0.67	93	0.0560
$BaBi_{0.67}Cu_{0.33}O_3$	1×10^2	0.30	—	—

[a] Calculated from the linear portion of the log ρ vs $1/T$ plots in the temperature range 300–600 K.
[b] At 1 MHz.

Thus for, no simple oxide of the type $ABi^{5+}O_3$ (A = monovalent cation) with perovskite structure is known. The compound $KBi^{5+}O_3$ is well known, but adopts the cubic $KSbO_3$-type structure which has an edge-shared octahedral network with the Bi–O–Bi angles far from 180° (17). For example, in $KBiO_3$, the angles are 98° and 127°. The factor which distinguishes the cubic $KSbO_3$ structure from the perovskite structure is the M–O–M bond angles (M = B-site cation). In the perovskite structure, these angles are ideally 180°. It has been argued that the strong covalent contribution to the M–O bonding inhibits 180° M–O–M angles for Bi^{5+} or Sb^{5+} cations (d^{10}) (18). The M–O–M angle of 180° found in the perovskite is favored in the case where the M cation is a d^0 transition metal (Nb^{5+} or Ta^{5+}). However, the stabilization of the 1 : 3 ordered perovskite structure for $Ba(B_{0.75}M_{0.25})O_3$ (B^{5+} = Sb or Bi, M = Li or Na) phases seems to contradict the above argument. This structure contains continuous 180° Bi–O–Bi or Sb–O–Sb bonds arranged in the form of chains along the a, b, and c axes. It is interesting to note that the 1 : 3 ordered structure is not observed in the case of $Ba(Nb_{0.75}M_{0.25})O_3$ or $Ba(Ta_{0.75}M_{0.25})O_3$, M = Li or Na. It is difficult to conclude why a 1 : 3 ordered structure is restricted to Sb^{5+} and Bi^{5+} cations and is not seen in the case of Nb or Ta. It is likely that the large difference in the ionic character between (Sb, Bi)–O and (Li, Na)–O bonds may play a crucial role in the stabilization of the 1 : 3 ordered structure. As pointed out by Alonso *et al.* (5), the 1 : 3 ordered structure is likely to be more favored for cations with high polarizing power such as Sb^{5+}, which arise from the electronic shell configuration ([Kr]$4d^{10}$). It is further interesting to note that the Bi^{5+}-containing perovskites with a 1 : 3 ordered structure can be stabilized at 700°C. This clearly shows that the much higher polarizing power of Bi^{5+} cation ([Xe]$5d^{10}$) seems to readily stabilize the 1 : 3 ordered structure at lower temperatures.

$Ba(Bi_{0.67}M_{0.33})O_3$ (M = Ba, Sr, Ca, Mg, Cd, or Cu) Perovskites

We could readily synthesize single-phase $Ba(Bi_{0.67}M_{0.33})O_3$ (M = Ba, Sr, Ca, Mg, Cd) compounds at 800°C under 3 kbar pressure. The color of the compounds varied from dark brown to black and the X-ray diffraction patterns showed characteristic reflections expected for a cubic perovskite unit cell (Fig. 1). However, the observed superlattice reflections in these compounds could be readily accounted for by a unit cell with a space group $Fm3m$ [$(NH4)_3FeF_6$ type] indicating a 1 : 1 ordering between $\frac{1}{2}Bi^{5+}$ and $\frac{1}{3}M + \frac{1}{6}Bi^{5+}$) at the B site of the ABO_3 perovskite structure. Prolonged heating of the samples even at higher temperatures (up to 1000°C, under pressure) did not result in the hexagonal 1 : 2 ordered phases.

TABLE 5

X-Ray Powder Diffraction Data for $Ba(Bi_{0.67}Ca_{0.33})O_3$

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}[a]
1 1 1	4.9424	4.9634	5.8	8.0
2 0 0	4.2898	4.2985	1.0	1.6
2 2 0	3.0367	3.0395	100.0	100.0
3 1 1	2.5910	2.5921	5.2	4.8
2 2 2	2.4820	2.4817	<1.0	0.9
4 0 0	2.1495	2.1493	27.6	29.0
3 3 1	1.9718	1.9723	1.5	2.2
4 2 2	1.7550	1.7546	43.0	39.2
5 1 1	1.6544	1.6545	<1.0	1.2
4 4 0	1.5201	1.5198	18.2	17.4
5 3 1	1.4531	1.4532	1.0	1.6
6 2 0	1.3593	1.3593	17.4	16.1
5 3 3	1.3113	1.3110	<1.0	0.6
4 4 4	1.2410	1.2409	4.8	5.5

[a] Relative peak height intensities are calculated on the basis of an ideal 1 : 1 ordered perovskite cell with $Fm3m$ symmetry. Atomic positions used are, Ba at 8(c), $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$; Bi at 6($a$), 0 0 0; Na,Bi at 4($b$), $\frac{1}{2}$ 0 0; oxygen atoms at (24e), $\frac{1}{4}$ 0 0.

Table 5 shows an indexed powder pattern for $Ba(Bi_{0.67}Ca_{0.33})O_3$ along with the observed and calculated intensities based on a face-centered lattice. Figure 2b shows the cation arrangement in $Ba(Bi_{0.67}M_{0.33})O_3$ and the unit cell parameters are listed in Table 1. A plot of pseudocubic unit cell parameter versus mean ionic radius r_{ave} [$(rBi^{5+} + rM^{3+})/2$ or $(0.67Bi^{5+} + 0.33M^{2+})/2$ or $(0.75\ Bi^{5+} + 0.25M^{1+})/2$] showed a linear behavior (Fig. 4). The lattice parameters of other well-established Bi^{5+} perovskite compounds such as $BaM_{0.5}Bi_{0.5}O_3$ (M = La, Dy, In) (1, 7) and $Ba(Fe_{0.5}Bi_{0.5})O_3$ (8) are also included in the plot along with the data for Nb^{5+}-containing

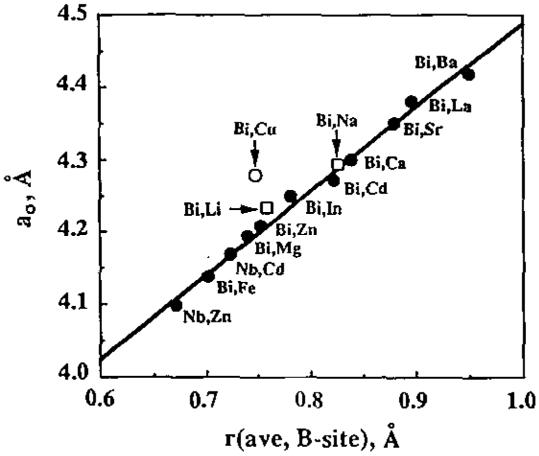


FIG. 4. The linear relationship between pseudocubic perovskite unit cell parameter (a_0, Å) and average ionic radius (Å) of [Bi(V), M] for $Ba(Bi, M)O_3$. Niobium(V)-containing compounds are included for comparison.

perovskite compounds. All the ionic radii used were taken from Shannon (14). The lattice parameters of all the compounds (except $Ba(Bi_{0.67}Cu_{0.33})O_3$, see below) fit very well in the plot showing that the effective octahedral ionic radius value (0.76 Å) given for Bi^{5+} by Shannon (14) is quite reasonable for perovskite-type compounds. Earlier, Knop *et al.* (15) found this value to be significantly high for octahedral Bi^{5+} in weberite-related compounds.

Electrical resistivity measurements showed that most of the compounds synthesized in this study are insulating, with the $Ba(Bi_{0.75}Cd_{0.33})O_3$ phase showing relatively high electrical conductivity (Table 4). The room temperature resistivity and activation energy of $Ba(Bi_{0.67}M_{0.33})O_3$ phases showed a noticeable decrease as the electronegativity of the octahedral M cation is increased (electronegativity varies according to Cd>Mg>Ca>Sr>Ba). This is probably due to the presence of some of the bismuth in the lower oxidation state, and the content of $Bi^{<5+}$ should increase as the electropositive character of the M cation is decreased. This is also clearly reflected in the oxygen content listed in Table 1.

Our attempts to synthesize copper(II)-containing perovskite of the type $Ba(Bi_{0.67}Cu_{0.33})O_3$ under 3kbar pressure by reacting BaO_2, CuO, and Bi_2O_3 at 700–900°C were not successful. However, the product obtained by reacting the above mixture at 800°C under 58 kbar pressure gave an X-ray diffraction pattern characteristic of a simple perovskite cell (Fig. 5). No superlattice reflections were seen and the pattern could be indexed on the basis of a primitive unit cell with $a = 4.268\ (\pm 0.002)$ Å.

In the case of $Ba(Bi_{0.67}Cu_{0.33})O_3$, the average ionic radius corresponding to $(\frac{2}{3}Bi^{5+}$ and $\frac{1}{3}Cu^{2+})/2$ does not fit well with the observed unit cell parameter (Fig. 4). The observed unit cell parameter is larger than the value calculated from the plot. This is probably due to the presence of one-half of the bismuth in the 4+ oxidation state and the copper existing as Cu^{3+} giving rise to a formula, $Ba(Bi^{5+}_{0.33}Bi^{4+}_{0.33}Cu^{3+}_{0.33})O_3$. This is further substantiated by the fact that the infrared spectrum of $Ba(Bi_{0.67}Cu_{0.33})O_3$, in addition to a band at 550 cm^{-1}, showed a broad band with a maximum at 435 cm^{-1} (Fig. 3 and Table 3). This band has been assigned to the Bi^{5+}–O–$Bi^{4+,5+}$ stretching mode ($\nu 3$) and has been clearly observed in the case of $BaBiO_3$ (13). More evidence for the presence of Bi in the lower valence state of $Ba(Bi_{0.67}Cu_{0.33})O_3$ can be seen in the electrical resistivity data. The electrical resistivity of this phase is many orders of magnetite lower than that of all the other Bi^{5+} perovskites (Table 4), and the observed high conductivity is probably due to the mixed valence state of Bi (Bi^{5+} and Bi^{4+}). In addition, if copper is present as Cu^{2+} in the above phase, a tetragonal distortion of the unit cell would be expected due to the Jahn–Teller effect. Such distortions were clearly seen in many other copper(II)-containing perovskites, viz. $BaCu_{0.5}U_{0.5}O_3$ and $BaCu_{0.5}W_{0.5}O_3$ (3, 16). High-resolution X-ray diffraction patterns obtained with a Guinier–Hägg camera for a $Ba(Bi_{0.67}Cu_{0.33})O_3$ sample did not show any line splitting due to any distortion from cubic symmetry. Our attempts to estimate the exact Cu^{3+}/Cu^{2+} content in the above phase by iodometric titration was complicated by the presence of Bi in the mixed valence state.

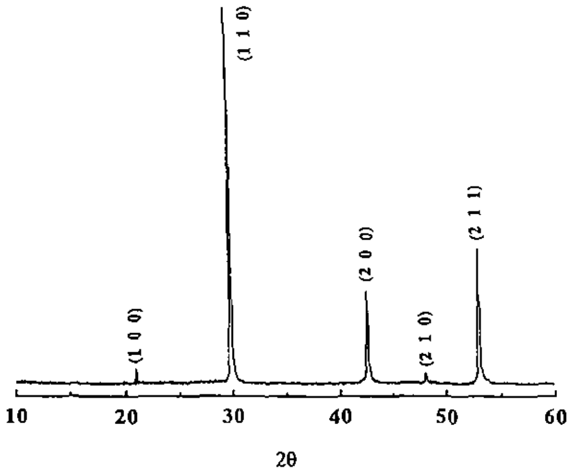


FIG. 5. X-ray diffraction pattern for disordered $Ba(Bi_{0.67}Cu_{0.33})O_3$. The 2θ values are in degrees.

CONCLUSIONS

Bismuth is difficult to stabilize in the pentavalent state. Obtaining an unusually high oxidation state in a given post-transition element such as Bi requires a very large covalence in the M–O bond. Stabilization of such a highly covalent M–O bond can be achieved by using countercations with a strongly electropositive character, viz. Li^+, Na^+, K^+, Ba^{2+}, and Sr^{2+}. In general, synthesis under high-pressure conditions stabilizes the metal cations in their highest oxidation states. Using the above principles, we have succeeded in the synthesis of new perovskites oxides of the type $Ba(Bi^{5+}_{0.67}M_{0.33})O_3$ (M = Mg Ca, Sr, Ba, or Cd) and $Ba(Bi^{5+}_{0.75}M_{0.25})O_3$ (M = Li or Na) with 1 : 1 and 1 : 3 ordered arrangement of B-site cations, respectively. Chemical analysis, infrared, spectra, and the trends in the unit cell parameters confirm the existence of Bi mainly in the pentavalent state in these perovskites.

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