

Bismuth(III)- and antimony(V)-based ceramics with anion-deficient fluorite structure

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Abstract

Original non-stoichiometric oxides with the formula $M_{2-2x}Bi_{3x}Sb_{2-x}O_7$ ($M \equiv Cd, Zn$) have been found in the $Bi_2O_3-Sb_2O_5-MO$ ($M \equiv Cd, Zn$) systems. These phases belong to the pyrochlore family. Niobium- and lanthanum-substituted $MBi_{1.5}Sb_{1.5}O_7$ ($M \equiv Cd, Zn$) solid solutions have been synthesized by solid state reaction. The composition ranges and the evolution of the lattice parameters as a function of the ionic radii of the substituting elements have been determined. The low frequency dielectric properties have been evaluated between room temperature and 473 K on sintered ceramic samples. Their variations are discussed in terms of the electronic structures of the involved cations and the relative polarisabilities of both the NbO_6 and SbO_6 octahedra.

1. Introduction

Among the devices which can be used in the microwave range, ceramic dielectric resonators are becoming more and more successful owing to their relative small dimensions and their ability to be used in both passive and active systems. Previous studies have shown that Bi_3SbO_7 [1, 2], $Bi_3Pb_4Sb_5O_{21}$ [3], lanthanum-, cadmium- and niobium-substituted $Bi_3Pb_4Sb_5O_{21}$ solid solutions [4] and $Pb(Cd)BiM^{IV}SbO_7$ ($M^{IV} \equiv Ti, Zn, Sn$) [5] should have dielectric properties, making them candidates for the elaboration of resonators. This work has been extended to the $Bi_2O_3-Sb_2O_5-MO$ ($M \equiv Cd, Zn$) systems, allowing us to discover an original non-stoichiometric phase $M_{2-2x}Bi_{3x}Sb_{2-x}O_7$ ($M \equiv Cd, Zn$) which belongs to the $M_2Sb_2O_7-Bi_3SbO_7$ pseudobinary system (Fig. 1). The $M_{2-2x}Bi_{3x}Sb_{2-x}O_7$ powders exhibit X-ray diffraction patterns characteristic of the pyrochlore structure: cubic symmetry, space group $Fd\bar{3}m$ for $M \equiv Zn$ ($0.435 \leq x \leq 0.575$ at 1100 °C) (Fig. 2(a)) and $M \equiv Cd$ ($0.40 \leq x \leq 0.43$ at 950 °C) (Fig. 2(b)); rhombohedral symmetry, space group $R\bar{3}m$ for $M \equiv Cd$ ($0.40 \leq x \leq 0.43$ at 950 °C) (Fig. 2(b)) [6].

In order to understand the influence of the different cations on the crystallographic and dielectric properties, it seemed of interest to investigate some related compounds obtained by homovalent chemical substitutions

from the prototype phase $MBi_{1.5}Sb_{1.5}O_7$ (Fig. 1). This paper deals with the crystallographic and low frequency dielectric properties of some solid solutions involving the following substitutions: niobium for antimony, $MBi_{1.5}(Sb_{1.5-x}Nb_x)O_7$ ($M \equiv Zn, Cd$), and lanthanum for bismuth, $M(Bi_{1.5-x}La_x)Sb_{1.5}O_7$ ($M \equiv Zn, Cd$).

2. Experimental details

Appropriate mixtures of reagent grade ZnO, CdO, Sb_2O_3 , Bi_2O_3 , Nb_2O_5 and La_2O_3 were thoroughly ground and homogenized in an agate mortar and calcined at 873 K for 24 h in open alumina crucibles (this step is necessary for a full oxidation of antimony (III) into antimony (V)). Subsequent thermal treatments (1073 K for 6 h and 1373 K for 15 h) ensured the completion of the reaction. X-ray diffraction data were obtained with a Guinier-Hägg camera using $Cu K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and silicon (NBS grade, $a = 5.4309 \text{ \AA}$) as an internal standard. The unit cell parameters were refined by the least-squares method.

Additive (2.5 wt.% $Bi_{12}PbO_{19}$) mixed powders were cold pressed into pellets at 200 MPa in a steel die and then sintered (1473 K for 12 h in air) in a Kanthal Al electrical furnace at a heating rate of 5 K min^{-1} . Relative densities were obtained from dimension measurements.

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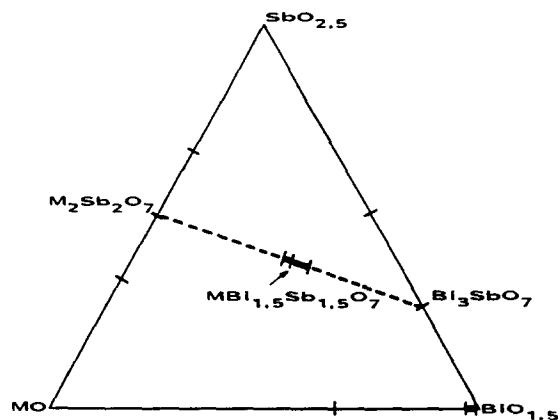


Fig. 1. Composition range of $M_{2-2x}Bi_{3x}Sb_{2-x}O_7$ solid solutions within the pseudoternary system $Bi_2O_3-Sb_2O_5-MO$ ($M \equiv Cd, Zn$).

Low frequency (10 kHz) dielectric constants and losses were measured between room temperature and 473 K under weak a.c. fields (about 0.5 V mm^{-1}) using a Wayne-Kerr (B905) automatic bridge. Disk-shaped samples (about 10 mm in diameter and about 1–2 mm thick) obtained from the sintered ceramics were coated using a low temperature silver paste (HPC 7323, 875 K, 5 min), aged overnight at 383 K and left for 2 days at room temperature before measurements.

3. Results

3.1. Crystallographic properties

The structural characteristics of $Zn(M^{III})_{1.5}Sb_{1.5}O_7$ ($M^{III} \equiv Bi, La$) have been determined using the powder neutron diffraction technique. As for the general $A_2B_2O_7$ cubic pyrochlore structures ($Fd3m$), the structure of $ZnBi_{1.5}Sb_{1.5}O_7$ can be described with mixed cations on both A ($Zn_{0.5}Bi_{1.5}$) and B ($Zn_{0.5}Sb_{1.5}$) sites. The $ZnLa_{1.5}Sb_{1.5}O_7$ has a distorted pyrochlore-type structure with rhombohedral symmetry (space group $R3m$). The detailed study of these structures will be the subject of a forthcoming paper [7].

All the substitutions investigated in the present study ($La \leftrightarrow Bi$ and $Nb \leftrightarrow Sb$) always lead to the formation of cubic or rhombohedral $MBi_{1.5}Sb_{1.5}O_7$ -type solid solutions. The composition ranges and the cell symmetry depend strongly on the nature of the substituting element (Table 1). Niobium and lanthanum substitutions in cadmium-based ceramics always lead to the rhombohedral pyrochlore-type structure, in agreement with previous observations [8]. In contrast, niobium and lanthanum substitutions in zinc-containing ceramics lead to either the cubic pyrochlore-type structure (whole $Nb \leftrightarrow Sb$ substitution; partial $La \leftrightarrow Bi$ substitution on bismuth-rich side) or the rhombohedral

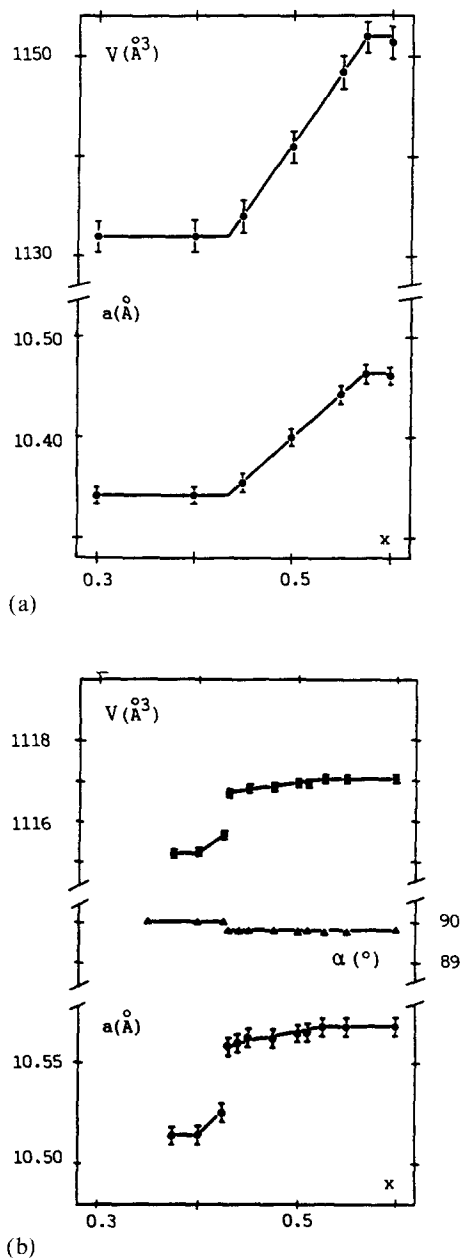


Fig. 2. Evolution of unit cell parameters and volume vs. composition for (a) $Zn_{2-2x}Bi_{3x}Sb_{2-x}O_7$ and (b) $Cd_{2-2x}Bi_{3x}Sb_{2-x}O_7$.

TABLE 1. Composition ranges and unit cell symmetry for $M^{II}Bi_{1.5}(Sb_{1.5-x}Nb_x)O_7$ and $M^{II}(Bi_{1.5-x}La_x)Sb_{1.5}O_7$ solid solutions

M^{II}	x	Symmetry
$M^{II}Bi_{1.5}(Sb_{1.5-x}Nb_x)O_7$	$0 \leq x \leq 1.50$	cubic
	$0 \leq x \leq 1.45$	rhombohedral
$M^{II}(Bi_{1.5-x}La_x)Sb_{1.5}O_7$	$0 \leq x \leq 0.17$	cubic
	$0.60 \leq x \leq 1.50$	rhombohedral
	$0 \leq x \leq 1.00$	rhombohedral

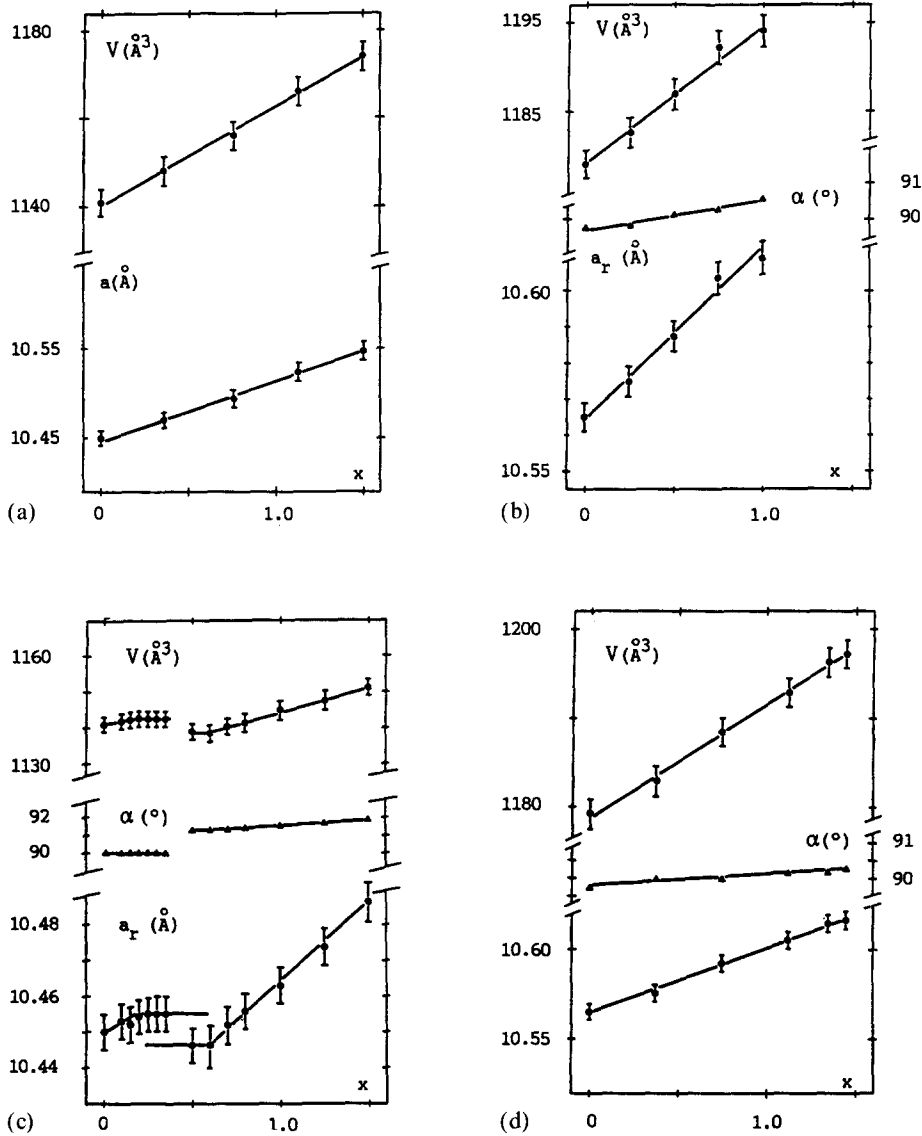


Fig. 3. Evolution of unit cell parameters and volume *vs.* composition for (a) $\text{ZnBi}_{1.5}(\text{Sb}_{1.5-x}\text{Nb}_x)\text{O}_7$, (b) $\text{CdBi}_{1.5}(\text{Sb}_{1.5-x}\text{Nb}_x)\text{O}_7$, (c) $\text{Zn}(\text{Bi}_{1.5-x}\text{La}_x)\text{Sb}_{1.5}\text{O}_7$ and (d) $\text{Cd}(\text{Bi}_{1.5-x}\text{La}_x)\text{Sb}_{1.5}\text{O}_7$.

pyrochlore-type structure (partial $\text{La} \leftrightarrow \text{Bi}$ substitution on lanthanum-rich side).

As shown in Fig. 3, the evolution of unit cell parameters and volume are consistent with the ionic radii of substituted species [9]. All the curves obey a linear law. Cadmium solid solutions show a more pronounced unit cell volume change than zinc solid solutions. This should be related to the larger size of Cd^{2+} cations with respect to Zn^{2+} cations.

3.2. Dielectric properties

The ceramic samples used for the determination of the dielectric properties have been sintered for 12 h at 1473 K using 2.5 wt.% sillenite-type $\text{Bi}_{12}\text{PbO}_{19}$ as a liquid phase sintering aid, except for $\text{Zn}(\text{Bi}_{1.5-x}\text{La}_x)$ -

$\text{Sb}_{1.5}\text{O}_7$ ceramics, for which all sintering attempts failed. The corresponding densities lie between 90% and 96.5% of the theoretical densities as shown in Table 2, which also gives the low frequency (10 kHz) dielectric characteristics of ceramics with various compositions. Except for some unexplained singular compositions, the density does not greatly influence the dielectric losses, which are generally in the 10^{-4} range.

The variations of the room temperature dielectric constants as a function of the substituting species depend strongly on the nature of the corresponding cations.

When Nb^{5+} is substituted for Sb^{5+} , the dielectric constant increases strongly with increasing x both for cadmium- as for zinc-based ceramics (Figs. 4(a) and

TABLE 2. Low frequency (10 kHz) characteristic of Nb-sustituted ceramics

x	$d_{\text{exp}}/d_{\text{th.}}(\%)$	Dielectric constant $\epsilon_r(\pm 0, 1)$	Dielectric loss $10^4 \cdot \tan \delta (1)$	Temperature coefficient of capacitance $10^6 \cdot \tau_c(\text{K}^{-1})$ $\tau_c = \frac{1}{\epsilon} \frac{\Delta \epsilon}{\Delta T}$
ZnBi_{1.5}(Sb_{1.5-x}Nb_x)O₇				
0	93.4	28.4	<1	-58
0.375	94.5	40.1	5	-80
0.6	90.1	42.1	8	-128
0.75	92.9	48.6	2	-142
0.85	92.7	59.6	10	-167
1.00	92.2	71.5	8	-203
1.125	93.4	92.2	29	-145
1.5	89.7	153.1	140	-323.
CdBi_{1.5}(Sb_{1.5-x}Nb_x)O₇				
0	94.8	22.9	8	+46
0.1	94.2	26.6	28	+25
0.15	95.7	30.5	4	+8
0.20	91.2	27.4	18	+5
0.25	94.3	29.2	8	-16
0.375	92.4	31.2	2	-49
0.60	96.0	48.9	3	-172
0.75	95.3	56.1	9	-249
0.85	96.3	66.3	7	-321
1.00	95.6	81.9	7	-418
1.125	96.5	104.2	12	-495
1.35	95.6	135.2	50	-487
1.45	95.2	122.6	20	-210

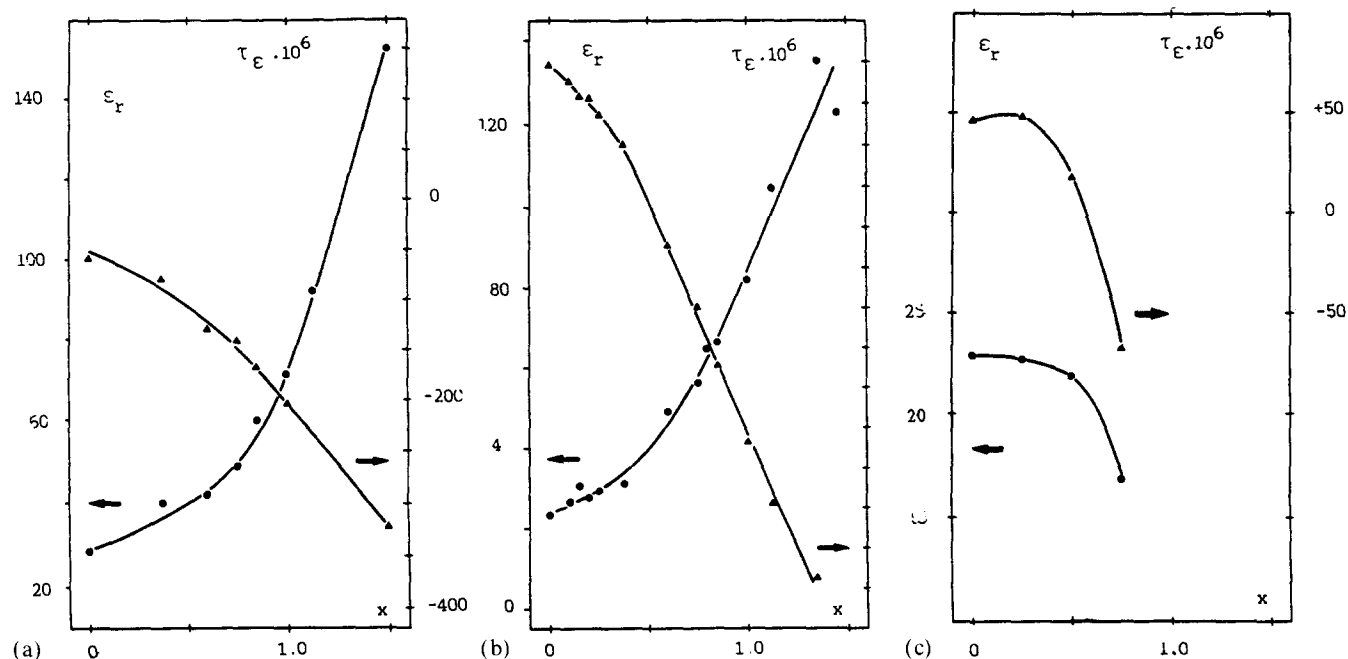


Fig. 4. Evolution of dielectric characteristics (ϵ_r , τ_c) vs. composition for (a) ZnBi_{1.5}(Sb_{1.5-x}Nb_x)O₇, (b) CdBi_{1.5}(Sb_{1.5-x}Nb_x)O₇ and (c) Cd(Bi_{1.5-x}La_x)Sb_{1.5}O₇.

4(b), Table 2). Here a cation with a closed 4d¹⁰ shell (Sb⁵⁺) is replaced by a 3d⁰ transition element cation (Nb⁵⁺). Such behaviour is similar to that observed

when Sn⁴⁺ (4d¹⁰) is substituted for Zr⁴⁺ (4d⁰) in ZrTiO₄ [10]. In both cases the dielectric constant behaviour should be related to the relative polarizability

TABLE 3. Low frequency (10 kHz) characteristics of Cd(Bi_{1.5-x}La_x)Sb_{1.5}O₇ ceramics

x	$d_{\text{exp}}/d_{\text{th.}}(\%)$	Dielectric constant $\epsilon_r(\pm 0, 1)$	Dielectric loss $10^4 \cdot \tan \delta (\pm 1)$	Temperature coefficient of capacitance $10^6 \cdot \tau_\epsilon(\text{K}^{-1})$ $\tau_\epsilon = \frac{1}{\epsilon} \frac{\Delta \epsilon}{\Delta T}$
0	94.8	22.9	8	+46
0.25	92.2	22.7	19	+48
0.5	91.8	21.9	7	+18
0.75	90.1	16.8	19	-67

of the NbO₆ octahedron with respect to the SbO₆ octahedron. As the niobium content increases, the number of electronic states which are likely to hybridize with the oxygen 2p states (which is zero for SbO₆ octahedra owing to the lack of empty 4d states) increases, leading to a significant increase in the polarizability and hence in the dielectric constant [11].

When La³⁺ is substituted for Bi³⁺, the opposite behaviour is observed (Fig. 4(c), Table 3). For Cd(Bi_{1.5-x}La_x)Sb_{1.5}O₇ the dielectric constant decreases with increasing x . This phenomenon could be expected: similar behaviour has been observed in many other bismuth compounds, e.g. (BiLa)₃SbO₇ and lanthanum-substituted Bi₃Pb₄Sb₅O₂₁ [2, 4]. The possible explanation is that a cation bearing a lone pair is replaced by a cation with a fully occupied d shell.

The variations of the temperature coefficients of the dielectric constants are also very sensitive to the substitution. When this involves bismuth sites (Fig. 4(c)), τ_ϵ decreases with x , crossing the zero value for a composition close to $x = 0.55$ for Cd(Bi_{1.5-x}La_x)Sb_{1.5}O₇ solid solution. In contrast, when substitution occurs into octahedral sites, the presence of Nb⁵⁺ ions not only makes the dielectric constant increase but also leads to a strong decrease in τ_ϵ , which reaches values close to -320×10^{-6} and $-600 \times 10^{-6} \text{K}^{-1}$ for ZnBi_{1.5}Nb_{1.5}O₇ and CdBi_{1.5}Sb_{0.05}Nb_{1.45}O₇ (maximum niobium content) respectively (Figs. 4(a) and 4(b)). The similitude of the observed behaviour for zinc- and cadmium-based ceramics confirms that niobium has the main influence on the dielectric properties with respect to the

cadmium or zinc presence. In addition, τ_ϵ crosses the zero value for a composition close to $x = 0.22$ for the CdBi_{1.5}(Sb_{1.5-x}Nb_x)O₇ series.

The fact that for high niobium content the dielectric constant presents a strongly negative temperature coefficient associated with an increase in dielectric losses could indicate the occurrence of a possible ferroelectric transition below room temperature. Further experiments to check this possibility are now in progress.

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