Ferroelectric Properties of Substituted Aurivillius Phases $SrBi_2Nb_{2-x}M_xO_9$ (M=Cr, Mo)

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Partially doped Aurivillius phases $SrBi_2Nb_{2-x}M_xO_9$ (M=Cr and Mo) were successfully synthesized and characterized. The extent of the substitution was limited at ~20 mole % because of the size differences between Nb^{5+} and Cr^{6+}, and between Nb^{5+} and Mo^{6+}. When the amount of substitution exceeded ~20 mole%, the phases began to collapse and the second phases were made. The dielectric constants of substituted compounds were enlarged nevertheless Cr or Mo is substituted. The increment is bigger in the Mo substituted compound than in the Cr doped one although the $Nb(Cr)O_6$ octahedra could be more strongly distorted than the $Nb(Mo)O_6$ octahedra since the ionic size difference between Nb^{5+} and of Cr^{6+} is much bigger than that between Nb^{5+} and Mo^{6+}. Consequently, the dielectric constant of the substituted Aurivillius phase $Bi_2A_{n-1}B_{n-x}M_xO_{3n+1}$ depends on the extent of distortion of the BO_6 octahedra and more strongly on the polarizability of the metal.

Key Words : Aurivillius phase, Ferroelectric property, Dielectric constant

Introduction

Aurivillius phases $Bi_2A_{n-1}B_nO_{3n+1}$[1] contain layered B_nO_{3n+1} perovskite structures which are regularly interleaved with Bi_2O_2 layers, where B typically represents an early transition metal (*e.g.*, Ti, Nb, Ta, Cr, W, Fe), A is an electropositive atom (*e.g.*, Na, K, Ca, Sr, Ba, Gd, La, Y, Pr, Sn, Pb, Bi), and n is the number of BO_2 layers within the perovskite slab.[2,3] After the pioneering work of Smolenski *et al.*[4] and Subbarao,[5] who extensively studied their ferroelectric properties as a function of composition, it has been well known that most Aurivillius compounds with $n \leq 5$ show ferroelectric property. The ferroelectricity found in the Aurivillius phases accelerated the work on these materials for electronic applications. As a result, the thin film of $SrBi_2Ta_2O_9$ (SBT) is now widely used as a capacitors, non-volatile ferroelectric random access memory (FRAM) and dynamic random access memory (DRAM) devices. Especially, the SBT compound shows significantly improved properties for the application over the existing $Pb(Zr, Ti)O_3$ based systems (*e.g.*, low coercive field, low leakage current, and no exhibition of fatigue up to 10^{10} cycles).[6-8]

It has been well known that the ferroelectricity in the Aurivillius phases originate from the structural distortions in the compounds. Withers and co-workers have suggested that the major cause of spontaneous polarization in the two-layer materials is the displacement of the A site cation in the perovskite block along the a-direction in the polar space group $A2_1am$ and not the movement of the B site cation away from the octahedral center.[9-12] On the contrary, the distorted O-B-O chains which construct perovskite layers, are thought to be the origin of the polarization in the Aurivillius phases.[6] So the high polarization is occurred along the a- and b-directions which are parallel to a layer. Although the contribution of the cation B to the polarization might be small, therefore, it has been understood that the spontaneous polarization in the ferroelectric Aurivillius phases originates from a complicated interplay of several displacive mechanisms involving rigid displacements along the polar a-axis, as well as rotations around the polar a-axis and the c-axis. As a result, not only the central cations B are dispaced along the a-axis with respect to the oxygen octahedral framework but also the cations A as well as the oxygen and Bi ions of the $(Bi_2O_2)^{2+}$ layer. The magnitudes of the contributions of the different displacements change with n; *e.g.*, for $BiWO_6$ (n = 1) the displacement of the B (*i.e.*, B = W) cation contributes most to the spontaneous polarization whereas for $Bi_4Ti_3O_{12}$ (n = 3) the displacement of the A (*i.e.*, A=Bi) cation is dominant.[12] Comparing the structures of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ also revealed that the nature of the electronic structure of the A cation influences strongly the interplay between the displacive mechanisms altering the importance of the role of the A cation for the ferroelectricity. In addition, a partial mixing of Bi and A cations on their respective sites, was reported by Lightfoot and co-workers.[13] The amount of mixing of Bi and A cations increases with increasing the size of the A site cation. So far a flood of work on the role of the A cation for the ferroelctricity have been made. However, not much effort has been done on the influence of different B metals. It is interesting to note that the two-layer (n = 2) Aurivillius phases niobates show higher Curie temperature than the corresponding tantalates.[14] In addition, $SrBi_2Nb_2O_9$ exhibits cation disorder and a more distorted niobium octahedral environments than the $SrBi_2Ta_2O_9$. Therefore, it is fruitful to know whether the ferroelectricity is affected by the different transition metals (*i.e.*, B metals) or not. In this study we substituted the niobium with chromium and molybdenum in the $SrBi_2Nb_2O_9$ if there is any change in the ferroelectricity.

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Experimental Section

To adjust the optimum conditions to prepare the $SrBi_2Nb_{2-x}M_xO_9$, the synthetic route of the pristine $SrBi_2Nb_2O_9$ was used as a reference. According to the preliminary tests to optimize the firing temperatures, times, atmosphere, and the stoichiometry, the following conditions were obtained. Appropriate amounts of reactants (Aldrich Bi_2O_3 99.99%, Aldrich Nb_2O_5 99.99%, Aldrich $SrCO_3$ 99.9%), and a substitute (Aldrich Cr_2O_3 99.99% or Aldrich MoO_3 99.5%) were throughly mixed using a mortar and pestle and pelletized in a 8 mm die under 170 MPa (2500 psi). The excess amount of Bi was added since it evaporates easily at the reaction temperature. Pellets were calcined in a electric tube furnace in 99.8% dense Al_2O_3 boats in air for 20 hr at 800 °C, then at 1100 °C for 10 hr with re-grinding after each heating step. Samples were examined by powder X-ray diffraction (XRD) using Rigaku diffractometer with Cu-K_α radiation after each step. The Rietveld refinement was under taken by the full-matrix least-square technique with a PC version of the computer program. The structural data of $SrBi_2Nb_2O_9$ reported by Ismunandar *et al.*[15] were used as a starting model. Isotropic thermal motions were included. The conductivity measurements on the samples were performed by using the KEITHLEY MULTIMETER 2000 at room temperature. In order to measure the dielectric constants the pellets were polished and coated with silver by using a microwave sputtering. A low-frequency impedance analyzer (HP 4192A) was used to measure the dielectric constants of the samples which were annealed after the silver coating at 600 °C for 1 hr and slow cooled in air.

Results and Discussion

The XRD pattern of $SrBi_2Nb_2O_9$ which was prepared at 800 °C for 20 hr, then 1100 °C for 10 hr in air, is shown in Figure 1. No impurities nor the unreacted compounds are found, which means that the given synthetic condition is appropriate. Partial substitution of Nb with Cr or Mo to prepare the $SrBi_2Nb_{2-x}M_xO_9$ (M=Cr, Mo) compounds was succeeded under the same condition that the pristine compound was synthesized. The black and dark green powder were obtained for the compounds substituted by Cr and Mo, respectively. The resistivity measurements on both samples reveal that the compounds are insulating at room temperature, which means that the oxidation states of Cr and Mo after the substitution are +6, as expected. The powder X-ray diffraction patterns for the $SrBi_2Nb_{2-x}Cr_xO_9$ (x = 0.2-1.0) and $SrBi_2Nb_{2-x}Mo_xO_9$ (x = 0.1-0.4) are given in Figure 2(a) and Figure 2(b), respectively. These XRD data are similar to that for the pristine $SrBi_2Nb_2O_9$ (see Fig. 1). All peaks are slightly shifted to the higher angle in the Cr substituted compounds, while those are almost unchanged in the Mo substituted compounds. This is due to the difference of ionic radii between Nb^{5+} and Cr^{6+}, and between Nb^{5+} and Mo^{6+} (*e.g.*, 0.58 Å, 0.73 Å, and 0.78 Å for Cr^{6+}, Mo^{6+}, and Nb^{5+} in the octahedral environment, respectively). The substitution with Cr and Mo for Nb was successful until the substitution amount was less than 20 mole%. When Cr or Mo substitutes Nb more than 20 mole%, the second phase peak begins to

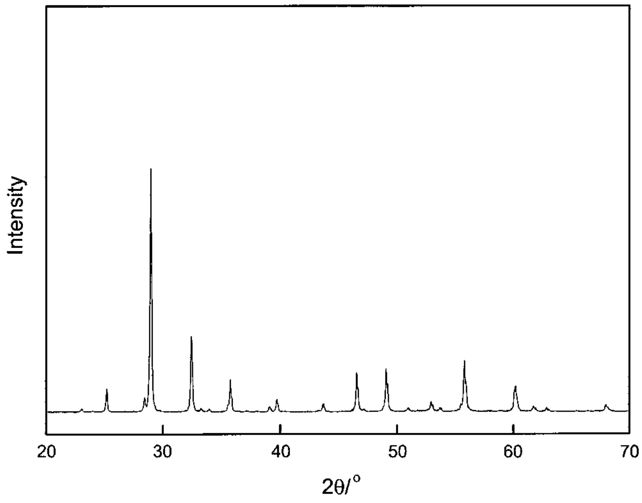

Figure 1. X-ray diffraction pattern of $SrBi_2Nb_2O_9$.

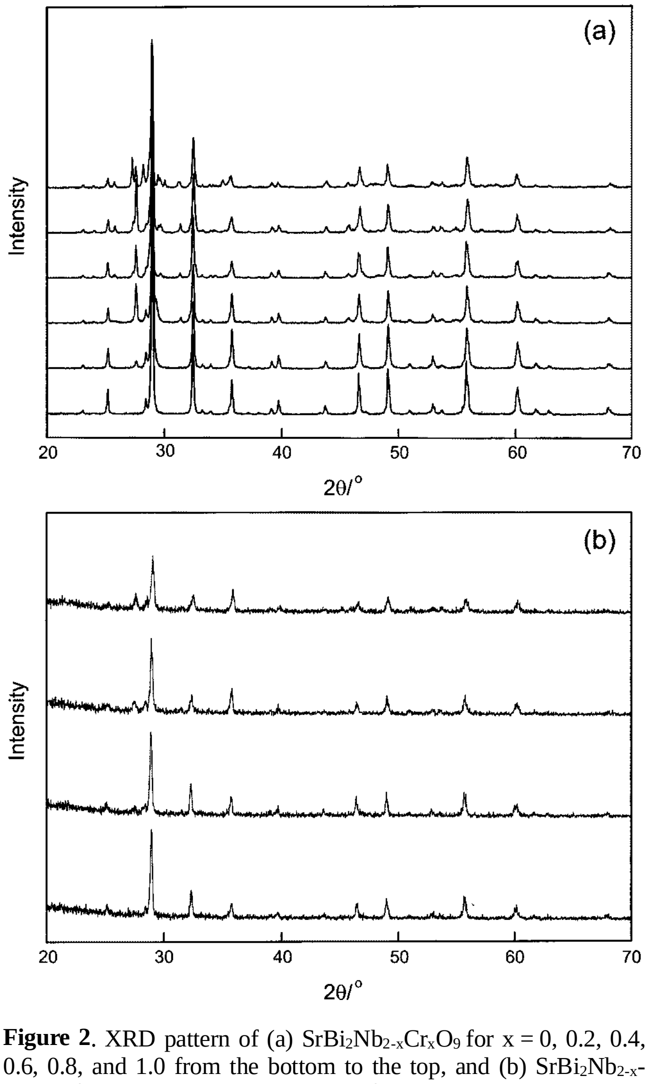

Figure 2. XRD pattern of (a) $SrBi_2Nb_{2-x}Cr_xO_9$ for x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0 from the bottom to the top, and (b) $SrBi_2Nb_{2-x}Mo_xO_9$ for x = 0, 0.1, 0.2, 0.3, and 0.4 from the bottom to the top.

Table 1. Positional parameters for $SrBi_2Nb_{2-x}Mo_xO_9$

atom	site	x	y	z	B
Sr	4a	0.0000	0.2322	0.0000	0.491
Bi	8b	0.2019	0.7370	0.4813	1.317
Nb/Mo	8b	0.4155	0.7562	0.4508	0.384
O(1)	4a	0.0000	0.1693	0.5588	1.570
O(2)	8b	0.3400	0.8290	0.4685	1.548
O(3)	8b	0.2500	0.0000	0.7660	1.697
O(4)	8b	0.1071	0.6795	0.9665	1.023
O(5)	8b	0.5738	0.9515	0.7450	1.446

Table 3. Bond distances (Å) of Nb-O or M-O in the $SrBi_2Nb_{2-x}M_xO_9$ Compounds

	$SrBi_2Nb_2O_9$[a]	$SrBi_2Nb_{1.9}Mo_{0.1}O_9$	$SrBi_2Nb_{1.8}Mo_{0.2}O_9$
Nb(Mo)-O(1)	2.189	2.2523	2.4726
Nb(Mo)-O(2)	1.835	1.9358	2.0819
Nb(Mo)-O(4)	1.900	1.8733	1.8084
Nb(Mo)-O(5)	1.890	1.9660	2.0145

[a] The data were collected from the report made by Ismunandar *et al.*

arise. The peaks are identified as Nb_2O_5 and $BiMO_3$ (M=Cr and Mo) which are supposed to be extracted when Cr or Mo fraction exceeded the threshold. Rietveld refinement data of $SrBi_2Nb_{2-x}M_xO_9$ show that the systems are orthorhombic with the space group $A2_1am$. The refined atomic fractional coordinates of $SrBi_2Nb_{1.9}Mo_{0.1}O_9$ are given in Table 1. Details of structural refinements including cell parameters and space groups for $SrBi_2Nb_{2-x}M_xO_9$ (M = Cr or Mo, x = 0.0, 0.06, 0.1 and 0.2) are given in Table 2. The contraction in the cell volume of the doped compounds tells us that the substitution process was successfully accomplished. The bigger contraction in the Cr substituted compounds with increasing the amount of Cr strongly suggests the above statement. Bond distances between Nb(Mo) and O in $SrBi_2Nb_2O_9$ and $SrBi_2Nb_{2-x}Mo_xO_9$ (x = 0.1 and 0.2) are given in Table 3. It is clear from the Table 3 that as increasing the amount of substitution, the distortion of the octahedral structure becomes stronger. Although not shown, similar results were obtained from the samples which were substituted by Cr. Although not shown, the occupancy of Nb in $SrBi_2Nb_{2-x}M_xO_9$ decreases as the stoichiometric amount of Cr or Mo added increases until x~0.4. This tendency is consistent with the result of the cell volume contraction.

The dielectric constant data measured for the $SrBi_2Nb_{2-x}Cr_xO_9$ (x = 0.2-1.0) and $SrBi_2Nb_{2-x}Mo_xO_9$ (x = 0.1-0.4) are shown in Figure 3(a) and Figure 3(b), respectively. The dielectric constant of unsubstituted compound is 120 within the frequency range of 10^4-10^7 Hz which is reasonable comparing to the references. When the substitution is made at 10 mole% the value increases to about 225 in the case of Mo insertion, while it becomes ~160 for Cr doping. Toward the upper limit, a slow increment of the dielectric constants is shown with increasing the amount of substitution

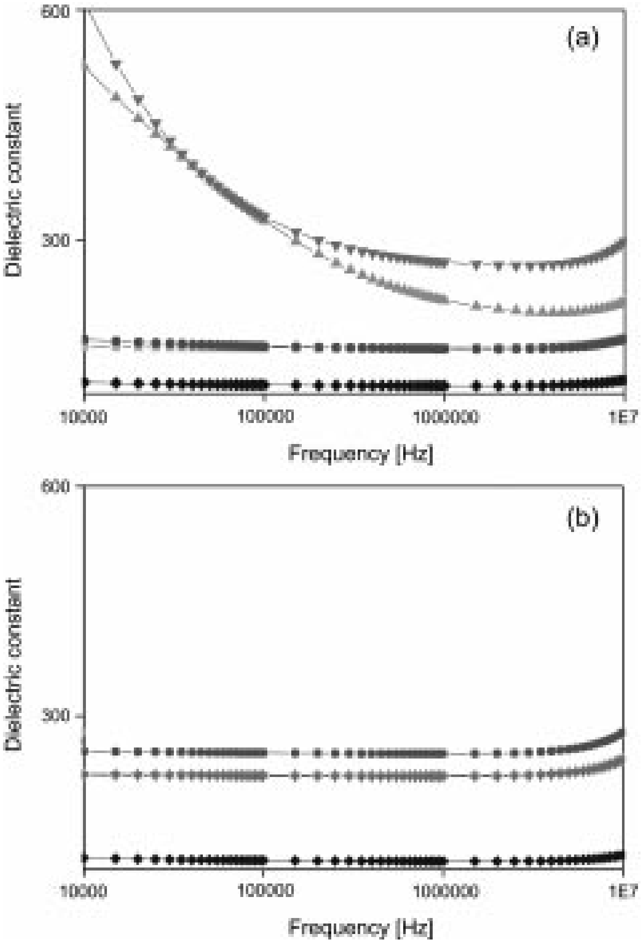

Figure 3. The dielectric constant data of (a) $SrBi_2Nb_{2-x}Cr_xO_9$ for x = 0.0, 0.2, 0.4, 0.6, and 0.8 from the bottom to the top, and (b) $SrBi_2Nb_{2-x}Mo_xO_9$ for x = 0.1, 0.2, 0.3, and 0.4 from the bottom to the top.

Table 2. Details of structure refinements for $SrBi_2Nb_{2-x}M_xO_9$

	$SrBi_2Nb_2O_9$[a]	$SrBi_2Nb_{1.94}Cr_{0.06}O_9$	$SrBi_2Nb_{1.9}Cr_{0.1}O_9$	$SrBi_2Nb_{1.9}Mo_{0.1}O_9$	$SrBi_2Nb_{1.8}Mo_{0.2}O_9$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space Group	$A2_1am$	$A2_1am$	$A2_1am$	$A2_1am$	$A2_1am$
a/Å	25.1124	25.0921	25.0816	25.0625	25.0663
b/Å	5.5154	5.5082	5.5031	5.5136	5.5130
c/Å	5.5189	5.5166	5.5104	5.5157	5.5183
V(Å^3)	764.39	762.46	760.58	762.19	762.57
Rwp, Rp	11.67, 9.22	–	–	11.31, 8.51	13.30, 9.52

[a] The data were collected from the report made by Ismunandar *et al.*

nevertheless Cr or Mo is substituted. It is interesting to note that the dielectric constant exceeds 300 in the sample in which Cr is substituted more than 30 mole%. But the value does not keep constant within the frequency range of 10^4-10^7 Hz, which is supposed to be due to the phase instability. This result is consistent with the XRD data to exhibit the second phases as the extent of substitution is getting higher. In general, the dielectric constants of the Aurivillius phases are known to be affected by the polarizability of the transition metals in them and by the extent of the distortion of the BO_6 octahedra. It is natural from the latter factor, therefore, to expect that the polarization becomes stronger in the $SrBi_2Nb_{2-x}M_xO_9$ compound when the difference of the ionic radii between Nb and M is bigger. However, the experimental results show that the dielectric constant in the Mo substituted sample is higher than that in the Cr substituted compound, albeit the ionic size difference between Nb^{5+} and of Cr^{6+} is much bigger than that between Nb^{5+} and Mo^{6+}. It is resonable, therefore, to conclude that the dielectric constants in the substituted compounds are weakly affected by the distortion of the octahedra but more strongly affected by the polarizability of the metal since the larger Mo^{6+} cation is more polarizable than the smaller Cr^{6+} cation.

Conclusions

Partial substitution of Nb with Cr or Mo to prepare the $SrBi_2Nb_{2-x}M_xO_9$ (M = Cr, Mo) compounds was succeeded at 800 °C for 20 hr, then 1100 °C for 10 hr in air. The extent of the substitution was limited at ~20 mole % because of the size differences between Nb^{5+} and Cr^{6+}, and between Nb^{5+} and Mo^{6+}. When the amount of substitution exceeded ~20 mole%, the phases began to collapse and the second phases were made. The success of the substitution process was proved from the cell volume contraction and the composition of Nb in the compounds. The dielectric constants of substituted compounds were enlarged nevertheless Cr or Mo is substituted. The increment is bigger in the Mo substituted compound than in the Cr doped one although the ionic size difference between Nb^{5+} and of Cr^{6+} is much bigger than that between Nb^{5+} and Mo^{6+}. It is noted, therefore, that the dielectric constants of the substituted Aurivillius phase $Bi_2A_{n-1}B_{n-x}M_xO_{3n+1}$ depends on the extent of distortion of the BO_6 octahedra and more strongly on the polarizability of the metal.

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