

Neodymium substituted $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ bismuth layered compound

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Abstract

In the present work, $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ($0 \leq x \leq 1$) ceramics were prepared and characterized. Although the substitution of Nd^{3+} for Bi^{3+} led to a decrease of tolerance factor t , the ferroelectricity in $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ was not enhanced but weakened. With increasing x , the Curie temperature of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ was lowered and the peak of dielectric constant was significantly suppressed. Besides, the variation of lattice parameters of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ showed an approach of a and b , which revealed a development trend from ferroelectric orthorhombic structure to the prototype tetragonal structure with the substitution. This strongly suggested that Bi^{3+} is crucial for the ferroelectricity in four-layered $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$, just like found in two-layered $\text{Bi}_3\text{TiNbO}_9$ and three-layered $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compounds. The importance of Bi^{3+} to the ferroelectricity should be due to the special electron configuration of Bi^{3+} but not its relatively small size, since Nd^{3+} is even smaller than Bi^{3+} . The size mismatch between A-site cations and the perovskite cuboctahedral cavity, indicated by t , seemed to play a secondary role in the contribution to the ferroelectricity of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ and its analogues. The dielectric properties of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics were also investigated at microwave resonant frequency.

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1. Introduction

Bismuth layered compounds are a family of ferroelectrics with high Curie temperature and have a general formula of $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, with A-site cations such as La^{3+} , Bi^{3+} , Ba^{2+} , Sr^{2+} , Pb^{2+} , Ca^{2+} and Na^+ in the perovskite cuboctahedral cavity, B-site cations such as W^{6+} , Nb^{5+} , Ta^{5+} , Ti^{4+} and Fe^{3+} in the oxygen octahedra. The structure of these compounds can be described as pseudo-perovskite $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ slabs separated by $(\text{Bi}_2\text{O}_2)^{2+}$ layers along the crystallographic c -axis. The number of the octahedra along c -axis between two neighboring $(\text{Bi}_2\text{O}_2)^{2+}$ layers is indicated by n .

These compounds were discovered more than 50 years ago by Aurivillius, and the interest in these compounds was renewed due to their fatigue-free properties against polarization switching, as the materials for ferroelectric random access

memory (FRAM).^{1,2} Detailed crystallographic studies on some ferroelectric bismuth layered compounds were carried out by several authors.^{3–6} It was found that the spontaneous polarization in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_3\text{TiNbO}_9$ is mostly attributed to the bonding requirement of Bi^{3+} in the perovskite A-site. Therefore, in these compounds, substitution of other cations for A-site Bi^{3+} can lower the Curie temperature because of the reduced driving force for ferroelectricity. In the previous work, we found a ferroelectric-relaxor-paraelectric development trend with increasing x in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($0 \leq x \leq 2$) ceramics at ambient temperature.⁷ In addition, the ferroelectric properties of bismuth layered compounds are also closely related to the structure tolerance factor t of perovskite slabs defined as Eq. (1), where R_A , R_B and R_O are the radii of the A-site cation, B-site cation and oxygen, respectively.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

When $t < 1$, the relatively small size of the A-site cation with respect to the perovskite cuboctahedral cavity can cause tilt-

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ing of the octahedra, and in consequence, cause the distortion of the whole structure. Smaller t usually corresponds to a more distorted structure.⁸ Suarez et al.⁹ concluded that in a broad range of bismuth layered compounds, the decrease of t generally accompanies an increase of Curie temperature.

In the present work, smaller Nd^{3+} is substituted for Bi^{3+} in bismuth layered compound $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$; the dielectric characteristics are evaluated together with the structure. The ferroelectricity may be weakened due to the reduction of bismuth in perovskite A-site, and Curie temperature may be lowered. On the other hand, the smaller average size of A-site cations will reduce the tolerance factor t , which may cause a more distorted structure and enhance the ferroelectricity. To study the variation of Curie temperature in such a case is interesting and will give further understanding to the origin of the ferroelectricity in bismuth layered compounds.

2. Experimental

$\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics with $x=0, 0.25, 0.5, 0.75,$ and 1.0 were prepared by a solid-state reaction process. Reagent-grade oxide or carbonate powders of $\text{Bi}_2\text{O}_3, \text{Nd}_2\text{O}_3, \text{TiO}_2$ and CaCO_3 were accurately weighed and fully mixed through ball milling with zirconia media in distilled water for 24 h. The powders were calcined at 800°C in air for 3 h, and then pressed into cylindrical compacts of 12 mm in diameter and 2–6 mm in height under a uniaxial pressure of 98 MPa. Sintering was performed at temperatures within the range from 1100°C to 1200°C in air for 3 h. The temperature at which the densest ceramics were attained increased with x .

Dielectric properties of the present ceramics were measured with an LCR meter (HP4284A). Phase constitution of the present ceramics was identified by powder X-ray diffraction (XRD) analysis with $\text{Cu K}\alpha$ radiation, and the microstructures were observed using a scanning electron microscope (JSM-5610LV) on the ground polished and thermally etched surfaces. The microwave dielectric properties were evaluated by the resonator method of Hakki and Coleman.¹⁰

3. Results and discussion

Non-substituted $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ is a four-layered bismuth compound with a high Curie temperature of 789°C . The structure distortion in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ with respect to the prototype $I4/mmm$ structure results in the $A2_1am$ space group, and Ca^{2+} and Bi^{3+} occupy A-sites in a random way.¹¹ Although half of the bismuth atoms are located in the $(\text{Bi}_2\text{O}_2)^{2+}$ layers, the Nd^{3+} substitution should mainly occur in the perovskite A-site, since the Bi^{3+} site in $(\text{Bi}_2\text{O}_2)^{2+}$ layers prefers cations with lone pair electrons.

Single phase $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ is found in the range of $0 \leq x \leq 1$, according to the XRD patterns (see Fig. 1). SEM photographs of the ground polished and thermal etched sur-

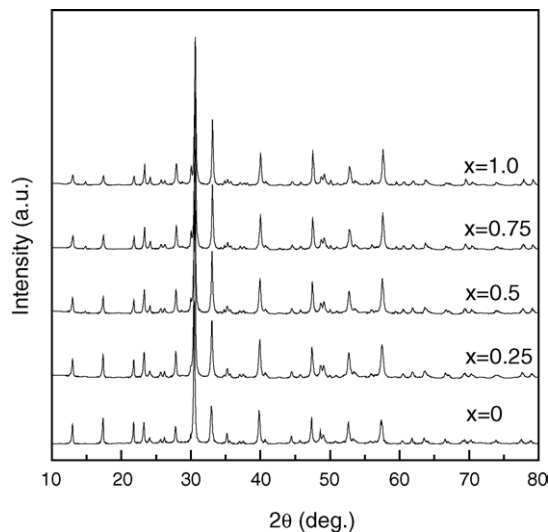


Fig. 1. XRD patterns of the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics.

faces of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics are given in Fig. 2. The randomly oriented grains are plate-like, which is due to the anisotropic growth rate along different crystal axis resulting from the anisotropic crystal structure. With increasing x , the grain size decreases, while no significant change is found in the morphology of grains.

Fig. 3 shows the temperature dependence of dielectric constant for $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics measured at different frequencies. For 10 kHz, 100 kHz and 1 MHz, the dielectric constant peak corresponding to the ferroelectric–paraelectric phase transition can be well defined. While for 1 kHz, the dielectric constant keeps ascending, which implies a high concentration of space charge at elevated temperatures. Fig. 4 shows the temperature dependence of the dielectric constant and the inverse dielectric constant of the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics measured at 1 MHz. With Nd^{3+} substitution, the Curie temperature is lowered and the peak dielectric constant is suppressed, which suggests the weakening of ferroelectricity. When $x=1$, the dielectric constant maximum is only 168. For all the compositions, there is little evidence of relaxor behavior around the phase transition temperature. Above the Curie temperature, the dielectric constant of the present ceramics follows the Curie–Weiss law defined as

$$\varepsilon_r = \frac{C}{T - T_0} \quad (2)$$

in a narrow temperature interval, with C being the Curie constant and T_0 the Curie–Weiss temperature. The Curie–Weiss temperature and the Curie constant for the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics have been extrapolated from the limited data with Eq. (2). The results are listed together with the Curie temperature in Table 1. The Curie constants are 10^4 , which are smaller than the values that usually found in displacive ferroelectrics.¹² Extrinsic contribution of space charge to the dielectric constant may be the reason for the de-

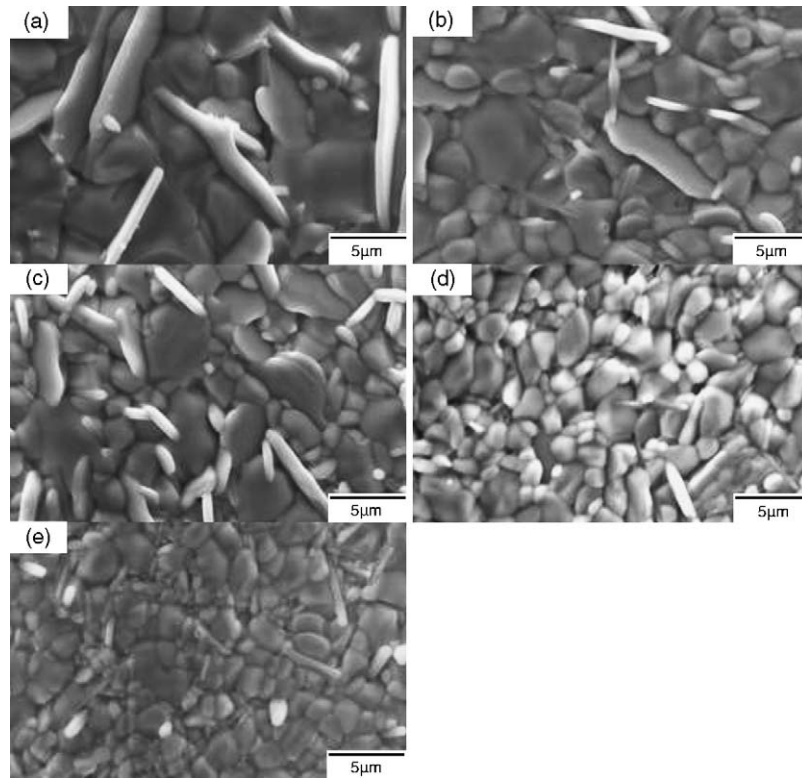


Fig. 2. SEM photographs of the ground polished and thermal etched surfaces of the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics. (a) $x=0$; (b) $x=0.25$; (c) $x=0.5$; (d) $x=0.75$; (e) $x=1.0$.

viation from the Curie–Weiss law above the phase transition temperature.

The lattice parameters of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ solid solutions are shown in Fig. 5. The unit cell shrinks with the Nd^{3+} substitution. This is reasonable since the smaller Nd^{3+} ion may have a shorter average bond distance with surrounding oxygen atoms than Bi^{3+} , which causes a contraction of

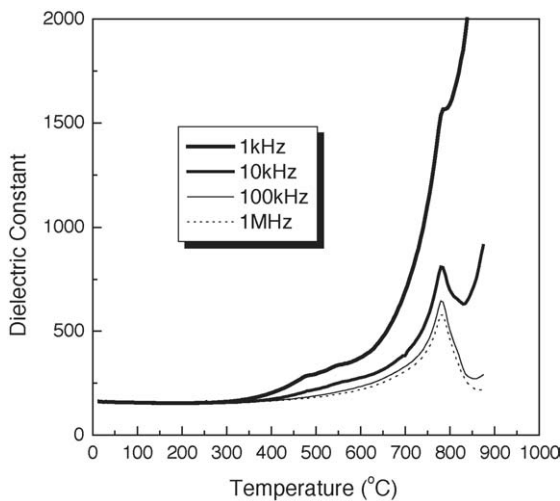


Fig. 3. Temperature dependence of dielectric constant for $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics measured at different frequencies.

the whole structure. The substitution leads to a reduction of the difference between the a and b parameters. This means a reduction in orthorhombic distortion in the structure. For $x=0.25$, lattice parameter a decreases compared to that of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ while b increases. For $x>0.25$, both a and b decrease and the unit cell shrinks as the values of a and b approach each other. This can be seen more clearly in Fig. 6, which gives the variation of orthorhombicity, defined as $2(a-b)/(a+b)$. The decrease of orthorhombicity with x suggests a trend from ferroelectric orthorhombic structure to the prototype tetragonal structure. This is consistent with the dielectric results that the ferroelectricity is weakened with Nd^{3+} substitution.

The tolerance factor (t) of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ was calculated from the effective ionic radii of Shannon ($R_{\text{O}} = 1.40 \text{ \AA}$, $R_{\text{Ti}} = 0.605 \text{ \AA}$, $R_{\text{Ca}} = 1.34 \text{ \AA}$ and $R_{\text{Nd}} = 1.27 \text{ \AA}$).¹³ However, the radius of Bi^{3+} in 12-fold coordination was not given in

Table 1

The Curie temperature (T_c), the Curie–Weiss temperature (T_0) and the Curie constant (C) for the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics

Composition	T_c ($^{\circ}\text{C}$)	T_0 ($^{\circ}\text{C}$)	C (K)
$x=0$	787	749	2.4×10^4
$x=0.25$	741	714	1.2×10^4
$x=0.5$	713	644	1.7×10^4
$x=0.75$	665	557	2.2×10^4
$x=1$	611	506	1.9×10^4

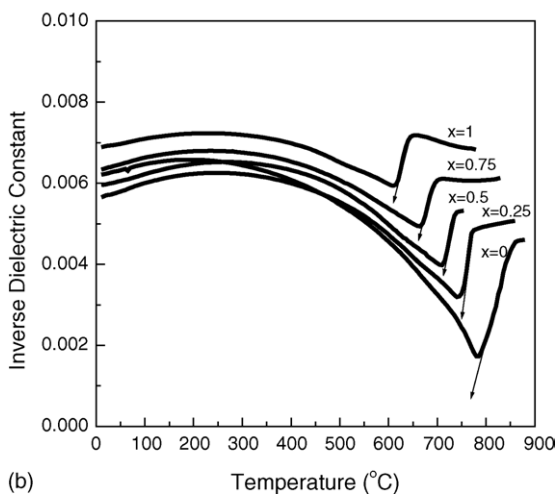
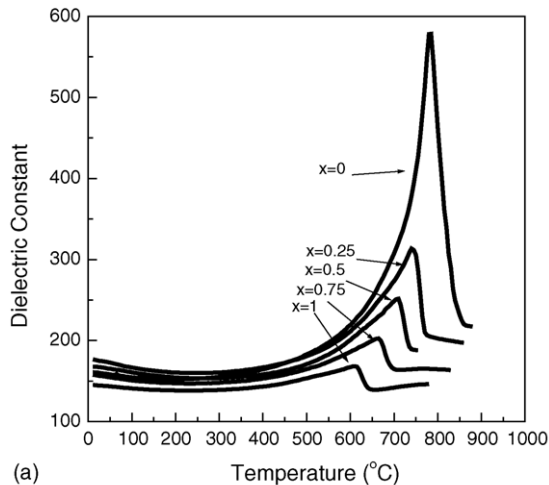


Fig. 4. Temperature dependence of (a) the dielectric constant and (b) the inverse dielectric constant for $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics measured at 1 MHz.

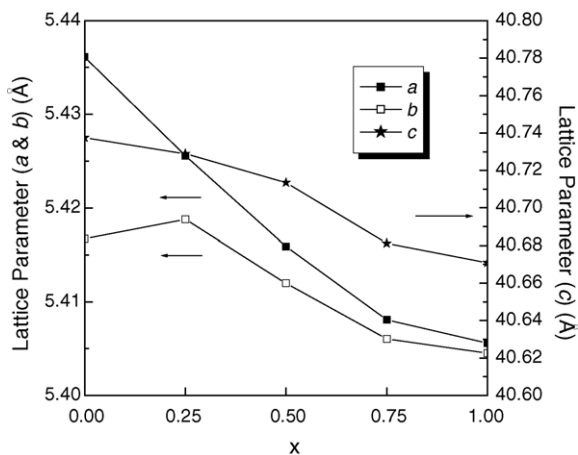


Fig. 5. Lattice parameters of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ solid solutions as a function of x .

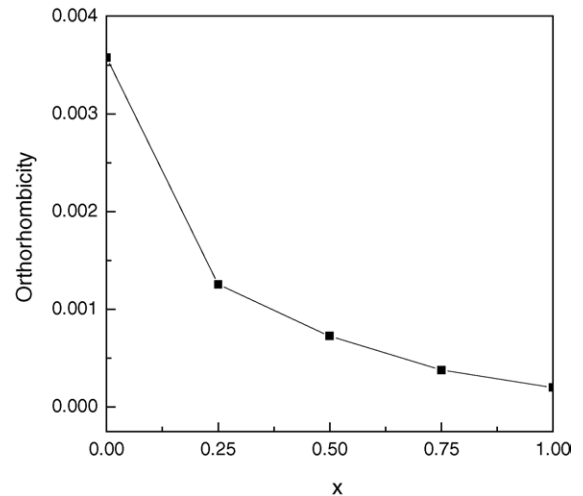


Fig. 6. Orthorhombicity of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ as function of x .

the work of Shannon. Since the radii of Bi^{3+} and La^{3+} are almost the same in six- and eightfold coordination, we adopt 1.36 Å, the radius of La^{3+} in 12-fold coordination, as the ionic radius of Bi^{3+} in 12-fold coordination. Fig. 7 gives the values of t in $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$. They decrease linearly with increasing x . It was concluded in the study of Suarez that the decrease of t usually accompanies an increase of Curie temperature in bismuth layered compounds.⁹ In the series of analogous compounds $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Sr}$ and Ca), the structural distortion is enhanced and Curie temperature increases as t decreases.^{11,14} Compared to $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, which shows a broad phase transition around 400 °C, $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ has a normal paraelectric-ferroelectric phase transition at a much higher temperature. The decrease of t indeed makes differences in the ferroelectric properties in these four-layered compounds. In the case of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$, albeit the substitution causes a further decrease of t and may reduce the size mismatch between the A-site cations and the perovskite

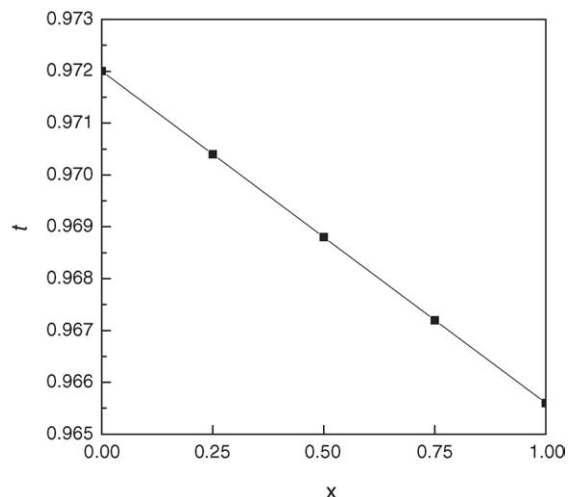


Fig. 7. Tolerant factor t as function of x in $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$.

Table 2
Dielectric properties of the $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics at microwave resonant frequency f_0

Composition	Dielectric constant	f_0 (GHz)	$\tan \delta$	Qf_0 (GHz)
$x=0$	163.9	2.354	0.0067	354
$x=0.25$	178.2	2.381	0.0043	549
$x=0.5$	173.8	2.370	0.0040	580
$x=0.75$	165.7	2.401	0.0042	577
$x=1$	151.9	2.651	0.0048	549

cuboctahedral cavity, the ferroelectricity is not enhanced. The Curie temperature is lowered and the orthorhombic distortion of the structure is greatly lessened with increasing x . This proves that Bi^{3+} is crucial for the ferroelectricity in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$, probably because of its special electron configuration but not its relatively small size. Decreasing the ferroelectric active Bi^{3+} results in weakened ferroelectricity. In addition, the orthorhombic distortion of the structure in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ is mostly attributed to the interaction between Bi^{3+} and surrounding oxygen atoms, while the size mismatch between A-site cations and the provskite cuboctahedral cavity does not seem to be important. In the present work, we cannot judge how much the Ca^{2+} in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ contributes to the ferroelectricity. However, it can be deduced that, compared to the large Ba^{2+} (1.61 Å) in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, the small Ca^{2+} (1.34 Å) has less effect against the structure distortion caused by the interaction between Bi^{3+} and surrounding oxygen atoms, and leads to a relatively high Curie temperature for $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$.

Dielectric properties of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ceramics at the microwave resonant frequency are listed in Table 2. The dielectric constant is above 150 in all the ceramics, and the Qf values are of several hundred GHz. In the previous work, we also found a high dielectric loss at microwave resonant frequency in $\text{Bi}_{4-x}\text{La}_x\text{Ti}_4\text{O}_{12}$ ceramics even in the paraelectric phase.⁷

4. Conclusions

In the present work, ceramics of $\text{CaBi}_{4-x}\text{Nd}_x\text{Ti}_4\text{O}_{15}$ ($0 \leq x \leq 1$) were prepared and single phase was found in all

the compositions. With the Nd^{3+} substitution, Curie temperature was lowered and orthorhombic distortion of the structure was lessened in spite of the decrease of tolerance factor t . We proposed that, in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$, the A-site Bi^{3+} is most important for the ferroelectricity, and the size mismatch between A-site cations and the provskite cuboctahedral cavity is favorable but not essential for the ferroelectricity. At the microwave resonant frequency, high dielectric constants more than 150, and Qf values of several hundred GHz were found in all the present ceramics.

Acknowledgments

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