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Products and microwave dielectric properties of ceramics with nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B' = Nb^{5+}$, Ta^{5+})

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Abstract

The products and microwave dielectric properties of ceramics with nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B' = Nb^{5+}$, Ta^{5+}) are investigated. When $x = 0.5$, i.e. $(Ba_{0.9}Ca_{0.1})(Y_{1/2}B'_{1/2})O_3$ ($B' = Nb^{5+}$, Ta^{5+}), the product contains a considerable amount of Y_2O_3 as well as the main perovskite phase. When $x = 0.3$ the product is single phase, equivalent to $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ or $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$. The lattice parameters of these new compounds are smaller than those of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$. The relative permittivities (ε_r) of these new compounds are larger than those of $Ba(Y_{1/2}B'_{1/2})O_3$ ($B' = Nb^{5+}$, Ta^{5+}). The increase in ε_r of the Nb-system is about 4 times larger than that of the Ta-system. The *Qf* values of the present ceramics are larger than the Ca-containing perovskite in the $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$ system. The sharp increase of ε_r in this study cannot be explained by the Ca^{2+} rattling ion model at the *A*-site, which applies to the case of the $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$ system. A new method to explain the increase in ε_r is discussed.

Keywords: Crystal chemistry; Dielectric properties; Functional applications; Perovskite; Porosity; (Ba,Ca)(Y,Nb,Ta)O_3

1. Introduction

The paraelectric properties of perovskite oxides change upon partial substitutions of their *A*-site alkaline-earth ions. Are there rules for the substitutions, to explain the changes in paraelectric properties—relative permittivity, and dielectric loss, and their changes with temperature? This inquiry has motivated many investigations[1–5] and this study. We investigate a new system with a nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B' = Nb^{5+}$, Ta^{5+}).

Previous studies have dealt with systems $(A_{1-x}A'_x)ZrO_3$ and $(A_{1-x}A'_x)(B_{1/3}B'_{2/3})O_3$ (A, $A' = $ Ba, Sr, Ca) including the pressure and temperature dependences of capacitances[1–3] and yielded very interesting experimental relationships among elastic parameters and dielectric properties.[4] Moreover, the systems, $(Ba_{1-x}Ca_x)(B_{1/2}B'_{1/2})O_3$ ($B^{3+} = Y^{3+}$, Nd^{3+}, Gd^{3+}; $B'^{5+} = Nb^{5+}$, Ta^{5+}), have been studied[5] for comparison with other reported systems.

2. Experimentals

The nominal composition of the two systems is expressed as $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B' = Nb^{5+}$, Ta^{5+}). The two compositions with x of 0.5—$(Ba_{0.9}Ca_{0.1})(Y_{1/2}B'_{1/2})O_3$—have been prepared by Ikawa and Takemoto.[5] Guaranteed grade reagents were used to prepare specimens according to normal ceramic processing. A micro pulverizer (Fritsch, P-5), setting 80 ml pots made of partially stabilized zirconia, was used after the first and second calcinations at 1200 °C for 9 h. The shaped powder was CIPed under 1.0 GPa (Sugino Machine, HPV-150C4). Ceramic disks about 8 mm in diameter and 4 mm length were prepared by sintering in air at 1600 °C for 5 or 6 h.

Specimens were characterized by XRD (Rigaku, RINT2500VHF), SEM, and density measurements (Micromeritrics, AccuPyc 1330). The microwave dielectric properties were measured by means of the Hakki–Coleman[6] and Kobayashi[7] method in the TE_{011} mode at about 9 GHz. A network analyzer (HP, 8722C) system was used in association with the program SU2-RODTE01 Ver.2.[7] The temperature dependence of the resonance frequency of the disk was measured from 0 to

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80 °C. The temperature coefficient of resonance frequency (*TCf*) was evaluated using data at 20 and 80 °C.

3. Results and discussion

3.1. Product and lattice parameter of perovskite

Figs. 1 and 2 show XRD patterns of crushed sintered pellets of selected x in the system $(Ba_{0.9}Ca_{0.1})(Y_xNb_{1/2})O_{(3x+4.5)/2}$ and $(Ba_{0.9}Ca_{0.1})(Y_xTa_{1/2})O_{(3x+4.5)/2}$, respectively. The XRD patterns of Figs. 1(a) and 2(a) show that there are considerable amounts of Y_2O_3 as well as the perovskites. This result confirms the work of Ikawa and Takemoto.[5] The XRD intensities of Y_2O_3 are weak when x is 0.4, and not seen when x is 0.3. All the diffractions peaks [Fig. 1(c) and 2(c)] were indexed according to the indices of $Ba(Y_{1/2}Ta_{1/2})O_3$ (JCPDS 19-0147). Therefore, they represent the spectra of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ and $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$. This means that all the Ca^{2+} ions occupy the *B*-site of perovskite in these systems. However, the authors cannot explain the difference in the intensities of Y_2O_3 between Figs. 1(a) and 2(a).

The lattice parameters are compared in Fig. 3. The parameters of the two perovskites are approximately independent of the composition ($0.3 \leqslant x \leqslant 0.5$). It is because the composition of the product is $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ or $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$. When the parameters are examined in detail it may be noted that the parameters have a slight tendency to decrease with the increase in x. It is inferred from this slight change in the parameters that the chemical composition of the compound is not strictly fixed at $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ or $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$, but there is slight change in chemical composition, taking into account point defects.

The lattice parameters[5] of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$ are also shown in Fig. 3; they are reasonably close to each other. In comparison, the parameters of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ and $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$ are almost identical, and they are significantly smaller than those of the former (Ca-free) compounds. The mean ionic radii[8] of *B*-site ions of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ are evaluated as follows. The weighted arithmetical mean radii and the cube root of mean cube radii of $Y_{1/2}Nb_{1/2}$ are 77 and 79.1 pm, respectively. These equivalent mean ionic radii for $Ca_{1/9}Y_{3/9}Nb_{5/9}$ are 76.7 and 79.4 pm, respectively. Nominally the ionic radii of Nb^{5+} and Ta^{5+} are identical.[8]

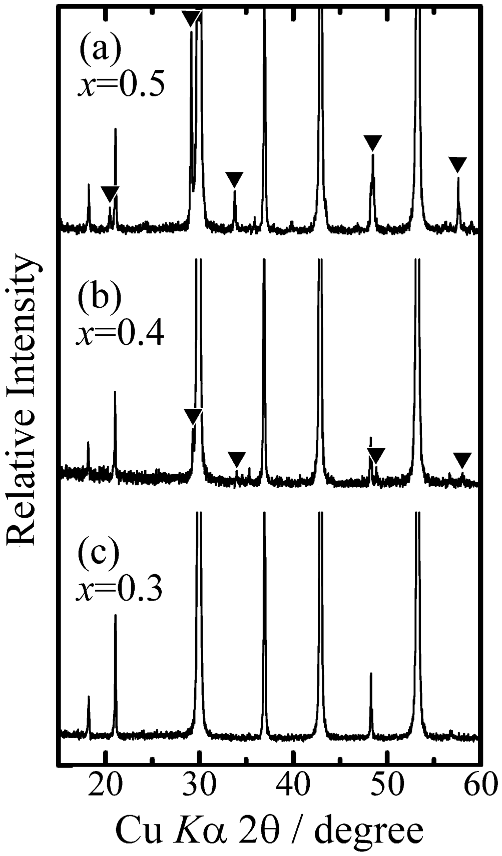

Fig. 1. XRD patterns of crushed sintered disks of the nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xNb_{1/2})O_{(3x+4.5)/2}$. Diffractions belonging to Y_2O_3 are marked by triangles.

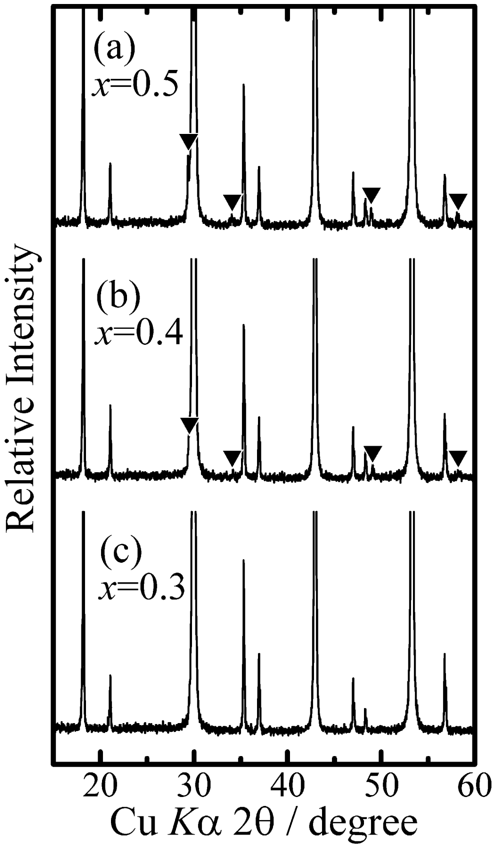

Fig. 2. XRD patterns of crushed sintered disks of the nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xTa_{1/2})O_{(3x+4.5)/2}$. Diffractions belonging to Y_2O_3 are marked by triangles.

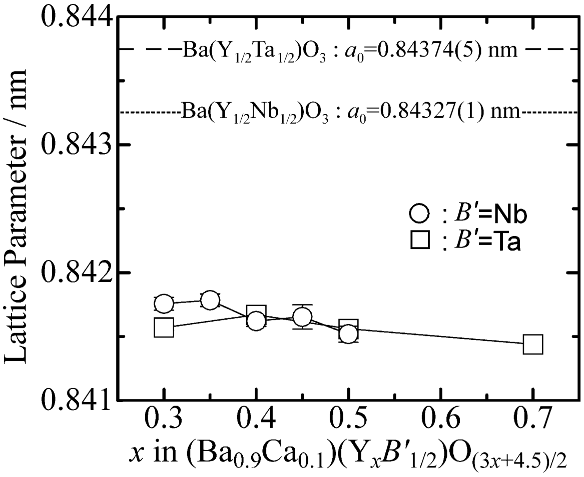

Fig. 3. Lattice parameter vs. composition parameter x in the nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B'=Nb^{5+}$, Ta^{5+}).

The respective arithmetical mean radii (77 and 76.7 pm) support the larger parameter of $Ba(Y_{1/2}Nb_{1/2})O_3$ than that of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ (Fig. 3). On the other hand, the respective cube root of mean cube radii (79.1 and 79.4 pm) are inconsistent with the experimental data (Fig. 3) although the cell volume could be evaluated by the sum of volumes of respective ion spheres.[5]

The observed densities (units of 10^3 kg m^{-3}) of disks are as follows: $(Ba_{0.9}Ca_{0.1})(Y_xNb_{1/2})O_{(3x+4.5)/2}$ system: $x=0.3$: 5.854(6) (96.9% of theoretical density); $x=0.35$: 5.782(5); $x=0.4$: 5.846(3); $x=0.45$: 5.855(5); $x=0.5$: 5.856(3). Then for the $(Ba_{0.9}Ca_{0.1})(Y_xTa_{1/2})O_{(3x+4.5)/2}$ system: $x=0.3$: 6.93(1) (97.2% of theoretical density); $x=0.4$: 6.63(1); $x=0.5$: 6.80(2); $x=0.7$: 6.54(2). These densities are sufficiently high for dielectric measurements.

3.2. Dielectric property

Fig. 4 shows ε_r and Qf values of the ceramic disks. The ε_r values[5] of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$ in the figure agree well with reported data.[9] The respective ε_r of 42.8 ($x=0.3$) and 33.4 of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ and $Ba(Y_{1/2}Nb_{1/2})O_3$ are compared with those ε_r of 33.2 ($x=0.3$) and 30.1 of $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$. The increase in ε_r due to the incorporation of Ca^{2+} is evident. Moreover, the sharp increase in ε_r of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ is outstanding; this increase in ε_r is about 4 times larger than the increase in $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$.

The Qf values are large when $x=0.3$, and they decrease sharply when $x=0.4$; they remain low values till $x=0.5$. All the Qf values of the $(Ba_{1-x}Ca_x)(B_{1/2}B'_{1/2})O_3$ systems[5] are very small, similar to those of $x=0.5$ in Fig. 4, when x is larger than about 0.05. Accordingly, the large Qf values in Fig. 4 when $x=0.3$ are impressive. For comparison, the Qf values of $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$ are 48.9 THz and 38.1 THz, respectively.[5] Even the large Qf values of this study at $x=0.3$ are far smaller than those of the terminal compositions.

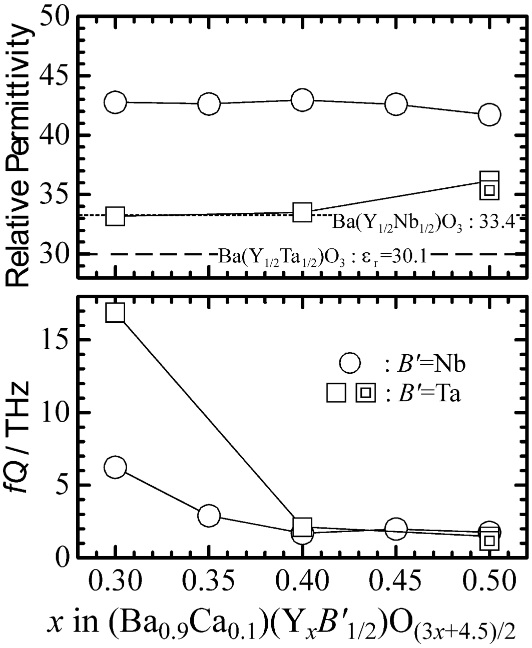

Fig. 4. Relative permittivity and the Qf value of the disk vs. x in the nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B'=Nb^{5+}$, Ta^{5+}).

The temperature dependence of resonance frequency for the Ca-free specimens was almost linear. Fig. 5 shows TCf vs. composition in the $(Ba_{0.9}Ca_{0.1})(Y_xNb_{1/2})O_{(3x+4.5)/2}$ system. The relationship is thought to be a typical one. Fig. 5 also shows TCf[5] for $Ba(Y_{1/2}Nb_{1/2})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$. It is evident that TCf of $Ba(Ca_{1/9}Y_{3/9}Nb_{5/9})O_3$ ($x=0.3$) is very large compared to that of $Ba(Y_{1/2}Nb_{1/2})O_3$. Similarly, TCf of $Ba(Ca_{1/9}Y_{3/9}Ta_{5/9})O_3$ ($x=0.3$) is larger than that of $Ba(Y_{1/2}Ta_{1/2})O_3$. The TCf vs. composition relationship of the figure is very

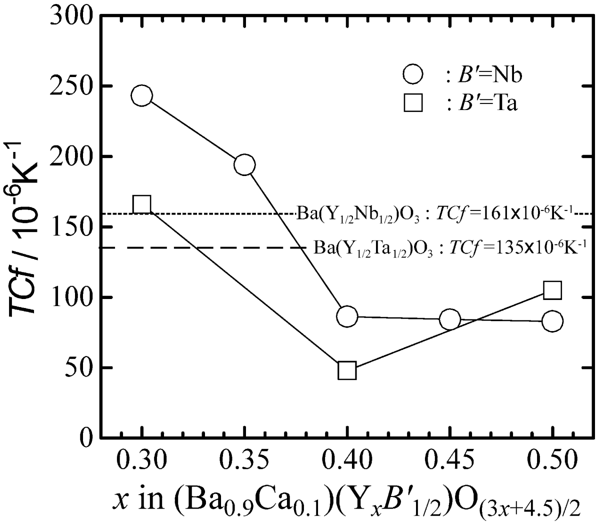

Fig. 5. Temperature coefficient of resonance frequency (TCf) vs. x in the nominal composition $(Ba_{0.9}Ca_{0.1})(Y_xB'_{1/2})O_{(3x+4.5)/2}$ ($B'=Nb^{5+}$, Ta^{5+}).

similar to the composition dependence of the *Qf* data (Fig. 4). It is inferred from this that both *Qf* and *TCf* are mainly controlled by a similar parameter.

The sharp increase in ε_r of the $(Ba_{1\text{-}x}Ca_x)(B_{1/3}B'_{2/3})O_3$ system (when x is smaller than about 0.25) is explained by the rattling of Ca^{2+} ion at the *A*-site.[5] Fig. 6 compares the observed normalized lattice parameters with the calculated ones.[5] The calculation was carried out by assuming that the cell volume can be evaluated by taking the sum of volumes of respective ion spheres[8] according to the chemical formula.[5] The rattling of Ca^{2+} ion is realized from the fact that the observed lattice parameters are larger than the calculated ones. Furthermore, the sharp increase in ε_r of the $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$ system occurs while there is a catastrophic decrease in the *Qf* value.[3]

It was noted that the ε_r values of $Ba(Ca_{1/9}Y_{3/9}B'_{5/9})O_3$ ($x = 0.3$) are larger than those of $Ba(Y_{1/2}B'_{1/2})O_3$ ($B' = Nb^{5+}$, Ta^{5+}) (Fig. 4) and the lattice parameters of the Ca^{2+} containing compounds are smaller than those of $Ba(Y_{1/2}B'_{1/2})O_3$ ($B' = Nb^{5+}$, Ta^{5+}) (Fig. 3). Furthermore, the calculated lattice parameters are larger than those observed. Accordingly, the sharp increase in ε_r cannot simply be explained by the rattling ion model. The authors are now focusing on the mass effects in perovskite ferroelectrics.[10,11] The difference in mass between the *A*-site ion and BO_6 octahedron may play an important role in determining the relative permittivities of some kinds of perovskites; namely, the smaller difference in mass between Ba^{2+} ion and $(Y_{1/2}Nb_{1/2})O_6$ than between Ba^{2+} ion and $(Y_{1/2}Ta_{1/2})O_6$ may be the main reason for the larger ε_r of $Ba(Y_{1/2}Nb_{1/2})O_3$ than the ε_r of $Ba(Y_{1/2}Ta_{1/2})O_3$.

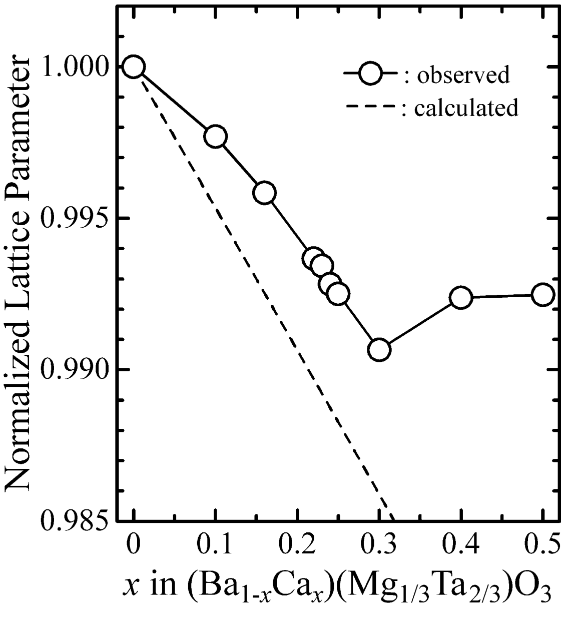

Fig. 6. Normalized lattice parameter vs. x in the nominal composition $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$.[5]

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