Microwave dielectric properties of BaTi$_4$O$_9$–BaSm$_2$Ti$_4$O$_{12}$ composite ceramics

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BaTi$_4$O$_9$ and BaSm$_2$Ti$_4$O$_{12}$ possess large dielectric performances and low dielectric loss, but their temperature-dependent properties could not meet with the practical use. In this paper, a composite ceramic system BaTi$_4$O$_9$/BaSm$_2$Ti$_4$O$_{12}$ (BaTi$_4$O$_9$ + xSm$_2$O$_3$, x = 20, 40, 60, 80 mol %) was prepared and their dielectric properties was presented. The composite ceramic precursor were modeled by a cool iso-static press (CIP) and calcined at 1300°C for 6 h. The measured densities of ceramic samples increased, but the relative densities decreased with the increase of x. XRD patterns showed there existed two phases of BaTi$_4$O$_9$ and BaSm$_2$Ti$_4$O$_{12}$ in the composite. The dielectric constants increased from 39.7 to 60.0, while the quality factors decreased from 8300 to 1500. At x = 40%, a near-zero temperature coefficient of +2.2 ppm/°C was achieved. The presence of pores, Ti$^{3+}$ and Ti$^{5+}$ was proposed to be the cause of the deviation from calculated dielectric properties.

Key-words : Dielectric ceramics, Dielectric loss, Titanate, Rare earth

1. Introduction

In the last three decades of 20th century, modern communications have been accelerated greatly by the rise of microwave dielectric resonators (MDRs) constructed by microwave dielectric ceramics (MDCs). So far as the MDCs is concerned, after 30 years’ development, a serial of pure compounds and composite ceramics with large constants ($\varepsilon_r$), low dielectric loss ($\tan \delta$), and low dielectric loss (Qf) have been developed, for instance, Ba$_7$Ti$_4$O$_{18}$, Ba$_2$Ln$_2$Ti$_4$O$_{13}$ (Ln = Nd, Sm), Sm$_2$O$_3$(Ti$_{1-x}$Zr$_x$)$_2$O$_5$ and Ba$(M'$)$_1$(M''$_{1/2}$)$_3$O$_5$ (M' = Zn and Mg; M'' = Nb and Ta).1-5

Accompanying the development of the dielectric ceramics is the rapid progress of communications technology, which demands much more high-performance dielectric ceramic systems. Composite ceramics technique provides a promising way to design dielectric ceramics composites with adjustable dielectric properties.6-8 Generally, the dielectric properties of mixed-phased compositions could be written as:

\[ \ln \varepsilon = \sum \ln \varepsilon_i \]  
(1)
\[ \tan \delta = \sum \tan \delta_i \]  
(2)
\[ \tau_f = \sum \tau_{f_i} \]  
(3)

where $\varepsilon_i$ is the molar ratio of the ith phase; $\varepsilon$, tan $\delta$ and $\tau_f$ are the dielectric constant, the dielectric loss and the temperature coefficient of the ith phase, respectively. The Formulas indicts that the composite could combine the excellent dielectric properties of at least 2 compounds, so the composite method is successful in elongating the list of dielectric ceramics. As mentioned above, Ba$_7$Ti$_4$O$_{18}$ and Ba$_2$Sm$_2$Ti$_4$O$_{12}$ possess excellent dielectric properties: a relative larger dielectric constant ($\varepsilon_r \approx 38.0$), low dielectric loss ($Q > 5000$ at 2 GHz, $Q = 1/\tan \delta$), and a positive temper-ature coefficient ($\tau_f \approx +15$ ppm/°C) for BaTi$_4$O$_9$ and a large dielectric constant ($\varepsilon_r \approx 80.0$), low dielectric loss ($Qf > 8000$, $Q = 1/\tan \delta$, $f$: resonating frequency), and a negative temperature coefficient ($\tau_f \approx -42$ ppm/°C) for BaSm$_2$Ti$_4$O$_{12}$.2,5 According to Formula (1)-(3), the combination of Ba$_7$Ti$_4$O$_{18}$ ceramics with Ba$_2$Sm$_2$Ti$_4$O$_{12}$ ceramics could provide a series of composite ceramics with adjustable dielectric properties. Therefore, in this paper, we prepared a series of Ba$_7$Ti$_4$O$_{18}$/Ba$_2$Sm$_2$Ti$_4$O$_{12}$ composite ceramics and analyze the variation of microstructure and dielectric properties with the relative content of Ba$_7$Ti$_4$O$_{18}$ and Ba$_2$Sm$_2$Ti$_4$O$_{12}$.

2. Experimental

The raw regents including TiO$_2$, Sm$_2$O$_3$, and BaCO$_3$, are all of A.R grade and used as purchased. All raw materials were weighed in a stoichemetric ratio and ball-milled for 24 h in an ethanol solution. After ball-milling, the mixed powder was dried in a oven at 60°C for 24 h and pressed by a 150 MPa cool iso-static press (CIP) into a stick with a diameter of c.a. 20 mm,. The pressed green bodies were dried in an oven at 80°C for 24 h, and then sintered at 1300°C for 6 h. The ceramic sticks were abraded into a cylinder, and then cut into disks.

The densities measurements of the samples were carried out using an Archimedes method. The crystal structure of sintered samples was examined by X-ray powder diffraction with monochromatic CuK$\alpha$ radiation (MO 3X HF Mac Science, Tokyo, Japan). The ceramic bulks were observed by SEM (Hitachi S4700, Japan) electroscope, and their surfaces were analyzed by XPS (Escalabmik II, VG. Co., U.K.). Before measuring dielectric properties, the ceramics was well polished. The microwave dielectric properties were experimentally determined by a parallel plate resonator method in the TE$_{011}$ dielectric resonator mode using a R3767CG network analyzer (Advantest, Japan).9 The dependance of resonant frequency on the sizes of the samples were listed in the Table 1. The temperature coefficients were measured at room temperature and 85°C, and calculated by the Formula (4):

\[ \tau_f = \frac{\Delta n}{n} \cdot \frac{\Delta T}{T} \]  
(4)

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\[f_t = \frac{f_{T2} - f_{T1}}{(T_2 - T_1) \times f_{T1}} \tag{4}\]

Where \(T_1, T_2, f_{T1}, f_{T2}\) stands for the room temperature, 85°C, resonating frequencies at 25°C and 85°C, respectively.

3. Results and discussions

3.1 Density measurement

The calculated densities of ceramic samples were estimated by a linear weighed addition of two separate phases:

\[d_{\text{theo}} = d_{BT4} \times (1 - x) + d_{BST4} \times x \tag{5}\]

\(d_{\text{theo}}\): theoretical density calculated by Formula (1); \(d_{BT4}\): theoretical density of \(\text{BaTi}_4\text{O}_9\), 4.54 g/cm\(^3\); \(d_{BST4}\): theoretical density of \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\), 5.80 g/cm\(^3\); \(x\): molar ratio of Sm\(_2\)O\(_3\).5)

The measured and relative densities were shown in Fig. 1. Although the green body was modeled by a CIP process with a 150 Mpa press, the relative densities in Fig. 1 were not larger than 95%. The measured densities increased with \(x\) from 4.49 to 5.12 g/cm\(^3\), but the relative densities decreased from 93.7 to 92.3%. Figure 2 was the SEM of the ceramic samples. The larger granular in Fig. 2 belonged to \(\text{BaTi}_4\text{O}_9\) phases, while the smaller granular to \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\) phases. When \(x < 60\) mol %, \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\) phases crystallized in a shape of fiber dispersed along the \(\text{BaTi}_4\text{O}_9\) crystalline boundary. With the increase of Sm\(_2\)O\(_3\) content, more and more \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\) phase crystallized and the shape of granular tended to be widened. In other words, more and more crystalline boundary forms, which could account for the decrease of relative densities.

3.2 XRD patterns

Both \(\text{BaTi}_4\text{O}_9\) and \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\) have an orthorhombic structure, but their space groups are different. The space group of \(\text{BaTi}_4\text{O}_9\) is Pnmm (No.59), while that of \(\text{BaSm}_2\text{Ti}_4\text{O}_9\) is Pbam (Table 1).

Table 1. The dependence of resonant frequency, dielectric constants, quality factors on the sizes of the samples

<table>
<thead>
<tr>
<th>No.</th>
<th>diameter × height (/mm × mm)</th>
<th>Resonating frequency (/GHz)</th>
<th>Dielectric const.</th>
<th>Quality factor (/GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.56 × 8.82</td>
<td>3.5807</td>
<td>39.7</td>
<td>8300</td>
</tr>
<tr>
<td>2</td>
<td>18.52 × 8.98</td>
<td>3.5465</td>
<td>42.0</td>
<td>5200</td>
</tr>
<tr>
<td>3</td>
<td>19.92 × 9.82</td>
<td>3.3565</td>
<td>44.0</td>
<td>2800</td>
</tr>
<tr>
<td>4</td>
<td>19.07 × 9.82</td>
<td>2.7824</td>
<td>60.1</td>
<td>1500</td>
</tr>
</tbody>
</table>

Fig. 1. Variation of measured and relative densities of \(\text{BaTi}_4\text{O}_9/\text{BaSm}_2\text{Ti}_4\text{O}_{12}\) composite ceramics with Sm\(_2\)O\(_3\) content.

Fig. 2. SEM of \(\text{BaTi}_4\text{O}_9 + x\text{Sm}_2\text{O}_3\) composite ceramics (\(x = 20, 40, 60\) and 80 mol %) (BT4: \(\text{BaTi}_4\text{O}_9\) phases; BST: \(\text{BaSm}_2\text{Ti}_4\text{O}_{12}\)).
Figure 3 presented the XRD patterns of ceramic samples. For all samples, there existed only two phases, i.e., BaTi$_4$O$_9$ phases with a JCPDF No. 34-0070 and BaSm$_2$Ti$_4$O$_{12}$ phases with a JCPDF No. 44-0062. In the quasi-ternary phase diagram of BaO–TiO$_2$–Sm$_2$O$_3$, BaTi$_4$O$_9$ and BaSm$_2$Ti$_4$O$_{12}$ are two of the most stable compounds. When preparing BaTi$_4$O$_9$ ceramic samples at high temperatures, Sm$_2$O$_3$ would diffuse into the lattice of BaTi$_4$O$_9$, and the solid state reaction could be written grossly as:

$$\text{BaTi}_4\text{O}_9 + \text{Sm}_2\text{O}_3 \rightarrow \text{BaSm}_2\text{Ti}_4\text{O}_{12}$$

3.3 Dielectric properties

The dielectric constant, quality factor and temperature coefficients of BaTi$_4$O$_9$/BaSm$_2$Ti$_4$O$_{12}$ composite ceramics were shown in Figs. 4(a)–4(c), respectively. In Fig. 4, all solid lines stood for the calculated values of dielectric constant, quality factor and temperature coefficient. The dotted line was calculated by Formulas (1)–(3) [2,5].

The dielectric constants in Fig. 4(a) increased from 39.7 to 60.0, meanwhile the calculated dielectric constants increased from 41.9 to 63.0. The difference between the calculated and measured dielectric constant should be attributed to the presence of pores in the composite, accompanying with the decrease of relative densities in Fig. 1. The same difference also presented in Fig. 4(b). The measured quality factors for $x = 20, 40, 60$ and $80 \text{ mol\%}$ were 8300, 5200, 2800 and 1500, respectively. On the other hand, the calculated quality factors for $x = 20, 40, 60$ and $80 \text{ mol\%}$ were 9100, 6800, 5200 and 3500, respectively.

But for temperature coefficient, the calculated values corresponded well with the measured ones. A near-zero temperature coefficient about $+2.2 \text{ ppm} / ^\circ\text{C}$ was gained at $x = 40 \text{ mol\%}$.

The facts indicated that for the Formulas (1)–(3) of composite dielectric properties, the temperature coefficients depend heavily on the composition of the composite, with the other two properties depends heavily on both the composition and the microstructure variations. For example, the density (or the amount of micropores) will exert marked influence on the dielectric loss and constant. The abrupt decrease of relative densities of the sample for $x = 60$ and $80 \text{ mol\%}$, corresponds to an abrupt decrease of the qualities factors, as well as that of dielectric constants. In Fig. 2, the relative densities of ceramic samples decreased with the increasing content of Sm$_2$O$_3$. Correspondingly, in Fig. 4(b), the discrepancies between the calculated and measured quality factors become larger and larger.

However, as illustrated in our precious work, the low valence titanium ions also play great roles in adjusting the dielectric properties, so XPS analysis was carried out to investigate the effects [10].

3.4 XPS analysis

In order to analyze the origin of difference in Fig. 4(b), XPS analysis of 20% Sm$_2$O$_3$ doped samples was carried out, as shown in Fig. 5.

The XPS peaks in Fig. 5 could be fitted by six peaks. The six peaks were 454.66, 457.11, 458.62, 461.14, 463.00, 464.43 eV. The peaks at 454.66 and 461.14eV corresponded with the binding energy of Ti2p3/2, Ti2p1/2 of Ti$^{2+}$, respectively. The peaks at 457.11 and 463.00 eV were the binding energy of Ti2p3/2, Ti2p1/2 of Ti$^{3+}$, respectively. And the peaks at 458.62 and 464.43 eV were the binding energy of Ti2p3/2, Ti2p1/2 of Ti$^{4+}$, respectively.

![Figure 3](image1.png)

**Fig. 3.** XRD patterns of BaTi$_4$O$_9$–xSm$_2$O$_3$ composite ceramics ($x = 20, 40, 60$ and $80 \text{ mol\%}$).

![Figure 4](image2.png)

**Fig. 4.** Variation of dielectric constant (a), dielectric loss (b) and temperature coefficients (c) as a function of the concentration of Sm$_2$O$_3$ [solid line: measured values; dotted line: Calculated values according to Formulas (1)–(3)].

![Figure 5](image3.png)

**Fig. 5.** XPS analysis of 20% Sm$_2$O$_3$ doped samples.
Such an abrupt increase of Ti$^{3+}$ and Ti$^{2+}$ content should be attributed to the heat diffusion of Sm$^{3+}$ into the lattice of BaTi$_4$O$_9$ ceramics, which could be written as:

$$\text{Sm}_2\text{O}_3 + \text{BaTi}_4\text{O}_9 \rightarrow \text{Sm}^{3+}_{\text{Ba}} + (1 - x)\text{Ti}^{4+}_{\text{Ti}} + x/2\text{Ti}^{2+}_{\text{Ti}} + 3\text{O}_2$$ (7)

Those low-valence titanium could also be represented by Ti$^{4+}$, circled by one or two electrons. If Sm ions occupy titanium sites (p-type doping), the amount of holes overwhelm that of electrons, which will lead to the decrease of the content of low-valence titanium. The fact that the amount of low-valence titanium cations increases could prove that trace amount of Sm$^{3+}$ could occupy the Ba-sites.10)

The charge balance equation could be written as:

$$[\text{Ti}^{4+}_{\text{Ti}}] + [\text{Ti}^{2+}_{\text{Ti}}] + [\text{e}^-] = [\text{Sm}^{3+}_{\text{Ba}}] + [\text{V}^{4+}_{\text{O}}] + [\text{h}^+]$$ (8)

Since the concentration of impurities was much higher than those of the carriers and oxygen defects, the concentration of electron and holes could be ignored:

$$[\text{Ti}^{4+}_{\text{Ti}}] + [\text{Ti}^{2+}_{\text{Ti}}] \approx [\text{Sm}^{3+}_{\text{Ba}}]$$ (9)

The equation above showed that the abrupt increase of Ti$^{3+}$ and Ti$^{2+}$ content was derived from the occupation of Ba-sites by Sm$^{3+}$. T. Negas had argued that the Ti$^{2+}$ should be the cause of dielectric loss.2) Therefore, the difference in Fig. 4(b) all although Sm$_2$O$_3$ content between the calculated and measured quality factor should be attributed to the large content of Ti$^{3+}$ and Ti$^{2+}$. But for the samples with high content of Sm$_2$O$_3$, the discrepancies become larger than that with low Sm$_2$O$_3$ content. For the convenience, the relative densities of ceramic samples were depicted again. The relative densities corresponded well with the quality factors, indicating the decrease of quality factor (esp. for the samples with high Sm$_2$O$_3$ content) should be ascribed to the decrease of relative densities.

Therefore, the decrease of quality factors should be attributed to the two aspects of reasons. The first is the low-valence titanium cations, which should be responsible for the discrepancies through the $x$ value ($x = 20, 40, 60$ and $80\text{ mol}\%$). Another one is the relative densities (or pores), which are the origin of the larger discrepancies when $x$ become larger and larger.

4. Conclusions

BaTi$_4$O$_9$/BaSm$_2$Ti$_4$O$_{12}$ composite ceramics in a form of BaTi$_4$O$_9$ + xSm$_2$O$_3$ ($x = 20, 40, 60, 80\text{ mol}\%$) was prepared at 1300°C for 6 h after a CIP process at 150 Mpa. XRD patterns showed the composite ceramics was composed of BaTi$_4$O$_9$ and BaSm$_2$Ti$_4$O$_{12}$ phases. When $x$ increased, the relative and measured densities decreased, while the dielectric loss and constant increased. For all value of $x$, the temperature coefficients varied linearly with $x$. At $x = 40\text{ mol}\%$, a near-zero temperature coefficient $+2.2\text{ ppm/}°\text{C}$ was obtained.

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