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# Co-Precipitation Synthesis and Characterization of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> Ceramic

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Strontium bismuth tantalate (SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>) was synthesized by a co-precipitation method. The sample was characterized by x-ray powder diffraction patterns (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results of the dielectric properties are reported at room temperature. No secondary phases were found while heating the powder at 850°C and the pure SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> phase was formed, as revealed by XRD. The characteristic bands for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> were observed by FTIR at approximately 619 cm<sup>-1</sup> and 810 cm<sup>-1</sup>. SEM micrographs for the sample displayed thin plate-like grains. The grain size was less than 1 μm and the crystallite size of about 24 nm. Dielectric response at room temperature shows that the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic has low loss values, and the flattening of the dielectric constant at higher frequencies. The observed Curie temperature is comparable with those reported in the literature.

**Key words:** SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, co-precipitation, dielectric

## INTRODUCTION

Aurivillius phases have the general formula (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup>(A<sub>n-1</sub>B<sub>n</sub>O<sub>3n+1</sub>)<sup>2-</sup>, where A stands for a divalent cation (e.g., Ca<sup>2+</sup>, Ba<sup>2+</sup>), B for a tetravalent or pentavalent (e.g., Nb<sup>5+</sup>, Ti<sup>4+</sup>), and are the perovskite blocks A<sub>n-1</sub>B<sub>n</sub>O<sub>3n+1</sub>.<sup>1</sup> Strontium bismuth tantalate (SBT), SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, belongs to the layered perovskite ferroelectrics where the crystal consists of the stacking of alternating layers of Bi<sub>2</sub>O<sub>2</sub> and pseudo-perovskite SrTa<sub>2</sub>O<sub>7</sub> units with double TaO<sub>6</sub> octahedral layers along the *c*-axis.<sup>2</sup> The layered perovskite-like ferroelectric of SBT is attractive for the development of non-volatile random access memories because of its excellent fatigue characteristic.<sup>3</sup> SBT is usually obtained through the mixture of oxides, Bi<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> and SrCO<sub>3</sub>, which gives large particles and requires high temperatures for

the synthesis of this compound.<sup>4</sup> Other methods used for the synthesis of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder are: the sol-gel method,<sup>5</sup> chemical routes,<sup>6</sup> solution combustion technique,<sup>7</sup> and hydrothermal process.<sup>8</sup> A study of many ceramics of the same chemical compound, but synthesized under different conditions, might reveal trends in the crystallite size, which in turn can be related to the properties of the product. For random access memory applications, it is necessary to obtain the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> materials with low dielectric loss, low conductivity and high fatigue properties.<sup>9</sup> To prevent the volatilization of Bi<sub>2</sub>O<sub>3</sub> during sintering above 1000°C, which could result in oxygen and bismuth vacancies, it is therefore desirable to dope SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> by rare earth elements.<sup>10,11</sup> Meanwhile, an accurate amount of Bi<sub>2</sub>O<sub>3</sub> oxide must be added to compensate experimentally for the loss characteristics of the Bi<sub>2</sub>O<sub>3</sub> oxide. To our knowledge, it does not resolve many practical physical issues such as the microstructure-property relationship and the physical nature leading to the change of the dielectric

properties of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramics. In this regard, we report a co-precipitation method to obtain SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> with sub-micron grain size. X-ray powder diffraction patterns (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) are used to characterize the synthesized material. Dielectric measurements were performed.

## EXPERIMENTAL

A flowchart of the co-precipitation procedure used is shown in Fig. 1. A stoichiometric amount of SrCl<sub>2</sub>·6H<sub>2</sub>O (Normatom) was dissolved in distilled water, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (Fluka Chemika, 99.0%) was dissolved in a minimum amount of dilute HNO<sub>3</sub> (Panreac, 65%) to avoid precipitation of Bi ions, and Ta<sub>2</sub>O<sub>5</sub> (Fluka Chemika, 99.9%) was dissolved in a minimum amount of HF (Riedel-de Haën, 40%). The three limpid solutions were mixed together, followed by the addition of KOH (Acros Organics) solution (10 M) until pH = 12 to ensure complete precipitation. The precipitate was filtrated by washing several times with distilled water. After drying in the oven, the precursor was heated in a furnace at 400°C for 12 h, and then at a rate of 5°C/min to 800°C and kept at this temperature for 24 h. The pellet was sintered at 850°C for 12 h. Both sides of the sintered sample were painted with silver paste and fired to form the electrodes.

X'Pert HighScore Plus software (PANalytical) was used to estimate the degree of crystallization. The dried sample was ground with KBr to form a mixture containing 1% mass of the sample, and a small pellet of the mixture was pressed and scanned by FTIR (KBr-pellet; Bruker Vertex 70 DTGS). The microstructure of the sintered pellet was analyzed by SEM with 10 kV of accelerating voltage in a high

vacuum. The dielectric properties were investigated at a range from room temperature to 400°C using a LCR meter HP 4284A.

## RESULTS AND DISCUSSION

Figure 2a shows the XRD pattern of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder. All Bragg peaks of this sample were found to correspond to the layered perovskite SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> crystal structure (JCPDS no 01-070-4062). No pyrochlore phase was found while heating the powder at 800°C. The refined lattice parameters are  $a = 5.51752 \text{ \AA} \pm 0.00085 \text{ \AA}$ ,  $b = 5.52500 \text{ \AA} \pm 0.00023 \text{ \AA}$  and  $c = 25.08384 \text{ \AA} \pm 0.00203 \text{ \AA}$ . These parameters are comparable with those reported ( $a = 5.5146 \text{ \AA}$ ,  $b = 5.5246 \text{ \AA}$  and  $c = 24.9017 \text{ \AA}$ ) in the literature.<sup>12</sup>

Crystallite size and micro-strain were measured according to the method of Williamson and Hall<sup>13,14</sup> (Fig. 2b).

$$\beta \cos \theta = \frac{0.89}{D} \lambda + 4\epsilon \sin \theta \quad (1)$$

where  $\beta$  is the integral breadth,  $D$  is the crystallite size, ( $\epsilon$ ) the micro-strain and ( $\theta$ ) the diffracted angle. The reflections with a low intensity of the peaks were excluded from the analysis. The slope corresponds to the strain and the intercept corresponds to the crystallite size. The average crystallite size was  $\sim 24 \text{ nm}$  and micro-strain was about  $\sim 7.26 \times 10^{-4}$ . The crystallite size/strain deduced from the  $\beta \cos \theta$  versus  $\sin \theta$  described the formation of nanoparticles.

Figure 3 shows the FTIR spectrum of the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder. The bands at 3452 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> are due to water molecules. The bands located at 2387 cm<sup>-1</sup> can be attributed to CO<sub>2</sub>. Bands at 1386 cm<sup>-1</sup>, 2853 cm<sup>-1</sup>, and 2929 cm<sup>-1</sup>

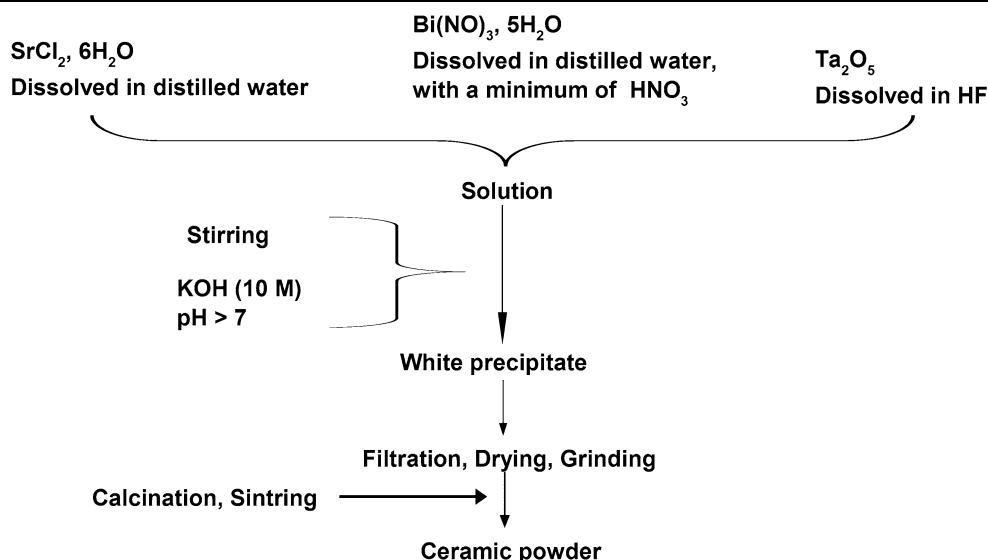


Fig. 1. Flowchart for the preparation of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> powder by co-precipitation.

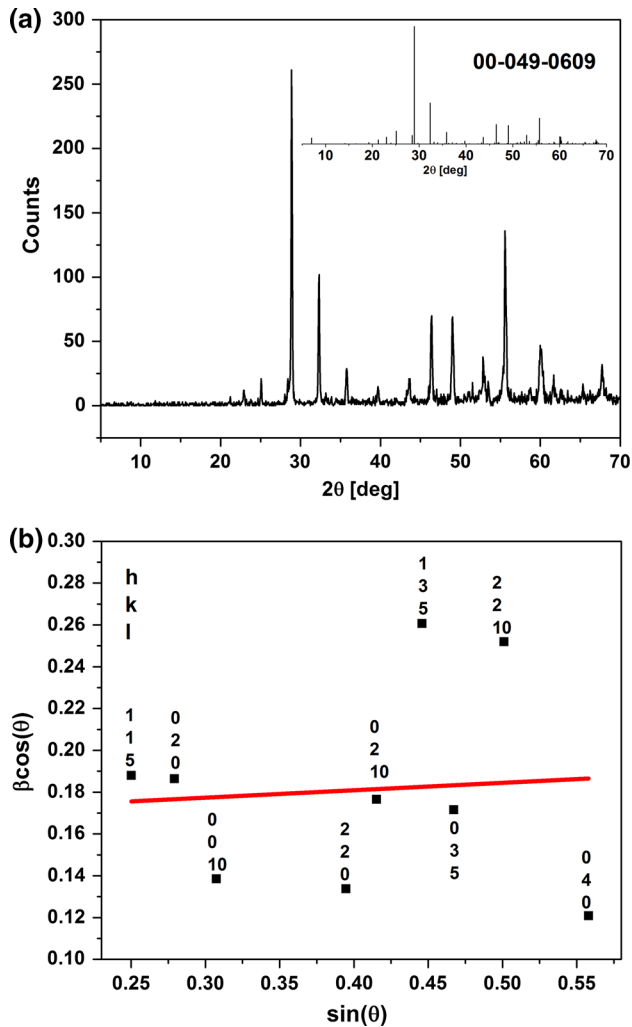


Fig. 2. (a) XRD pattern and (b) corresponding Williamson–Hall plot for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder.

indicate the presence of residual organics, and 619 cm<sup>-1</sup> and 810 cm<sup>-1</sup> are expected for octahedral stretching TO<sub>6</sub>. These two infrared absorption bands are related to the crystallization of the phase SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>.<sup>12,14</sup> Also, note there is no presence of residual precursors or unwanted secondary phases at a temperature of 800°C.

Figure 4 shows the cross-sectional microstructure investigated by SEM of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic. The sintered pellet exhibits less porosity, relatively dense structure, small rod-like and plate-like shaped grains. The plate-like morphology has been considered to be the characteristic grain growth of Aurivillius microstructures.<sup>15–17</sup> The obtained samples are micro- to nanograined and therefore contain well developed grain boundaries and free surfaces. It has recently been demonstrated that the physical properties of pure and doped fine-grained oxides strongly depend on the presence of defects like interphase boundaries and grain boundaries.<sup>7,14</sup>

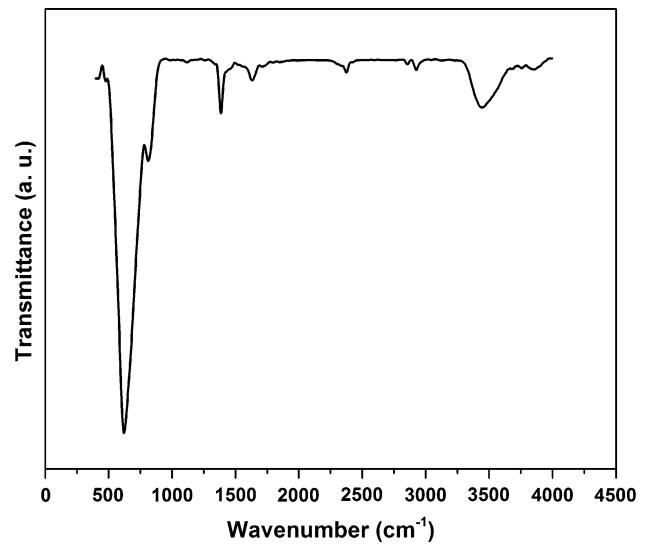


Fig. 3. FTIR spectrum of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder.

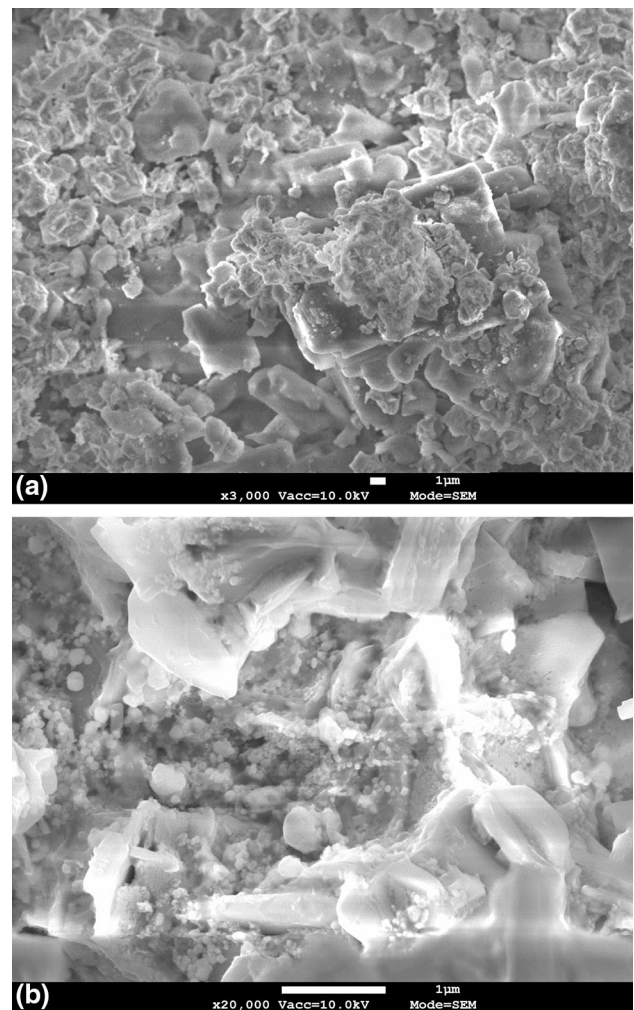


Fig. 4. (a, b) SEM images of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic.

Figure 5 shows the temperature-dependent dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan\delta$ ) for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic at room temperature. Both the  $\epsilon'$  and  $\tan\delta$  values decrease with increasing frequency. The dielectric constant decreases significantly with frequency and ranges from 287 to 94 in the frequency range of 100 Hz–10 kHz. In general, for all materials, the dielectric constant continuously decreases with frequency, due to the space charge polarization and interface effect.<sup>17</sup> Another explanation suggests that these observations may be due to the fact that the dipoles cannot follow the rapid variation of the applied field.<sup>15,18</sup> For the analysis of frequencies below 10 kHz down to 1 MHz,  $\epsilon'$  remains constant around a value of  $\sim 86$ . The dielectric loss is found to be less than  $\sim 0.005$  when measured at 100 kHz, which is lower than those reported from SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramics prepared by a solid-state method.<sup>19,20</sup> The frequency dependence of the dielectric properties at room temperature shows low loss values at higher

frequencies and the flattening of dielectric constant, which are very desirable in nonvolatile ferroelectric random access memory applications. The plot of the temperature-dependent dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan\delta$ ) at different frequencies for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic is shown in Fig. 6. A Curie temperature is observed at 330°C, which is in good agreement with the reported value (310°C  $\pm$  20°C).<sup>17,21</sup> It may also be noted that the values of dielectric loss do not exceed the value of 0.5 over the temperature range of 50–400°C.

As noted in the “Introduction”, the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramics suffer from high dielectric loss due to the volatilization of bismuth during the sintering process at temperatures greater than 1000°C. The losses are attributed to increased conduction arising from lattice defects induced through volatilization of the bismuth oxide.<sup>22</sup> With the synthesis conditions described above, the grain sizes are found to be extremely small, and may give rise to resistive and capacitive grain boundaries. As

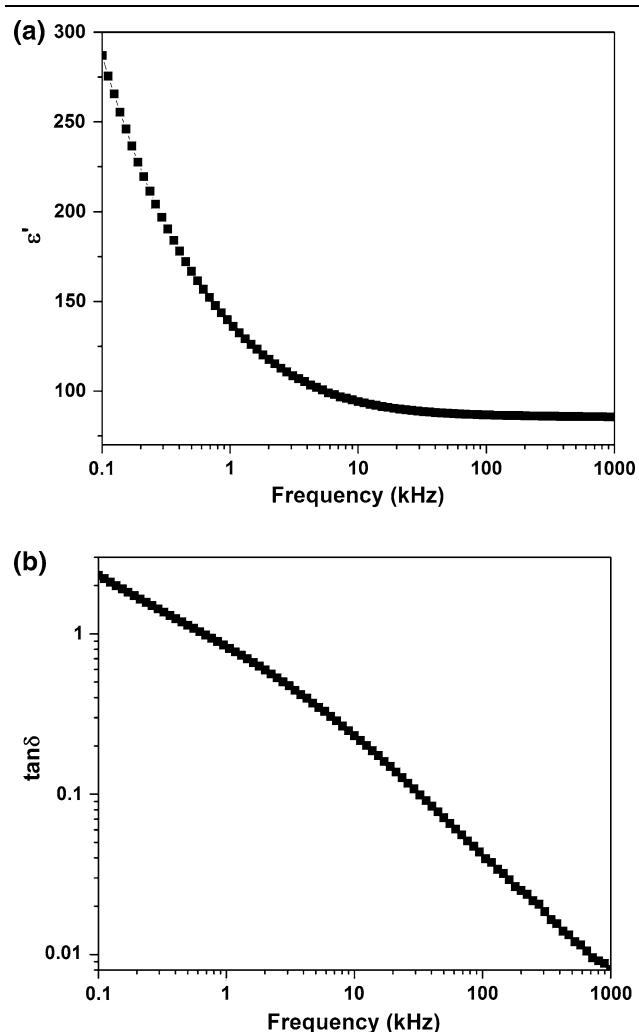


Fig. 5. (a) Frequency dependence of dielectric constant and (b) dielectric loss at room temperature for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic.

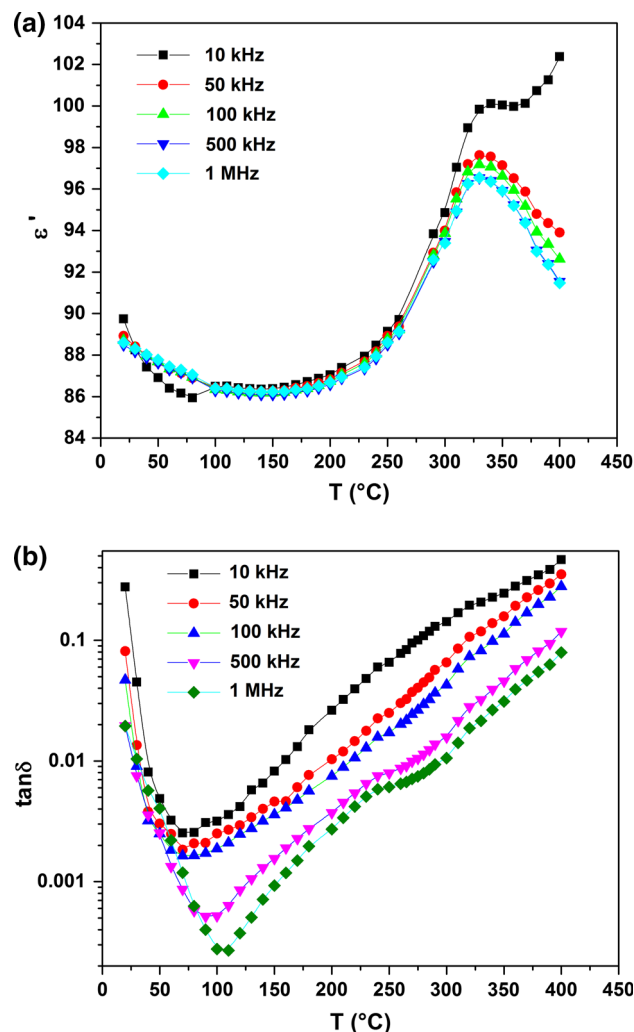


Fig. 6. (a) Temperature-dependent dielectric constant and (b) dielectric loss at different frequencies for SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic.

improved elsewhere,<sup>23,24</sup> the dielectric loss appears to be a strong function of grain size. Thus, the decrease in loss can be understood from the fact that the lower conductivity of the fine-grained ceramics is due to the higher density of resistive grain boundaries. It can be concluded that our ceramic processing conditions may reduce lattice defects, which increases the resistivity and reduces dielectric loss.

### CONCLUSION

Nanosized SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic powder was synthesized through a simple co-precipitation method. This process seems to afford a means towards an environmentally friendly and inexpensive aqueous synthesis. The Williamson–Hall method was used to understand the contributions of lattice strain and crystalline size to the XRD peaks. The dielectric properties at room temperature of the proposed material can match those of the SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> ceramic prepared by solid-state reaction. The dielectric constant remains constant with a loss of 0.005 at a frequency of 100 kHz. The co-precipitation route for sample preparation shows advantages over the solid-state reaction approach, such as no evidence for bismuth volatilization in the processing condition.

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