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Spark-plasma-sintering of bulk $SrBi_2Ta_2O_9$ materials

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$SrBi_2Ta_2O_9$ is a layered-type perovskite ferroelectric material. It was first synthesized and investigated by Aurivillius in 1949 [1]. Because $SrBi_2Ta_2O_9$ possesses excellent electrical properties such as low leakage current, low operating voltage etc., it is an attractive material for ferroelectric random access memory (FRAM). However, layered-type perovskite ferroelectrics suffer from high processing temperature, low remanent polarization and high dielectric loss [2]. It is reported that $SrBi_2Ta_2O_9$ decomposes at temperatures higher than 1150 °C [3]. Therefore, it is very difficult to get dense ceramics with good dielectric and ferroelectric properties via conventional sintering. Some attempts to improve the properties of $SrBi_2Ta_2O_9$ have been carried out by doping with various metal oxides [4, 5]. However, the densification improvement by controlling sintering conditions has not been reported.

Spark plasma sintering (SPS) is a new rapid sintering method, which has been developed recently for the fabrication of ceramics and composites. The most important feature of SPS is the pressed powders are heated by the spark discharge between the particles. As a result the samples can be sintered uniformly and rapidly and dense ceramics with fine grains can be obtained in a very short holding time. It has been reported that SPS has been used to fabricate a variety of materials such as ZrO_2 [6], Nb/Nb_5Si_3 [7] and Ni_2MnGa [8]. However, few reports have been found on its applicability to bulk $SrBi_2Ta_2O_9$ materials.

In the present study, $SrBi_2Ta_2O_9$ powders were prepared using a conventional solid-state reaction method from commercial powders of Bi_2O_3, $SrCO_3$ and Ta_2O_5, which were ball-milled for 24 h. The dried mixture was calcined at 950 °C for 2 h in air and then crushed into powder. The obtained powder was placed into a graphite die (2 cm in diameter) and sintered using spark-plasma-sintering. The applied pressure was 39 MPa and the heating rate approximately 200 °C min^{-1}. After holding at the desired temperature for approximately 3 min, the applied current was dropped to zero, the pressure was released and the sample was cooled to room temperature, cooling rate of about 600 °C min^{-1}. The as-sintered pellets were black in appearance due to the contamination of carbon from the die. After annealed at 800 °C for 2 h, the yellow-white appearance of the pellets was restored. For comparison, $SrBi_2Ta_2O_9$ ceramic samples were also sintered using conventional methods. The bulk densities of the pellets were measured using Archimedes method. The crystal phases of pellets were determined by X-ray diffraction (XRD) using Cu K_α radiation. The fracture structures of the samples were observed using a scanning electron-microscope (SEM, JSM 6301F). The permittivity was measured at 1 KHz from room temperature to 400 °C via an impedance analyzer (Mode HP4194A, Hewlett Packard Co. Ltd., Tokyo, Japan).

Fig. 1 shows XRD patterns of SPS pellets sintered at different temperatures. Below 1100 °C, a well-developed crystal structure of $SrBi_2Ta_2O_9$ is identified, and no secondary phase is observed. However, at temperatures higher than 1100 °C, secondary phase(s) can be found, which indicates the decomposition of $SrBi_2Ta_2O_9$. This can be attributed to the evaporation of Bi_2O_3. A similar phenomenon has been found in $SrBi_2Ta_2O_9$ sintered by a conventional method [3] .

The relative densities after annealing are plotted as a function of sintering temperature in Fig. 2. It is observed that at 900 °C greater than 95% of theoretical density has been reached in the SPS sample while for the conventional sintering method the density is found to be only about 78% of theoretical density. This indicates higher density $SrBi_2Ta_2O_9$ can be obtained at a relatively low temperature by SPS and thus decomposition can be avoided effectively. The decrease in density for SPS pellets at sintering temperatures higher than 1150 °C might result from the decomposition of $SrBi_2Ta_2O_9$. As follows:

$$SrBi_2Ta_2O_9 \longrightarrow SrTa_2O_6 + Bi_2O_3 \qquad (1)$$

To quantify the degree of decomposition the following equation is used:

$$\text{Decomposition ratio} = 1 - \Sigma I_{SBT(hkl)} / \Sigma \left(I_{SBT(hkl)} + I_{ST(hkl)} \right) \qquad (2)$$

where $I_{SBT(hkl)}$ and $I_{ST(hkl)}$ are the intensities of the diffraction peaks of $SrBi_2Ta_2O_9$ and $SrTa_2O_6$, respectively, appearing from $2\theta = 20$ to 45 °C. The effect of the sintering temperature upon the decomposition of $SrBi_2Ta_2O_9$ is presented in Fig. 3. Compared with conventional sintering, the rate of decomposition for SPS is relatively low although decomposition starts earlier. This might be related to the heating method in SPS. During the SPS process, the powders were encapsulated in a graphite mold and sintered under uniaxial pressure and thus the evaporation of Bi_2O_3 can be suppressed and the decomposition rate slowed down. Fig. 4 shows typical fractures of pellets sintered at 1000 °C using SPS

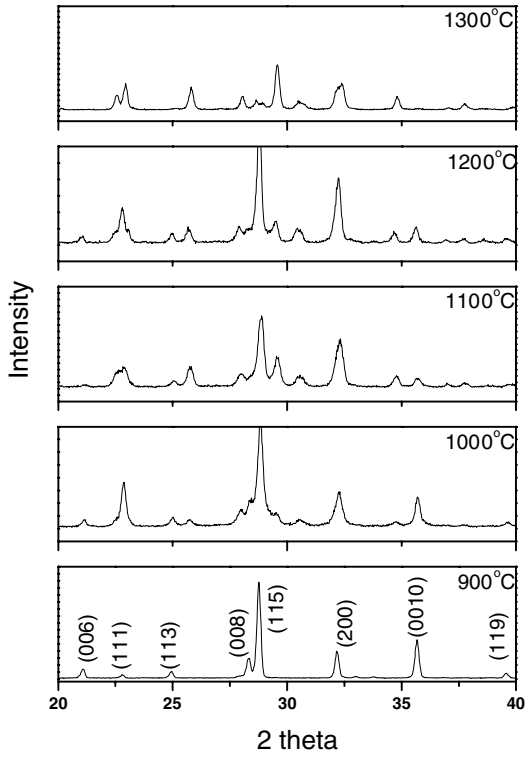


Figure 1 XRD patterns curves of SPS pellets sintered at different sintering temperatures.

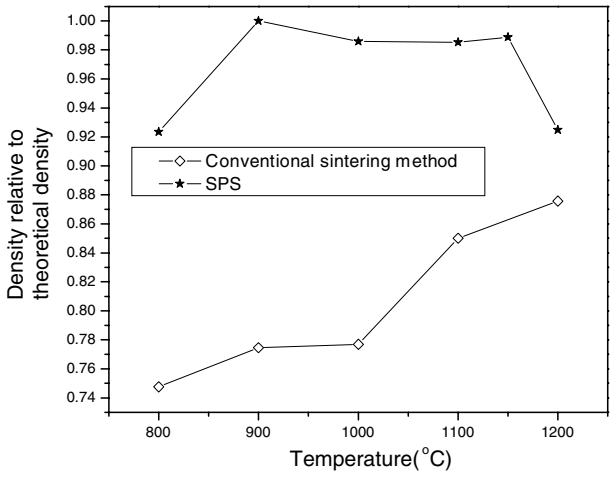


Figure 2 The curve of relative densities versus sintering temperatures.

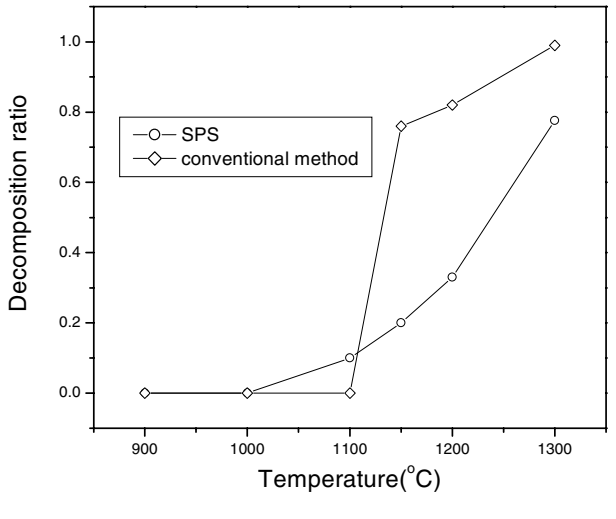
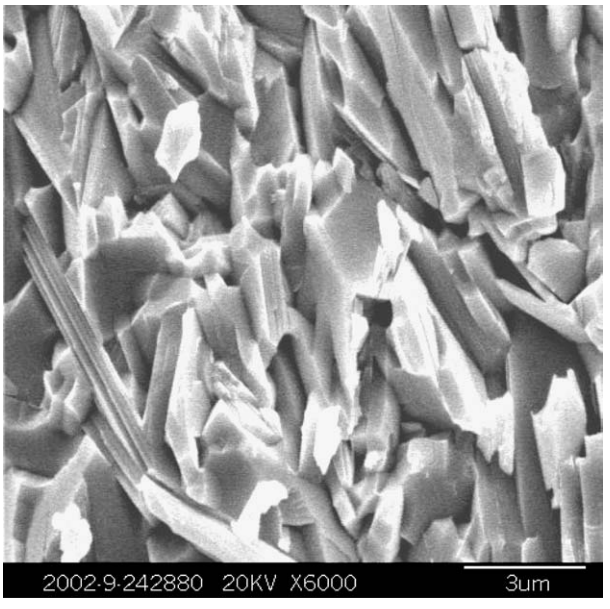
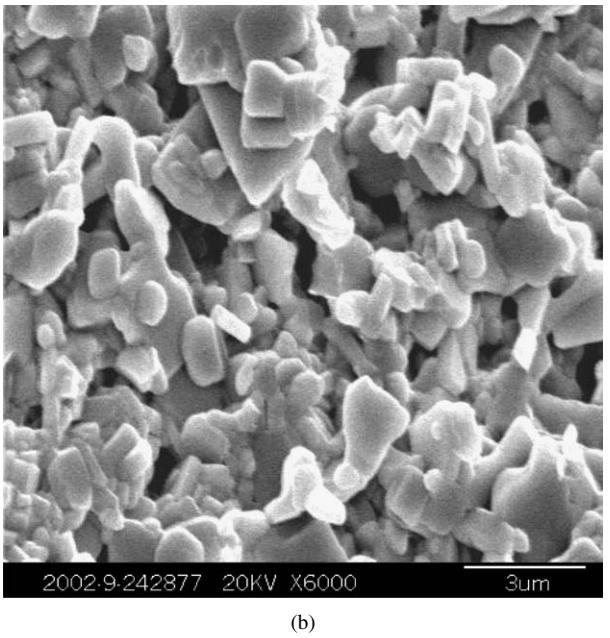


Figure 3 The curve of decomposition ratio versus sintering temperatures.



(a)



(b)

Figure 4 SEM photographs of pellets sintered at 1000 °C by (a) SPS and (b) conventional sintering method.

and conventional sintering. For the samples prepared by a conventional method, a porous microstructure can be observed, confirming the lower sinterability. However, for SPS samples anisotropic grain growth and a relatively high density are observed.

In order to quantify the degree of anisotropic grain growth, the following equation was used:

$$F = (P - Po)/(1 - Po) \tag{3}$$

where $P = \Sigma I_{SBT\,(h00)}/\Sigma I_{SBT\,(hkl)}$, and $I_{SBT(h00)}$, $I_{SBT\,(hkl)}$ are the sum of the intensities of (h00) reflections and (hkl) reflections in the sintered specimens, respectively. P_0 is the value of P for random orientation powders.

Fig. 5 shows F as a function of temperature for both sintering methods. For samples made by conventional sintering there is obvious preferred orientation, while

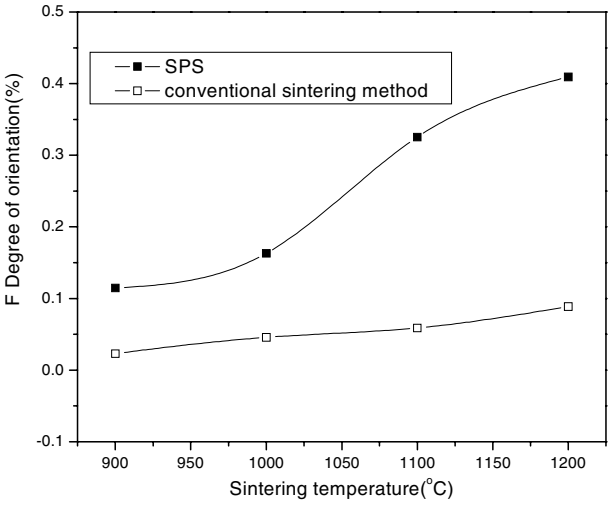


Figure 5 F factor of $SrBi_2Ta_2O_9$ as a function of temperature.

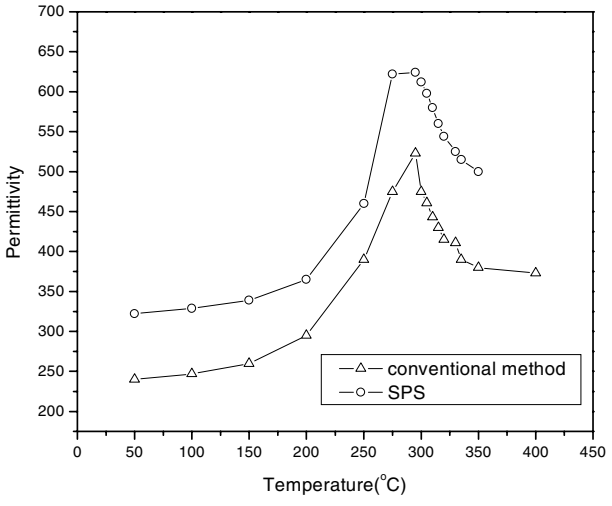


Figure 6 Temperature dependence of permittivity at 1 KHz for $SrBi_2Ta_2O_9$ ceramics.

for SPS specimens, F increases with increasing temperature, which illustrates $SrBi_2Ta_2O_9$.

SPS is actually a combination of hot-pressing and the plasma generation. During the heating process, a uniaxial pressure was applied to the sample. When the sintering temperatures were higher than 814 °C, which is the melting point of Bi_2O_3, molter Bi_2O_3 tends to flow along a-b planes under pressure and enhances anisotropic grain growth. Since polarization occurs parallel to the *a*-axis [9, 10], SPS would be expected to improve the ferroelectric properties of $SrBi_2Ta_2O_9$. The permittivities at 1 KHz for SPS and conventional sintered pellets over the temperature range 25–400 °C are shown in Fig. 6. It can be seen that the permittivities of SPS samples are higher than those of conventional method products and that a broader peak is also observed for SPS samples. Thus, the improved densification and orientated growth resulting from SPS enhance the dielectric behavior of $SrBi_2Ta_2O_9$ [11] and broader transition can be attributed to the fine grains resulting from the fast heating rate during SPS [12].

It can be concluded that higher density $SrBi_2Ta_2O_9$ ceramics can be obtained at relatively low temperature by SPS. SPS suppresses decomposition and enhances anisotropic grain growth such that the obtained pellets exhibit good dielectric properties.

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