Microstructure and characteristics of BaTiO₃ ceramic with 4PbO–B₂O₃ (sintering aid)

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Many lead-free materials, such as Bi-based compounds, BaTiO₃ or alkaline niobate compound, have been intensively studied. The microstructure and characteristics of BaTiO₃ ceramic are significantly influenced by addition of 4PbO–B₂O₃. Under low sintering temperatures, the grain growth of BaTiO₃ ceramic is enhanced by capillary action, rearrangement and solution-replication of the liquid phase. At high sintering temperatures, exaggerated grain growth of BaTiO₃ ceramic is restrained by the presence of a liquid phase. The glass frit also has significant effect on the dielectric and piezoelectric properties of BaTiO₃ ceramic. The measured density of BaTiO₃ ceramic with suitable addition of 4PbO–B₂O₃ glass frit and sintering temperature can get 95.7–98.8% dense. The peak value of the $K_{33}$ was 2500 with addition of 0.2 mol% glass frit at the sintering of 1250°C for 4 h. The maximum value of the $k_p$ was 0.36 with addition of 0.2 mol% glass frit at the sintering of 1350°C for 4 h. With suitable amounts of glass frit and an optimized sintering temperature, the density is enhanced and the values of the dielectric and piezoelectric properties are improved.

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1. Introduction

Recently, lead-free or low-lead-content piezoelectric materials are being extensively investigated to replace PZT-based ceramics. Barium titanate (BaTiO₃), a well-known ferroelectric material, possesses a high dielectric constant, chemical stability, mechanical stability, and ease of preparation and use in the form of ceramic samples. Sintering of BaTiO₃ ceramic under 1350°C–1450°C is required for densification of samples. Thus, the solidified intergranular phase exists in many sintered disks, causing a decrease in the dielectric constant. Therefore, a liquid phase should be introduced to induce complete sinterability and lower the sintering temperature. In the past, there were many oxides added as flux for lowering the sintering temperature, such as MgO, LiF, BaLiF₃, V₂O₅–P₂O₅, B₂O₃, and Bi₂O₃. The desirable characteristics of a liquid phase used as a sintering aid are: (i) low melting point (<800°C), (ii) no reaction with BaTiO₃ ceramic, (iii) low viscosity at the sintering temperature.

The properties of PbO-based glass were reported by Fajans and Kreidl. They found this glass not only to have a low flow temperature, but also to show high polarizability which is helpful to polarization of the ceramics. Lead oxide has frequently been used in sintering aids for barium titanate ceramics: PbO in the flux is a readily soluble isovalent substitute for Ba²⁺. Inclusion of lead oxide in the BaTiO₃ ceramics generally improves densification, thus sintering could be carried out either with lower amounts of glass-former, or at lower temperatures. The PbO–B₂O₃ glass frit has been used as a sintering aid for the densification of BaTiO₃ ceramics by Wang et al. They studied the densification of hydrothermal BaTiO₃ sintered with 70 mol% PbO–30 mol% B₂O₃ and 30 mol% PbO–70 mol% B₂O₃ glasses at 850°C for 2 h. They indicated that, with the same amount of glass addition, BaTiO₃ sintered with 70 mol% PbO–30 mol% B₂O₃ shows a better densification compared with that sintered with 30 mol% PbO–70 mol% B₂O₃. The better fluidity and the higher reactivity (better wettability) of the glass with higher PbO content may be the main reason.

In the present work, 4PbO–B₂O₃ was taken as a sintering aid on account of high lead (Pb) content (about 92%) and low flow temperature. Glass containing more than 92% PbO could not be obtained because of crystallization. The eutectic temperature of the 4PbO–B₂O₃ was around 500°C, so it would provide a liquid phase during the sintering process. The effect of the amounts of the 4PbO–B₂O₃ glass frit addition and sintering temperature on the dielectric and piezoelectric properties of the BaTiO₃ ceramic were investigated. By means of SEM observation, grain growth in BaTiO₃ ceramic sintered with glass frit was analyzed.

2. Experimental procedure

The ceramic used in this study was BaTiO₃ and the glass frit used was 4PbO–B₂O₃. The raw materials used for the frit were reagent-grade PbO and B₂O₃. After mixing, the mixture was placed in an alumina crucible and melted in an electric furnace. Because PbO and B₂O₃ will be lost through vaporization, several precautions were taken to ensure compositional accuracy. The glass was melted very rapidly at 900°C–1000°C and all the melts were held no longer than a total of 30 min at 950°C, even for repeated meltings. Once melting was complete, the crucible was removed from the furnace and the molten glass was poured into a bucket of cold water. After drying, the glass was ground in a mortar and pestle and passed through a 325-mesh screen (ASTM size).

The host BaTiO₃ powder was formulated and fabricated by conventional ceramic technology with reagent-grade BaCO₃ and TiO₂. After weighing, the raw materials were mixed with acetone in an alumina ball mill for 4 h. The mixtures were dried and calcined at 1100°C for 4 h. After that, the calcined BaTiO₃ powders

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were mixed with 4PbO–B2O3 glass powder. The mixtures of host BaTiO3 powder and glass powder were homogenized with acetone in the ball mill for 24 h. After drying, the mixtures were pressed into disk 14 mm in diameter and 1 mm in thickness. The samples were covered with an alumina crucible and fired under different temperatures for 4 h. After sintering, the sintered disks were polished and silver paste electrodes were fired on both sides. The poling technique generally involved immersing the samples in silicone oil and subjecting them to a high DC field of 3 kV/mm at 100°C for 30 min. Twenty-four hours after poling, the dielectric and piezoelectric properties were measured with a HP4192A LF impedance Analyzer in reference of the IRE Standards.15)

In order to determine crystal structure, crystal system and lattice constant, the sintered ceramic samples were polished and measured at room temperature by the X-ray diffraction (XRD) method. By using the scanning electron microscope (SEM), the free surface of the sintered ceramic body was observed. The mean grain size was calculated by the line intercept method.16) The density was measured by water immersion measurement method.

3. Results and discussion

The influence of 4PbO–B2O3 glass frit (0–16 mol%) and sintering temperature on the measured density of BaTiO3 ceramic is shown in Fig. 1. At the same temperature, the density increases first, reaches a maximum point, and then decreases with increasing amounts of glass frit. For sintering at 1350°C, the peak value of the density occurs with addition of 0.2–1 mol% glass frit; for sintering at 1250°C, the peak value occurs with the addition of 4 mol% glass frit; and for sintering at 1150°C, the peak value occurs with the addition of 10 mol% glass frit. Figure 2 shows the planar coupling factor kP of BaTiO3 ceramic as function of the amount of glass frit and sintering temperature. The curve of the planar coupling factor shows a similar tendency to that of the measured density. The maximum value of the kP is at the addition of 0.2 mol% glass frit for 1350°C. Figure 3 shows the poled dielectric constant K33 and the dielectric loss tangent of BaTiO3 ceramics as function of the amount of glass frit and sintering temperature. The peak value of the K33 was 2500 and 1950, respectively, with addition of 0.2 mol% glass frit for 1250°C and with addition of 1 mol% glass frit for 1150°C. However, the dielectric constant of the BaTiO3 ceramic for 1350°C decreases with increasing amounts of 4PbO–B2O3. Moreover, BaTiO3 ceramic have higher K33 value for 1250°C than other temperatures. At the same sintering temperatures, the dielectric loss tangent decreases with increasing amounts of 4PbO–B2O3, because the dielectric loss tangent of 4PbO–B2O3 frit has a value below 0.005.

The variation of the dielectric and piezoelectric properties of BaTiO3 ceramic with amounts of 4PbO–B2O3 glass frit can be correlated to variation in microstructure. The influence of the glass frit (0 and 2 mol%) on the microstructure of BaTiO3 ceramic after sintering at 1350°C for 4 h is shown in Fig. 4. As the glass frit is added to the BaTiO3 ceramic, the grain sizes of ceramics with additives are smaller than those of ceramics without additives. Figure 5 shows the microstructure of BaTiO3 ceramic with addition of (A) 0 mol%, (B) 2 mol% and (C) 7 mol% 4PbO–B2O3 after sintering at 1150°C for 4 h. The grain...
sizes of ceramics with additions of glass frit are larger than those of ceramics without additives. In order to find out the distribution of Pb\(^{2+}\) in the BaTiO\(_3\) ceramic, a mapping method is used as shown in Fig. 5(D), which compared to the area shown in the SEM picture of Fig. 5(C). Figure 6 shows the Curie point temperature (determined electrically) of the BaTiO\(_3\) ceramic as a function of the amount of glass frit after sintering at 1350\(^\circ\)C for 4 h. Table 1 shows the effect of the glass frit addition on the lattice parameter in BaTiO\(_3\) ceramic after sintering at 1350\(^\circ\)C for 4 h. The crystalline phase was confirmed by X-ray diffraction, which was a single perovskite phase. In the BaTiO\(_3\) solid solutions, both c and a (the lattice constants) increase as the glass frit addition is increased. This causes the tetragonal \(c/a\) ratio and the Curie temperature of BaTiO\(_3\) ceramic to increase. It is confirmed that Pb\(^{2+}\) is distributed homogeneously in the grain regions. It is believed that BaTiO\(_3\) ceramic sintered with 4PbO–B\(_2\)O\(_3\) can form substitutional solid solution owing to Pb\(^{2+}\) substituting Ba\(^{2+}\) at the A-site.

For the purpose of studying the effect of grain size, the samples were sintered under different temperatures for 4 h. The relationships between the grain size and sintering temperature of BaTiO\(_3\) ceramic with different 4PbO–B\(_2\)O\(_3\) doping amounts are...
shown in Fig. 7. Therefore, the grain sizes of BaTiO$_3$ ceramic increase with increasing amounts of glass frit under a low sintering temperature (1150°C and 1250°C). On formation of a liquid phase, there is a rearrangement of particles to give more effective packing. There is solution of smaller particles and growth of larger particles of material transferred through the liquid phase during the sintering process. When the liquid phase penetrates between particles, the pressure at the contact points leads to an increased solubility such that there is material transfer away from the contact areas, so that the particles’ centers approach one another and shrinkage results. The surface of BaTiO$_3$ ceramic showing liquid capillary depressions between crystals is illustrated in Fig. 5(C). Hence, the grain sizes of BaTiO$_3$ ceramic increase with increasing amounts of glass frit under a low sintering temperature (1150°C and 1250°C). At a high sintering temperature (1350°C), exaggerated grain growth commonly occurs for BaTiO$_3$ ceramic. During the sintering process, when the boundary curvature and the driving force for boundary migration are high, pores are often left behind. The grain growth processes must be actively prevented in order to obtain complete densification. With 4PbO–B$_2$O$_3$ addition to BaTiO$_3$ ceramic, it is a satisfactory way to obtain pore elimination and inhibition of grain growth as shown in Fig. 4. Therefore, the grain sizes of BaTiO$_3$ ceramic decrease with increasing amounts of glass frit under a high sintering temperature (1350°C).

The influence of the glass frit (4 mol%) on the microstructure of BaTiO$_3$ ceramic for different sintering times at 1350°C is shown in Fig. 8 (A) no soaking, (B) 10 min, (C) 30 min and (D) 1 h. The grains contain subgrains in Fig. 8(B). It means BaTiO$_3$ ceramic has a strong tendency for crystallization. Dramatic microstructural changes occur during the initial sintering stage. The events involve particle penetration and fragmentation. Penetration refers to liquid flow through the pore and grain structure by means of a combination of reaction and capillary action. A consequence of penetration is fragmentation of the solid particles. A microstructure of the fragmentation process is shown in Fig. 8(C). The particles undergo rearrangement upon melt formation. Subsequently, liquid penetration are accompanied by swelling occurs and the grains are separated by the penetrating liquid. Subsequent densification occurs as repacking and solution-reprecipitation begin. Fragmentation requires solubility of the solid in the liquid. Solubility of the solid in liquid further aids rearrangement because of particle smoothing concurrent with capillary attraction. Rearrangement is often composed of two stages. Primary rearrangement involves the individual particles, as shown in Fig. 8(B). Secondary rearrangement can also involve particle disintegration and subsequent repacking of fragment, as shown in Fig. 8(C). During the period when the liquid forms and spreads, rearrangement events occur rapidly. Although solution and reprecipitation of the solid occurs concurrently with rearrangement, the rearrangement events dominate the early response. During the second stage of liquid phase sintering, rearrangement ends and solution-reprecipitation processes become dominant. Solution reprecipitation requires solid solubility in the liquid. It is characterized by grain growth, dissolution of small grains, grain rounding and densification, as shown in Fig. 8(D). Particle penetration and fragmentation are the main reasons to slow the grain growth rate.

As for the effect of the 4PbO–B$_2$O$_3$ glass frit on the microstructure of the BaTiO$_3$ ceramic, the grain growth is enhanced in the presence of a liquid phase under a low sintering temperature (1150°C), but is restrained in the presence of a liquid phase under a high sintering temperature (1350°C). The 4PbO–B$_2$O$_3$ glass frit also has significant effect on the dielectric and piezoelectric properties of BaTiO$_3$ ceramic. The theoretical density of BaTiO$_3$ ceramic at room temperature is 6.017 g/cm$^3$. The relative density of BaTiO$_3$ ceramic influences the dielectric constant and the electromechanical coupling factor. Previous reports$^{[5]}$ of BaTiO$_3$ ceramic without sintering aid were 92–95% dense and had $K'_{33}$ of 1700–1800. In this system, BaTiO$_3$ ceramic without addition of 4PbO–B$_2$O$_3$ glass frit, a density of 5.55 g/cm$^3$ (about

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**Table 1. Lattice Constant of BaTiO$_3$ Ceramic as a Function of Amount of 4PbO–B$_2$O$_3$ after Sintering at 1350°C for 4 h**

<table>
<thead>
<tr>
<th>Composition</th>
<th>0 mass%</th>
<th>2 mass%</th>
<th>7 mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>$a = 3.995$</td>
<td>$a = 3.997$</td>
<td>$a = 3.999$</td>
</tr>
<tr>
<td></td>
<td>$c = 4.029$</td>
<td>$c = 4.036$</td>
<td>$c = 4.046$</td>
</tr>
<tr>
<td></td>
<td>$c/a = 1.009$</td>
<td>$c/a = 1.010$</td>
<td>$c/a = 1.012$</td>
</tr>
</tbody>
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Fig. 6. Influence of glass frit 4PbO–B$_2$O$_3$ (0–10 mol%) and the sintering temperature on the Curie temperature of BaTiO$_3$ ceramic.

Fig. 7. Influence of glass frit 4PbO–B$_2$O$_3$ (0–10 mol%) and the sintering temperature on the grain size of BaTiO$_3$ ceramic (a) 1150°C, (b) 1250°C, (c)1350°C.
92.2% dense), a planar coupling factor of 0.34, a dielectric constant of 2000 and a dissipation factor of 0.0155 can be attained at the sintering of 1350°C for 4 h. The $k_p$ and $K_{33}^3$ of BaTiO$_3$ ceramic with suitable addition of 4PbO–B$_2$O$_3$ glass frit were increased resulting from the porosity decreasing and the density increasing. The measured density of BaTiO$_3$ ceramic with suitable addition of 4PbO–B$_2$O$_3$ glass frit and sintering temperature can get 95.7–98.8% dense. The peak value of the $K_{33}^3$ was 2500 with addition of 0.2 mol% glass frit at the sintering of 1250°C. The maximum value of the $k_p$ was 0.36 with addition of 0.2 mol% glass frit at the sintering of 1350°C. In this system, it was found that the electrical properties depended on the material parameters such as porosity, and densification. The grain size has not significant effect on the dielectric and piezoelectric properties of BaTiO$_3$ ceramic. The curve of the planar coupling factor shows a similar tendency to that of the measured density as shown in Fig. 1 and Fig. 2. But the $k_p$ and $K_{33}^3$ of BaTiO$_3$ ceramic with addition of 4PbO–B$_2$O$_3$ glass frit were decreased, especially $K_{33}^3$, by adding excess 4PbO–B$_2$O$_3$. For that may be caused by the dilution of high dielectric constant (BaTiO$_3$ ceramics) with low dielectric constant glass frit (4PbO–B$_2$O$_3$). At the same sintering temperatures, the dielectric loss tangent decreases with increasing amounts of 4PbO–B$_2$O$_3$, because the dielectric loss tangent of 4PbO–B$_2$O$_3$ frit has a value below 0.005.

With suitable addition of glass frit and sintering temperature, a dense structure was obtained. A density of 5.93 g/cm$^3$, a planar coupling factor of 0.36, a dielectric constant of 1875 and a dissipation factor of 0.014 can be attained in BaTiO$_3$ ceramic with 0.2 mol% 4PbO–B$_2$O$_3$ after sintering 1350°C for 4 h. A density of 5.84 g/cm$^3$, a planar coupling factor of 0.32, a dielectric constant of 1750 and a dissipation factor of 0.013 can be attained in BaTiO$_3$ ceramic with 7 mol% 4PbO–B$_2$O$_3$ after sintering at 1250°C for 4 h. A density of 5.76 g/cm$^3$, a planar coupling factor of 0.22, a dielectric constant of 1550 and a dissipation factor of 0.013 can be attained in BaTiO$_3$ ceramic with 10 mol% 4PbO–B$_2$O$_3$ after sintering at 1150°C for 4 h. According to Wang’s results,$^{14}$ a density of 5.35 g/cm$^3$ and a dielectric constant of 1500 were achieved for hydrothermal BaTiO$_3$ sintered with 10 mol% PbO–30 mol% B$_2$O$_3$ contents at 850°C for 30 min. Therefore, good densification and high dielectric constant of BaTiO$_3$ sintered with PbO–B$_2$O$_3$ glass are obtained in the PbO-rich range.

4. Conclusions
The 4PbO–B$_2$O$_3$ flux appears to be a densification promoter for BaTiO$_3$ ceramic. At low sintering temperatures, the grain growth of the ceramics was enhanced by capillary forces, rearrangement and solution-reprecipitation of the liquid phase. At high sintering temperatures, exaggerated grain growth of BaTiO$_3$ was restrained by the presence of a liquid phase. After the liquid forms, the action is primary rearrangement. The solid particles repack under capillary forces form a wetting liquid. Subsequently, the liquid penetrates the grain boundaries and gives fragmentation. Particle penetration and fragmentation are the main

![Fig. 8. Influence of the glass frit (4 mol%) on the microstructure of BaTiO$_3$ ceramic under different sintering time at 1350°C (a) no soaking, (b) 10 min, (c) 30 min and (d) 1 h [Bar = 10 μm].](image-url)
reasons to slow the grain growth rate.

In this system, BaTiO$_3$ ceramic without addition of 4PbO–B$_2$O$_3$ glass frit, a density of 5.55 g/cm$^3$ (about 92.2% dense), a planar coupling factor of 0.34, a dielectric constant of 2000 and a dissipation factor of 0.0155 can be attained at the sintering of 1350°C for 4 h. The 4PbO–B$_2$O$_3$ glass frit has significant effect on the dielectric and piezoelectric properties of BaTiO$_3$ ceramic. The measured density of BaTiO$_3$ ceramic with suitable addition of 4PbO–B$_2$O$_3$ glass frit and sintering temperature can get 95.7–98.8% dense. The peak value of the $K_{33}$ was 2500 with addition of 0.2 mol% glass frit at the sintering of 1250°C for 4 h. The maximum value of the $k_p$ was 0.36 with addition of 0.2 mol% glass frit at the sintering of 1350°C for 4 h. With suitable additions of glass frit, the sintering temperature and the porosity are decreased and the density is increased. Hence, the dielectric and piezoelectric properties of BaTiO$_3$ ceramic with additives are improved comparing to those of ceramics without additives.

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