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Influence of synthesis methods on the dielectric properties of $(Ba_{0.2}Pb_{0.8})TiO_3$ ceramics

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The dielectric properties of $(Ba_{0.2}Pb_{0.8})TiO_3$ prepared by several methods related to dispersion have been studied. The sol–gel derived specimens without dispersion have lower density, and lower dielectric constant at the Curie temperature. The sol–gel specimens derived from a well-dispersed suspension with pH 11 and 13, and 2% PMMA show higher dielectric constant at the Curie temperature, and higher density, because the grains grow homogeneously in the well-dispersed system. The sol–gel derived specimens have a higher Curie temperature than that of calcined mixed oxides and molten salt synthesis derived specimens.

1. Introduction

Since 1943, when the ferroelectric $BaTiO_3$ was found, the Curie point changes which can take place in solid solution with $SrTiO_3$ or $PbTiO_3$ have been studied. In particular, the use of Pb^{2+} ions alone has been found to be effective to shift the Curie point higher in solid solution with $BaTiO_3$. Up to now, materials with Curie points in the temperature range of -30–300 °C have been developed commercially. The production of materials with Curie points above 300 °C is required to utilize the solid solution at higher temperatures. Therefore, in this work, the dielectric properties of $(Ba_{0.2}Pb_{0.8})TiO_3$ ceramics which has a high Curie temperature above 300 °C, have been studied. The substitutional solid-solution method is widely used in the $BaTiO_3$–$PbTiO_3$ system for dielectric and piezoelectric applications [1]. Factors which control dielectric and piezoelectric characteristics are as follows: heating condition, compositional variation, properties of raw materials, porosity, and the degree of abnormal grain growth [2]. The problem with keeping the stoichiometric composition in the (Ba, Pb) TiO_3 solid solution is the evaporation of lead. To solve this problem, fine powders are synthesized by the sol–gel method. This method has several merits as follows [3–5]: high homogeneity, high purity and high surface area. In this work, the dielectric properties of $(Ba_{0.2}Pb_{0.8})TiO_3$ derived by the sol–gel method have been studied and compared with those of calcined mixed oxides (CMO) and molten salt synthesis (MSS) methods. The purpose of the present work was to investigate dielectric properties of $(Ba_{0.2}Pb_{0.8})TiO_3$ ceramics prepared by several methods related to dispersion.

2. Experimental procedure

$BaCO_3$, PbO and TiO_2 with purities above 99.9% were used as the starting materials in the CMO and MSS methods. KCl was used as flux in the MSS method. For the sol–gel method, barium acrylate and lead acetate salts were used as the barium and lead sources with purity of 95% and 99%, respectively, and titanium isopropoxide alkoxide was used as the titanium source with purity of 95%. Barium acrylate was dissolved in dry ethyleneglycol and methoxyethanol, 1:4 molar ratio, in a three-necked flask at room temperature. In the separate vessel, lead acetate was dissolved in dry methoxyethanol, 1:4 molar ratio, and the titanium isopropoxide was added into this vessel

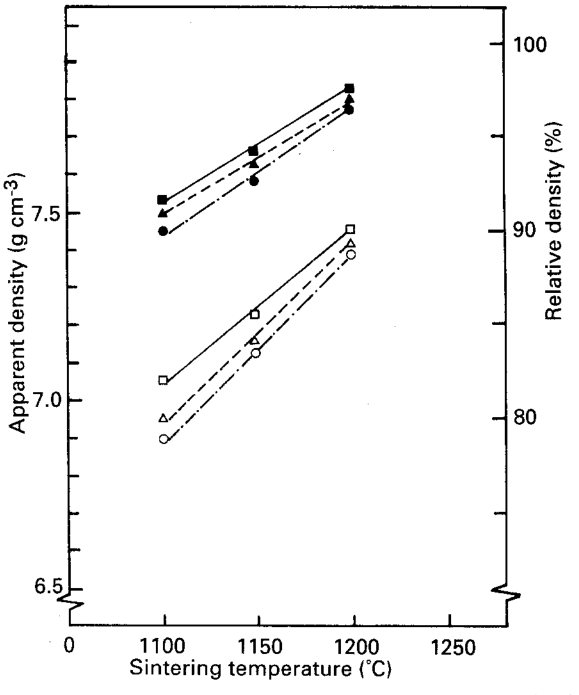

Figure 1 (○, △, □) Apparent and (●, ▲, ■) relative density of $(Ba_{0.2}Pb_{0.8})TiO_3$ prepared by various synthesis methods, sintered at various temperatures for 0.5 h. (○, ●) Undispersed sol–gel, (△, ▲) MSS, (□, ■) CMO.

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at 70 °C. Then the lead acetate, dry methoxyethanol and titanium isopropoxide solution were added to the barium acrylate, dehydrated ethyleneglycol and methoxyethanol solution as drops with continuous stirring. Hydrolysis was subsequently performed by introduction of a solution of methoxyethanol and doubly distilled deionized water (1 : 2 ratio) in excess proportions (100 mol water/mol alkoxide). After sufficient hydrolysis, the solution was peptized within 0.07 mol acrylic acid. The gel formed was then dried [5]. The polymer used in the experiment was poly (methylmethacrylate) (PMMA), prepared from methylmethacrylate monomer, purity 99%, and condensed with vigorous stirring using 0.01 wt % aa'-Azobis-iso-butyronitie as the polymerized accelerator, and kept at 70 °C [6]. The polymers are more effective as good dispersants in suitable solvents. Therefore, we investigated the solvent solution which can dissolve PMMA completely. The CMO procedure for powder preparation follows the general ceramic process. The calcination conditions for the CMO method were 900 °C for 2 h. In the MSS method, the washing process was repeated until free Cl^- ions were no longer

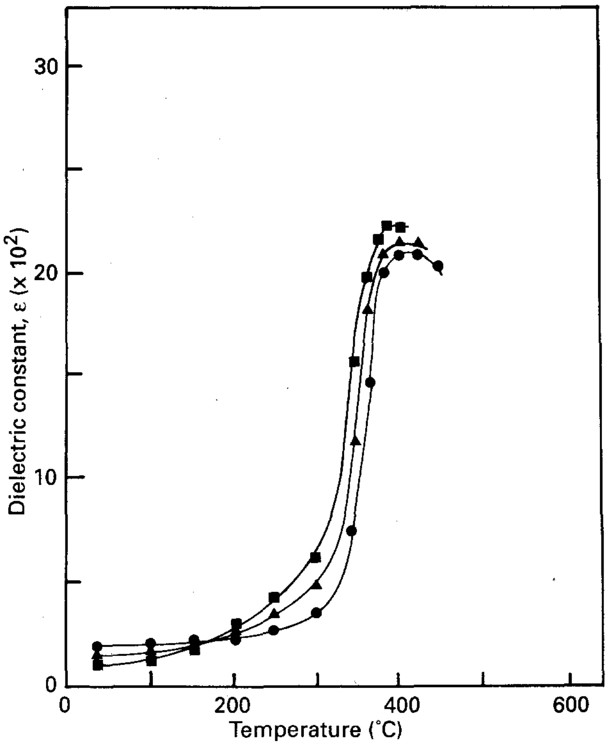


Figure 2 Dielectric constant versus temperature of $(Ba_{0.2}Pb_{0.8})TiO_3$ prepared by various synthesis methods, sintered at 1200 °C for 0.5 h without dispersion. (●) Undispersed sol–gel, (▲) MSS, (■) CMO.

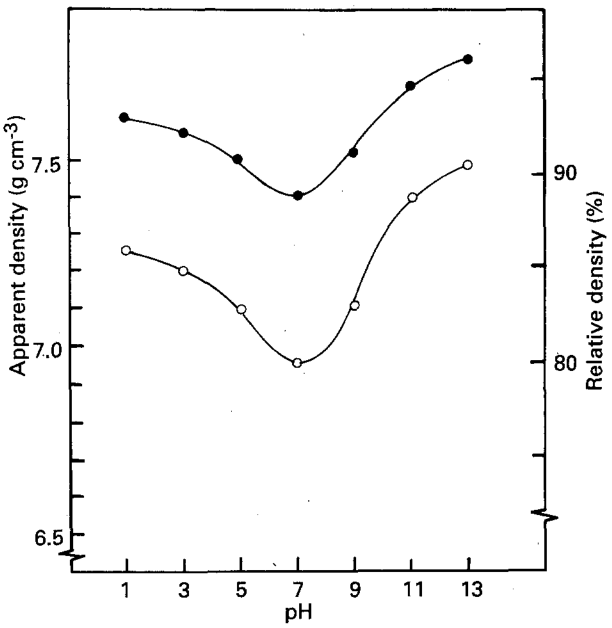


Figure 4 (○) Apparent and (●) relative density versus pH for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h.

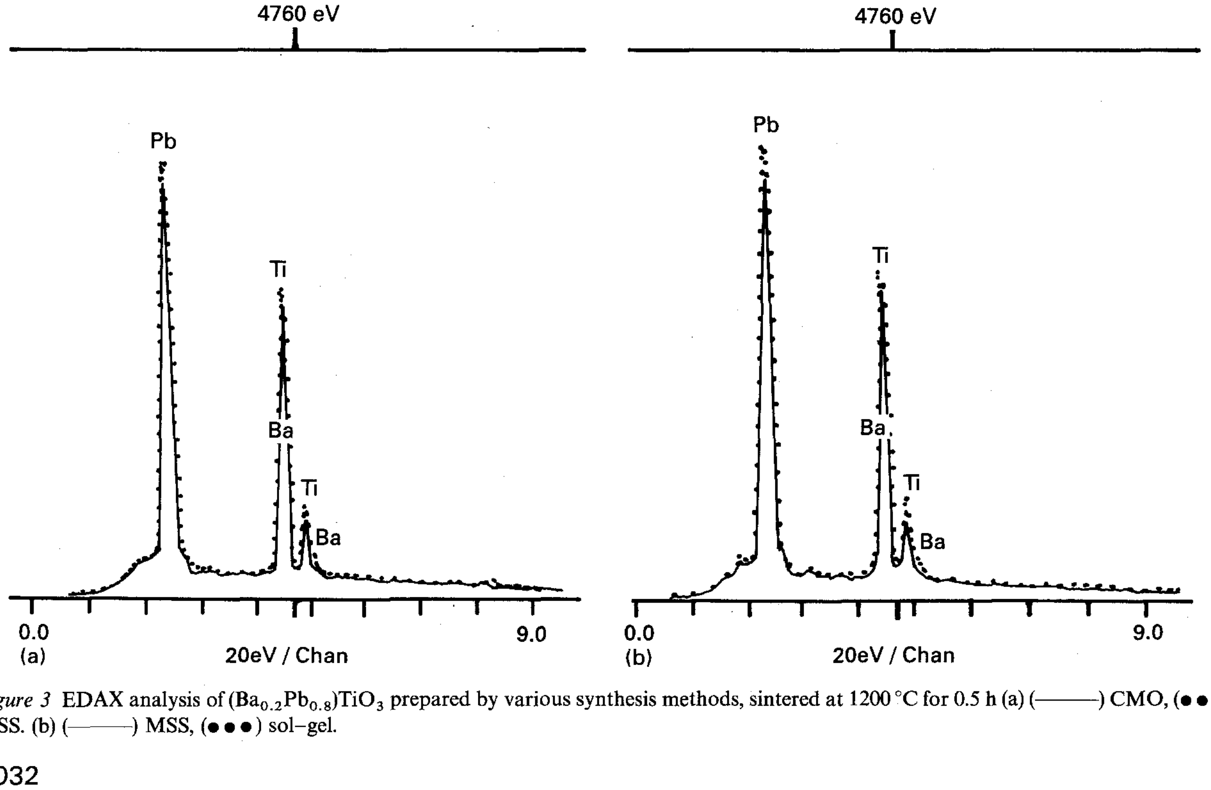


Figure 3 EDAX analysis of $(Ba_{0.2}Pb_{0.8})TiO_3$ prepared by various synthesis methods, sintered at 1200 °C for 0.5 h (a) (———) CMO, (● ● ●) MSS. (b) (———) MSS, (● ● ●) sol–gel.

detected by $AgNO_3$ solution [7]. Powders prepared by the MSS methods were calcined at 800 °C for 6 h. For sol–gel derived powders, the calcination conditions were 600 °C for 1 h. The calcined powders were pressed into pellets with 0.5 wt % PVA binder by the application of a pressure of 700 kg cm^{-2}. Then these samples were cold isostatically pressed again under 1500 kg cm^{-2} pressure. The pellets were sintered in the range 1100–1350 °C for 0.5 h in air. After sintering, high-temperature silver paste was deposited on both surfaces of the polished specimens as electrodes by the screen method, and these pellets were heated to 800 °C for 10 min. The dielectric constant characteristics of the specimens were

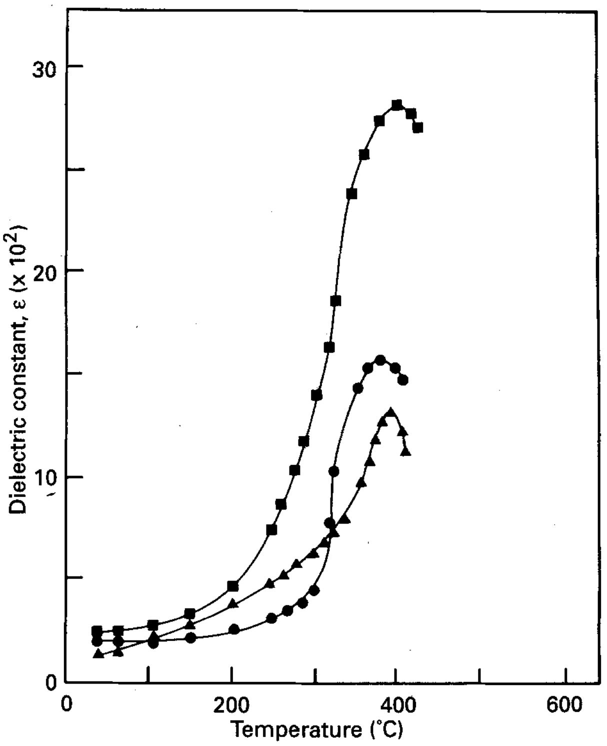


Figure 5 Dielectric constant versus temperature for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h under various pH dispersion conditions. pH: (●) 3, (▲) 7, (■) 11.

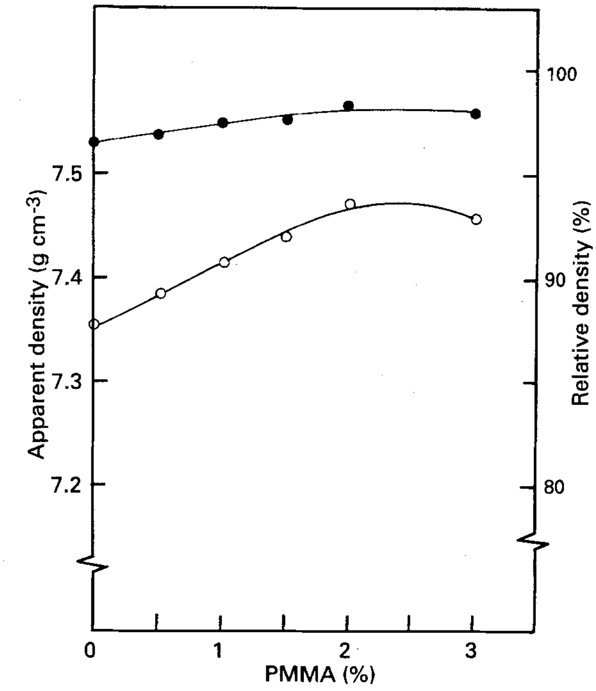


Figure 6 (○) Apparent and (●) relative density versus PMMA content for the sol-gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h.

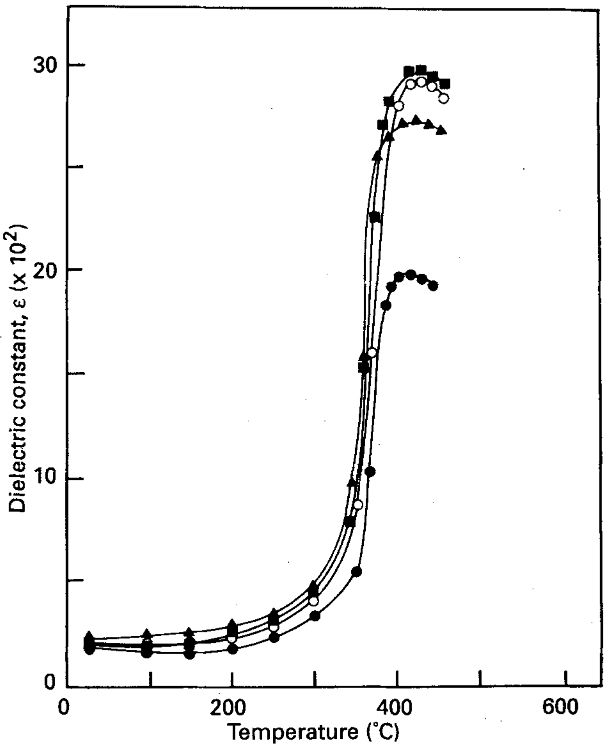


Figure 7 Dielectric constant versus temperature for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h with various PMMA contents: (●) 0, (▲) 1.0% (■) 2.0%, (○) 3.0%.

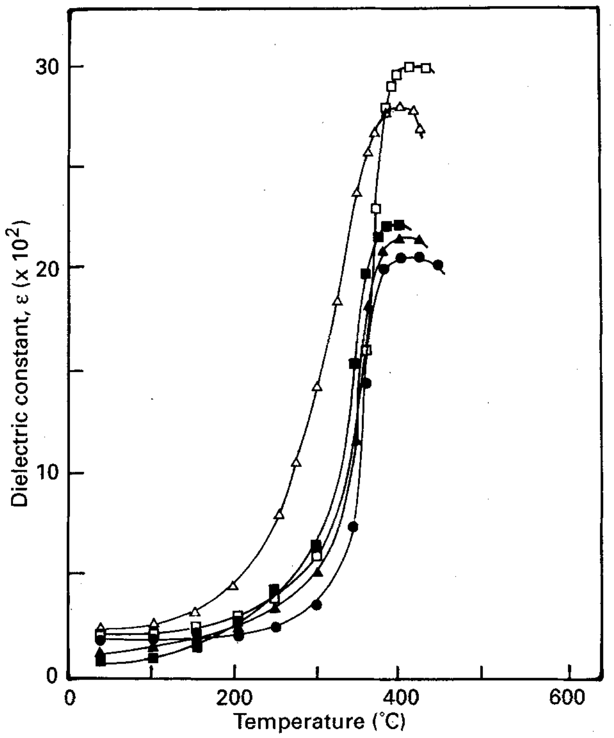
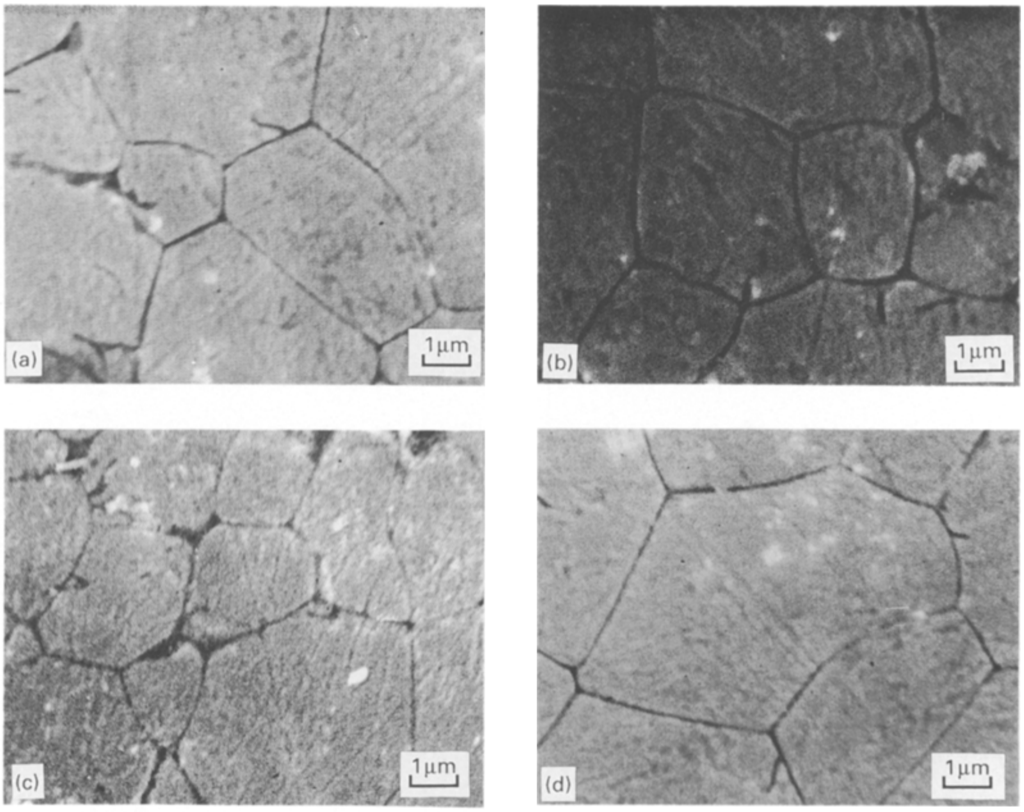


Figure 8 Dielectric constant versus temperature of $(Ba_{0.2}Pb_{0.8})TiO_3$ prepared by various synthesis methods, sintered at 1200 °C for 0.5 h. (▲) MSS, (■) CMO, (●) sol-gel undispersed, (△) sol-gel dispersed at pH 11, (□) sol-gel dispersed with 2.0% PMMA.



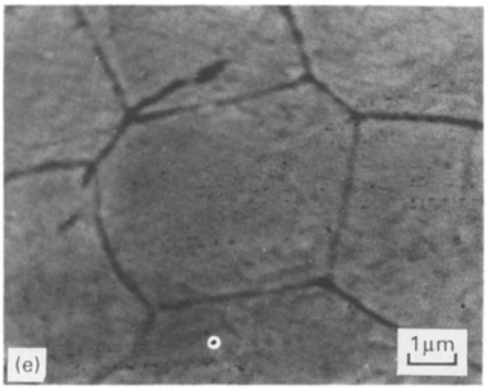


Figure 9 Scanning electron micrographs of $(Ba_{0.2}Pb_{0.8})TiO_3$, sintered at 1200 °C with various synthesis methods (a) CMO, (b) MSS, (c) sol–gel undispersed, (d) sol–gel dispersed at pH 11, (e) sol–gel dispersed with 2.0 % PMMA.

measured using an LCR meter in the range 100–500 °C.

3. Results and discussion

Fig. 1 shows the apparent and relative densities of the sintered specimens prepared by several methods. The sintered specimens prepared by the CMO method have higher density at various sintering temperatures. For the sol–gel derived specimens, the small grains with high reactivity resulted in agglomeration between particles, and this caused the low density. The microstructures of sintered specimens are influenced by the initial particle size of the powder and the sintered density depends on the agglomerate size [8]. Fig. 2 shows dielectric constant plotted against temperature for the specimens sintered at 1200 °C for 0.5 h by various synthesis methods. The dielectric constants at room temperature increase in the order CMO, MSS and non-dispersed sol–gel derived specimens. The maximum dielectric constants at the Curie temperature decrease in the order CMO, MSS and non-dispersed sol–gel derived specimens. For the sol–gel derived specimen, the width of the dielectric constant peak was broader. Merz [9] found that the width of the dielectric constant curve decreased and the maximum dielectric constant at the Curie temperature increased with an increase of hydrostatic pressure. Figure 3 shows the EDAX analysis for the CMO, MSS and sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$. When the titanium intensity is fixed, the lead intensity of MSS derived specimens is higher than that of CMO derived specimens, and that of the sol–gel derived specimen is the highest. Therefore $(Ba_{0.2}Pb_{0.8})TiO_3$ in the sol–gel method compared to the other methods reduces the evaporation of lead at lower temperature. This result is in accordance with the highest Curie temperature shown in Fig. 2.

In Fig. 4, the apparent and relative densities of the sol–gel derived specimens sintered at 1200 °C for 0.5 h after dispersion at various pH are shown. The specimen dispersed at pH 7 shows that the lowest density resulted from bad dispersion characteristics. The badly dispersed powders which result in large voids or void clusters can agglomerate easily [10]. The dielectric constant variation of the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h after dispersion at various pH is shown in Fig. 5. In the specimen dispersed at pH 7, the low density and the maximum dielectric constant at the Curie temperature resulted from large agglomerates in contrast to the well-dispersed specimen at pH 11. The density and maximum dielectric constant at the Curie temperature in the specimen dispersed at pH 3 are higher than those of the specimens dispersed at pH 7. However, because of the low degree of crystallization, the dielectric constant curve of the specimen dispersed at pH 3 appears broad.

Figure 6 shows the apparent and relative densities of sintered $(Ba_{0.2}Pb_{0.8})TiO_3$ after dispersion with PMMA. The density increased up to 2 % PMMA, and then did not increase with further addition of PMMA. The powder dispersed with 2 %PMMA shows the highest density. This powder has well-dispersed characteristics resulting from the particle groups broken up with 2 % PMMA. The PMMA acted in the role of dispersant and binder. The dielectric constant variation in the sintered $(Ba_{0.2}Pb_{0.8})TiO_3$ after dispersion with PMMA is shown in Fig. 7. An increase in sintered density due to good packing density, results in a dielectric constant increase up to 2 % PMMA. Agglomerates make abnormal grain growth and irregular void shapes. Brewer *et al.* [11] reported that residual voids and agglomerates formed microflaws and were detrimental to the mechanical and electrical properties of sintered specimens. Fig. 8 shows the variation of dielectric constant for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ after dispersion, compared with those of CMO and MSS. The sol–gel derived specimens have lower dielectric constant at the Curie temperature without dispersion, but a higher value after dispersion with 2 % PMMA or after dispersion at pH 11, compared with those of the CMO and MSS derived specimens. The ultra-fine powders without dispersion agglomerate actively and result in a low dielectric constant at the Curie temperature. After dispersion, the sinterability increases, resulting in a high dielectric constant at the Curie temperature.

Figure 9 shows scanning electron micrographs of $(Ba_{0.2}Pb_{0.8})TiO_3$ obtained by various synthesis methods. The grain size of the sol–gel derived specimens is the smallest compared with those of CMO and MSS derived specimens. However, in the well-dispersed system (pH 11 and 2 % PMMA), the grains grow homogeneously, resulting in high density.

4. Conclusions

1. The sol–gel derived specimens without dispersion have a lower density and dielectric constant at the Curie temperature compared to those of specimens prepared by CMO and MSS methods.
2. The sol–gel specimens derived from good dispersion with pH 11, 13 and 2% PMMA show a higher dielectric constant at the Curie point than those of the CMO and MSS derived specimens.
3. The sol–gel specimens derived from well-dispersed systems show higher density because the grains grow homogeneously compared to the CMO and MSS specimens.

Acknowledgement

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