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Ferroelectric Glass-Ceramic Sintering Aid for Lead Titanate Ceramics

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Abstract

Silicate-based glass that devitrifies on heating to form ferroelectric lead titanate has been developed. The potential for use as sintering aid in PbO-based electroceramics has been evaluated by studying the densification of $PbTiO_3$ (PT) with increasing wt% addition of glass powder. As the wt% glass content increased, the density increased, the maximum and room temperature relative permittivity decreased and there was also a decrease in T_c and the c/a ratio. The decrease in T_c is believed to be due to increased clamping from neighbouring grains as the density of the PT increases. The decrease in maximum and room temperature relative permittivity is related to the presence of secondary phases.

Key words: lead titanate, glass-ceramics, sintering aids, dielectric, impedance spectroscopy

Introduction

One of the significant costs in the manufacture of electroceramics is the energy consumed during thermal processing. From this perspective lower sintering temperatures are desirable. Moreover, high sintering temperatures necessitate the use of expensive electrode materials such as platinum and palladium in many co-fired multilayer devices.(1) Finally, there are environmental concerns over PbO volatilization during high temperature sintering. As a result, much attention has been aimed at reducing the sintering temperature of a wide range of electroceramic products such as barium titanate (BT) and lead zirconate titanate (PZT)(2-5) $PbTiO_3$ (PT) is a tetragonal perovskite with a c/a ratio of 1.063 at room temperature, which is the largest known for lead-based perovskite compounds. Single crystal data have shown that the relative permittivity, ε_r, obeys the Curie-Weiss law above the Curie temperature, T_c~490°C. The large ionic displacements in PT lead to a particularly large spontaneous polarization (>53 $\mu C/cm^2$) and strain (c/a ratio = 1.06) at room temperature.(6) PT exhibits large pyroelectric coefficients, low relative permittivity (~100-200) and dielectric properties stable with time, temperature and frequency. However, these excellent properties are not yet fully realised in bulk polycrystalline samples due to difficulty in fabricating undoped PT. PT ceramics microcrack and fracture on cooling below T_c as a result of the large spontaneous strain generated when the structure changes from cubic to tetragonal. Normally, the fabrication of dense PT ceramics is achieved by reducing the spontaneous strain using dopants and/or inhibiting grain growth. The densification occurs with a reduction of c/a ratio which also affects electrical properties. Palkar *et al.*(7, 8) studied Si-doped PT prepared by a co-precipitation technique. They found that the presence of Si in PT did not alter its crystal structure and Si was not found to occupy the Pb or Ti sites in the perovskite lattice. Instead, they suggested that Si was dispersed in either a glassy matrix or at interstitial lattice positions. In addition, they reported the presence of a non-ferroelectric metastable, pyrochlore phase ($Pb_2Ti_2O_6$). More commonly, either CaO(9) or Sm_2O_3 [10, 11] are added to $PbTiO_3$ to inhibit microcracking and fracture on cooling. The defect chemistry associated with these substitutions is poorly understood but T_c and the c/a ratio decrease in each case.

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In this work, high dielectric permittivity (ε_r) sintering aid based on silicate glass has been developed follwing Shyu and Yang glass composition.[12] This glass composition is easy to melt and it crystallizes as high volume fraction PT-based glass-ceramics (~40 vol%). Therefore the effect of these sintering aids on the microstructure and properties is investigated and their suitability for potential commercial usage assessed.

Experimental and Characterization

Processing

The glass composition utilized was 39PbO-1BaO-25TiO_2-9.8Al_2O_3-24.2SiO_2-1B_2O_3 (mol%). Glass batch was prepared from Pb_3O_4, $BaCO_3$, TiO_2, $Al(OH)_3$, B_2O_3 and Loch Aline (SiO_2) (all with purity ≥99%) and transferred to a platinum crucible for melting. Melting was carried out in an electric furnace for 2h at 1200-1250°C, using a platinum stirrer after 1h. The melt was poured onto a preheated metal block and quickly transferred to a pre-heated muffle furnace for annealing at 500-550°C for 1h followed by cooling to room temperature at 3°C/min.

A solid state mixed oxide route was used to prepare $PbTiO_3$ powder. Mixed powder was calcined at 750°C/4h with a 5°C/min heating and cooling rate. The calcined powder was then crushed and sieved through 180 μm mesh. Glass was crushed in a percussion pestle and mortar and sieved through a 106 μm mesh to yield powder suitable for further ball milling. For each composition, the appropriate amounts (Table 1) of glass and $PbTiO_3$ powder were ball milled for 24h in distilled water using ZrO_2 milling media. The slurry was then dried and crushed using pestle and mortar and sieved through a 180 μm mesh. Mixed/milled glass and $PbTiO_3$ powders were cold pressed to form pellets using a 10 mm diameter steel die with an applied load of ~ 125 MPa. The thickness of each green compact was about 2 mm. The green compacts were sintered in air according to the sintering conditions given in Table 1. Sintering was carried out in a lidded crucible with green pellets embedded in PT powder and using a heating and cooling rate of 5ºC/min and 2 ºC/min, respectively. Density measurements were carried out using the Archimedes technique. The apparent density of the ceramic/glass composites were compared to their theoretical density, assumed to be a summation of the density of the glass and $PbTiO_3$ in appropriate ratios.

Table 1. Compositions and sintering conditions for glass-PT ceramics.

Sintering conditions	**Composition wt% glass A : wt% PT**		
1100 ºC/2h	10:90	5:95	3:97
1000 ºC/2h	10:90	5:95	3:97
900 ºC/2h	10:90	5:95	3:97

Characterisation

X-ray Diffraction (XRD) was used to identify phases of the sintered pellets. Pellets were crushed and XRD was performed using a Siemens D500, operated at 40 kV and 30 mA, scanned from 10° to 80° with a scan speed of 1°/min and step interval 0.02° using Cu K_α radiation with a wavelength of λ = 1.5406 Å. The samples were first calibrated with a Si internal standard to eliminate errors due to detector misalignment. Lattice parameters of $PbTiO_3$ were calculated from a least squares programme against XRD traces of the $PbTiO_3$ phase. The data were analyzed using Stoe WinXPow (v.2.1) software. Microstructural analysis was carried out using a JEOL JSM6400 SEM operated at 20 kV. Qualitative chemical analysis was obtained by Energy Dispersive X-ray (EDS) spectroscopy on JSM 6400 SEM.

Dielectric properties as a function of temperature were obtained using an HP 4284A, LCR meter connected to a vertical tube furnace. An accurate determination of the tetragonal-cubic transition temperature, T_c, was obtained using an Agilent 4294A, precision impedance analyzer. Before the measurements, samples were electroded with gold paste on the top and bottom faces. Electrodes were fired at 800°C for 1h with a heating rate of 10°C/min.

Results and Discussion

Ceramic Densification

Figure 1 shows the % density obtained at various sintering temperatures with different wt% addition of glass. Densities are calculated from that of the glass and the theoretical density of PT. Density of parent glass was measured as 5.49 gcm^{-3}

and theoretical density of PT 7.96 gcm^{-3} (as calculated from XRD pattern of calcined PT powder). In general, the greater the wt % of glass the higher was the density at any given temperature. Below 1100ºC, densities were typically <94% theoretical but unlike conventional ceramic PT, the glass-powder composites did not fracture on cooling after sintering provided >2wt % glass was added.

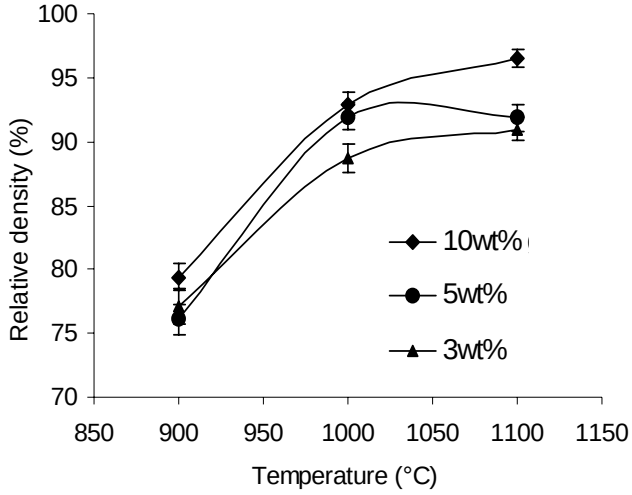

Figure 1. Density measurements of $PbTiO_3$ with 3, 5 and 10 wt% glass addition, sintered for 2h between 900ºC and 1100ºC.

Phase Analysis by XRD

XRD traces are shown Figure. 2 for pellets that contain 10 wt% glass addition, sintered at 1100°C/2h and as-calcined $PbTiO_3$ powder. The as calcined powder has particle size ~ 0.3-1 μm according to SEM analysis (not shown here). Samples with glass addition gives similar XRD trace to that obtained from the as-calcined PT powder with no second phases observed. However, ceramic samples with glass additions showed peak broadening associated with a smaller average crystallite size. The separation of (001) and (100) is slightly reduced in the glass-PT composites (c/a = 1.058 for glass addition) with respect to as calcined PT (c/a = 1.062). This marginal difference may be due to the incorporation of impurities such as Al, B or Si from the glass into the PT lattice, the residual stress with ceramics or as a result of clamping within the dense PT ceramics that is associated with a smaller average crystallite size.
At this stage, clamping within the dense PT ceramics and residual stresses are possible causes of XRD peak broadening but impedance spectroscopy data presented in Section 3.5 indicates no measurable compositional variation in the PT.

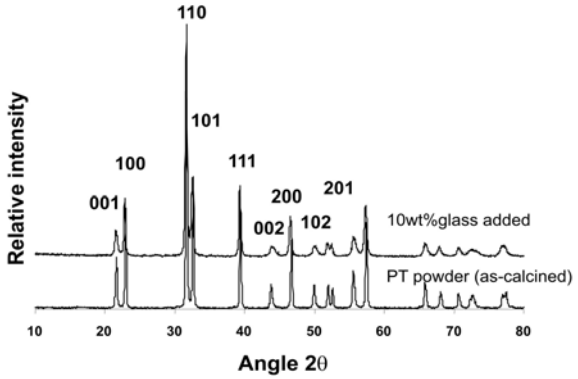

Figure 2. XRD traces of PT powder (as-calcined) and PT sintered at 1100 ºC/2h with 10 wt% glass added.

Microstructural Analysis

To illustrate typical microstructures, samples sintered at 1100°C/2h with 3 and 10 wt% glass additions were selected for SEM analysis. Low magnification images, Figures.3(a) and (b) illustrate that pellets with 10wt% glass generally exhibit fewer microcracks compared with 3 wt%. The crack lengths in all cases are~100 μm. Between the microcracks, however, a similar microstructure was observed in all pellets Figure 4 with grain size varying from 0.4–1.0 μm. In addition, some secondary phase was observed which was Ti-rich (TiO_2) compared with the lighter contrast matrix (PT), according to EDS analysis. The most likely second phase is therefore TiO_2 rejected from PT phase as a result of PbO loss during reaction or sintering. Figure. 5 is a cross section SEM image of a bulk and surface region of a sample with 3 wt% glass added to PT, sintered at 1100°C/2h. The darker contrast region at the edge reveals evidence of PbO volatilization during sintering.

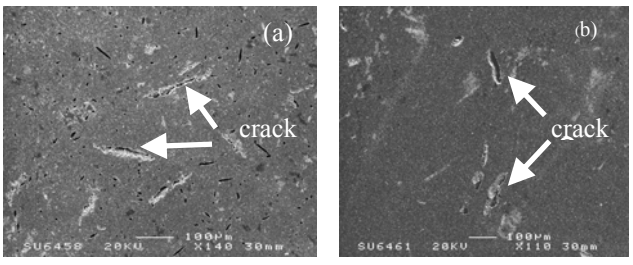

Figure 3. SEM images of (a) 3 wt% and (b) 10 wt% glass added to PT and sintered at 1100°C/2h.

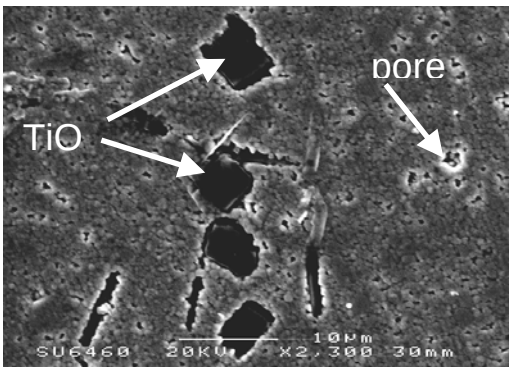

Figure 4. Higher magnification SEM image of 3wt% glass addded to PT, sintered at 1100°C/2h.

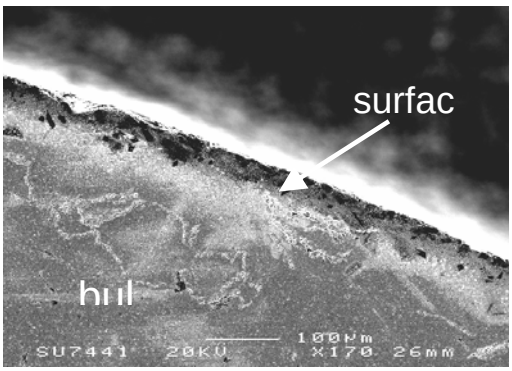

Figure 5. SEM image of bulk and surface region of 3 wt% glass added to PT, sintered at 1100°C/2h.

To study the densification and grain growth, samples with 10% glass was sintered at 1100ºC for 10h rather than 2h. The subsequent SEM image was shown in Figure 6. After 10h, there was a bimodal distribution of grain size, indicating the likely presence of liquid phase consistent with the differential thermal analysis data presented by Sooksaen *et al.* 2005[12].

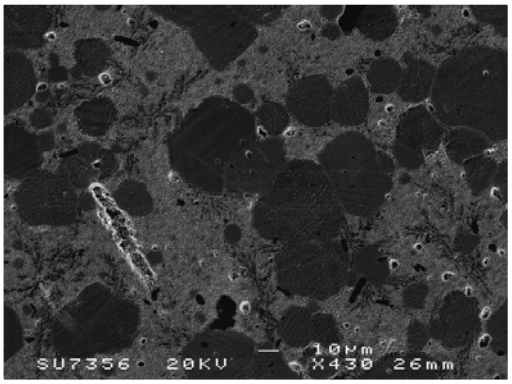

Figure 6. SEM image of sample with 10 wt% glass, sintered for 10h.

Dielectric Properties

Figure 7. shows the relative permittivity plots for samples with 3, 5 and 10 wt% glass added to PT and sintered at 1100°C/2h. Similar trends are observed in each plot. In general, the greater the wt% addition of glass, the lower the peak and room temperature permittivity possibly due to the presence of secondary phases (e.g. TiO_2) and residual glass phase which have lower relative permittivities compared to $PbTiO_3$ phase. Above T_c (~ 490°C), the ε_r follows the Curie-Wiess law as expected for a ferroelectric PT. Insets in Figure 7 are tan δ curves between 450 and 550°C. Careful scrutiny of Figure 7 suggests that as the wt% of glass addition increases, T_c decreases. In sample with 10 wt% glass addition T_c decreased to ~472°C. In order to investigate whether this effect was real and not instrument related the impedance analyzer was calibrated against known standards and further measurements obtained.

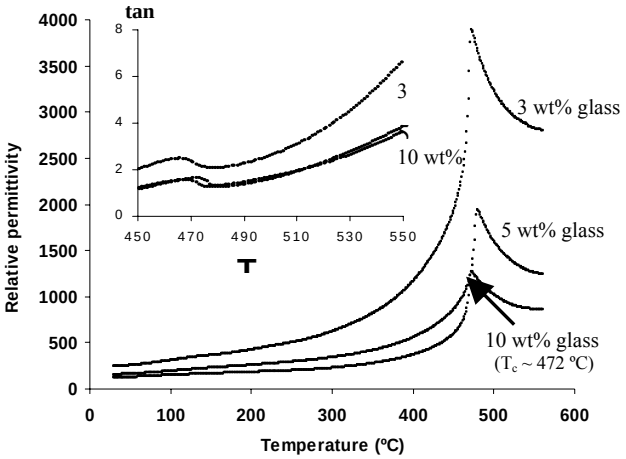

Figure 7. Dielectric permittivity plot of 3, 5 and 10 wt% glass added to PT, sintered 1100°C/2h. Samples were run on LCR meter at 100 kHz. Inset is tan δ curves between 450 and 550 °C.

Impedance Spectroscopy (IS)

An impedance analysis confirmed the downshift in T_c for samples sintered for 2h but increased when sintered for longer times (Table 2). However, there was no measurable compositional change as all samples showed similar values of characteristic time constant.(14) Hence the clamping effect, rather than a change in composition, is the most likely reason for the downshift in T_c by suppressing the c/a ratio.

The IS analysis has also showed an increase in sample conductivity for samples

sintered for 10h with glass addition. From the SEM image in Figure 6 the grain growth mechanism, although unknown, maybe related to Pb-loss. This may link to an increase in the number of charge carriers as a result of Pb-loss and/or oxygen deficiency for samples sintered for extended periods at 1100ºC.

Table 2. T_c values for samples with 10 wt% of glass addition, sintered for 2 and 10h. Temperatures were accurate to ±3 ºC.

Sintering at 1100 °C	**T_c (ºC)**
2 hours	465 ±3
10 hours	490 ±3

Conclusions

It has been demonstrated that silicate-based glasses which contain a high mol% of TiO_2 and PbO act as sintering aids for densification of $PbTiO_3$ ceramics. The density increases with increasing amount of glass addition and the level of microcracking is reduced. Sintering for 10h at 1100ºC, results in a bimodal grain distribution. The room temperature and maximum ε_r of the lead titanate ceramics decrease along with the phase transition temperature as the wt% glass addition increases. These effects are accompanied by a decrease in the c/a ratio which according to impedance analysis is likely to be due to clamping of the grains rather than incorporation of dopants from the glass.

In conclusion, the novelty of using PT based glasses as sintering aids from an environmental perspective is that the reduction in sintering temperature would decrease volatilisation of PbO without the addition of high dopant concentrations previously used to fabricate dense PT ceramics.

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