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Dispersion characteristics of sol–gel derived $(Ba_{0.2}Pb_{0.8})$ TiO_3 as a function of PMMA

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The suspension behaviour of sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ powder, was observed as a function of PMMA content (0 to 3%). The suspension shows an optimum dispersion in 70% benzene/30% hexane. The effect of PMMA concentration on the sedimentation density in 70% benzene/30% hexane shows the best dispersion at about 2% PMMA concentration. The sol–gel specimens derived from a well-dispersed suspension with 2% PMMA show a higher dielectric constant at the Curie temperature and a higher density than those in other PMMA concentrations. These results can be explained by the increase in sinterability due to the stable suspension behaviour.

1. Introduction

High-tech ceramics are currently being developed to satisfy conditions of high performance and good capacity [1–3]. It is necessary that fine and homogeneous powder preparation, homogeneous packing and void-free sintered specimens be developed. Chemical powder preparation methods, via a liquid phase, exist by which it is easy to prepare fine particles and control the properties of the powder product, such as the sol–gel method. This method has the merits of yielding high purity, homogeneity, stoichiometric composition and fine particles [4–6], and (Ba, Pb)TiO_3 fine powder was prepared with high reactivity and homogeneity by this method [7]. The extent to which individual particles exist as aggregates obviously has a major influence on the behaviour of the suspension during processing and on the properties and performance of the final product. Therefore, the primary emphasis is on the preparation of fine particles, and the extension of most of the general concepts to high density and homogeneous grain growth is assured [8]. The sintered green samples, which are homogeneously packed with fine spherical particles, have high density, a reduced sintering cycle and enhanced stability against abnormal grain growth. It is hoped that by preparation of fine powders and manipulation of the dispersion characteristics, a uniformly packed, high-density green compact and stable dispersion will result.

There are two types of dispersion mechanism used, electrostatic repulsion and steric interaction with adsorbed polymers. Sterically stabilized dispersions result from the effect of non-ionic polymers attached to the surface of the colloid particles where stability is imparted by the polymer molecules that interrupt the approach between particles. Electrostatic stabilization is explained by the control of pH and addition of electrolytes. There currently exist just two general ways [9] in which the steric stabilization mechanism can be imparted: bridging flocculation and charge neutralization. Bridging is considered to be a consequence of the adsorption of the segments of individual polymeric flocculent molecules on to the surfaces of more than one particle. Such bridging links the particles together into loose aggregates, which often sediment rapidly or are easily removed by filtration. Charge neutralization is found to be effective only with polymeric flocculants whose charge is opposite in sign to that of the particles. Sterically stabilized dispersions are comparatively insensitive to the presence of the electrolyte concentration. This contrasts sharply with the electrical double layers which are strongly dependent upon the ionic strength. So steric stabilization is equally effective in aqueous and non-aqueous dispersion media. The suspension behaviour associated with polymer adsorption has been studied. By using submicrometre powder from a suspension with well-dispersed PMMA, the adsorption effect on the characteristics of a sintered body has been studied.

2. Experimental procedure

The alkoxide and salts used in the sol–gel method are extremely moisture prone and carbon dioxide-sensitive materials, and so these were kept under a nitrogen atmosphere. Barium acrylate and lead acetate salts were used as the barium and lead sources with purities of 95% and 99%, respectively, and titanium isopropoxide alkoxide was used as the titanium source with a purity of 95%.

Barium acrylate was dissolved in dry etyleneglycol and methoxyethanol, 1:4 molar ratio, in a three-neck flask at room temperature. In a separate vessel, lead acetate was dissolved in dry methoxyethanol, 1:4 molar ratio, and the titanium isopropoxide was added into this vessel at 70 °C. Then the lead acetate, dry methoxyethanol and titanium isopropoxide solution

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was added to the barium acrylate, dehydrated etyleneglycol and methoxyethanol solution as droplets with continuous stirring. After that hydrolysis was performed by introducing a solution of methoxyethanol and doubly-distilled deionized water (1:2 ratio) in excess proportions (100 mol water/mol alkoxide) [10]. After sufficient hydrolysis, the solution was peptized with in 0.07 mol acrylic acid. The gel which formed was then dried. The suspension behaviour of the gel was observed with various additions of polymer. The polymer used in the experiment was PMMA (poly(methylmethacrylate)), 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.

The polymers are more effective as good dispersants when in suitable solvents. So we investigated the solvent solution which can dissolve PMMA completely. The sedimentation density was determined by putting 20 g $(Ba_{0.2}Pb_{0.8})TiO_3$ powder in a dry 10 ml graduated cylinder and adding a solvent to give a total volume of 10 ml. The relative density was obtained from the measured sediment height. Suspension rheological flow curves were determined using a BL viscometer and the temperature dependence of the reaction was studied using TGA. Metallurgical micrographs of the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$, dispersed ultrasonically and stirred continuously, were observed to confirm the degree of dispersion and aggregate size.

The powder was calcined at 600 °C for 1 h and mixed with 0.5 wt % PVA binder. The powders were pressed isostatically under 1500 kg cm^{-2} into pellets of 10 mm diameter and 3 mm thick. These were sintered at 1200 °C for 0.5 h mixed in a powder of the same composition and industrial ZrO_2 powder to maintain the lead atmosphere. The densities of the specimens were determined by ASTM test method C373–72 (1977). The specimens sintered provided that high-temperature silver-plate electrodes heated at 800 °C for 10 min, were used. The dielectric constant was calculated from the capacitance measured by an LCR meter at 1.02 kHz.

3. Results and discussion

The polymer was tied to the surface at a number of points but for some of its length it was able to extend into the solution. Segments attached to the surface formed trains which were separated by loops, while the ends of the polymer were usually able to extend into the solution as tails. The complete dissolution of the polymer allowed the outer segments to extend into the solution and the inner segments to become attached to the particle surface. Polymers can be good dispersants only in suitable solvents. Therefore, various solvents were observed to determine which can dissolve PMMA the best. PMMA is reported to dissolve completely in n-hexane and benzene with zero contact angle. Therefore n-hexane and benzene were used as the dispersing medium in this experiment. The sedimentation density of the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ in various benzene/n-hexane mixtures was measured. The results, illustrated in Fig. 1 in terms of sedimentation density, show an optimum dispersion in the 70% benzene/30% hexane mixture. Above 40% n-hexane, the θ point is reached and the sedimentation density decreases drastically. The Θ-point represents the transitional point with respect to segment–solvent interactions [9]. At this point, the polymer segments change from exhibiting a net mutual repulsion to a net mutual attraction. A solvent is "good" when the polymer–solvent contacts are energetically favoured over polymer–polymer and solvent–solvent contacts. In good solvents, the polymer chains repel one another.

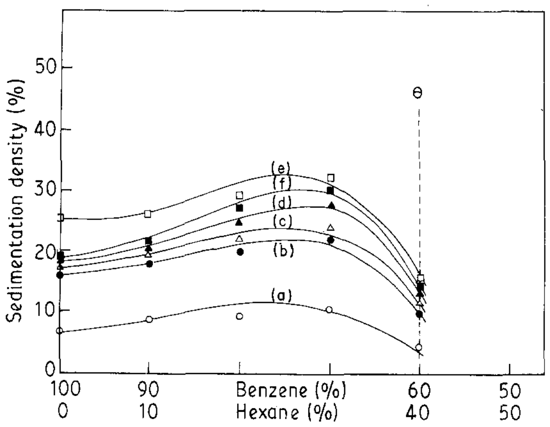

Figure 1 Sedimentation of $(Ba_{0.2}Pb_{0.8})TiO_3$ powder dispersed in solution of various PMMA content in benzene/hexane mixtures. (a) 0%, (b) 0.5%, (c) 1.0%, (d) 1.5%, (e) 2.0%, (f) 3.0%

Fig. 2 shows the effect of PMMA concentration on $(Ba_{0.2}Pb_{0.8})TiO_3$ sedimentation density in 70% benzene/30% hexane. The results show the best dispersion at about 2% PMMA concentration, with a slight decrease in packing at higher concentrations. The effects of a polymer on the stability of a colloidal dispersion have been represented schematically by Napper [11]. If the adsorption density on the particle surface is too high, aggregation is found to occur by linking between one tail and another in this diagram. Linke and Booth [12] review the work on silica-polyacrylamide and suggests that the tails of the

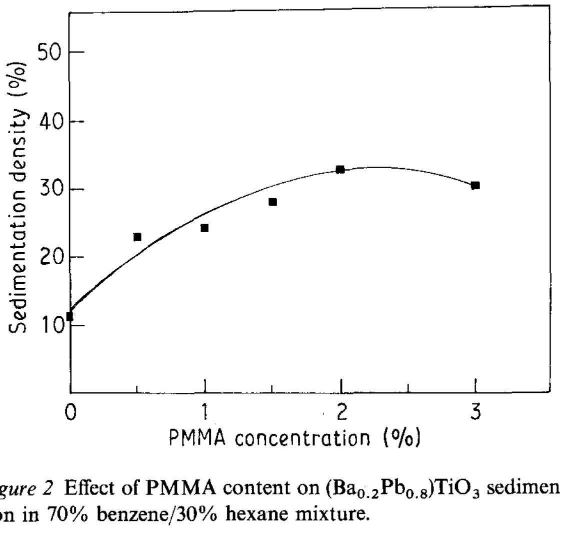

Figure 2 Effect of PMMA content on $(Ba_{0.2}Pb_{0.8})TiO_3$ sedimentation in 70% benzene/30% hexane mixture.

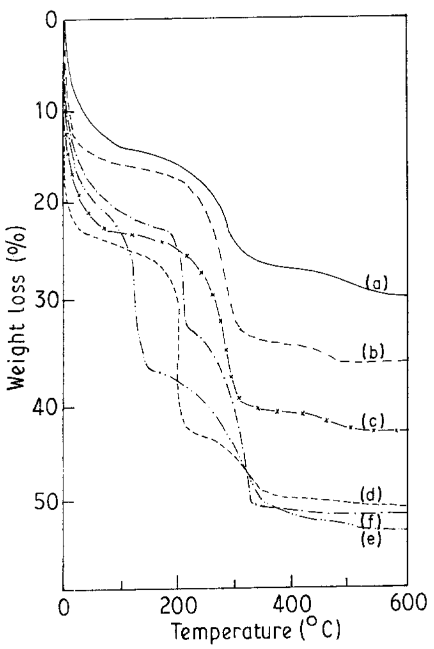

Figure 3 Thermogravimetry curves as a function of PMMA content for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$. For (a) to (f), see Fig. 1.

excess polymers attached on the particle surfaces, extend into the solution and bridge each other. Our results show a similar tendency to those of reports.

TGA curves for $(Ba_{0.2}Pb_{0.8})TiO_3$ as a function of PMMA concentration are shown in Fig. 3. Dehydration and removal of the organic residue increased with increasing concentration of polymer up to 2% PMMA, above which it decreased. The weight loss is independent of the concentration of PMMA as a dispersant. This is similar to the report of Heath and Tadros [13], for sodium montmorillonite. According to these authors, poly(vinyl alcohol) in aqueous solution takes up much space, which results in the brisk dehydration.

Fig. 4 shows the weight loss taken from the TGA curves as a function of PMMA concentration. The 2% PMMA solution shows the highest weight loss and the best dispersed suspension. Up to 2% PMMA the weight loss is higher with increasing PMMA concentration, above which the reverse is true. These results show a tendency similar to that of the sedimentation density. Metallurgical micrographs for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ powders dispersed in 70% benzene/30% hexane mixture as a function of PMMA concentration are shown in Fig. 5: optimum dispersion appears at about 2% PMMA concentration. This result backs up those for sedimentation density and weight loss.

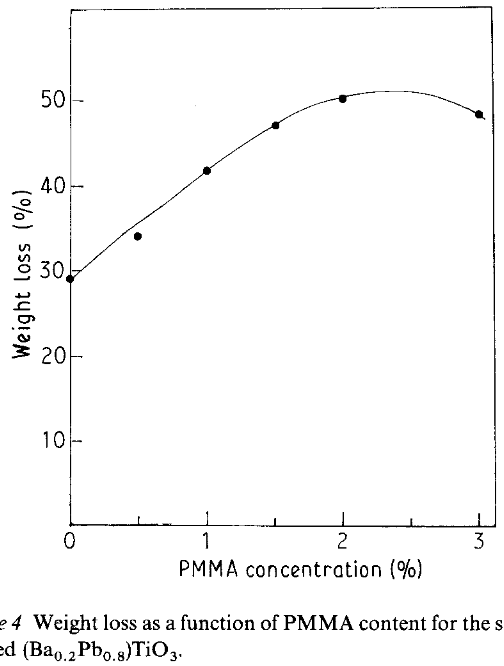

Figure 4 Weight loss as a function of PMMA content for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$.

Fig. 6 presents plots of suspension viscosity against shear rate for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ as a function of PMMA concentration. The viscosity decreased with increasing shear rate in the 0% PMMA solution. This result agrees with the report by Nakamae *et al.* [14] on the dispersion behaviour of γ-Fe_2O_3 in poly(vinyl butyral) solution. In this study, the suspension with no polymer addition shows extensive low shear-rate aggregation, as indicated by the highly shear-thinning behaviour. The viscosity becomes independent of shear rate, Newtonian behaviour, with PMMA addition. The high viscosities resulting from the high molecular weight polymer addition (1.2×10^5) and the Newtonian behaviour observed with the polymer are characteristics of a well-dispersed suspension. For the interaction between polymer and mica sheet, explained in detail by Klein [15], the viscosity of the suspension with polymer is higher than that of the suspension without polymer. The reason for this is the high molecular weight of the polymer itself. Fig. 7 shows the apparent and relative density of sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h after dispersion in the PMMA solution. The sintered density increases with increasing PMMA concentration up to 2% PMMA, above which it decreases. The highest sedimentation density at 2% concentration is characteristic of well-dispersed suspension. Addition of a polymer enhances the strength, flexibility, and workability of the ceramic in its green state, prior to sintering. It might be preferable for the polymer to function not only as a dispersant but also as a binder. The effect of a dispersant on the green and sintered specimens has been studied by Calvert *et al.* [16].

Molecular packing plays a crucial role in determining the characteristic of the green and sintered specimens. The high packing density satisfies the conditions for a pore-free and dense, sintered body.

In Fig. 8, the dielectric constant of $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h is given as a function of PMMA concentration. The packing density increases with increasing PMMA concentration and a good packing density results in high sintered density and high dielectric constant. However, at higher PMMA concentrations (3%), poor dispersion behaviour causes decreasing density, which results in a decrease in the dielectric constant. The agglomeration causes grain growth and void formation. The residual pores and agglomerates in the sintered body act as microflaws which adversely affect the mechanical and electrical properties. This agrees with Brewer *et al.*s report [17].

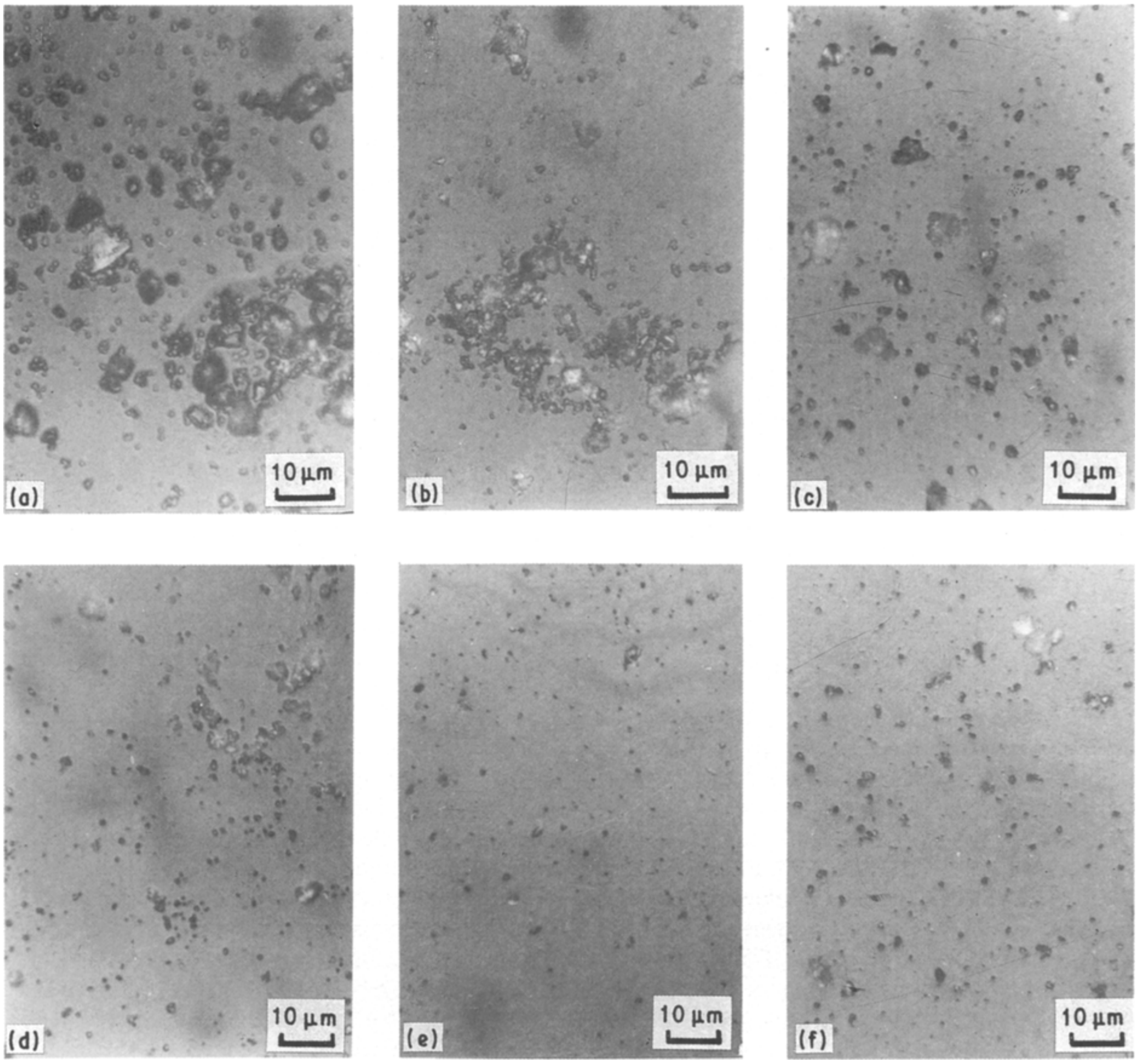

Figure 5 Metallurgical micrographs for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ powder dispersed in 70% benzene/30% hexane as a function of PMMA content: (a) 0.0%, (b) 0.5%, (c) 1.0%, (d) 1.5%, (e) 2.0%, (f) 3.0%.

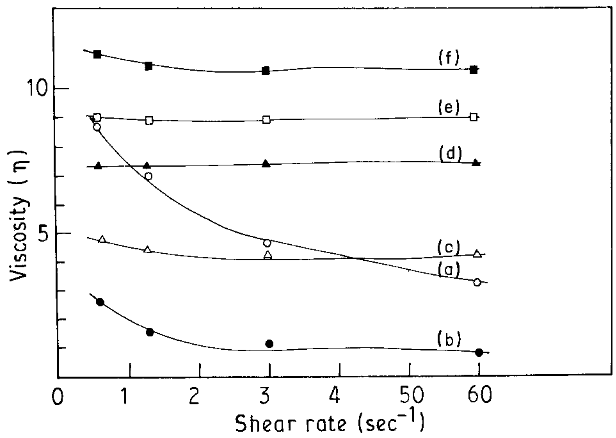

Figure 6 Suspension viscosity plotted against shear rate for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ as a function of PMMA content. For (a) to (f), see Fig. 1.

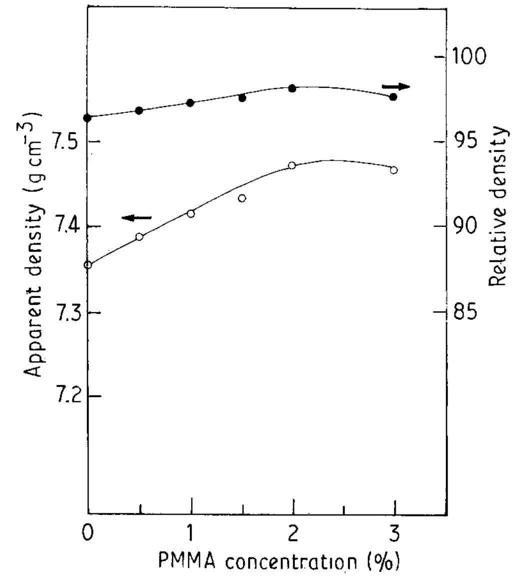

Figure 7 Apparent and relative density plotted against PMMA content for the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h.

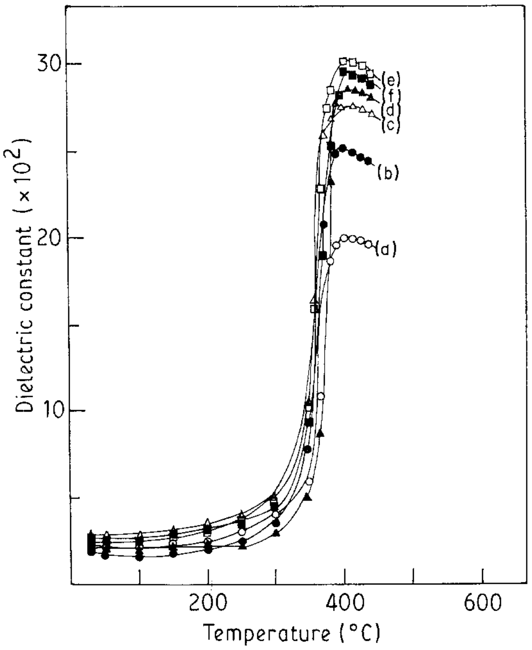

Figure 8 Dielectric constant plotted against temperature of the sol–gel derived $(Ba_{0.2}Pb_{0.8})TiO_3$ sintered at 1200 °C for 0.5 h with PMMA content. For (a) to (f), see Fig. 1.

4. Conclusions

1. PMMA can be effectively dispersed in 70% benzene/30% hexane.

2. A 2% PMMA addition gave the best dispersion, with a 33% sedimentation density.

3. The specimens derived from well-dispersed suspension with 2% PMMA showed a 98% relative sintered density.

Acknowledgement

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