JOURNAL OF MATERIALS SCIENCE 29 (1994) 4256–4259

Thermodilatometric behaviour of pure and doped $ZrTiO_4$–SnO_2

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Thermodilatometric tests have been performed to investigate the shrinkage of green compacts of pure and ZnO-doped $4ZrO_2$–$5TiO_2$–SnO_2 prepared by dry ball milling, flo-deflocculation and coprecipitation. Experiments have shown that the powder preparation procedure has a significant influence on the sintering process. Optimizing the homogeneity composition, which is enhanced from dry ball milling to coprecipitation, raises the starting sintering temperature. The reduction of the dimension of the starting particles increases the sintering rate and the addition of ZnO favours the shrinkage of the green bodies. Coprecipitated products lead to the highest final density because the evaporation of tin oxide on firing is reduced.

1. Introduction

Zirconium titanate solid solutions are known to have a high dielectric constant, high Q value and low temperature coefficient of resonant frequency [1]. Therefore, they are of great interest as a material for applications in the microwave frequency regime. The addition of SnO_2 produces better electrical properties [2].

However, reactive calcination from oxides leads to synthesis of these compounds at elevated temperatures. Moreover, powders do not readily sinter by simple solid-state diffusion and previous treatments as well as sintering aids are required to obtain good densities at moderate temperatures.

ZnO seems to be effective, compared with other oxides, in achieving a good densification between 1200 and 1400 °C. In fact, the liquid phase, through which the sintering process takes place, has lower viscosity and higher volatility at relatively low temperature and allows the formation of compacts with good electrical properties [3].

The preparation of particles of uniform size, shape and composition is of great importance [4, 5]. These requirements imply fully dense, uniform microstructures which, according to some postulates proposed recently [6], can be obtained from small, uniform, unagglomerated particle, assemblies. The formation and characterization of uniform particles is not only of technological importance but also provides a means for elucidating the validity of various sintering models, which have been developed by assuming a uniform particle size and shape [7].

In general, a powder preparation method should meet several important criteria: an oxide precursor should have the desired morphology and chemistry which will decompose to the required product at relatively low temperatures. Moreover, the method should be relatively simple, reproducible and economically feasible [8].

Commercial powders have sometimes inadequate composition and it is necessary to resort to a mixing of different products; this fact requires a processing which breaks up agglomerates formed during powder preparation, reduces the particle dimensions, helps the homogenization and uniformity of the composition.

Powder processing involves four basic steps: manufacture, preparation for consolidation, consolidation to an engineering shape, and densification. Each step has the potential for introducing heterogeneities which will persist during further processing into a new heterogeneity during densification and microstructural development [9, 10]. Many of the heterogeneities can be eliminated by manipulating and controlling interparticle forces, as practiced in colloid science. Powders disperse and form a system of separated particles when repulsive forces dominate, and floc to a low-density network of touching particles when attractive forces dominate [11–13]. In the case of zirconium and titanium oxides, powders disperse under acid and floc in a basic environment. Suspensions of disperse particles are indicated to break up agglomerates and homogenize powders of different composition.

Another way to manipulate powders is wet or dry ball milling which is known to be an efficient method for promoting various kinds of solid-state reactions [14], such as structural transformations, chemical reactions, displacement reaction, extension of the solid

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solubility, production of new nanostructural materials or high-temperature crystalline phases. On the other hand, the highly energetic treatment, even if effective in powder processing, presents a non-negligible influence on the material's starting composition because the abrasive action of the powders will generate new material through the wear of the grinding media.

Sometimes, commercial powder processing is insufficient for the presence of many different oxides and it is necessary to prepare the products directly from solutions of different salts. This leads to the production of highly homogeneous particles with controlled dimensions, shape and composition.

The sol–gel and coprecipitation synthesis routes have been widely investigated to obtain ultrafine, very homogeneous and high-purity materials. In these ways it is possible to prepare highly reactive precursors which allow the sintering temperature to be lowered and the microstructure to be controlled.

In the present work, the sintering of $4ZrO_2$–$5TiO_2$–SnO_2 has been investigated to evaluate the influence of the powder preparation methods as well as the addition of ZnO as sintering aid on their reactivity and densification; commercial powder homogenization was conducted by the flo-deflocculation route and/or highly energetic dry ball milling; the coprecipitation method via hydrolysis from different salts was followed to synthesize the amorphous and/or crystallized products.

2. Experimental procedure

In the flo-deflocculation route, different amounts of ZrO_2(Tosoh TZO), TiO_2 (Fischer 99.9%), SnO_2 (Aldrich Chemicals 99.9%) and ZnO (Aldrich Chemicals 99.9%) were weighed in appropriate proportions. Powders were dispersed in deionized water and the pH value was adjusted to 2 by adding HCl, then vigorously stirred for 2 h. The suspensions were then flocced at pH 8 by NH_4OH. The resulting powders were washed several times with deionized water and dried.

In the dry ball milling process, powders were treated for 1 h with zirconia balls and high-density polyethylene containers using a highly energetic SPEX equipment.

For the coprecipitation process, great care must be taken with titanium chloride because it easily reacts with water at room temperature and hydroxide precipitates, so 0.05 M solutions of the other chloride salts were first prepared. They were stored at 4 °C using melting ice and then, while stirring, titanuim chloride was poured dropwise. The solution was aged (10 h) at this temperature until it became completely clear.

The hydrolysis was performed by pouring the solution into concentrated ammonia (28 wt %); under these conditions, the pH value never falls below 10 and very fine particles precipitate.

The hydroxides were washed several times with deionized water to remove chloride and ammonium ions, then twice with ethanol and acetone to remove the physically adsorbed water; after this treatment, powders were set in an oven at 80 °C to evaporate the entrapped solvents, softly crushed in an agate mortar, and calcined at different temperatures.

The amorphous nature of the starting powders was verified through X-ray and infrared spectra. On the basis of the thermogravimetric (TG) and differential thermal analysis (DTA) curves, obtained using a Netzsch equipment, powders were divided into two batches: one batch was calcined at 580 °C, for 1 h, the other at 700 °C for the same time, the former, being below and the latter above the crystallization range; in this way it was possible to evaluate the densification behaviour of the green compacts starting either from amorphous or crystalline products.

All the powders were sieved through a 50 μm sieve and pressed into cylinders at 100 MPa, then subjected to the dilatometric test from room temperature to 1350 °C with a heating rate of $10\,°C\,min^{-1}$.

3. Results and discussion

Coble [15] identified four stages in the sintering process which have the following major characteristics.

(a) the early step for loosely packed particles with low initial relative densities when the pores form an interconnected network through the material; as the body sinters there is no change in the mean grain size;

(b) takes over from (a) at low relative density (0.6) when the pore shape is the same as during stage (a); densification is now accompanied by grain growth;

(c) occurs during the later stages of sintering when the pores coalesce. The grains continue to grow; the transition to this stage occurs at a relative density of about 0.95;

(d) intervenes when the migrating grain boundaries break away from the pores, leaving them isolated in mid-grain; densification virtually ceases after this point, but grain growth continues, often at an accelerated rate.

The mechanism responsible for stages a and b have been described by Swinkels and Ashby [16], Helle *et al.* [17], and McMeeking and Kuhn [18] who have obtained general constitutive relationships for deformation and densificaton when grain-boundary diffusion is the dominant mechanism, while Kellet and Lange [19, 20] described the interactions between grain growth and densification. Although their discussions are exact, they do not explore the effect of an aggressive and fluid phase during the early stage of sintering for a material with high melting temperature.

During the first step, the reaction between the starting oxides generates the $4ZrO_2$–$5TiO_2$–SnO_2 solid solution through the presence of a liquid phase. In fact, as above pointed out, SnO_2 has a low melting temperature and, in appropriate mixtures, can form a liquid at temperatures which are correct for the early stages of sintering.

This fact is more important for application of $4ZrO_2$–$5TiO_2$–SnO_2 in microwave components and requires low porosity, uniform composition and low shrinkage during densification in order to avoid the distortion of the starting shape.

Fig. 1 shows the sintering behaviour of the coprecipitated and calcined at 700 °C (curve 1), ball-milled (curve 2), and flo-deflocculated powders (curve 3), of pure $4ZrO_2$–$5TiO_2$–SnO_2, while Fig. 2 elucidates the shrinkage of pure and doped, $4ZrO_2$–$5TiO_2$–SnO_2 powders coprecipitated and calcined 1 h at 700 °C.

With the coprecipitated powders the chemical aspect described above is minimized because the starting powders are not constituted of a mixture of independent chemical oxides, but of a solid solution; therefore, SnO_2 is bonded within a more complex network which strongly reduces the possibility of it melting and partially evaporating.

The different mechanisms, together with the small particle dimensions of the coprecipitated powders, lead to a continuous, uniform and progressive densification with a limited or almost absent presence of liquid phase, giving higher final densities. This fact may be considered positive, because it leads to highly dense bodies, but it implies greater shrinkages which can induce the distortion of the starting shape. On the other hand, when one of the components melts several degrees earlier than the others, densification takes place through the presence of a liquid phase which reacts with other particles.

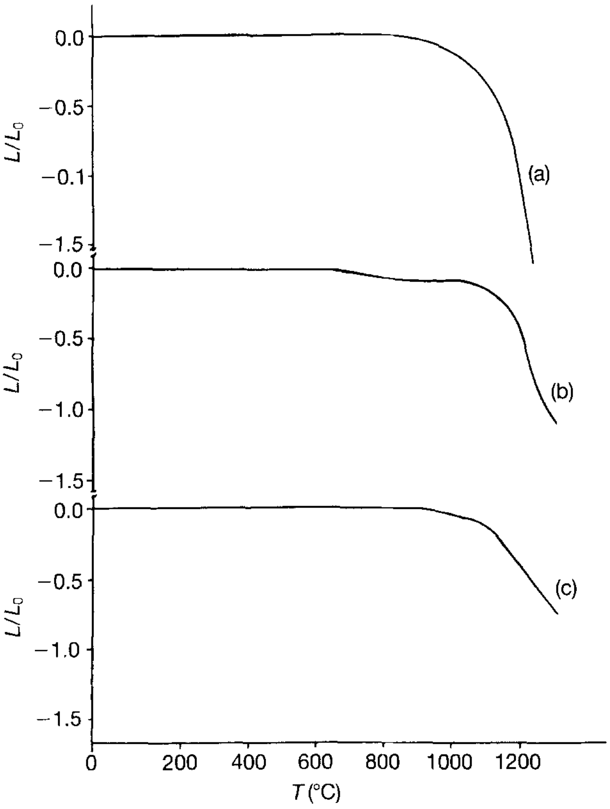

Figure 1 Shrinkage curves of pure green compacts: (a) coprecipitated and calcined 1 h at 700 °C, (b) ball-milled, and (c) flo-deflocculated powders.

Dry ball-milled powders start to sinter at the lowest temperature while flo-deflocculated and coprecipitated products densify later. Samples obtained from commercial oxides exhibit a major difference in the homogenization and in crystal dimensions. This fact suggests that the homogenization of the different components is effective in the starting sintering temperature, while the crystal size has an influence on the global shrinkage of the fired samples, because the smaller the crystal size, the higher is the shrinkage.

The best homogeneity of samples obtained by flo-deflocculation, induces sintering at a higher temperature; this is associated with a reduced quantity of liquid phase derived from the melting of SnO_2 more strictly bonded to the other oxides.

Densification of commercial oxides begins at lower temperature than for coprecipitated products, but has a lower rate of sintering. The increase in liquid phase is associated with a partial evaporation of SnO_2-rich phase from the sample surface and is balanced by the diffusion of other SnO_2 from the core of the specimen. The fast diffusion of this compound is not balanced by the shrinkage of the body and causes a higher inner porosity which is difficult to remove during later steps of sintering: the sintering process is slowed and the sintering rate decreases.

In some cases, the arrest temperature of the dilatometric curve is lower than the previously reported limit, owing to the effect of the behaviour of the samples. In fact, it was observed that samples containing free SnO_2 (ball-milled and flo-deflocculated powders) had a marked loss of material when the temperature exceeded 1300 °C, causing a chemical reaction with the thermocouple of the instrument and giving rise to a non-negligible deposition of material in the dilatometer chamber.

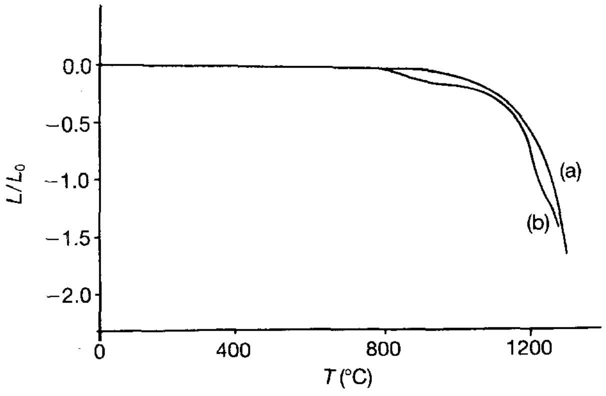

Figure 2 Thermodilatometric curves of (a) pure and (b) doped coprecipitated and calcined 1 h at 700 °C powders.

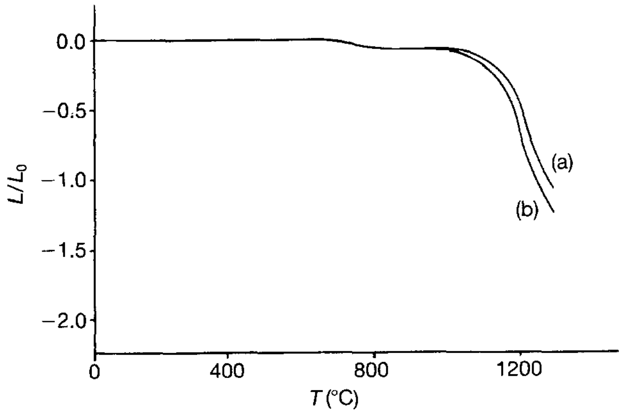

Figure 3 Thermodilatometric curves of (a) pure and (b) doped ball-milled commercial powders.

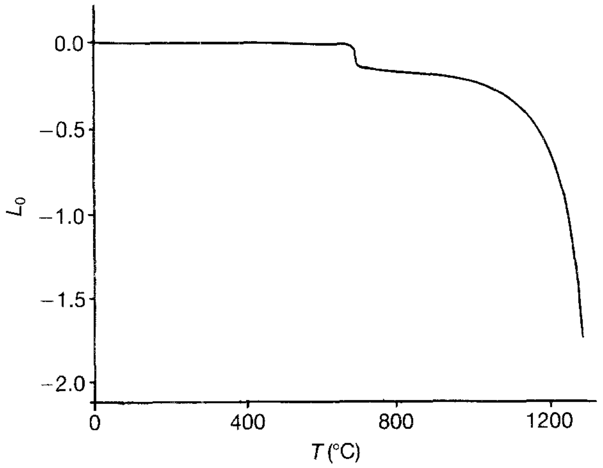

Figure 4 Sintering behaviour of pure $4ZrO_2$–$5TiO_2$–SnO_2 coprecipitated and calcined 1 h at 580 °C.

The curves in Fig. 2 show the effect of ZnO in the coprecipitated powders: it is possible to observe that this component induces densification at a lower temperature, but shrinkage is less regular. Tests performed on specimens prepared with mixtures of different commercial oxides also explain the efficiency of ZnO as a sintering aid, as is seen in Fig. 3, which shows the dilatometric behaviour of pure and doped ball-milled powders.

Fig. 4 shows the sintering behaviour of the coprecipitated powder when the calcination temperature (580 °C) is maintained below the crystallization range of the amorphous oxides. In this case crystallization occurs during sintering and is marked by a step in the dilatometric curve which occurs, as expected, at 650 °C. The second step of the sintering process is, in this case, retarded, but, because of the small size of the starting particles, the sintering rate, although at a higher temperature, is higher, so that samples reach a stronger driving force to reduce the starting dimensions and therefore lead to a higher final density.

4. Conclusions

Thermodilatometric tests on pure and ZnO-doped $4ZrO_2$–$5TiO_2$–SnO_2 prepared by dry ball-milling, flo-deflocculation and coprecipitation showed that:

1. the powder preparation procedure has a significant influence on the sintering process;
2. the homogeneity composition improvement increases the starting sintering temperature;
3. reduction of the starting particle dimensions increases the sintering rate;
4. in all the cases, the addition of ZnO favours the shrinkage of the green bodies;
5. coprecipitated products have a higher sinterability and a reduced amount of liquid phase during sintering than mixtures of different oxides.

Acknowledgement

This work was supported financially by the Italian Ministry of University and Scientific Research.

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Received 10 May
and accepted 9 September 1993