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Screen printed barium strontium titanate films for microwave applications

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Abstract

Powders to be used in inks for screen printing of $Ba_{0.5}Sr_{0.5}TiO_3$ thick films have been prepared by two different routes — calcination of $BaCO_3$, $SrCO_3$ and TiO_2 by a conventional solid-state reaction, and thorough mixing of uncalcined nano-sized $BaTiO_3$ and $SrTiO_3$. The effect of these two different production routes on the microstructural properties in terms of grain size and density has been assessed using SEM. Electrical measurements at 1 kHz indicate that both permittivity and dielectric loss are affected by the density of the films. Permittivity also appears to be affected by the grain size of the films, which increases dramatically above a particular sintering temperature. The Curie temperature also decreases as sintering temperature increases and this has been linked to observed Ba diffusion from the film into the alumina substrate.

Keywords: Dielectric properties; Diffusion; Microstructure—final; Sintering; (Ba,Sr)TiO_3

1. Introduction

The need for miniaturisation of electronic devices has led to investigations into new potential dielectric materials. Ferroelectrics, such as barium strontium titanate (BST) are promising candidates for use in microwave circuits. For example, when used in phase shifters in phased array antennae ferroelectric materials would be cheaper, lighter and smaller than the ferrite materials currently used. BST can be engineered to possess the required properties in terms of permittivity, dielectric loss and tunability, and when in thick film form allows lower bias voltages to be used for applications that require tuning.[1]

$Ba_{0.5}Sr_{0.5}TiO_3$ has been produced from two different methods in the present study; from pre-calcined carbonates and from commercially supplied nano-sized titanates. Initial studies of bulk material produced by these two methods have shown that samples produced from nano-sized titanates are able to achieve much higher densities on sintering at all temperatures, but especially in the region from 1250–1350 °C. This is important because studies on thick films produced so far indicate interaction with the alumina substrate at sintering temperatures above 1250 °C,[2] which can have deleterious effects on the microstructural and electrical and dielectric properties of the films. Therefore, BST thick films using both these methods have been produced and are compared and contrasted in terms of their microstructure and electrical and dielectric properties.

2. Experimental

Powder to be used in ink production was produced by two different routes, as follows:

Route 1: BST powder was produced by the conventional mixed oxide method by the calcination at 1150 °C of $BaCO_3$ (Fluka, >99%), $SrCO_3$ (Riedel-deHaen, >97%) and TiO_2 (Toho, >99.7%) according to Eq. (1).

$$BaCO_3 + SrCO_3 + 2TiO_2 \rightarrow 2Ba_{0.5}Sr_{0.5}TiO_3 + 2CO_2. \tag{1}$$

The powder was milled after calcination to reduce the particle size to <10 μm, and then freeze-dried to reduce agglomeration on drying.

Route 2: Nano-sized $BaTiO_3$ and $SrTiO_3$ powders (provided by TPL, >99%) were mixed thoroughly in deionised water on a ball mill in equal proportions.

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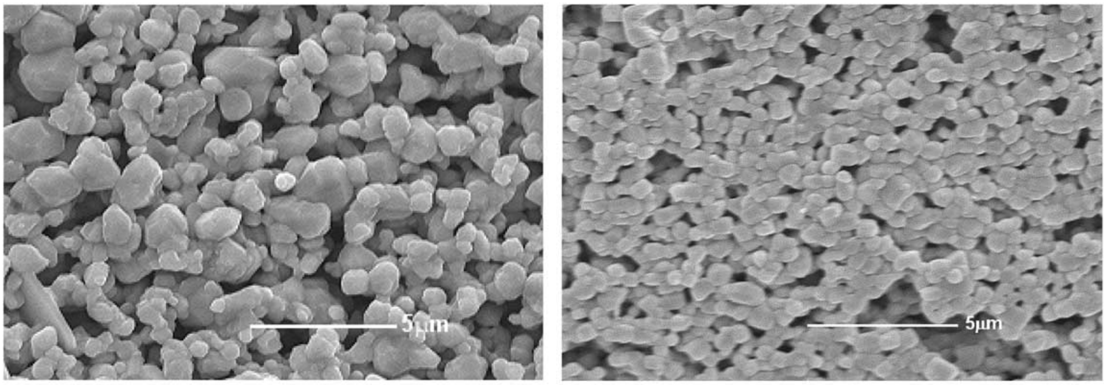
No calcination step was used, as previous experiments have indicated that the nano-sized titanates are able to achieve high density at relatively low sintering temperatures for bulk ceramics without a calcination step. The particle size of the starting powders was 60 nm.

Inks suitable for screen printing were made by mixing powder, vehicle (Blythe) and 1 mass% dispersant (phosphate ester, PS-21A, Witco) in acetone using zirconia balls on a ball mill overnight. The jar was then left in a fume cupboard with the top off to allow the acetone to evaporate. Before printing the ink needed a short amount of time on a roll mill in order to re-mix the powder and vehicle which tended to separate out. 45 vol.% (79 mass%) solids loading of $Ba_{0.5}Sr_{0.5}TiO_3$ was used for powder from the carbonate route, while 30–35 vol.% (67–72 mass%) was used for nano-sized powders as their small particle size made higher solids loading impractical.

Thick films were screen printed onto platinum coated alumina substrates. The films were sintered in air at temperatures between 1250 and 1500 °C for 1 h. A silver top electrode was sprayed onto the sintered BST and fired at 800 °C, to enable electrical measurements to be made through the film. SEM was used to evaluate the microstructure of the films, in terms of density and grain size. EDX was used to determine the chemical composition of both the films and the alumina substrate where diffusion had occurred. Permittivity and dielectric loss of the samples were measured in air using a HP4194A impedance analyser, over a temperature range of −70–70 °C at a frequency of 1 kHz.

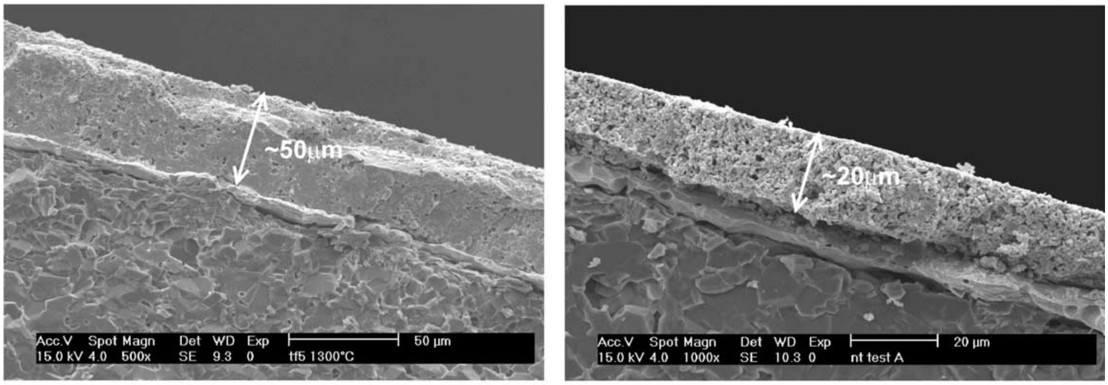
3. Results and discussion

The microstructure of films from the carbonate and nanotitanate powders sintered at 1250 °C are shown in Fig. 1. It can be seen that there is a high level of porosity, the density and grain size being very similar in both cases, although the grain size shows more variation for carbonate-derived films (grain size ~1 μm for nanotitanate-derived films, and 0.5–2 μm for carbonate-derived films). However, as shown in Fig. 2, after sintering at 1300 °C the carbonate films have started to become more dense and show a slight increase in grain size to ~1.0–3.0 μm whilst the nanotitanate films



(a) (b)

Fig. 1. SEM micrographs of fracture surfaces of thick films sintered at 1250 °C: (a) carbonate-derived film; (b) nanotitanate-derived film.



(a) (b)

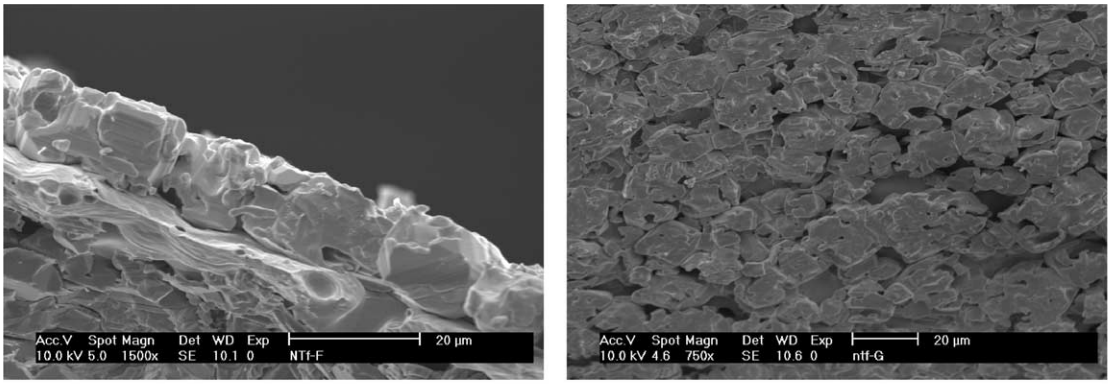
Fig. 2. SEM micrographs of thick films sintered at 1300 °C: (a) carbonate-derived film; (b) nanotitanate-derived film.

appear unchanged. It should be noted that the film thickness for the nanotitanate samples is much smaller, due to the lower solids loading used in the ink.

Both sets of films undergo a rapid increase in grain size above a certain sintering temperature, here called T_{gg} (grain growth temperature) for simplicity. For nanotitanate films T_{gg} is between 1300 and 1350 °C, and the grain size increases to 20–30 µm. For carbonate films T_{gg} is between 1400 and 1450 °C, and the grain size increases to 20–50 µm. The microstructures after grain growth for nanotitanate-derived and carbonate-derived films are illustrated in Figs. 3 and 4, respectively. For carbonate films the grain growth is accompanied by considerable densification. However, nanotitanate films are still very porous. Previous studies on bulk samples made from nanotitanate powders have shown that the majority of densification occurs by 1300 °C therefore, in the case of films, although grain growth removes small scale porosity there is still large scale porosity remaining.

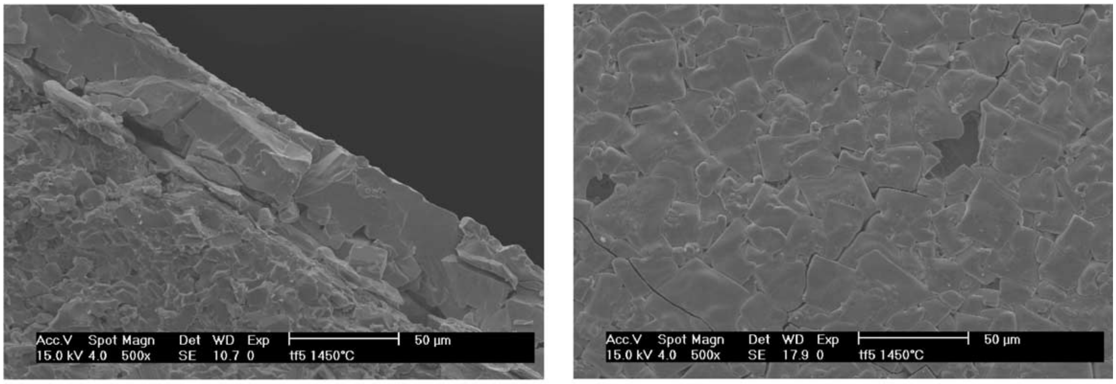
Measurement of the electrical properties over a temperature range of −70–70 °C enabled the Curie peak at the Curie temperature, T_c, to be observed and also gave an idea of the possible effects of temperature variation in the room temperature region which is important for most applications. The dielectric properties of the films are shown in Fig. 5. The permittivity values for samples from both routes sintered at 1250 °C are very similar and both profiles are very diffuse with no clear Curie peak. Below $T_{gg,}$ the value of permittivity at T_c increases with sintering temperature for both routes, as would be expected as the density increases.[3] Above T_{gg}, values of permittivity increase dramatically as a result of the densification and grain growth. Values of permittivity for nanotitanate-derived films sintered above 1250 °C are lower than those for carbonate-derived films, possibly due to their lower overall density and the increased influence of any interfacial effects as a result of their lower thickness.

For both sets of films, T_c decreases with sintering temperature, so much so for nanotitanate-derived films the peak in permittivity is no longer visible on the scale of the measurements. The expected value of T_c for this composition is ~ -30 °C. This can be related to diffusion of the film into the alumina substrate. $Ba_{1-x}Sr_xTiO_3$ has been reported to react with alumina substrates at sintering temperatures >1250 °C.[2,4] Observation of polished sections of the films using a SEM show that



(a) (b)

Fig. 3. SEM micrograph of nanotitanate-derived film sintered at 1350 °C: (a) cross-section; (b) surface.



(a) (b)

Fig. 4. SEM micrograph of carbonate-derived film sintered at 1450 °C: (a) cross-section; (b) surface.

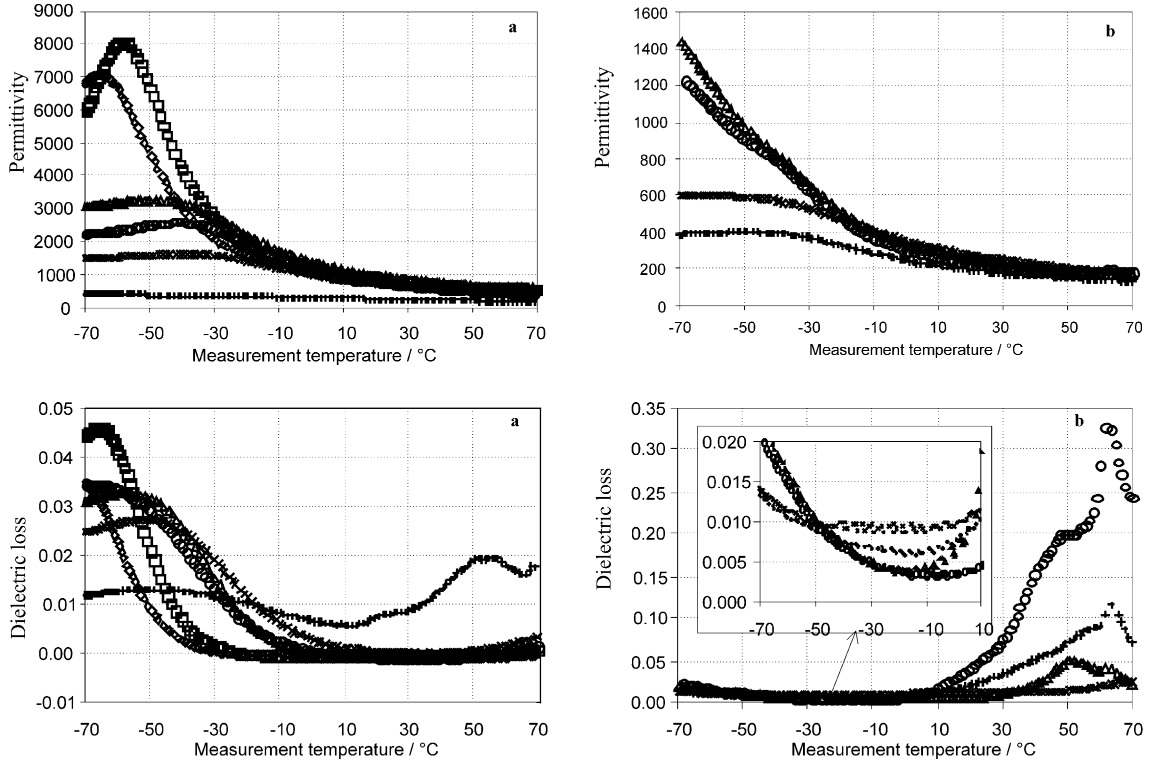


Fig. 5. Temperature dependence of permittivity and dielectric loss at 1kHz between −70 and 70 °C for (a) carbonate route and (b) nanotitanate route; + 1250 °C, × 1300 °C, ○ 1350 °C, △ 1400 °C, ◇ 1450 °C, □ 1500 °C.

diffusion and interaction of the film and the substrate has occurred, as illustrated in Fig. 6. Immediately below the Pt layer a Ba-rich layer can be observed in the alumina substrate. Below this is a layer in which there is a Ba-rich intergranular phase. EDX analysis of the $Ba_{0.5}Sr_{0.5}TiO_3$ film layer shows a smaller percentage of Ba than would be expected, presumably as a result of the diffusion of Ba into the substrate. The shift in T_c can seen to be a consequence of the increasing Sr-content of the $Ba_{1-x}Sr_xTiO_3$ layer as the Ba diffuses out.

Dielectric loss can also be seen to be dependent on sintering temperature as a result of the changes in composition and density, but appears to be less dependent on changes in grain size (Fig. 5). Properties can be separated to those in the ferroelectric and paraelectric regions. A loss peak occurs just below T_c for carbonate-derived films sintered at all temperatures, although the peak becomes better defined when the permittivity-temperature peak is also well-defined (⩾1450 °C). Losses generally increase with increasing sintering temperature in the ferroelectric region and peak at ~0.046 for the sample sintered at 1500 °C. Nanotitanate-derived films do not show loss peaks at low measurement temperatures, possibly as a result of their diffuse permittivity-temperature profile. Losses do however start to increase at low temperatures, as shown in the inset of Fig. 5, but the maximum measured is still only ~0.022. As this loss peak depends on the position of the paraelectric-ferroelectric phase transition, its position is also composition dependent. Therefore, the value of losses, as well as permittivity, at particular temperatures will be dependent on the level of Ba diffusion from the BST film.

In the paraelectric region, losses appear to be dependent on density. All the nanotitanate-derived films and the carbonate-derived film sintered at 1250 °C have large peaks in losses at high temperatures. These are probably due to the low density of the samples allowing moisture to be introduced during the measurement procedure which increases the dielectric loss and are not thought to be indicative of the intrinsic loss of the films. The measured losses are as high as ~0.02 in

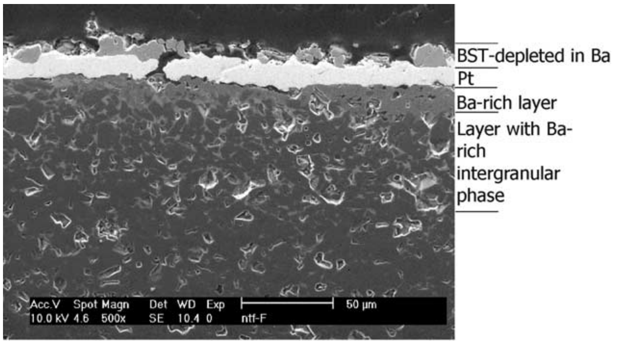


Fig. 6. SEM micrograph of cross-section of nanotitanate-derived film showing Ba diffusion.

carbonate-derived films, and ~0.33 in nanotitanate-derived films. For the higher density carbonate-derived films (i.e. those sintered at ⩾1300 °C), dielectric loss generally decreases with increasing sintering temperature and is generally <0.004.

4. Conclusions

BST thick films of carbonate- and nanotitanate-derived inks have been prepared and characterised. Both carbonate- and nanotitanate-derived films undergo rapid grain growth above a certain sintering temperature, denoted T_{gg} where the grain size increases from ~0.5-6 μm to 20–50 μm. This increase occurs at >1400–>1300 °C for the carbonate-derived and nanotitanate-derived films, respectively.

Below T_{gg}, permittivity increases with density and hence sintering temperature. Above T_{gg}, it is thought that higher levels of Ba diffusion into the alumina substrate result in a lowering of T_c.

Values of permittivity also increase above T_{gg}, due to the increased density of the films. Peaks in dielectric loss occur at low temperature for carbonate-derived films resulting in losses up to ~0.045. Nanotitanate-derived films do not show peaks in dielectric losses at low temperatures and therefore losses are lower in the paraelectric region and are generally <0.02.

Further work is required to investigate the suitability of films for use in microwave devices with dc bias fields and at high frequencies.

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