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Cofiring characteristics and dielectric properties for dielectric composites with macroscopic inhomogeneity and X7R characteristics

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Abstract

A multilayer dielectric composite with a compositional gradient and temperature-stable characteristic was successfully prepared through the conventional tape casting technique. The cofiring behaviors and dielectric properties of the composite were investigated. It was shown that processing parameters not only affected the physical integrity of the composites, but also altered their final dielectric properties. The processing sensitivity was attributed to the interfacial interdiffusion and mismatched sintering shrinkage. Microstructural observation and compositional analysis indicated that the sintered dielectric composite had macroscopic inhomogeneity and layer-like structure. By suitable structural and processing designs, the X7R EIA specification of the composite was obtained, together with low-sintering temperature and high dielectric constant. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Capacitors; Composites; Dielectric properties; Diffusion; Perovskite; Tape casting

1. Introduction

A great deal of effort has been dedicated to the manufacturing of high-performance ceramic capacitor materials with low temperature coefficient of capacitance (TCC). Currently, two kinds of material systems, $BaTiO_3$-based and/or Pb-containing relaxor-based ferroelectrics, were largely developed.[1–5] Although the dielectric-temperature feature of above-mentioned material systems can realise the Electronics Industries Association (EIA) X7R specification,[6] the dielectric constant (K) is not sufficiently large, i.e. below 5000. Moreover, lots of attempts were made to synthesize heterogeneous relaxor materials by mixed-sintering.[7] Unfortunately, the Pb-based relaxor perovskite structure provides high Pb^{2+} mobility such that the various compositions homogenize and the resultant dielectric response is a single peak corresponding to the dielectric characteristics of the average composition.

Recently, we prepared a novel dielectric composite with high K and X7R characteristics, based on a parallel-type structure model, as shown in Fig. 1. Four Pb-containing relaxor dielectric compositions with different diffusion phase transition temperatures (T_{max}) were juxtaposed in a certain volume ratio. The green multilayer compact was then sintered into a monolithic body under suitable processing conditions. It merits in the combination of high dielectric constant, flexible design, low TCC, and low sintering temperature. Thus, compared with conventional $BaTiO_3$ based and/or Pb-containing relaxor based plate capacitors, the capacitors made of the dielectric composite easily obtain a large capacitance and a highly thermal-stable property. Moreover, the composite structural design may be applied in X7R-type high voltage capacitors because the high dielectric constant allows the increased active thickness of the dielectric composite in the same capacitance, which further improves breakdown tolerance. These possible practical applications become the main driving force for investigating the dielectric composite.

Because the preparation of the dielectric composites involves the cofiring of different dielectric compounds,

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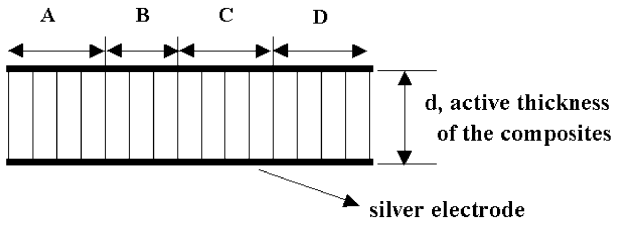

Fig. 1. Schematic diagram of the dielectric composite with four different compositions.

possible interfacial interaction and different sintering behaviors causes the dielectric composites to have a strong sensitivity to the processing parameters. In this paper, some experimental results about the cofiring characteristics, microstructure and dielectric properties was reported. It may be considered that the work will help towards the development of a reliable dielectric composite.

2. Experimental procedure

The detailed procedures of preparing four kinds of Pb-containing perovskite solid solutions and multilayer dielectric composites were referred to elsewhere.[8] The green films of various dielectric compositions prepared by the tape-casting technique were cut and then laminated according to a certain volume ratio under the pressure of ~10 MPa at ~65°C for 5 min to develop a good binding among the layers. Table 1 lists the main compositions and T_{max} of each layer. All starting materials are reagent grade oxides. 2 wt.% excess PbO was used to compensate for the loss of Pb at high temperature and to decrease the sintering temperature to a certain degree. Because of the use of two-step calcination process,[9] nearly pure perovskite phases were obtained, especially after being sintered at high temperature, as demonstrated by X-ray diffraction (XRD).

Green compacts of each dielectric composition and as-laminated multilayer samples were used as densification tests. The sintering densification behaviors were measured by a differential-thermal dilatometer (LCP-1) continuously recording the relative change of the sample length. The microstructures were observed by scanning electron microscope (SEM, Jeol6301F) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Link ISIS300, Oxford). EDS was used to quasi-quantitatively analyze the compositions near the interface. The as-sintered multilayer dielectric composites were polished on both sides perpendicular to the layer and then printed by In–Ga alloy as testing electrodes. The dielectric properties of multilayer composites were measured pseudo-continuously at 1 V_{rms} and 1 kHz at the temperature of −60–130°C using an impedance analyzer (HP4192A), a Delta 2300 automatic temperature control box, and a computer-monitoring system.

Table 1
The compositions and T_{max} of various dielectric layers

Sample No.	Composition		T_{max} (°C)	Volume ratio (%)
A	PNN–PMN–PT	0.36–0.62–0.02	−45	65
B	PMN–PZN–PT	0.92–0.04-0.04	25	10
C	–	0.60–0.36–0.04	65	10
D	–	0.28–0.68–0.04	120	15

3. Results and discussion

3.1. Sintering behaviors and microstructural characteristics of dielectric composites

Because the dielectric composites consist of four kinds of Pb-containing complex relaxor ferroelectric ceramics by cofiring, the sintering behaviour of each dielectric composition will greatly affect the physical integrity of the resultant composites in view of the mismatched densification rate, as shown in Fig. 2(a). The difference of sintering rates mainly depends on the different compositions of these layers even though each layer owns the same perovskite structure. The only difference among B, C and D lies in the relative content of Mg and

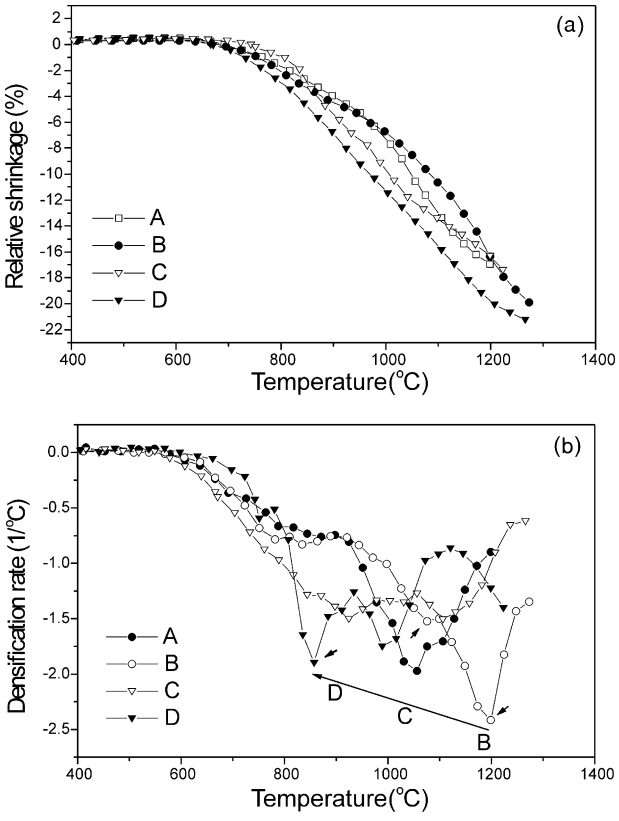

Fig. 2. Sintering characteristics of different dielectric compositions: (a) sintering shrinkage; (b) densification rate.

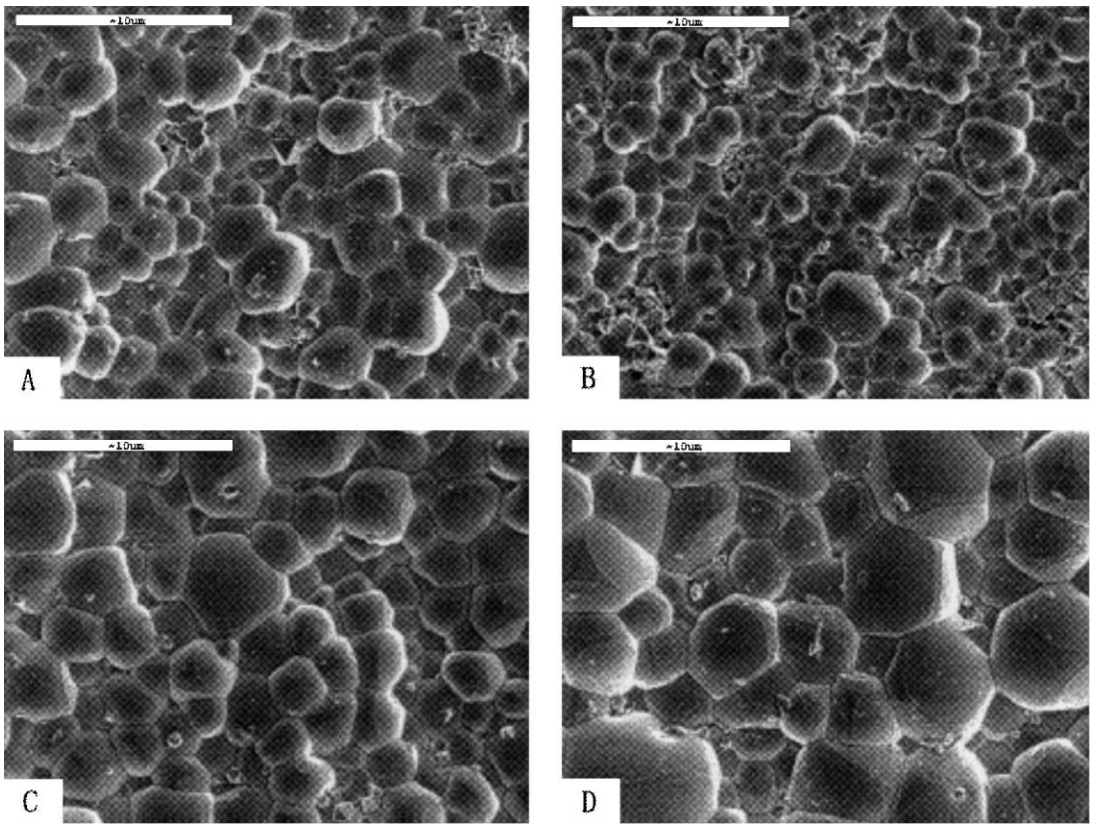

Fig. 3. Grain morphology of four kinds of dielectric compositions (A)–(D) sintered at 1020°C for 2 h.

Zn. Fig. 2(b) shows that the increase in the Zn content can promote the sintering of the ceramics. The arrows indicate the reduced temperature corresponding to the maximum densification rate with the increase of Zn content in the samples. According to the phase diagram,[10] the role of Zn lies in the formation of the eutectics between PbO and ZnO at lower than 900°C. This is also confirmed by the change of the grain sizes of B, C and D layers, as indicated in Fig. 3.

According to the mismatched sintering densification behaviors among different layers, the dielectric composites should be structurally designed carefully to remove the final warping or deformation. This is because a rational laminating order may compensate for the mismatch of the sintering densification. Fig. 4 indicates the influence of different structural design on the sintering densification of dielectric composites. For the dielectric composites with ACDB order, larger densification rate is reached at ~800°C but then reduced with an increase of the sintering temperature up to ~920°C. For DABC composites, the monotonous shrinkage occurs during the total sintering of green multilayer composites. By comparison, the anomalous change of sintering shrinkage for ACDB composites at ~920°C can be attributed to the warping or deformation caused by the mismatched sintering densification. The physical integrity of ACDB composites should come from the counteracting of the shrinkage mismatch between different layers caused by the suitable structural design. In conclusion, the different structural design will affect the physical integrity of the dielectric composites. Moreover, by comparing Figs. 2 and 4, green multilayer dielectric composites with various laminating orders are more easily sintered than each single component. This change can be attributed to the interfacial interdiffusion and chemical reactions happened at the interfaces between different dielectrics.

3.2. Processing dependence of dielectric properties for multilayer composites

Based on a parallel-type computational formula $K = \sum_i ViKi$, the dielectric composite easily realises low

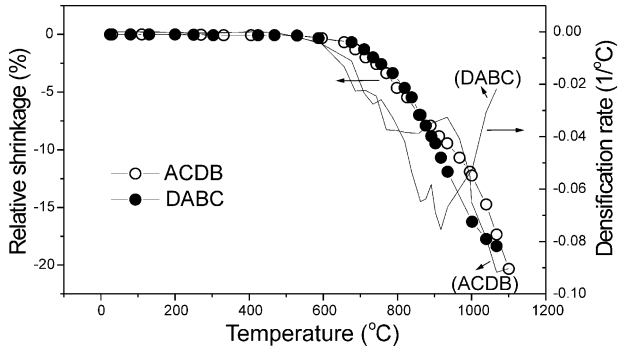

Fig. 4. Sintering densification of different dielectric composites.

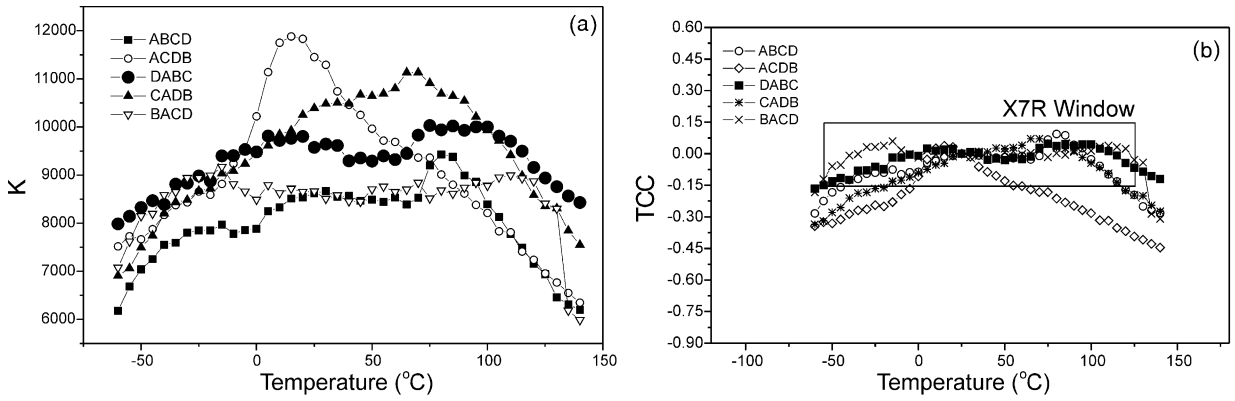

Fig. 5. Dielectric properties of multilayer composites with various laminating orders sintered at 1020°C for 2 h: (a) dielectric-temperature characteristic; (b) temperature coefficient of the dielectric constant.

TCC and high dielectric constant. However, because of the interfacial interaction, the dielectric properties of the composites present strong processing sensitivity. Fig. 5 shows that the dielectric-temperature characteristics of the dielectric composites change with different laminating orders. Among them, the dielectric composites with DABC order present X7R characteristics and high dielectric constant (above 9000) at room temperature, and the dielectric-temperature curves of other composites have evident changes in the amount and location of dielectric curie peak. All these changes will finally cause the fluctuation of TCC. Fig. 6 indicates cross-sectional back-scattering image of the dielectric composites. The brightness and darkness obviously show the existence of four different dielectric compositions in the as-sintered samples. Line scanning results along certain cross section are indicated in Fig. 7. The change of signal intensity for Mg, Ni and Zn elements shows an evident interdiffusion happened at the interface during cofiring.

Moreover, Fig. 8 indicates the effect of sintering conditions on dielectric-temperature characteristics. With the increase in the sintering temperature and time, the amount of the peaks on the K–T curve is evidently reduced. Finally, a single K–T peak is formed because of strong interdiffusion under the high temperature and long time, which causes the formation of nearly single-phase solid solution. Because the diffusion-reaction layers at the interface tend to have an average composition of neighboring dielectric layers, according to the

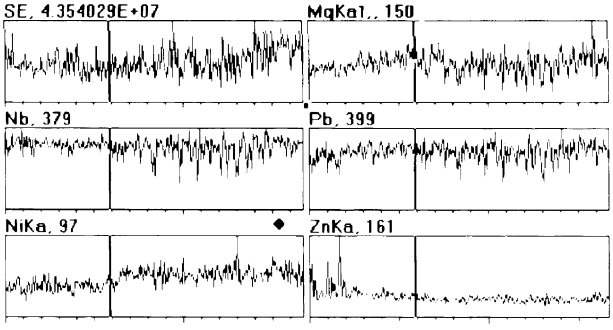

Fig. 7. Line scanning results of different elements across the cross-section (Fig. 6).

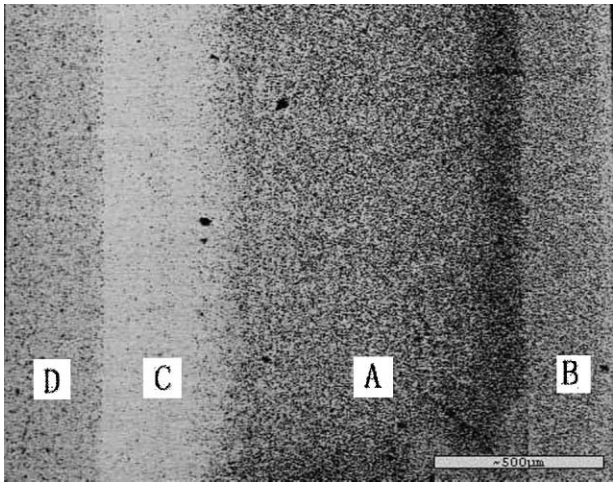

Fig. 6. Cross-sectional back-scattering image of multilayer dielectric composite.

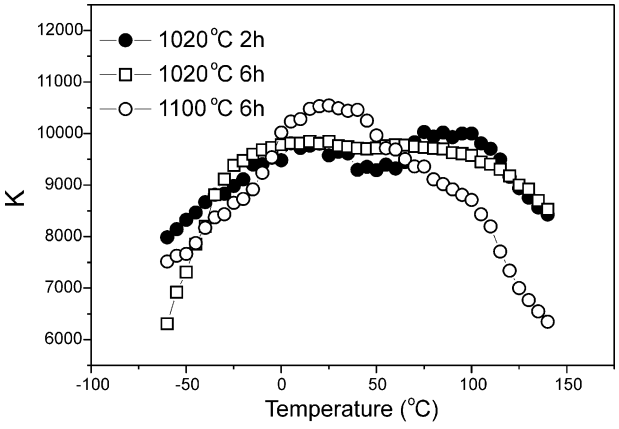

Fig. 8. Influence of sintering conditions on dielectric-temperature properties of multilayer dielectric composite with the laminating order of DABC.

peak-moving characteristics of doped complex perovskite relaxors, the T_{max} value of the compositions at the reaction layers must lie between those of the original dielectrics. All these will lead to the increase of the diffusion feature of each original dielectric peak. Therefore, even though excessive elemental interdiffusion easily degrades dielectric properties, a suitable interfacial diffusion controlled by rational structural design and sintering conditions will be required for temperature-stable and reliable dielectric composites, in view of interfacial integrity and formation of interfacial reaction layers with different T_{max}. Furthermore, the appearance of different dielectric maxima in the dielectric-temperature curves of Fig. 5 also implies that this kind of multilayer dielectric has a composite structure. The macroscopic inhomogeneity is the base of obtaining X7R and high dielectric constant.

4. Conclusions

Low-sintering temperature-stable dielectric composites with layer-like structure and macroscopic inhomogeneity were prepared successfully. The dielectric composites with monolithic structure owned a strong processing sensitivity. The choice of processing parameters not only greatly affected the physical integrity of the sintered composites, but also altered their final dielectric properties. The strong processing sensitivity originated from interfacial interaction during cofiring. The dielectric composite with ideal laminating design under certain sintering process easily realised X7R characteristics and high dielectric constant (above 9000). Both the existence of Pb^{2+} and Zn^{2+} and interfacial interaction greatly decreased the sintering temperature of the composite to $\sim$1000°C.

Acknowledgements

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