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Short communication

Co-firing behavior of $ZnTiO_3$ dielectric ceramics/Ag composites for MLCCs

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Abstract

Ag is frequently used as an internal electrode in multilayer ceramic capacitors (MLCCs). Controlling the co-firing process and interface between the electrode and ceramic is of great importance to obtain highly reliable MLCCs. In this paper, the sintering behavior of the co-firing system of $ZnTiO_3$ dielectric and Ag internal electrode material is studied. Chemical reaction, interfacial microstructure and inter-diffusion are discussed, respectively, based on XRD, SEM and EDS analysis. It is shown that the introduction of Ag can affect the dielectric properties of the ceramic matrix heavily based on dielectric property measurements.

Keywords: B. Interfaces; C. Diffusion; Dielectrics; $ZnTiO_3$; Microstructure; Co-firing

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1. Introduction

Current trends towards smaller size, better performance, higher reliability and lower cost have led to a revolution on manufacturing techniques of multilayer ceramic capacitors (MLCCs) based on advanced tape-casting and surface mounting technologies, which is characterized by the development of MLCCs with base metal internal electrode and thinner dielectric layers [1].

MLCCs, with alternative ceramic layers and electrode layers, may include many defects, such as delaminations, cracks, and holes. Interfacial inter-diffusions as well as chemical reactions would inevitably exist, caused by unsuitable sintering processes and structural design [2–4]. Great efforts have been made to optimize the sintering process and adjust the dielectric ceramic composition, which are considered as two key processes for acquiring advanced MLCC components with high quality and reliability. Unfortunately, the effect of interaction between the internal electrode and the dielectric ceramic layers on the component properties has not yet been fully understood.

$ZnTiO_3$, with relatively low sintering temperature (below 945 °C) and good dielectric properties, have been considered as a suitable candidate for low-temperature co-firing compatibility [5–7]. In this paper, we investigated the co-firing compatibilities of $ZnTiO_3$ dielectric and Ag. The effect of diffusion of Ag addition on the co-firing step, electrical and dielectric properties is also discussed.

2. Experimental procedure

$ZnTiO_3$ was prepared by solid-state reaction method with the chemical reagent powders of ZnO and TiO_2. In order to investigate the effect of Ag on the co-firing behavior, $ZnTiO_3$ powder was mixed with different amount of Ag powder and ball milled for 24 h so as to get uniform mixture. Appropriate amount of B–Pb glass (3 wt.%) was introduced into $ZnTiO_3$ as sintering aids to improve the densification. The ground powder mixture was dried and finally pressed into discs (10 mm in diameter and 1.5 mm thick) and pellet

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samples. The composite samples were sintered at 900 °C for 4 h for microstructure and electrical property measurements.

Phase identification on the sintered discs was performed using X-ray diffraction (XRD, Model D/max-RB, Rigaku, Japan). The microstructure and element diffusion at the interface of silver/ceramic composites were examined by a scanning electron microscopy (SEM, Model JEOL JSM-6301F, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS), respectively. The dielectric measurements were performed using HP4292A Impedance/Gain Phase Analyzer controlled by a PC.

3. Results and discussion

3.1. Shrinkage behavior

The sintering curves of pure Ag, $ZnTiO_3$, and the mixture of $ZnTiO_3$ and Ag powders (20 wt.% Ag) were measured, respectively, by TMA technique in order to study their densification characteristics. Powders were pressed into pellets about 10 mm in diameter and 5 mm thick under 4 MPa. Then, the three samples were heated up at 10 °C/min to 900 °C, 1150 °C and 1050 °C for Ag, $ZnTiO_3$ and the composite of them, respectively.

Figs. 1 and 2 show the shrinkage curves and shrinking rate curves of pure Ag, $ZnTiO_3$, and the mixture of $ZnTiO_3$ with Ag powders (20 wt.% Ag), respectively. It can be seen that the sintering temperature of Ag (about 500 °C) is far below that of $ZnTiO_3$ (nearly 880 °C). Ag finishes its densification at around 700 °C, while at that temperature $ZnTiO_3$ is just starting to densify. For the composite of $ZnTiO_3$/Ag, one can observe at low temperature an expansion of the material, which is unfavorable to the combination of the $ZnTiO_3$ and Ag interfaces. Furthermore, the associated differential shrinkage of the composite would result in interfacial defects like deformations, cracks, and warps [8,9].

Densities of samples sintered at 900 °C for 4 h were measured by Archimedes method. The measured density of $ZnTiO_3$ was 5.08 g/cm^3, and Ag's density was 10.43 g/cm^3.

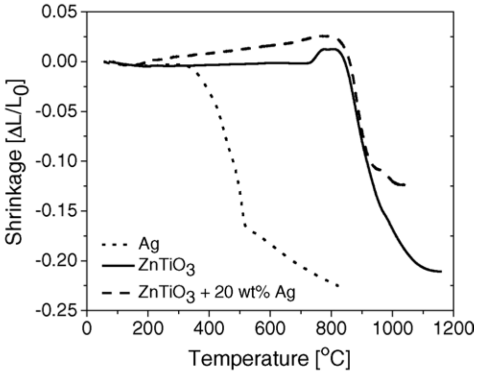

Fig. 1. Shrinkage curves of Ag, $ZnTiO_3$ and their composite.

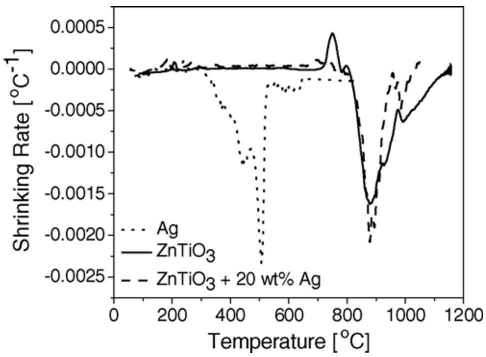

Fig. 2. Shrinking rate curves of Ag, $ZnTiO_3$ and their composite.

The measured, theoretical and relative density of the composite samples, abbreviated as ρ_M, ρ_T and ρ_R hereafter, are all given in Table 1. Here, ρ_T and ρ_R are calculated by the following equations:

$$\rho_T = \rho_{Ag}\frac{\rho_{ZnTiO_3}}{\rho_{Ag} + (\rho_{ZnTiO_3} - \rho_{Ag})x} \qquad (1)$$

$$\rho_R\,(\%) = \frac{\rho_M}{\rho_T} \times 100\% \qquad (2)$$

where ρ_{Ag}, ρ_{ZnTiO_3} is the measured density of pure Ag and $ZnTiO_3$, and x is the weight content of silver in the Ag/$ZnTiO_3$ composites. On the one hand, the density (ρ_M) of the composite increases with the increasing amount of Ag, which partly results from the higher density of Ag. On the other hand, the relative density of the composite also increases with the addition of Ag. This means that Ag addition could lead to an increase of the densification of $ZnTiO_3$.

3.2. Interfacial reaction

To study the interfacial reactions during sintering process, $ZnTiO_3$ dielectric powder was mixed with different weight proportion of Ag powder. The reference was pure $ZnTiO_3$. All the samples were sintered at 900 °C for 4 h. XRD was performed on the sintered discs to characterize the phase transformation of the composite according to the content of Ag addition (samples A–D). The results are shown in Figs. 3 and 4.

It can be seen from Fig. 3 that the XRD patterns of the sintered mixtures are similar to that of $ZnTiO_3$ dielectric. Consequently, there is no significant chemical reaction between $ZnTiO_3$ and Ag to form new compounds, and one

Table 1
The density for a series of samples sintered at 900 °C for 4 h

Sample	$(1-x)ZnTiO_3 + xAg$				
Composition (x, wt.%)	0.000	0.005	0.010	0.050	0.100
Measured density (ρ_M) (g/cm^3)	4.60	4.82	4.84	4.86	5.12
Theoretical density (ρ_T) (g/cm^3)	5.08	5.09	5.11	5.21	5.35
Relative density (ρ_R) (%)	90.55	94.70	94.79	93.28	95.62

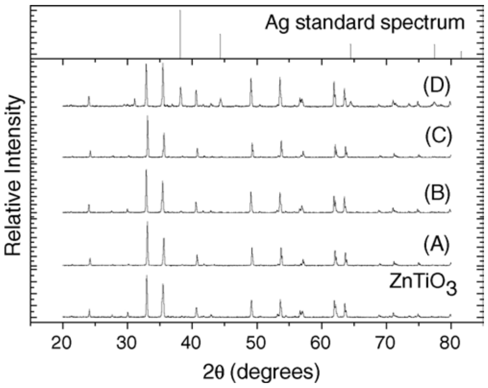

Fig. 3. XRD patterns of $ZnTiO_3$ with different contents of Ag: (A) 0.5 wt.%; (B) 1.0 wt.%; (C) 5 wt.%; (D) 10 wt.%; sintered at 900 °C for 4 h.

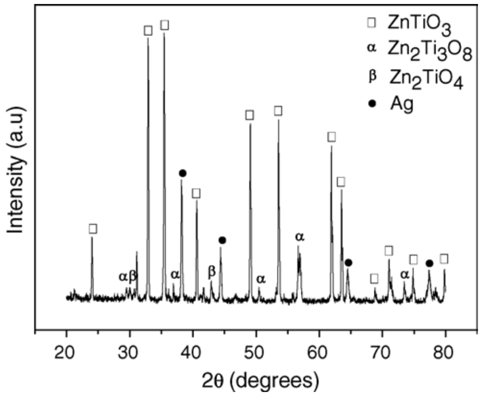

Fig. 4. Phase analysis of $ZnTiO_3$/Ag composite (sample D).

can conclude that Ag particles are located at the interface of $ZnTiO_3$ grains. However, Fig. 4 shows that the content of $Zn_2Ti_3O_8$ and Zn_2TiO_4 has increased obviously with Ag additions, which is due to Ag's effect on the decomposition of $ZnTiO_3$.

3.3. Interfacial structure and diffusion

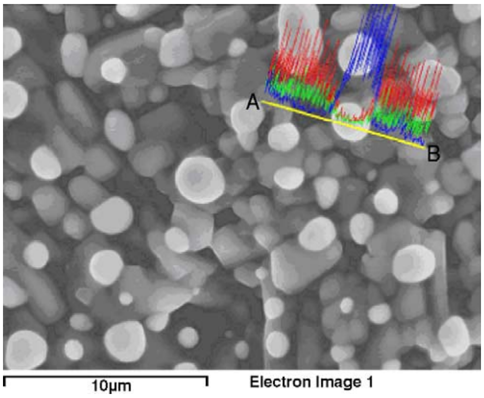

Fig. 5. SEM image of $ZnTiO_3$/Ag composite (sample D).

The microstructure of the mixture sintered at 900 °C was characterized by field emission SEM. The fracture surface of sample D was polished and then etched by 1 M HF acid for 1 min. Fig. 5 shows a cross-section view of the interface between $ZnTiO_3$ and Ag of the sintered sample D. EDS analysis was carried out on the polished section to analyze the main element distribution and diffusion along the thickness direction, as marked by the dark line (AB) in Fig. 5. Fig. 6 shows the line scanning results (along AB) of EDS for concerned elements, Ti, Zn, and Ag, near the interface in sintered sample D.

It can be seen from Fig. 5 that Ag particles distribute separately in the $ZnTiO_3$ dielectric ceramic matrix. This indicates that silver does not enter into the lattice structure of $ZnTiO_3$. EDS results shown in Fig. 6 also reveal that there is no obvious Ag diffusion into the grain of $ZnTiO_3$ dielectric. This is in agreement with the XRD analysis discussed above.

3.4. The effect of Ag particles on the dielectric properties

Fig. 7 illustrates the dielectric constant and the dielectric losses of disc samples with different content of Ag addition. The dependence of dielectric properties on silver content is complex. The perovskite $ZnTiO_3$ has no vacancy in its crystal lattice large enough for Ag diffusion silver, but unavoidably, a small amount of Ag could exist in $ZnTiO_3$. Due to the co-firing mismatch of $ZnTiO_3$ and Ag indicated in Figs. 1 and 2, the entering Ag in $ZnTiO_3$ matrix could lead to stresses and defects, which are deterimental to the dielectric properties. So, a nominal introduction of Ag, less than 0.5 wt.%, can apparently decrease the dielectric constant and increase the dielectric losses as Ag particles dissolve into the interspaces of $ZnTiO_3$. After Ag particles fulfill the vacancies of $ZnTiO_3$, the dielectric constant increases strongly with the increase of the Ag content. For the dielectric losses shown in Fig. 7, it also increases gradually with the increase amount of Ag when the Ag content is over

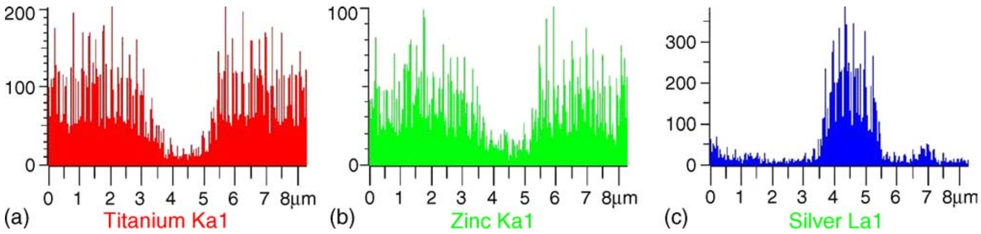

Fig. 6. EDS analysis along the scanning line AB.

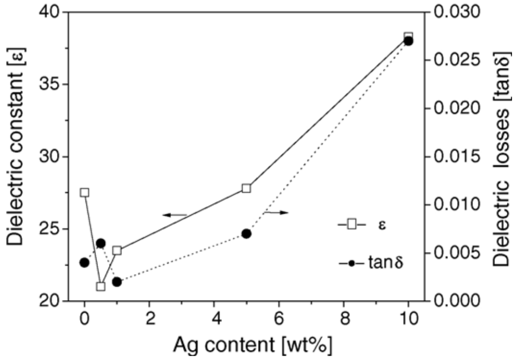

Fig. 7. The dependence of the dielectric constant and losses of the composite on Ag content.

1 wt.%. A large amount of Ag added to the $ZnTiO_3$ matrix could lead to much more defects. These defects such as holes could significantly increase dielectric losses and decrease the dielectric constant to some degree. As indicated in Fig. 4, Ag addition can also accelerate the decomposition of $ZnTiO_3$ into $Zn_2Ti_3O_8$, whose dielectric constant is larger than that of $ZnTiO_3$ [9]. In a word, at this stage, the increase of dielectric constant mainly results from the addition of a large amount of Ag. The increase of dielectric losses is the result of the defects arising from the mismatch between Ag and $ZnTiO_3$.

4. Conclusions

This paper mainly discussed shrinkage behavior, interfacial diffusion and reaction between $ZnTiO_3$ dielectric and Ag, and the effects of Ag addition on the dielectric properties. No obvious chemical reaction or elemental diffusion between $ZnTiO_3$ and Ag was observed. Significant co-firing mismatches exist between $ZnTiO_3$ and Ag, which greatly increase the dielectric losses. Due to the high conductivity of Ag and the mismatch between Ag and $ZnTiO_3$, the addition of Ag could affect the dielectric properties heavily as shown by the dielectric measurements.

Acknowledgements

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