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Interfacial investigation of the Co-fired NiCuZn Ferrite/PMN composite prepared by tape casting

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Abstract The co-firing behavior and interfacial diffusion of the co-fired system of NiCuZn ferrite (abbreviated as NiCuZn) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (abbreviated as PMN) relaxor ferroelectric are studied in this work. NiCuZn layers and PMN layers prepared by tape casting were stocked alternately. X-ray diffraction analysis shows no new phase appeared in the mixture of NiCuZn and PMN. Scanning electronic microscopy observation of the bi-layer composite indicates obvious warp at the interface due to the sintering mismatch between ferrite and ferroelectrics. The co-firing property of NiCuZn and PMN is modified by doping appropriate content of Bi_2O_3. By pressing a mixed composition interlayer in the ratio 50:50 between the ferrite and ferroelectric layers, a crack-free multilayer structure could be obtained.

Keywords Co-firing · Ferrite · Interface · LTCC

1 Introduction

With the rapid development of the surface mounting technique(SMT) and multilayer co-firing technology, multilayer monolithic ceramic chips having a small size and high efficiency, are in great demand as the main components of large-scale integrated circuits [1–3]. Many of the devices involve co-firing different functional ceramic layers. Previous studies have shown that the mismatch of sintering properties would lead to a lot of co-firing defects but lacked a systematic study on the co-firing behavior of multilayer ceramic sample prepared by tape casting method [4–9].

NiCuZn ferrites are widely used in multilayer chip inductors (MLCIs) applications because of their relatively low sintering temperature and high resistivity [10, 11]. Lead-based complex relaxor ferroelectrics have been extensively used for functional ceramic devices due to their anomalously large dielectric constant, large electrostrictive strain, and relatively low firing temperature [12–14]. Multilayer ceramics based on ferrites and lead-based relaxors are absorbing more and more interest because of their excellent ferromagnetic and ferroelectric properties. However, interfacial problems in these multilayer materials have not been thoroughly resolved. The co-fired mismatch of ferrites and lead-based relaxors is often serious. This has greatly affected the reliability and electronic properties of these multilayer devices.

In this work, the appropriate matching condition of the co-firing system NiCuZn/PMN was studied and an improvement on the co-firing match between NiCuZn and PMN is established through adding sintering aid in ferrite and inserting interlayers between ferrite and ferroelectric layers.

2 Experimental

NiCuZn powders were mixed and milled in a ball mill for 16 h with the mixture of propyl acetate and iso-butyl alcohol as solvent firstly. Then plasticizer (dioctyl phthalate, DOP) and binder (polyvinyl butyral, PVB) were added and mixed for another 16 h to obtain the uniform slurry.

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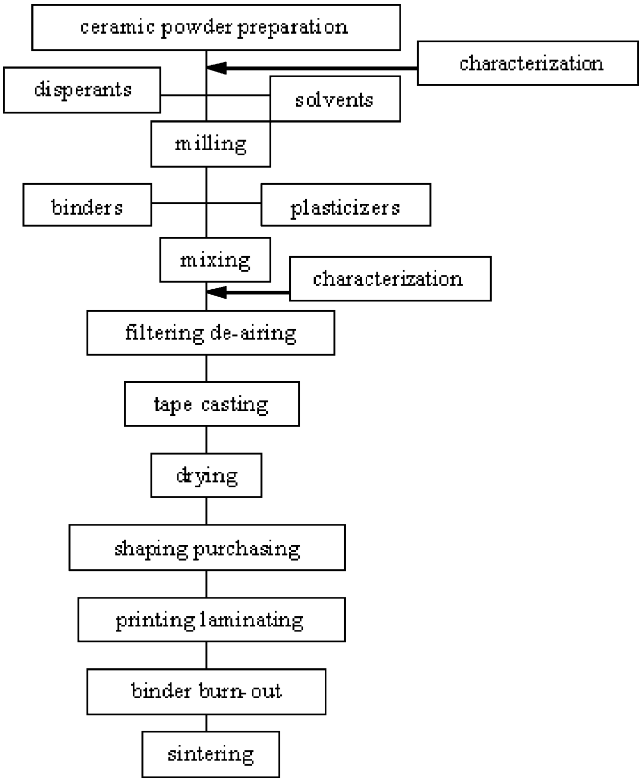

Fig. 1 Flow chart for the preparation of NiCuZn ferrite and PMN multilayer ceramics

The slurry preparation procedure of PMN was the same with that of NiCuZn. A laboratory-type caster with a doctor blade was used to produce green tapes. Casting was conducted at about 30 cm/min. Multilayer samples were fabricated by stacking ferrite and ferroelectric green tapes alternately and then pretreated by warm-stacking at 65 °C under 3 MPa for 15 min to develop a good bonding between layers. The flowchart for the preparation of the multilayer composites is shown in Fig. 1. The burning-out temperature for organic components in the cast tapes was determined by thermogravimetric analysis (TG). The sintered multiplayer samples were used to observe the interfacial microstructure.

Mixture of ferrite and ferroelectrics is made up in 50:50 wt% ratios to be used as interlayers. It was ground together by ball milling for 12 h to ensure a homogeneous mixture.

Several cylindrical samples of NiCuZn and PMN (10 mm in diameter, 5 mm thickness) pressed under 5MP were used to measure the sintering densification characteristics as a function of sintering temperature in the air at a heating rate 5 °C /min by a thermomechanical analyzer (Model TMA92, Setaram, Caluire, France).

An X-ray diffractometer (XRD: Rigaku, Tokyo, Japan) with CuKα radiation was used to identify the chemical reactions between NiCuZn and PMN. The grain morphology and interfacial microstructure of the samples sintered at 950 °C were observed by SEM (JEM-6301F) in secondary electron(SE) or back-scattered(BS) mode.

3 Results and discussion

To study the phase transformation during the sintering process, NiCuZn and PMN powders were mixed in the weight proportion of 0.4:0.6. The references were pure NiCuZn ferrite and pure PMN. These three kinds of powders were added with PVA and then pressed into pellet and sintered at 950 °C for 4 h in the air.

Figure 2 shows the XRD spectra of the as-sintered NiCuZn ferrite/PMN composite together with those of single-phase NiCuZn and PMN. XRD analysis shows no any new phase and it indicates that there is no any chemical reaction between NiCuZn and PMN. It is well known that the main problem in the fabrication and sintering of pure perovskite PMN samples is the formation of the unwanted pyrochlore phase that would decrease the dielectric and electromechanical performances of the material. However, in our work, XRD patterns show no pyrochlore phase after sintering at this temperature and the perovskite phase of PMN in the mixture remained stable.

The sintering curves of ferrite and relaxor ferroelectrics were measured using TMA technique. Seen from Fig. 3, an apparent sintering mismatch between NiCuZn and PMN is noted. The accumulative shrinkage of PMN is much smaller than that of NiCuZn before 920 °C, which densified slowly in a long temperature range from 750 °C to 920 °C. Also, NiCuZn densifies much slower than PMN relaxor ferroelectric at temperatures below 920 °C, but becomes slightly faster at higher temperatures. Moreover, NiCuZn

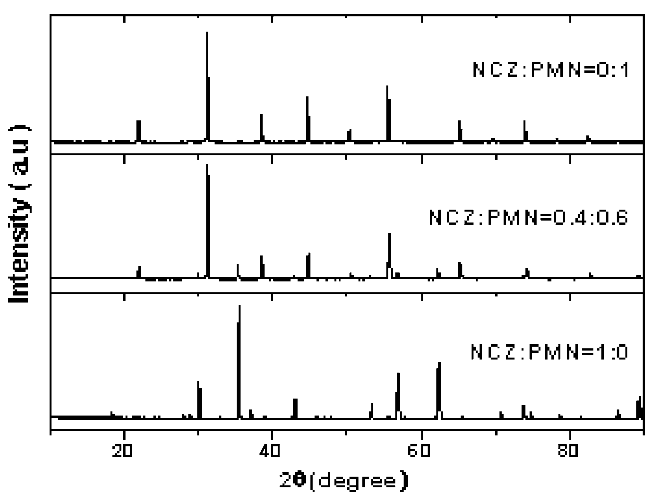

Fig. 2 XRD spectra of pure NiCuZn ferrite, PMN and their mixture (all sintered at 950 °C)

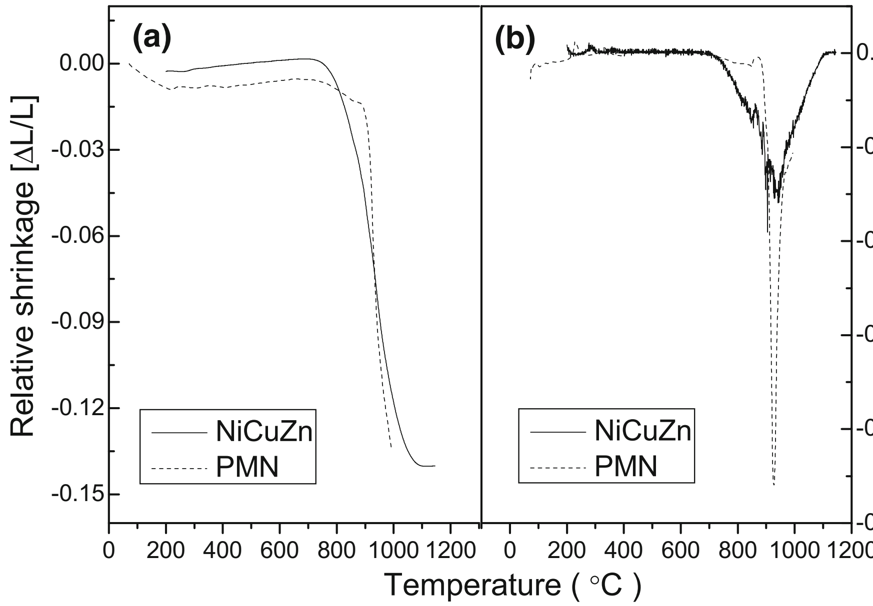

Fig. 3 Densification characteristics of the ferrite and ferroelectric ceramics: (a) shrinkage; (b) shrinking rate

reaches its maximum densification level at about 1,100 °C, which is nearly 200 °C higher than that of PMN. The inconsistent shrinkage explains the formation of interfacial stress and warping deformation. As a result, more than two-third of the co-fired multilayer samples have broken up into pieces.

Figure 4 shows a micrograph of the interface in a bi-layer sample co-fired at 950 °C for 4 h. An obvious warp exists at the interface between the ferrite and ferroelectric ceramic layer. It is believed that a mismatch in the sintering densification characteristics between these two different ceramics should be responsible for the interfacial defects.

As seen from Fig. 3, the ferroelectric layer underwent less shrinkage than did the ferrite layer after 920 °C, and hence the associated differential shrinkage would establish interfacial stresses, including tensile and compressive stress. As clearly shown in Fig. 4, the ferroelectric layer was placed in a state of compression and the sample relieved the inter stress by bending and delamination.

From the analyses above, a suitable modification of line shrinkage profiles is a prerequisite for a successful co-fired system. Considering to retaining the best electromagnetic properties of NiCuZn and PMN, we added different content (all below 2 w%) Bi_2O_3 as the sintering additives for NiCuZn. Fig. 5 shows that the sintering behaviors of the NiCuZn have been considerably modified after being added Bi_2O_3 additives. Although the onset sintering temperature is slightly changed, the sintering shrinkage rate apparently modified. The differential shrinkage is clearly reduced. Particularly, the shrinkage profiles of NiCuZn with 1.0 wt% Bi_2O_3 shows an outstanding resemblance with that of PMN, which demonstrates a good co-firing matching condition between these two ceramics.

Figure 6a shows back-scatter morphology near the interface between PMN and NiCuZn doped with Bi_2O_3 (1.0 wt%) in a multilayer sample prepared by tape casting and sintered at 950 °C for 4 h. Alternate heterogeneous layers are in good connection, with no evidence of cracks or delaminations. Both ferrite and ferroelectric layer show a dense microstructure and the corresponding grains grow normally. The melting of Bi_2O_3 at the grain boundary leads to the transient liquid sintering of the ceramic at high temperature and will help the sintering of the composites.

In order to further improve the sintering behavior, we insert an interlayer between ferrite and ferroelectric layers. This interlayer consists of half-and-half NiCuZn and PMN. From Fig. 7a it can be seen that by using an intermediate

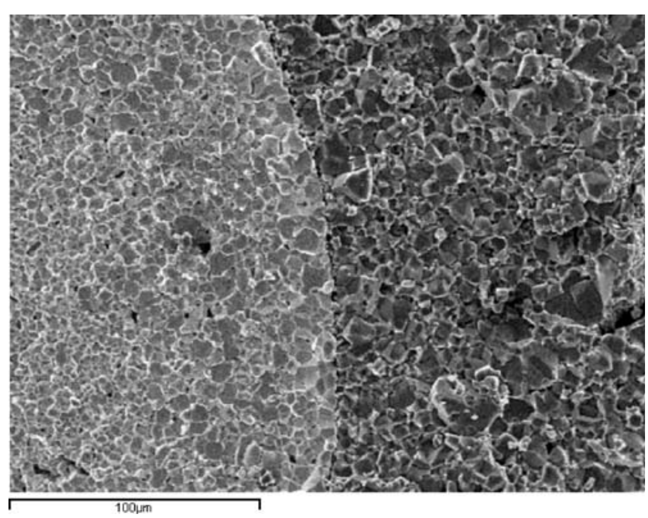

Fig. 4 Cross-sectional microstructure of a bi-layer sample (sintered at 950 °C for 4 h)

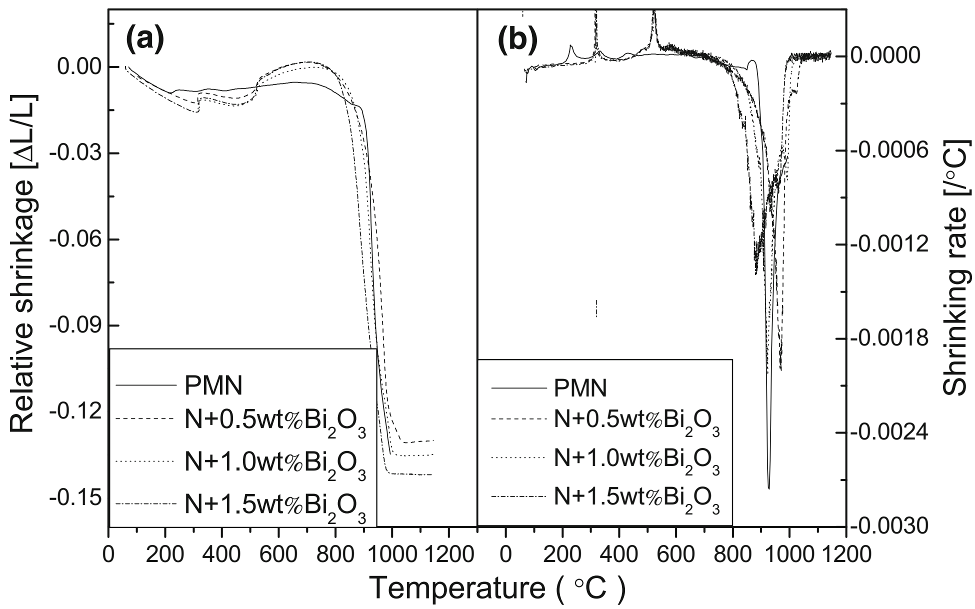

Fig. 5 Densification characteristics of the ferrite added with sintering aids: (a) shrinkage; (b) shrinking rate

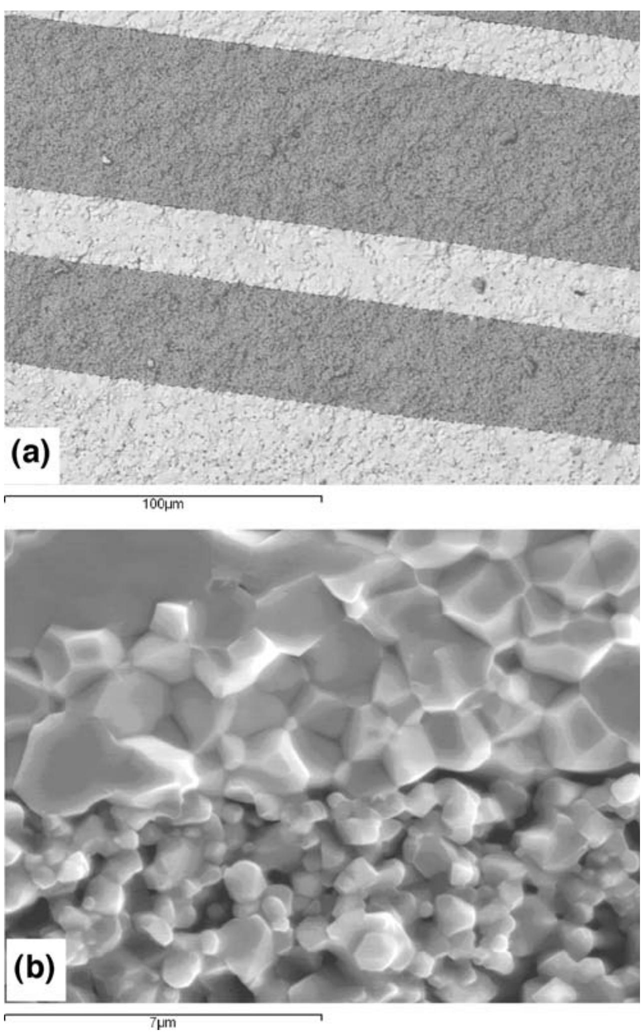

Fig. 6 SEM image of the cross-sectional view of the interface between NiCuZn ferrite doped with 1.0 wt% Bi_2O_3 and PMN ferroelectrics: (a) back-scatter image of multilayer samples; (b) SEM image of interfacial microstructure

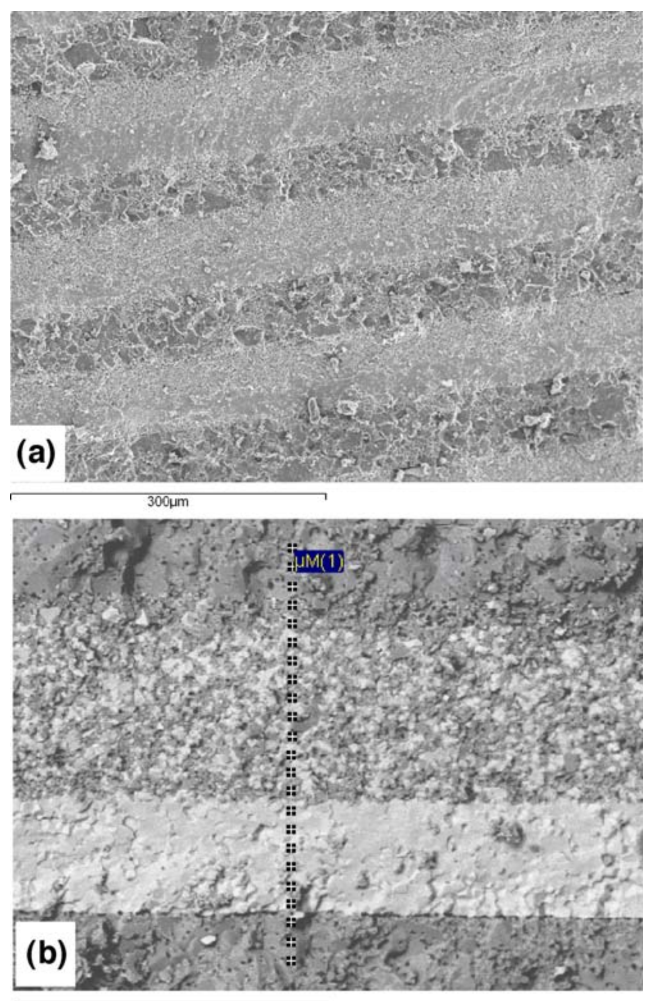

Fig. 7 (a) SEM image of the multilayer composite with interlayer; (b) BS image of (a)

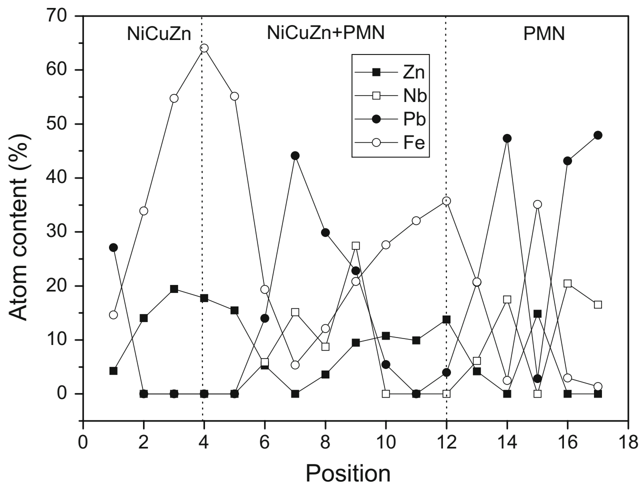

Fig. 8 The concentration profiles for the concerned elements along the line in Fig. 7b

50:50 interlayer a crack-free multilayer sample can be fabricated. This interlayer has partially similar structure with ferrite and ferroelectrics and it also has the same elements with those of NiCuZn and PMN. So, beyond regulating the sintering of the composites, it can also increase the affinity between the NiCuZn and PMN layers. Compared with this, interfacial bonding is weaker for composites without interlayer indicated in Fig. 6b. BS image of interfaces in Fig. 7b shows a continuous element diffusion area near the interface between NiCuZn and interlayer as well as the interface between PMN and interlayer. In other words, the interfaces here are blurred by the element diffusion. Fig. 8 further demonstrate element such as Fe, Zn and Pb diffuse obviously at the heterogeneous interfaces. Interfacial element diffusion has greatly improved the interface boding and mechanical integrity, as shown in Fig. 7a and b.

4 Conclusions

An investigation of the co-firing behavior of NiCuZn and PMN has been fully carried out. Undesired interfacial defects, such as delaminations and warping were observed. Sintering aids were successfully used to regulate the co-firing behaviors and improve the bonding and mechanical integrity at the interface. A mixed composition interlayer has the chemical and structural affinity with both ferrite and ferroelectrics and therefore greatly promote the interfacial bonding.

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