Article ID: 1003 - 6326(2005)02 - 0225 - 04

Cofiring behavior of NiCuZn ferrite/PMN ferroelectrics di-layer composites①

MIAO Chun-lin(缪春林), ZHOU Ji(周 济),
YUE Zhen-xing(岳振星), LI Long-tu(李龙土)
(State Key Laboratory of New Ceramics and Fine Processing,
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China)

Abstract: The cofiring compatibility between ferrite and relaxor ferroelectrics materials is the key issue in the production of multilayer chip LC filters. The cofiring behavior, interfacial microstructure and diffusion of di-layer composites of NiCuZn ferrite/PMN relaxor ferroelectrics are studied. In order to analyze the matching condition of thermodynamic properties between ferrite and relaxor ferroelectric ceramics, TMA is performed on PMN ferroelectrics and NiCuZn ferrite with certain percentage of Bi_2O_3, respectively. EDS results demonstrate that serious element diffusions exist at the interface, which is in accordance with the phase analysis based on XRD patterns.

Key words: NiCuZn ferrite; cofiring; multilayer; interface

CLC number: TB323 **Document code:** A

1 INTRODUCTION

Recently, with the rapid development of the surface mount technology (SMT) for miniaturization, high efficiency and reliability, multilayer ceramic devices have been widely used in electronic circuits, such as multilayer ceramic capacitors (MLCC), multilayer chip inductors (MLCI) and multilayer piezoelectric transducers (MLPT)[1-3].

Multilayer chip LC filter, which is combined with capacitor layers and inductor layers alternately, is a type of advanced surface mount devices. The cofiring comparability between different ceramic materials and the role of the cofired interface on properties of the devices are two key issues for manufacturing the multilayer chip LC filters. Because of the mismatching of the sintering kinetics, sintering densification behaviors and various thermodynamic parameters between ferrite and dielectric materials, undesirable cofiring defects such as delaminations, cracks and cambers are easily introduced in the final products. Moreover, phase transformation and chemical reaction may occur at heterogeneous interfaces. The effect of this interaction on the interfacial microstructure is generally considered one of the root reasons for the deterioration of electrical properties[4]. Therefore, the research on the cofiring behaviors between different ferrite and ferroelectric ceramic materials has become an important base for developing multilayer LC filters.

During the past few years, much research work was dedicated to studying the cofiring behaviors of multiplayer chip LC filters based on different systems, such as $ZnTiO_3$/NiCuZn[5], PNNT/NiCuZn[6, 7], $BaTiO_3$/ferrite[8] and TiO_2/NiCuZn[9]. However, the cofiring properties and interfacial interactions between NiCuZn ferrite and PMN ferroelectrics composites have not been studied. NiCuZn ferrite, which has excellent magnetic properties and can be sintered at low temperature with appropriate amount of sintering aids, is an important material for producing low-temperature sintered MLCI[10-12]. Lead magnesium niobate (PMN)-based relaxor ferroelectrics have become one of the most important material systems in MLCC applications owing to their valuable properties such as low sintering temperatures and high dielectric constants[13-15]. Both are promising candidates for multilayer chip LC filter applications.

In this work, the multilayer composites were prepared by cofiring NiCuZn ferrite (abbreviated as NiCuZn) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ ferroelectrics. The sintering characteristics of single ferrite and ferroelectrics were analyzed first. In addition, the cofiring properties including chemical reaction, interfacial diffusion and interface microstructure of ferrite/ferroelectrics composite were investigated.

2 EXPERIMENTAL

2.1 Specimen preparation

① **Foundation item:** Project(2001AA320502; 2003AA32G030) supported by Hi-tech Research and Development Program of China; Project (2002CB613306) supported by the National Basic Research Program of China

Received date: 2004 - 11 - 20; **Accepted date:** 2005 - 01 - 18

Correspondence: ZHOU Ji, Professor, PhD; Tel: +86-10-627-84579; Fax: +86-10-627-71160; E-mail: zhouji@mail.tsinghua.edu.cn

The NiCuZn ferrite was prepared by the traditional solid-state reaction method. The analytically pure NiO, CuO, ZnO and Fe_2O_3 were used as raw materials, which were mixed according to stoichiometric composition and then calcined at 700 ℃. Different amounts of Bi_2O_3 were added to the ferrite in order to modify the densification properties of the NiCuZn ferrite and to lower the sintering temperature, and then mixed in ball mill for 24 h and dried. The $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor ferroelectric ceramic powders were provided by Fenghua Electronic Ceramic Company (Guangdong, China). The NiCuZn ferrite and PMN powders were separately added with PVA for granulation, shaped into pellets (10 mm in diameter and 1.5 mm in height) and then cold-isostatically pressed at 150 MPa. The di-layer composites of NiCuZn/PMN were prepared by first pressing NiCuZn ferrite powder in a mould, then adding PMN powder and pressing again at 1.5 MPa and finally cold-isostatically pressing the resulting pellets at 150 MPa for 3 min. The resulting samples were sintered at 950 ℃ for 4 h.

2.2 Characterization

Shrinkage curves were produced by a thermomechanical analyzer (TMA, SETARAM). The sintered densities were measured by the Archimedes method. The phase structure for the specimens was identified using X-ray diffractometer (XRD, Rigaku). The microstructure and element distribution on the cross section of the composites were examined by scanning electron microscopy (SEM, JEM-6301F) and energy dispersive X-ray spectroscopy (EDS), respectively.

3 RESULTS AND DISCUSSION

3.1 Phase analysis

To determine whether any interfacial reaction between these two materials would occur, the 50/50 (mass fraction, %) mixture of NiCuZn ferrite and PMN ferroelectrics was prepared and sintered at 950 ℃ for 4 h. Fig. 1 shows the XRD pattern of the as-sintered mixture sample, together with that of single-phase NiCuZn ferrite and PMN.

As indicated in XRD patterns, the mixture sample contains pyrochlore phase after the addition of NiCuZn ferrite, although pure PMN sintered at 950 ℃ is of single perovskite phase. This illustrates that potential chemical reactions may exist between NiCuZn ferrite and PMN ferroelectrics to form new phases, such as pyrochlore, which is detrimental to electronic properties. Moreover, the interdiffusion around the interface between NiCuZn grains and PMN grains is also responsible for the formation of new phases, which can be demonstrated from the energy dispersive X-ray analysis.

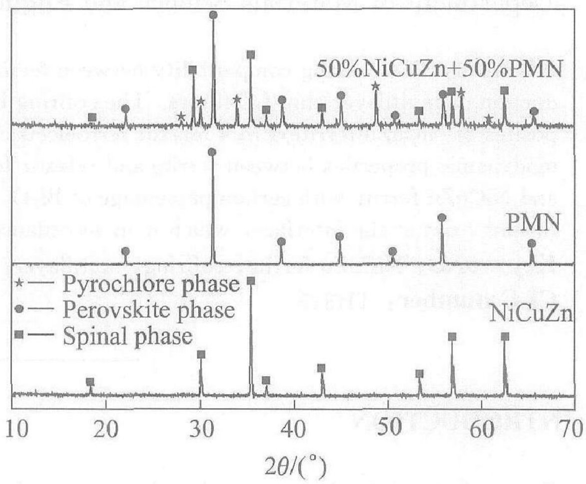

Fig. 1 XRD patterns of mixture sample, ferroelectrics and ferrite sintered at 950 ℃

3.2 Shrinking behavior

Fig. 2(a) shows the shrinkage curves of PMN, NiCuZn and NiCuZn ferrite with certain proportion of Bi_2O_3 sintering aid fired at a heating rate of 10 ℃/min. The onset temperature of NiCuZn ferrite (about 800 ℃) is much lower than

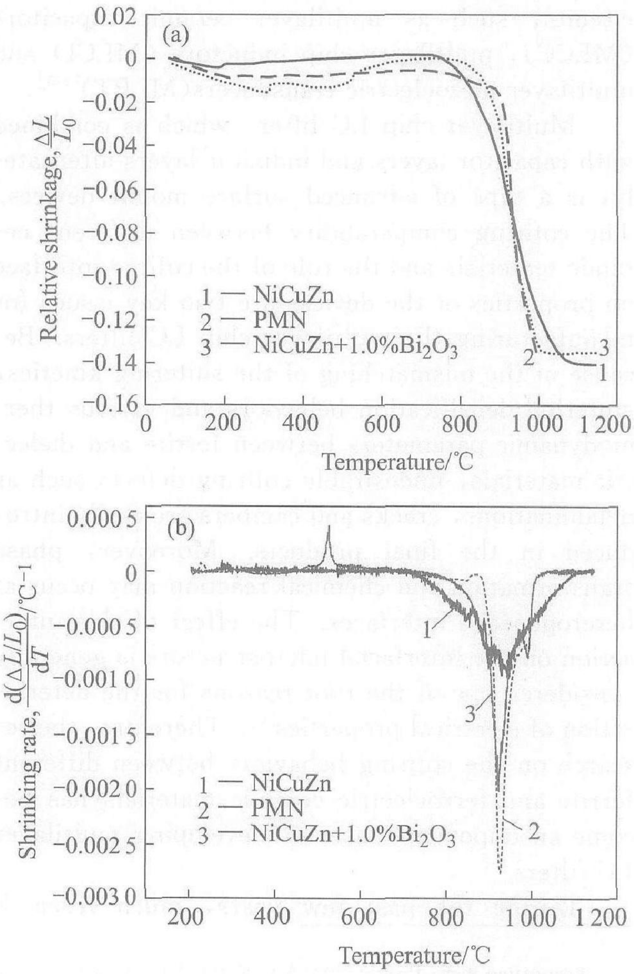

Fig. 2 Densification characteristics of NiCuZn, PMN and NiCuZn added with Bi_2O_3

(a) —Shrinkage; (b) —Shrinking rate

that of PMN. Once the PMN ferroelectrics begin to densify, the densification is completed at a higher densification rate over a narrow temperature range compared with the shrinking process of NiCuZn ferrite. Only one peak appears in the differential shrinkage rate shown in Fig. 2(b). The maximum densification rate for pure PMN ferroelectrics is much higher than that of NiCuZn. A comparison between the densification behaviors of NiCuZn ferrite with Bi_2O_3 and the pure one reveals that the sintering additives can favorably modify the sintering mismatching between the ferrite and ferroelectrics.

3.3 Interfacial microstructure

Fig. 3 shows SEM micrographs of the interfacial microstructure of Bi_2O_3-doped NiCuZn/PMN composites (labeled as sample 1, 2 and 3) that were sintered at 950 ℃ for 4 h. It can be seen from Fig. 3(a) of sample 1 that the interface is in good

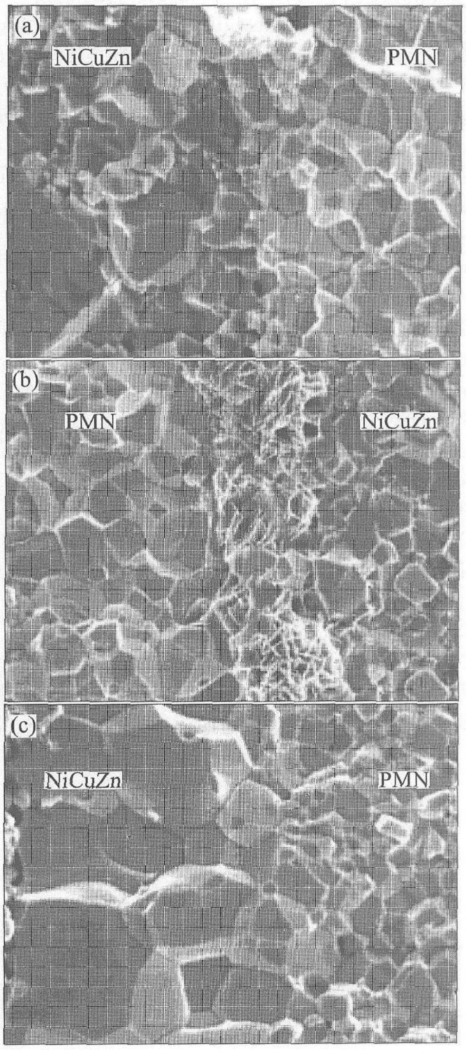

Fig. 3 SEM images of cross-sectional morphology of interface between NiCuZn ferrites doped with 1.0% Bi_2O_3 and PMN ferroelectrics cofired at 950 ℃
(a) —Sample 1; (b) —Sample 2; (c) —Sample 3

connection. The grain sizes of NiCuZn ferrite and PMN ferroelectrics are about 2 μm and 3.5 μm, respectively. Obviously, new phase is observed at the interface in sample 2. The heating treatment at temperatures above 800 ℃ can lead to the loss of PbO by evaporation, which will cause the formation of pyrochlore phase, and the lead diffusion at the interface of NiCuZn/PMN composites can aggravate this trend. Hence Pb^{2+} deficiency arising from lead content near the interface less than the content in the ferroelectrics body promotes the formation of pyrochlore. In addition, as shown in sample 3, abnormal grain growth is also found near the interface between NiCuZn ferrite and PMN grains, which may be promoted by the liquid phase of Bi_2O_3 due to its low melting point (about 750 ℃) when Bi_2O_3 migrates towards the interface. It is evident that the small amount of new heterogeneous phases like pyrochlore near the interface can promote different sintering mechanisms leading to very different microstructures[16].

3.4 Interfacial diffusion

Fig. 4(a) shows the cross-sectional back-scattered (BS) image of the NiCuZn/PMN composite. The darkness and brightness apparently indicate the existence of the two different ceramic compositions, NiCuZn and PMN, in the as-sintered sample 1.

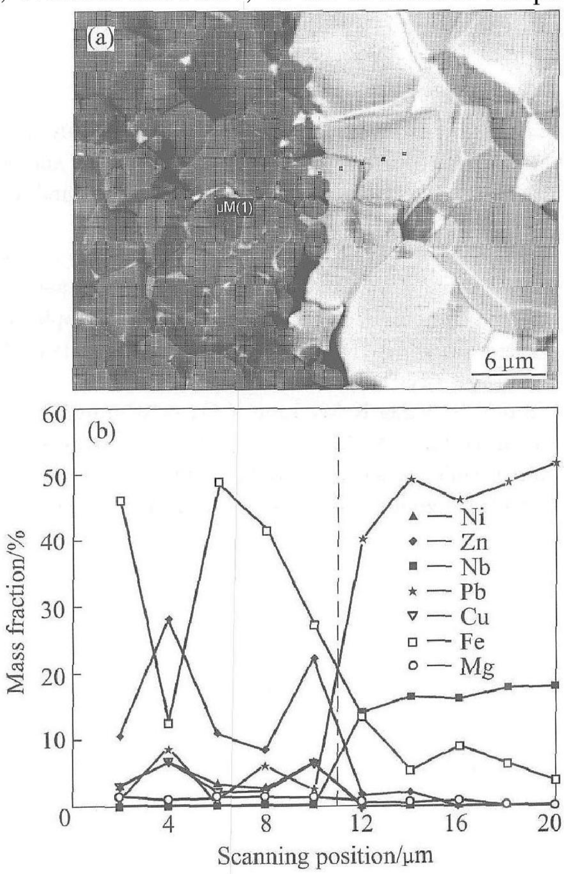

Fig. 4 Back-scattered image of interface in sample 1(a) and content profiles for concerned elements(b)

Element diffusion across the cofired interface between NiCuZn ferrite and PMN ferroelectrics was examined using EDS analysis. The ordinal points in the BS image correspond to the position numbers in Fig. 4(b), where the contents of main elements (Ni, Cu, Zn, Fe, Nb, Mg and Pb) detected with EDS are plotted. It can be seen that contents of Zn, Fe and Pb change gradually, which reveals that the intense interdiffusions exist between the ferrite and ferroelectrics during the cofiring. The above result is in agreement with the X-ray diffraction patterns based on Fig. 1.

4 SUMMARY

The di-layer composites with good interfacial bonding are prepared by cofiring PMN ferroelectrics and NiCuZn ferrite added with appropriate amount of sintering aid. Analyzed by the XRD patterns, potential chemical reaction between NiCuZn ferrite and PMN ferroelectrics exists. Additionally, significant element diffusion at the interface between ferrite and ferroelectrics is confirmed by EDS, which leads to the formation of new phase and the exaggerated grain growth near the interface. Potential adverse chemical reactions and the serious element distribution will be well studied and eliminated for the practical application of multilayer LC filters.

REFERENCES

[1] CAO Jiang-li, LI Long-tu, GUI Zhi-lun. Interactions at the cofired interface of Ag/Pd electrode and lead-based ferroelectrics [J]. Materials Science and Engineering B-Solid, 2003, 99: 127-130.

[2] Kim D W, Hong K S, Yoon C S, et al. Low-temperature sintering and microwave dielectric properties of $Ba_5Nb_4O_{15}$-$BaNb_2O_6$ mixtures for LTCC applications [J]. Journal of the European Ceramic Society, 2003, 23: 2597-2601.

[3] Shin Y S, Kang K M, Jung Y G, et al. Internal stresses in $BaTiO_3$/Ni MLCCs [J]. Journal of the European Ceramic Society, 2003, 23: 1427-1434.

[4] ZUO Ru-zhong, LI Long-tu, GUI Zhi-lun, et al. TEM and EDS investigation of heterogeneous interfaces in cofired multilayer ceramic capacitors [J]. Materials Science and Engineering B-Solid, 2002, 95: 1-5.

[5] WANG Mao, YUE Zhen-xing, ZHOU Ji, et al. Co-firing behavior and interfacial structure of dielectric/ferrite composites for multiplayer LC filters [J]. Key Engineering Materials, 2002, 224-226: 151-154.

[6] GAO Feng, YANG Zu-pei, HOU Yu-dong, et al. Co-firing properties and camber development of ferroelectric/ferrite multiplayer composites [J]. Journal of Materials Science, 2003, 38: 1523-1528.

[7] GAO Feng, QU Shao-bo, YANG Zu-pei, et al. Interface and ionic interdiffusion in cofired ferroelectric/ferrite multiplayer composites [J]. Journal of Materials Science Letters, 2002, 21(1): 15-19.

[8] Aran R, Yurii G K, Ramesh R. An investigation of co-fired varistor-ferrite materials [J]. Journal of the European Ceramic Society, 2004, 24: 2005-2013.

[9] Hsiang H I, Lia W C, Wang Y J, et al. Interfacial reaction of TiO_2/NiCuZn ferrites in multilayer composites [J]. Journal of the European Ceramic Society, 2004, 24: 2015-2021.

[10] Nakamura T. Low-temperature sintering Ni-Cu-Zn ferrite and its permeability spectra [J]. Journal of Magnetism and Magnetic Materials, 1997, 168: 285-291.

[11] Jean J H, Lee C H, Kou W S. Effects of lead oxide on processing and properties of low-temperature-cofirable Ni-Cu-Zn ferrite [J]. Journal of American Ceramic Society, 1999, 82(2): 343-350.

[12] Jean J H, Lee C H. Low-fired NiO-CuO-ZnO ferrite with Bi_2O_3 [J]. Japanese Journal of Applied Physics, 1999, 38: 3508-3512.

[13] Gupta S M, Kulakarni A R. Synthesis and dielectric properties of lead magnesium niobate—a review [J]. Materials Chemistry Physics, 1994, 39: 98-109.

[14] Smirnova E P, Rubinshtein O V, Isupov B A. Dielectric and electrostrictive properties of PMN-based complex perovskites [J]. Ferroelectrics, 1993, 143: 263-270.

[15] Chae M C, Kim N K. Effect of Zn substitution on dielectric responses of 0.2PMT · 0.8PMN ceramics [J]. Journal of the European Ceramic Society, 2002, 22: 1857-1861.

[16] Costa A L, Galassi C, Roncar E. Direct synthesis of PMN samples by spray-drying [J]. Journal of the European Ceramic Society, 2002, 22: 2093-2100.

(Edited by YANG Bing)