Current Applied Physics 11 (2011) 37–42

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Structure and magnetoelectric property of low-temperature sintering $(Ni_{0.8}Zn_{0.1}Cu_{0.1})Fe_2O_4$/[0.58PNN-0.02PZN-0.05PNW-0.35PT] composites

Renbing Sun [a,b,c], Bijun Fang [a,*], Limin Zhou [a], Qinhui Zhang [b,c], Xiangyong Zhao [b], Haosu Luo [b]

[a] School of Materials Science and Engineering, Changzhou University, 1 Gehu Road, Changzhou, Jiangsu 213164, China
[b] Shanghai Institute of Ceramics, Chinese Academy of Sciences, 215 Chengbei Road, Jiading, Shanghai 201800, China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form
14 June 2010
Accepted 16 June 2010
Available online 25 June 2010

Keywords:
Ceramic composites
Solid-state reaction method
X-ray diffraction
Electrical properties
Magnetoelectric property

ABSTRACT

$(1-x)(Ni_{0.8}Zn_{0.1}Cu_{0.1})Fe_2O_4/x0.58Pb(Ni_{1/3}Nb_{2/3})O_3-0.02Pb(Zn_{1/3}Nb_{2/3})O_3-0.05Pb(Ni_{1/2}W_{1/2})O_3-0.35PbTiO_3$ ($(1-x)$NZCF/xPNZNWT) magnetoelectric composites were prepared by conventional solid–state reaction method via low-temperature sintering technique. The low-temperature sintering technique can prepare dense composites, where the ferrite and piezoelectric phases coexist in the synthesized particulate composites, and no apparent mutual solubility takes place between the two phases. The $(1-x)$NZCF/xPNZNWT ceramic composites exhibit excellent integrated electrical properties, where diffused dielectric response peaks, typical P-E hysteresis loops and excellent piezoelectric property can be obtained. The $(1-x)$NZCF/xPNZNWT composites prepared by the low-temperature sintering process can be electrically and magnetically poled to exhibit apparent magnetoelectric effect, indicating that such technique is convenient to develop excellent particulate magnetoelectric materials in the future.

1. Introduction

Magnetoelectric materials with coexistence of ferroelectric and ferromagnetic have attracted increasing interest due to their potential applications as multi-state memories, spintronics and heterogeneous read/write devices [1,2]. The magnetoelectric (ME) effect can be dated back to 1894, however, single-phase compounds exhibit poor inherent multiferroic coupling and low Neel or Curie temperature, which hinder their applications. Alternatively, multiferroic magnetoelectric composites composed of piezoelectric and magnetic materials have drawn significant interest in recent years, where the coupling interaction between the piezoelectric and magnetic materials could produce a large ME response [3–6]. Such excellent ME effect provides opportunities for potential applications as multifunctional devices such as magnetoelectric sensors, transducers and actuators.

As compared to single-phase magnetoelectric compounds, the ME effect in composites is extrinsic multiferroic response, which depends greatly on the composite microstructure and the coupling interaction across magnetic–piezoelectric interfaces. So far, 0–3 particulate and 2-2 laminate bulk magnetoelectric composites have been investigated in experimental and theoretical [7–13]. The laminate structures exhibit the magnitude of V/(cm Oe) ME voltage coefficient, which is two or three orders in magnitude of that of the single-phase ones and especially appropriate for commercial devices. However, due to the limitation in the feature size and miniaturizing difficulty of the layer structure, and the brittleness of ceramics, it is hard to prepare laminate composites. As a comparison, sintered particulate composites show inferior ME property due to the drawbacks such as low resistivity, interface diffusion, mismatch in elastic compliance, and degradation in individual material parameters. However, due to the advantages of cost effectiveness and fabrication process easiness, it practically and economically needs novel particulate magnetoelectric composites.

It is known that low anisotropy favors the magnetomechanical coupling in crystal, therefore, $NiFe_2O_4$ with low anisotropy and high initial permeability is a promising candidate to give rise to the high ME effect. Furthermore, a larger net magnetic moment can be obtained by substituting some zinc into nickel ferrite, which also favors the ME effect [8]. On the other hand, $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ with the morphotropic phase boundary (MPB) composition is known to exhibit large piezoelectric response. Addition of slight content of $Pb(Zn_{1/3}Nb_{2/3})O_3$ can improve piezoelectric property and mechanical factor of the ferroelectric system [14].

In this paper, a novel particulate magnetoelectric composite consisting of ferromagnetic $(Ni_{0.8}Zn_{0.1}Cu_{0.1})Fe_2O_4$ (NZCF) and

* Corresponding author. Tel.: +86 519 86330100; fax: +86 519 86330095.
E-mail addresses: fangbj@cczu.edu.cn, fangbj@sohu.com (B. Fang).

1567-1739/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2010.06.015

relaxor-based ferroelectric 0.58Pb($Ni_{1/3}Nb_{2/3}$)O_3-0.02Pb($Zn_{1/3}Nb_{2/3}$)O_3-0.05Pb($Ni_{1/2}W_{1/2}$)O_3-0.35$PbTiO_3$ (PNZNWT) was prepared by conventional solid–state reaction method. To inhibit interdiffusion between the ferrite and piezoelectric phases, WO_3 and CuO were used as sintering aids to decrease sintering temperature [15,16] and improve densification of the sintered particulate ceramic composites, which will improve the ME effect. The electrical properties and ME effect of the $(1-x)$NZCF/xPNZNWT composites were studied systematically together with the observation of microstructure and the analysis of chemical composition and elemental diffusion across the ferrite–piezoelectric interfaces in order to clarify the possible mechanism of the ME effect.

2. Experimental procedure

Particulate magnetoelectric ceramic composites $(1-x)$NZCF/xPNZNWT were prepared by conventional solid–state reaction method. Analytical-purity oxides, NiO, ZnO, CuO, Fe_2O_3, PbO, Nb_2O_5, WO_3, and TiO_2, were used as raw materials. To maintain stoichiometry the raw oxides were dried separately before weighing and the synthesized columbite precursors were weighed and introduced into the batch calculation. Stoichiometric mixture of NiO, ZnO, CuO and Fe_2O_3 was ball-milled in distilled water for 12 h, and then the well-mixed slurry was filtrated, dried and calcined at 1000 °C for 3 h to prepare ferrite NZCF. Ferroelectric PNZNWT was prepared by the columbite precursor method, where the columbite precursors, $NiNb_2O_6$ and $ZnNb_2O_6$, were prepared by calcining of the stoichiometric mixtures of NiO and Nb_2O_5, and ZnO and Nb_2O_5 at 1000 °C for 4 h, respectively. Then the other oxides with the stoichiometric weight were added to the above precursors. After wet ball-milled using ZrO_2 milling media, the well-mixed stoichiometric mixture was calcined at 900 °C for 2 h to prepare perovskite PNZNWT.

$(1-x)$NZCF/xPNZNWT composites were prepared by conventional ceramic processing using the above synthesized ferrite and ferroelectric precursors according to the formula $(1-x)$NZCF/xPNZNWT ($x = 1.0, 0.9, 0.8$ and 0.7, in weight ratio). The well-mixed powders were dry-pressed into pellets with the addition of 3 wt% polyvinyl alcohol (PVA) binder and sintered at 950 °C for 2 h. CuO and WO_3 were used as sintering aids, which could decrease sintering temperature of the particulate ceramic composites and improve densification and electrical properties of the sintered composites [15,16].

The sintered ceramic composites were ground and polished to obtain flat and parallel surfaces. Crystal structure of the sintered composites was characterized by X-ray diffraction measurement (XRD, D/max-2500/PC Rigaku X-ray Diffractionmeter). Microstructure was observed by scanning electron microscopy (SEM, Hitachi S-4800 Field Emission Scanning Electron Microscope) using free surfaces of the specimens. X-ray elemental analysis was performed by a INCA energy dispersive X-ray analysis (EDX) attached to the SEM equipment in order to identify any elemental interdiffusion across the ferrite–piezoelectric interfaces. For electrical properties measurements, silver paste was fired on both surfaces of the well-polished pellets to provide robust electrodes. Detailed electrical properties measurement procedures were described elsewhere [17].

3. Results and discussion

3.1. Phase structure and microstructure morphology

XRD patterns of the sintered $(1-x)$NZCF/xPNZNWT ceramic composites are shown in Fig. 1. The end members exhibit spinel and perovskite structure, respectively, where the characteristic

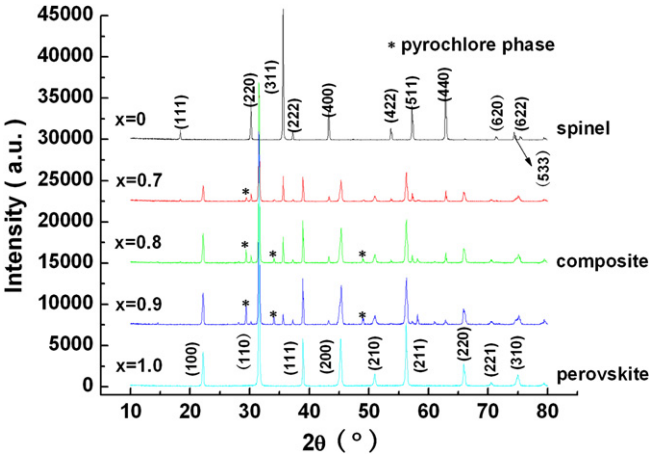

Fig. 1. XRD patterns of the $(1-x)$NZCF/xPNZNWT particulate ceramic composites sintered at 950 °C for 2 h.

diffraction peaks can be indexed well based on the JCPDS data of spinel ferrite $NiFe_2O_4$ and perovskite ferroelectric Pb($Ni_{1/3}Nb_{2/3}$)O_3 (JCPDS files 34-0103 and 74-2081). In the composite compositions, the coexistence of ferrite NZCF and ferroelectric PNZNWT is confirmed by the XRD patterns, indicating that no apparent

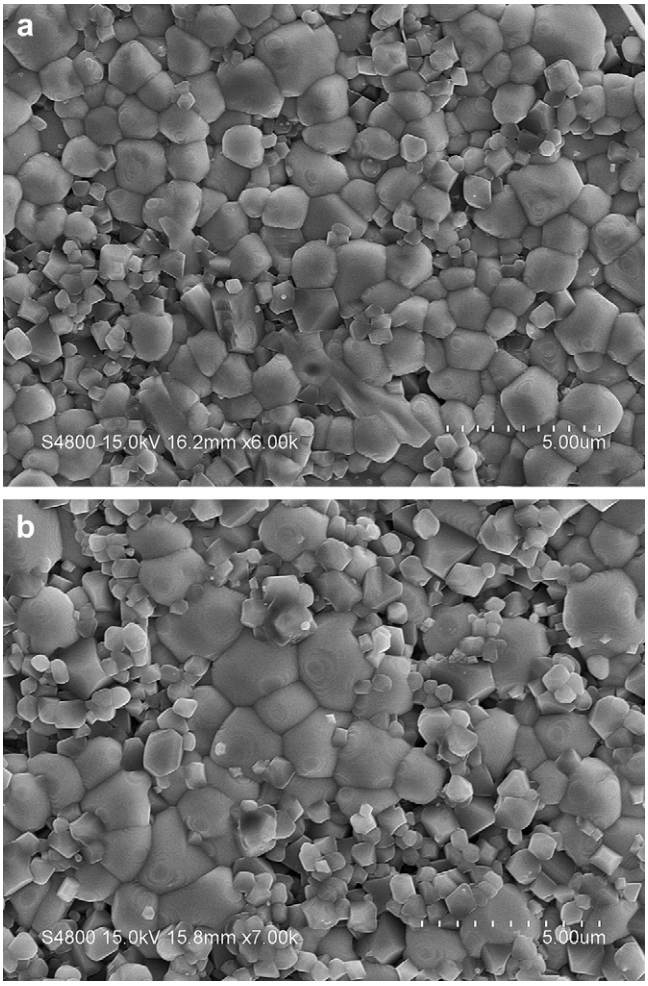

Fig. 2. Secondary electron images of free surfaces of the (a) 0.1NZCF/0.9PNZNWT and (b) 0.3NZCF/0.7PNZNWT ceramic composites sintered at 950 °C for 2 h after thermal etching at 825 °C for 30 min.