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PZT-cobalt ferrite particulate composites: Densification and lead loss controlled by quite-fast sintering

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ABSTRACT

During densification at 1100–1200 °C of particulate lead zirconate titanate (PZT)/cobalt ferrite (CF, 26–81 mol%) composites, side reactions do occur that are detrimental to the properties of the so-obtained material. Such reactions are promoted by initial PbO loss, the extent of which can be determined by means of XRD analysis of the densified samples taking into account the amount of ZrO_2 and the variations of the perovskite's tetragonality. In this process, titania is produced which reacts with CF to form cobalt titanate. Microstructural characterization showed that CF grain size distribution can be mono- or bi-modal, and CF overgrowth was found to affect the coercivity of the material. In the case of the PZT:CF 74:26 composites, full densification and prevention of unwanted side reactions were achieved by designing a quite-fast sintering process. The high coercivity (789 Oe) displayed by these composites is related to the good dispersion of 250 nm euhedral CF grains in the PZT matrix and limited PZT grain growth (240 nm).

1. Introduction

The increasing interest in advanced materials with coupled ferromagnetic and ferroelectric ferroic orders is motivated by modern technological requirements of multifunctionality, integration and high performance of transducers, actuators, sensors, filters, phase shifters, storage applications and miniaturized antennas [1,2]. Magnetoelectric (ME) composites can be developed in several different combinations by mixing magnetostrictive and piezoelectric materials displaying different connectivity, such as particulate composites [3,4], laminated composites [5,6], nanoparticulate thin films [7,8], nanopillar film structures [9], ultrathin films [10]. Particulate ceramic composites have the advantages of low cost, simple production technology, good ME effect and easy control of electrical and magnetic properties when the ferroelectric phase (generally a perovskite) and the ferromagnetic phase (a ferrite with spinel structure) are mixed in a favourable proportion under the percolation threshold of the ferromagnetic phase, characterized by a lower dielectric constant [11–13]. The macroscopic ME properties are affected by the degree of magnetic phase dispersion and distribution, and also by the final density which, for a particulate composite with a given dispersion and distribution, is proportional to the solid/solid interface density. Therefore, achieving full density extent is of paramount importance as the fact that the quasi-intrinsic ME effects are originated from the interfacial strain-mediated coupling of piezoelectricity and magnetostriction [14]. The bonding between magnetic and ferroelectric particles must be strengthened and the influence of low resistance ferromagnetic phase on the polarization of the ferroelectric one must be decreased as well. This can be achieved by producing fully densified microstructure where an as high as possible amount of ferromagnetic phase (below the percolation threshold) is dispersed and homogeneously distributed in the ferroelectric matrix. A great research effort is in progress to improve the fabrication of PZT–$CoFe_2O_4$ (PZT–CF) composites due to the excellent piezoelectric properties showed by the PZT material and the large magnetostrictive coefficient of CF [15–17]. Many papers reported the ME properties of said composites and claim that PZT and CF do not react during the sintering process, while less attention is given to the densification and the effects of the porosity on the ME coupling [16–18]. Sentences like: "densely sintered" are often reported with no actual density values being mentioned. Recently, 97% relative density was achieved by microwave-sintering of PZT/CF (80/20) composites produced by a novel sol-gel route [4]. A further issue is the lead volatilization that occurs during the sintering process, which causes residual porosity to be present in the material and decreases the piezoelectric response of the composite. Atkin and Fulrath [19] found that in the multiphasic system the PbO

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activity, defined as the ratio of PbO partial pressure above the lead-compound (PZT), must be constant at a value between zero and one. Thus, when PZT and CF particles are pressed together, if reactions occur able to produce zirconium and/or titanium oxides, the PZT particles can lose PbO to maintain the PbO activity constant [19,20]. In this work PZT-CF particulate composites with increasing CF content, from 26 to 81 mol%, were produced, and the focus was placed on densification process issues like PbO losses and reactivity of the CF particles with titanium oxide. The densification parameters were optimized in order to achieve full densification and control of the microstructure, and to reduce mechanical defects and interphase diffusion, using a conventional, but optimized, ceramic process. An easy method to calculate the PbO loss was proposed by quantifying the lead-deficient phases through X-Ray Powder Diffraction (XRPD) analysis.

2. Experimental

$(1\text{-}x)Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3\text{-}(x)CoFe_2O_4$ (PZTN-CF) composites were produced by a two-step solid-state-reaction method. Perovskite PZTN powders were prepared by the mixed oxides route, calcined at 800 °C and milled down to 0.7 μm [21]. Spinel CF powders were prepared by the mixed oxides route, calcined at 1000 °C and milled down to 0.2 μm [22]. The composites were prepared by mixing the as-synthetized powders according to the $(1-x)PZTN-xCF$ molar compositional scheme, with $x = 0.26$, 0.32, 0.58, and 0.81, which were labelled as PZTN-CF26, PZTN-CF32, PZTN-CF58, and PZTN-CF81, respectively. The powder mixtures were wet ball-milled, dried and subjected to cold linear pressing at 50 MPa to produce 10 mm diam., 2 ÷ 3 mm thick disks. Isostatic pressing at 250 MPa was applied to the disks to obtain green homogeneous PZTN-CF bodies. The sintering treatments were performed in lead-saturated atmosphere setting soaking temperature and time at 1200 °C for 2 h, 1150 °C for 2 h and 1100 °C for 0.5 h. A constant heating rate of 6 °C/min was employed to reach the sintering temperature plateau, and the sintered samples were brought back to room temperature by natural cooling of the furnace.

The crystalline phases were identified by XRPD using a Bruker D8 Advance X-ray diffractometer (θ–θ) with Cu Kα. The samples were scanned in $15^\circ \le 2\theta \le 80^\circ$ range of at 2.4°/min scanning rate. The quantitative determination of the phases was performed with the commercial BRUKER EVA program, obtaining a weighted residual value R_{wp} between 3.5 and 7.7.

The microstructure of the sintered samples was investigated by SEM analysis of cross-sections performed on a ZEISS SIGMA Field Emission Scanning Electron Microscopy (FE-SEM) system. The relative density of the sintered samples was calculated from the density determined by the Archimedes' method normalizing to the theoretical density obtained as the average of PZTN and CF theoretical densities (8.006 g cm^{-3} and 5.304 g cm^{-3}, respectively). Magnetic hysteresis loops were measured at room temperature at magnetic field strengths in the range of (0–10 kOe) on a vibrating sample magnetometer (MicroMagTM VSM model 3900 from Princeton Measurements Co.).

3. Results and discussion

3.1. Phase analysis and microstructure

Fig. 1 shows the XRPD patterns of the sintered samples. All the diffraction peaks for the compositions sintered at 1100 °C for 0.5 h were indexed to the cubic spinel structure of $CoFe_2O_4$ (PDF No 22-1086, for the sake of clarity, only the strongest I_{CF} (3 1 1) peak was marked with a rhombus), and to the tetragonal perovskite structure of PZTN (PDF No 70-4060, I_{PZTN} (1 0 1), circle). As was expected, the intensity of the $CoFe_2O_4$ diffraction peaks increases vs. increasing $CoFe_2O_4$ content, while the intensity of the PZTN peak decreases. Upon temperature increase to 1150 °C and 1200 °C, XRPD shows that the starting Zr/Ti ratio ($\tau = Zr/Ti$) is not kept constant in the perovskite phase, as pointed out by the split of the (0 0 2) and (2 0 0) diffraction peaks (at $2\vartheta \approx 44^\circ$ and 45°, respectively). In fact, according to the crystal geometry equations, which correlate the d-spacings with the Miller indices, for the tetragonal symmetry the d-spacing of the (0 0 2) diffraction peak is directly proportional to the *c* lattice parameter ($2d_{(002)} = c$) while the d-spacing of the (2 0 0) diffraction peak is directly proportional to the *a* lattice parameter ($2d_{(200)} = a$). In particular, this is most clearly seen in the sample with the highest PZTN amount (see magnified view on the right of Fig. 1, covering the 43.5°–46° 2ϑ region) but this is also true for all the other samples. The (0 0 2) diffraction peak widens towards smaller 2ϑ degrees with increasing sintering temperature, whereas the *a*-axis dimension is not as strongly affected. This feature reveals that the crystal tetragonality, *c/a*, of the PZTN phase increases vs. increasing sintering temperature, owing to the formation of perovskite phases with lower Zr/Ti ratio. Moreover, peaks belonging to the undesired phases of baddeleyite, ZrO_2 (PDF No. 65-1022, I_{ZrO2} (1 1 1), square) and $CoTiO_3$ (PDF No. 65-1022, I_{CoTiO3} (0 1 2), cross) were also identified in the sample sintered for 2 h at 1200 °C and 1150 °C. These results are reliable as their magnitude is well above the detection limit of the equipment. Other phases possibly present in the sample (such as Fe_2O_3, Nb_2O_5, $FeNbO_4$, etc...) were not detected, maybe because their XRPD features were hidden by those of the main phases. The presence of the baddeleyite phase justifies the stoichiometry change of the PZTN phase, depending on the sintering temperature. This suggests that PbO depletion occurred during heat treatment at temperature higher than 1100 °C. The relative intensity of the highest ZrO_2 peak, normalized to the starting PZTN amount, increases with the increasing of the sintering temperature, which confirms that ZrO_2 forms due to PbO volatilization. Lead evaporation is not a consequence of cobalt titanate formation or other reactions between PZTN and CF particles, because the extent of these reactions should be directly correlated with the $CoFe_2O_4$ content in the composites. On the other hand, cobalt titanate formation may promote PbO volatilization to the following reactions:

$$\begin{aligned} &Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3 \leftrightarrow (0.988{\cdot}f)PbO_{(g)} \\ &\quad + (0.50752{\cdot}(1-y+fy))ZrO_2 + (0.46848{\cdot}(1-z+fz))TiO_2 \\ &\quad + (0.012{\cdot}f)Nb_2O_5 + (1-f)Pb_{0.988}(Zr_{0.52{\cdot}y}Ti_{0.48{\cdot}z})_{0.976}Nb_{0.024}O_3 \end{aligned} \tag{1}$$

where f is a molar fraction representing the amount of PbO losses; y and z are the molar fractions that define the Zr/Ti molar ratio in the produced PZTN perovskite phases. The amount f of PbO loss can be calculated from the Zr/Ti ratio variation ($\tau = 0.52y/(0.48z) = 0.52y/(1-0.52y)$) if the amount of one of the products is known. As regards to the Zr/Ti ratio variation, the (0 0 2) diffraction peak's broadening at smaller 2ϑ values is the result of a convolution of several diffraction peaks each of them reflecting the presence of a specific amount of perovskite phase characterized by a specific lattice elongation along the tetragonal *c*-axis, as defined by the Zr/Ti ratio. In the present study, no attempt was made to quantify the amount of each perovskite stoichiometry that could be present in the sample. It was assumed that, besides the starting perovskite phase, characterized by a Zr/Ti ratio of 52/48, there was only another one with a Zr/Ti ratio of 52y/48z – chosen so that the weighted residual value R_{wp} was minimized. It is convenient to choose baddeleyite (ZrO_2) formation as the reference process rather than that of other products since, as it can be seen

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