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Effects of Nd and Co co-doping on phase, microstructure and ferromagnetic properties of bismuth ferrite ceramics

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Abstract

In this work, the samples of $Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ (BNFCO) with $x=0$, 0.03, 0.05 and 0.07 mol fraction, were prepared by a solid state reaction. The effect of Nd and Co co-doping concentration on phase, densification, microstructure and ferromagnetic properties were examined. The BNFCO powders were prepared using a mixed-oxide method and calcined at 800 °C for 2 h before being pressed and sintered at various temperatures in the range of 825–900 °C for 2 h. An increase in Co co-doping content increased density of the ceramics. Phase analysis by X-ray diffraction indicated the existence of rhombohedral phase for all BNFCO powders and ceramics. Microstructural investigation using the scanning electron microscope showed a reduction of grain size with increasing Co content. Magnetic hysteresis loops showed that remanent magnetization and coercive magnetic field of the Co-doped samples were improved.

Keywords: A. Sintering; B. X-ray methods; C. Magnetic properties; D. Ferrites

1. Introduction

The multiferroic compound of $BiFeO_3$ or BFO has drawn a great amount of interest because of its rhombohedrally distorded perovskite-type structure that can be represented by a general formula ABO_3, which belongs to the space group R3c at room temperature. This allows a coexistence up to quite high temperature of ferroelectricity ($T_C \sim 850$ °C) and G-type antiferromagnetism ($T_N \sim 370$ °C) [1,2]. Therefore, it has attracted considerable attention because of their possible uses for future technology in information storage and sensors [3]. However, it has been known that BFO has a high leakage current and low resistance due to defects such as secondary phases and oxygen vacancies [4]. One way that has been investigated to improve properties of BFO is an A-site substitution, by displacement of the volatile Bi with rare earth elements such as La and Nd which used as substitute for Bi in BFO [5–10]. Mishra et al. reported that Nd-substituted BFO nanoceramics showed high dielectric constant at high temperature and improvement in ferroelectric properties of BFO [9].

Recently, many research groups attempted to further improve magnetic characteristic of BFO, particularly enhancement of ferromagnetic properties of BFO ceramics by B-site substitution, by displacement of Fe in BFO with magnetic elements such as Co [11–13]. Apart from this, Zheng et al. reported that the substitution of Co in BFO ceramics had high remanent magnetization and improvement in magnetic properties of BFO [13].

The aim of this present work is to prepare and study the effect of Nd and Co co-doping on phase, densification, microstructure and ferromagnetic properties of BFO ceramics. The ceramic processing was carried out using a simple and cost effective solid-state mixed-oxide method. Phase, microstructure and ferromagnetic properties were investigated and discussed.

2. Material and methods

$Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ or BNFCO ($x=0$, 0.03, 0.05, and 0.07 mol fraction) powders were prepared using the

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solid-state mixed-oxide method. The starting binary oxide powders were Bi_2O_3 (99.9%, Aldrich), Nd_2O_3 (99.9%, Aldrich), Co_3O_4 (99%, Aldrich) and Fe_2O_3 (99%, Riedel-de Haën). The powders were weighed according to their stoichiometric compositions with 5% Bi_2O_3 excess. These oxides were mixed in ethanol, ball milled for 24 h, and dried in an oven for 24 h. The dried mixtures were calcined at 800 °C for 2 h and then ground. The BNFCO powders were then pressed under uniaxial hydraulic at a pressure of 1 t using a few drops of 3 wt% polyvinyl alcohol as a binder. The pellets were sintered at various temperatures in the range of 825–900 °C for 2 h. The optimum sintering temperature for high density ceramics was determined and selected for further characterizations. Phases of the selected ceramics were characterized using an X-ray diffractometer (XRD, Philips model X-pert). Density was measured by Archimedes' method. Microstructure of the ceramics was investigated by scanning electron microscope (SEM, JEOL JSM-6335F). Magnetic hysteresis (M–H) loops were characterized using a vibrating sample magnetometer (VSM, Lake Shore 7400 Series).

3. Results and discussion

X-ray diffraction patterns of $Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ (BNFCO) powders were obtained at a calcination temperature of 800 °C for 2 h dwell time as shown in Fig. 1. The patterns of BNFCO powders with different concentration of Co_3O_4 dopant were well matched with JCPDS No. 86-1518, which indicated an existence of polycrystalline rhombohedral distorted perovskite structure with a space group R3c. These patterns could be well indexed with the pattern of BFO, but there was also a small amount of a second phase presented. This phase was identified to be $Bi_{25}FeO_{40}$ which likely occurred due to an excessive Bi used for compensating volatilization during synthesis [14].

X-ray diffraction patterns of BNFCO ceramics sintered at 850 °C for 2 h are shown in Fig. 2. The patterns for all samples were indexed as rhombohedral distorted perovskite structure similar to those found in the powders but without the presence of a second phase.

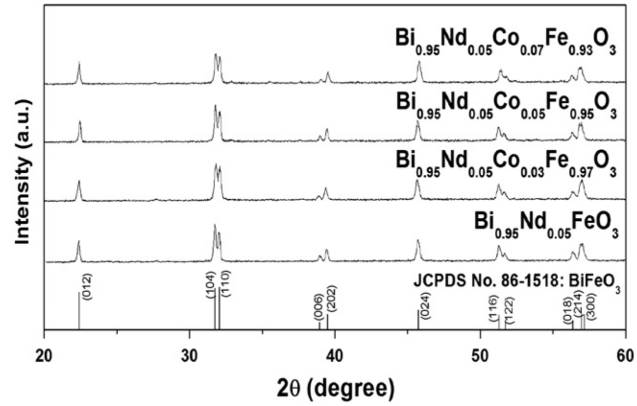

Fig. 2. X-ray diffraction patterns of $Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ ceramics sintered at 850 °C for 2 h.

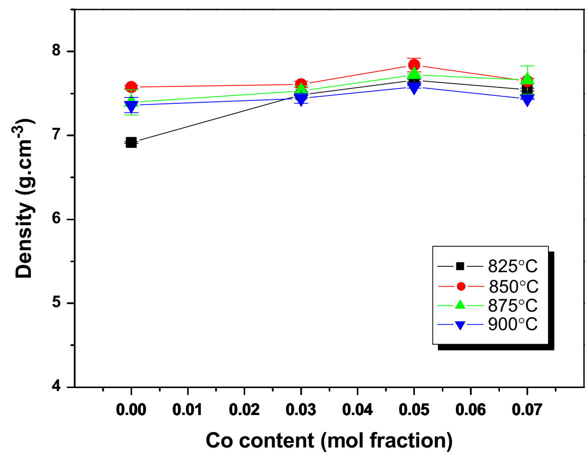

Fig. 3. Relationship between density and Co doping content of $Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ ceramics.

Fig. 3 illustrates a relationship between density of BNFCO ceramics and content of Co dopant at different sintering temperatures. Densities of the BNFCO ceramics were found to increase with increasing Co content. At 850 °C, it could be seen that the density values were rather similar for all samples. Increasing sintering temperature > 850 °C tended to reduce densities of all ceramics. From the density results, it was quite clear that the optimum sintering temperature for BNFCO ceramics was found to be 850 °C. However, the density values obtained at each temperature were rather close in a range of 7.6–7.8 g cm^{-3}.

SEM micrographs of sintered surfaces of BNFCO ceramics are shown in Fig. 4. Grain sizes of all samples were found to decrease with increasing Co content and homogeneous microstructure was also developed. Increasing Co content, the grains of BNFCO ceramics had more angular shape. It is believed to occur due to the surface energy of Co (2695 ergs/cm^2) being higher than that of Fe (2525 ergs/cm^2) [15], thus it is reasonable that Co doped

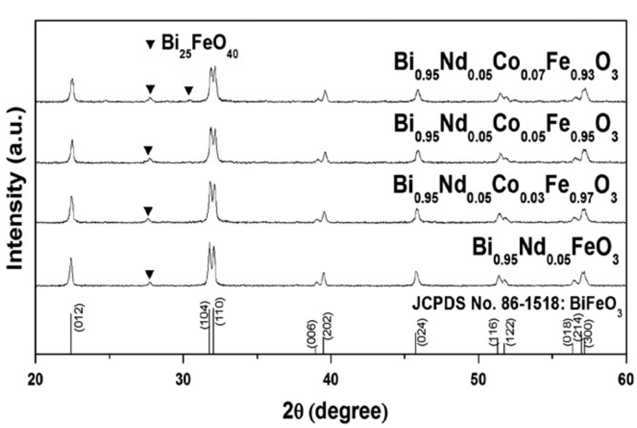

Fig. 1. X-ray diffraction patterns of $Bi_{0.95}Nd_{0.05}Co_xFe_{1-x}O_3$ calcined powders.