Ni doping effects in $\text{YBa}_2\text{Fe}_3\text{O}_{8+w}$

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Abstract: By doping Ni into $\text{YBa}_2\text{Fe}_3\text{O}_{8+w}$ (YBFO) system, we obtained the phase $\text{YBa}_2\text{Fe}_{3-x}\text{Ni}_x\text{O}_{8+w}$ (YBFNO, $x=0, 0.05, 0.10, 0.15, 0.30, 0.50, 1.00$). This paper discusses the changes in crystal structural, resistivity and magnetoresistivity (MR) of YBFO samples due to the incorporation of transition metal Ni. The results show that Ni substitution for partial Fe in YBFO does not substantially transform the structure of parent phase, but results in tiny changes in the lattice parameters. The YBFO crystal with Ni doped is semiconducting.

Key words: $\text{YBa}_2\text{Fe}_3\text{O}_{8+w}$; Ni doping; crystal structure; magnetoresistivity

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1. Introduction

Compound $\text{YBa}_2\text{Fe}_3\text{O}_{8+w}$ (YBFO) is an antiferromagnet (AFM) with Neel temperatures (T_N) around 660 K [1-2]. The crystal structure of YBFO is triple perovskite as it is formed by merging Y and Ba, and by disordering of the oxygen atoms and vacancies. The oxygen stoichiometry $8+w$ varies in a narrow range of $-0.2 < w < +0.1$ [3]. The crystal is the only analogue of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) where Cu is fully replaced by another transition metal. There is a wide miscibility gap in two phases as iron is unable to adopt a square-planar coordination. Fe^{3+} is stabilized in the environment of one octahedral and two square-pyramidal per unit cell, where YBFO composition is generated. YBFO and YBCO differ in their arrangements and the number of oxygen atoms on the basal plane of their unit cell. When $w > 0$, chemical analysis conducted to locate the oxygen in excess of the eight atoms per formula unit showed that the sites available for such oxygen were those in the Y layer at 0, 0, 1/2, assigned as O(4) [4]. The structure diversification of introducing Fe into YBCO has been widely studied in an attempt to detect possible correlations between structural modifications due to the presence of iron and the lack of superconductivity.

Ref. [4] discussed the nucleus and magnetic structure of YBFO, samples of which were prepared from liquid-mixed citrate precursors. The cooperative magnetic structure for all compositions was based on a larger cell related to the nuclear cell by the transformation matrix $[1, -1, 0/1, 1, 0/0, 0, 2]$ [4]. The tetragonal crystal structure of $\text{YBa}_2\text{Fe}_3\text{O}_8$ became orthorhombic once oxygen vacancies were included into the iron coordination octahedron [4]. The antiferromagnetic ordering of the iron magnetic moments was below 630–670 K, indicating that the variation in oxygen content was too small to significantly affect the magnetic exchange interactions.

Huang et al. [5] investigated the accommodation of Co in the oxygen-saturated solid-solution phase $\text{YBa}_2(\text{Fe}_{1-z}\text{Co}_z)_3\text{O}_{8+w}$ using techniques of powder X-ray and neutron diffraction, and ^{57}Fe Mossbauer spectroscopy. In the nominal composition range $0.00 \leq z \leq 1.00$, the solid-solution limit under syntheses 950 °C in 1 bar O_2 was $z=0.47(5)$ [5]. No symmetric change in the nuclear and magnetic structures was observed due to the Co substitution. The Co atoms were distributed evenly over the two sites, which were square-pyramidally and octahedrally coordinated for $w=0$. The value of w was viewed as nearly constant and Co adopted valence close to 3.00.

At present, the research on doping transition metals into Fe position in YBFO system, such as Ni and Mn, has not been reported. This paper investigates the Ni doping effects on crystal structure, resistivity and magnetoresistivity (MR) of YBFO system.

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2. Experimental program

Conventional sol-gel method was followed to prepare samples $\text{YBa}_2\text{Fe}_{3-x}\text{Ni}_x\text{O}_{8+w}$ ($x=0, 0.05, 0.1, 0.15, 0.3, 0.5, 1$, for short YBFNO).

Step 1: Weighed high-purity stoichiometric Y_2O_3 , $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and Fe powders.

Step 2: Raw materials were uniformly and slowly dissolved into acetic solution with continuous stirring during a gradually heating process. The heating process continued until the solution became dry.

Step 3: Grinded the xerogel for 60 min to gain the well proportioned powder and then pressed the powder

into tablets.

Step 4: Sintered at 1100°C in the atmosphere for 350 h and cooled in the furnace.

To improve the sample homogeneity, intermediate grinding and palletizing must be ensured. The sintering processes are shown in Fig. 1. A Philips X'Pert MRD diffractometer with Cu-K α radiation recorded the θ - 2θ XRD patterns, which characterized the phase purity of the series samples. Each sample was in single phase with tetragonal structure. The resistance-temperature curves were obtained by PPMS (physical property measurement system).

Fig. 1 Heat processes of YBFNO samples

Fig. 2 XRD patterns of YBFNO

3. Results and discussion

3.1. XRD test and analysis

Typical XRD θ - 2θ patterns for YBFNO are shown in Fig. 2. Similarities between spectra of $\text{YBa}_2\text{Fe}_{3-x}\text{Ni}_x\text{O}_{8+w}$ ($x=0.05, 0.1, 0.15, 0.3, 0.5, 1$) and YBFO ($x=0$) reveal that incorporating a small amount of Ni into the YBFO lattice will not substantially transform tetragonal structure of parent phase since only tiny changes of the lattice parameters are observed. In Fig. 2, the intensity of the (100) peaks gradually become smaller, meaning that the tendency towards a-axis preferential orientation is weakened as Ni content increases. Impurities peaks of $\text{Ba}_2\text{Fe}_2\text{O}_5$ and BaFe_2O_4 can occasionally be detected, indicating that they are close to YBFO in phase graph. Only a few impurities peaks of Ni oxides are found. This is because most of Ni is incorporated into octahedral or square-pyramidal environments in YBFO lattice in the substitution for Fe. In addition, in samples of $x > 0.3$, the typical peaks intensity of objective products are not prominent and the impurity peaks such as $\text{Ba}_2\text{Fe}_2\text{O}_5$, BaFe_2O_4 , Y_2BaNiO_5 and NiO become stronger. When $x \leq 0.3$, the intensity of characteristic peaks in YBFNO spectra dominates even though there are a few negligible impurities. As a result, we presume that the solid-solution limit of Ni in YBFO is in the vicinity of $x=0.3$ under the condition of adequate oxygen atmosphere.

Peaks for a series of samples of YBFNO in Fig. 3 shift slightly to the right so as to conform a strong dependence of peak position on the content and radius of the Ni^{2+} incorporated into YBFO system.

Fig. 3 The enlarged diffraction peaks (006) and (200) in YBFNO

For instance, the lattice parameters of YBFNO gradually become smaller as Ni content increases. However, if Ni enters in YBFO crystal and does not substitute Fe, the lattice parameters of YBFNO will be larger than those of

the parent phase, and the new crystal will expand. Thus, we are convinced with the partial substitution of Fe by Ni in octahedral and square-pyramidal coordinations of YBFO crystal. The lattice parameters change because the radius of Ni ion is smaller than that of Fe. And the oxygen content in the unit cell is nearly a constant when oxygen is adequate.

Table 1 lists the values of the lattice parameters versus Ni content within its solid-solution limit. These data are obtained by a least-squares fit to a large number of the Bragg diffraction.

Table 1 The calculated unit cell parameters of YBFNO

Ni content	Unit cell parameter on the x axis	Unit cell parameter on the z axis	Volume of unit cell
0.00	3.916 45	11.813 68	181.20
0.05	3.916 38	11.813 58	181.19
0.10	3.913 02	11.802 57	180.72
0.15	3.910 62	11.795 40	180.39
0.30	3.910 20	11.793 44	180.32

3.2. Resistance analysis and MR of YBFNO

Fig. 4 shows curves in logarithmic scale between resistance and temperature of YBFNO samples in 0 T and 1 T magnetic fields. Samples of YBFNO in the two magnetic fields remain semiconducting like YBFO. It was reported that the resistivity function of $\text{LaBa}_2\text{FeO}_{8.3}$ ($150 \text{ K} < T < 300 \text{ K}$) acted as Arrhenius-type behavior with an activation energy of about 0.2 eV [6]. Elzubair et al. [7] formulated an evident variable-range hopping (VRH) process:

$$\rho = \rho_{\infty} \exp(T_0/T)^{1/4},$$

where T_0 is characteristic temperature related to the density of state at the Fermi level. The VRH process was suitable for describing the resistivity of $\text{RBa}_2\text{Fe}_3\text{O}_{8+w}$ ($R=\text{La, Nd, Sm, Eu, Gd}$) when measurement temperature range was increased to 620 K [8]. We find that the VRH process also fits for YBFO when measurement range was 10–300 K, and there was a direct link between the resistivity and temperature. Comparing Fig. 4(b) with Fig. 4(a), we notice limited effects of application field on the resistivity of YBFNO.

To compare the density of states at the Fermi level, we investigated the relationship between the resistivity and the Ni content in YBFNO at 300 K. The curves in Fig. 5, as a whole, are very similar to two curves in 0 T and 1 T magnetic fields at 300 K, except for $x=0.15$. It is shown that except for $x=0.15$ at 300 K, the application field has limited effects on the resistivity. Moreover,

when Ni content is 0, 0.15, or 1, the resistivity of samples in 0 T and 1 T fields at 300 K is noticeably different from other samples, as is probably related to the onset of spatial charge or magnetic ordering.

Fig. 4 Representative logarithmic resistance of $\text{YBa}_2\text{Fe}_{3-x}\text{Ni}_x\text{O}_{8+w}$ in 0 T (a) and 1 T (b) fields. The continuous line is a fit to a VRH process. For convenience, only several lines were given.

Fig. 5 The relationship between the resistivity and Ni content in YBFNO at 300 K

Fig. 6 shows the relationship between the resistance and the temperature for different Ni-content samples in 1 T field. With the decrease in temperature, the crystals experience Insulator-Metal (IM) phase transition. The temperatures of this phase transition T_{IM} (nearly 110 K) are much lower than the Neel transition temperature, T_{N} (nearly 660 K for pure YBFO). This is because T_{IM} is closely relevant to the factors such as synthesizing conditions, crystal boundary, and magnet ordering. Moreover, the oxygen content in crystal also plays a role in the low T_{IM} .

Fig. 7 shows the relationship between the magnetoresistivity (MR) and the temperature. MR is obtained by

$$\rho = \rho_{\infty} \exp(T_0/T)^{1/4},$$

where ρ_0 and ρ_H are resistivities in 0 T and 1 T fields, respectively.

The different intensity peaks corresponding to $x=0.1$, 0.15, 0.3, and 0.5 appear within a low-temperature range of 90–130 K and a high-temperature range of 240–300 K.

Fig. 6 The relationship between the resistance and the temperature of YBFNO in 1 T field

Fig. 7 The relationship between the MR and the temperature of YBFNO samples in 0 T field

This phenomenon can be attributed to the effects of Colossal Magneto resistance (CMR). The maximum positive MR value at $x=0.1$ reaches nearly 600%. Other CMR peaks in the low-temperature range are flat and small, because of the phase transition between Paramagnetic-Metal (PM) and Ferromagnetic-Insulator (FI), instead of the one between PM and Ferromagnetic-Metal (FM). Impurities such as $\text{Ba}_2\text{Fe}_2\text{O}_5$ and BaFe_2O_4 are rarely seen in the synthesized products. In addition, phase transitions probably exist between PM and FM at $x=0$, 0.05, and 1 within the both temperature ranges.

4. Ending remarks

We used the wet chemical method to prepare YBFNO samples. A small amount of Ni does not tremendously transform the space structure of YBFO system. The main reason for the decrease of lattice parameters is that Ni has smaller ionic radius than Fe. In YBFNO, Ni can arbitrarily substitute partial Fe in the parent phase. YBFNO samples exhibit the semiconducting feature like YBFO. The VRH process is suitable to describe the resistivity of YBFNO samples.

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