Fe-Doping Effect on the Bi \(_3\)Ni Superconductor Microstructure

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The substitution effects of Fe ion on the structure of the intermetallic Bi\(_3\)Ni\(_x\)Fe\(_{3-x}\) (0 ≤ \(x\) ≤ 0.10) superconductor were studied. The morphology of samples consists of an inhomogeneous laminar slab-like microstructure. The main phase corresponds to Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\) with an orthorhombic structure (Pnma), but with very small quantities of impurities of BiNi and Bi as revealed by X-ray diffraction. SEM and AFM reveal that the Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\) phase consists of two regions. One region is Bi richer and Ni and Fe poorer than the other region. Raman spectroscopy revealed two phonon modes at room temperature. No significant changes were observed in the spectra with Fe doping and in different regions of the Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\) phase. Superconductivity is observed below a transition temperature \(T_c = 4\) K and regardless of iron doping.

Keywords: Bi\(_3\)Ni, Superconductor, Intermetallic alloys, Iron

1. Introduction

The coexistence of superconductivity and magnetism is a phenomenon of great interest in condensed matter physics. In almost all materials, these two fundamental states are highly competitive and destroy the superconductivity. Compounds based in Bi-Ni, such as LaO\(_{1-\delta}\)NiBi\(_3\), CeNiBi\(_2\) and Bi\(_2\)Ni\(_2\), present this complex phenomenon. In the intermetallic Bi\(_3\)Ni compound, with critical temperature \(T_C\) around 4.1 K, the coexistence of superconductivity and ferromagnetism is observed, with superconductivity emerging in the ferromagnetically ordered phase\(^4\).

The stoichiometric Bi\(_3\)Ni is described as an intermetallic alloy with an orthorhombic crystallographic structure of CaLiSi\(_6\)-type, 16 atoms per unit cell and space group Pnma\(^3\). Ruck \textit{et al.} studied the crystal structure of Bi\(_3\)Ni using quantum chemical calculations. According to their results, the Ni atoms have a capped trigonal prismatic coordination of Bi atoms with strong bonds Ni-Bi and Ni-Ni. Besides the Ni-Bi phase diagram, others phase diagrams such as Rh-Bi\(_7\) and Co-Bi\(_8\) have been explored for new superconductors. For RhBi\(_4\) and Rh\(_2\)Bi\(_{13}\), superconductivity was observed at a critical temperature \(T_c\) of 2.8 K and 3.2 K, respectively. For the CoBi\(_3\) compound, synthesized using a high-pressure and high-temperature technique, \(T_c\) is around 0.5 K.

Although the Bi\(_3\)Ni compound is known as a superconductor since 1948\(^7\), there were few reports about this material. Pineiro \textit{et al.} studied the possible coexistence of superconductivity and magnetism in Bi\(_3\)Ni and showed that it presents a ferromagnetic characteristic up to 750 K, well above the Ni Curie temperature\(^8\). Herrmannsdorfer \textit{et al.} demonstrated the coexistence of ferromagnetic and superconducting states in Bi\(_3\)Ni nanostructures. Superconductivity confined in Bi\(_3\)Ni emerges in the ferromagnetically ordered phase and is stable up to high magnetic fields\(^9\). Zhu \textit{et al.} investigated anisotropy in superconducting and normal state properties of Bi\(_3\)Ni single crystals\(^10\). They demonstrated from electron spin resonance that ferromagnetic fluctuations exist on the surface of the crystal below 150 K.

In this study, we describe the substitution effects of Fe ion in the structure of the Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\) (\(x = 0.00, 0.05\) and 0.10) superconductor. The samples were prepared by the solid-state reaction method and characterized by X-ray diffraction, optical and scanning electron microscopy with energy dispersive spectroscopy, atomic force microscopy and Raman spectroscopy. It was observed that the main phase corresponds to Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\), but with small quantities of BiNi and Bi as impurities. From SEM and AFM, two regions were observed in all samples: white and gray. The white region is richer in Bi and poorer in Ni and Fe than the gray region. Observations from atomic force microscopy experiments, in magnetic mode, showed the presence of magnetic interactions in the range of 500 nm. Raman spectra were obtained and two phonon modes were observed, with no peak shift dependence with Fe doping.

2. Experimental Details

Polycrystalline samples of Bi\(_3\)Ni\(_{1-x}\)Fe\(_x\) (0 ≤ \(x\) ≤ 0.10) were prepared by the solid-state reaction method using Bi
samples, the behavior of $\chi^2 = \sqrt{\chi^2}$ and $\chi^2 = 2.315$ for Bi$_{x}$Ni$_{1-x}$Fe$_{0.05}$ samples. Numbers in parentheses indicate the standard deviation.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Cell Parameters (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{x}$Ni$</em>{1-x}$Fe$_{0.05}$</td>
<td>$a = 8.8837 (1)$</td>
<td>$b = 4.0997 (1)$</td>
</tr>
<tr>
<td>Bi$<em>{x}$Ni$</em>{1-x}$Fe$_{0.05}$</td>
<td>$a = 11.4830 (2)$</td>
<td>$b = 4.1002 (1)$</td>
</tr>
<tr>
<td>Bi$<em>{x}$Ni$</em>{1-x}$Fe$_{0.05}$</td>
<td>$a = 4.10283 (9)$</td>
<td>$b = 4.1002 (1)$</td>
</tr>
</tbody>
</table>

Figures 2(a) and 2(b) show the microstructure of the polycrystalline Bi$_{x}$Ni$_{1-x}$Fe$_{0.05}$ sample as revealed by SEM using backscattered electrons. From panel (a), we can clearly observe a granular structure with several pores. It also shows that the sample is inhomogeneous at micrometric scale, with
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The same structure is observed for all samples. Their composition measured by EDS will be discussed later. Figure 2(b) shows in higher magnification several microcracks that are aligned approximately parallel to a horizontal direction in the photograph. The origin of these cracks may be due to thermal expansion anisotropy as observed in REBa$_2$Cu$_3$O$_{7-\delta}$ (RE = rare earth)$^{15}$ or due to weak bonding between the laminar grains as observed in iron-based superconductors$^{16}$.

Figure 2. (a) Backscattered electrons SEM image of the polycrystalline sample of Bi$_3$Ni$_1$Fe$_{0.00}$ ($x = 0.00$) sample. The stacked lamellar structure is shown in more detail in (b).

Figure 3 show the microstructure of polycrystalline samples of Bi$_3$Ni$_{1-x}$Fe$_x$ with (a) $x = 0.00$ and (b) $x = 0.10$ in more detail. Two regions, labeled white and gray, are clearly observed. If the same image of the polycrystalline sample with $x = 0.00$ is observed by optical microscopy, two regions are also distinguished in the upper inset. In the lower inset, the surface morphology of the polycrystalline Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ sample was analyzed with atomic force micrograph in phase mode using a Si probe and revealed also two regions, one darker on the right side and another white on the left side of the figure. We cannot distinguish each of these two regions corresponds to the two regions observed by SEM, but they maybe correlated.

If Figure 3(b) is magnified, several lamellae are observed in both white (Figure 4(a)) and gray (Fig. 4(b)) regions. Their thickness is around 500 nm and they are aligned across several grains. While in the white region the porosity appears to be low, in the gray regions, the porosity is higher. Also the pores appear to be aligned parallel to the lamellae in the gray region. It is possible to observe also in Figs. 3(b) and 4 that this microstructure runs across several white and gray regions, leaving the possibility our samples to be textured.

In view of the different regions observed from X-ray and SEM at different samples, we decided to analyze the chemical composition using energy dispersive spectroscopy (EDS). Local composition of the Bi$_3$Ni and Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ samples was determined by EDS in different positions on the sample surface and in using areas of 4 x 4 $\mu$m$^2$. Table 2 shows the compositions measured in different regions. The results
ambient conditions in (a) phase mode and (b) topographic mode using a magnetized Co-coated probe for the same region. In the upper inset, image (a) is shown in more detail. While Figs. 5(a) and 5(b) show different regions in respect of the interaction between the AFM probe and the sample surface with no clear observed pattern, in the inset of Fig. 5(b) it is observed several magnetic fringes with a width of approximately 500 nm. These results may show that our sample is magnetically inhomogeneous. The structure was observed in all samples with Fe concentration equals to $x = 0.00$, $x = 0.05$ and $x = 0.10$. The $x = 0.00$ and $x = 0.10$ samples were rotated 90$^\circ$ degrees and the observed magnetic fringe pattern did not change orientation with the sample. We do not think that this observed magnetic fringe pattern is related with the lamellae structure observed in Figs. 4 since this pattern was also observed in samples with $x = 0.00$ (Fig. 4(a)).

Figure 4. SEM micrograph of polycrystalline sample of Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ for (a) white and (b) gray regions.

showed that there is variation in the chemical composition between the white and gray regions. This chemical composition difference is smaller in the Bi$_3$Ni than in the Bi$_3$Ni$_{0.90}$Fe$_{0.10}$. The white region is richer in Bi and poorer in Ni than the gray region for Bi$_3$Ni samples. When Fe is added, its solubility is higher in the gray region (14 %) than in the white region (8 %). Also, the ratio between Bi/Fe is constant (10) for the gray phase for the Bi$_3$Ni and Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ samples. For the white region, this ratio increases when Fe is added. The XRD experiment shown in Figs. 1(a-c) revealed that the white and gray regions have the same atomic structure, despite of the slight different chemical composition due to the different solubility of the elements revealed in the SEM.

Figure 5 show AFM images of 10 x 10 μm$^2$ area for Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ sample. Both images were obtained under

Table 2. Local composition of the Bi$_3$Ni and Bi$_3$Ni$_{0.90}$Fe$_{0.10}$ samples, as determined by EDS in different positions on the sample surface. The EDS analyses were performed in areas of 4 x 4 μm$^2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region</td>
</tr>
<tr>
<td></td>
<td>White</td>
</tr>
<tr>
<td></td>
<td>Bi (%) Ni (%) Fe (%)</td>
</tr>
<tr>
<td>Bi$<em>3$Ni$</em>{0.90}$Fe$_{0.00}$</td>
<td>95.2 4.7 0.0</td>
</tr>
<tr>
<td>Bi$<em>3$Ni$</em>{0.90}$Fe$_{0.10}$</td>
<td>90.5 1.6 7.9</td>
</tr>
<tr>
<td></td>
<td>Gray</td>
</tr>
<tr>
<td></td>
<td>Bi (%) Ni (%) Fe (%)</td>
</tr>
<tr>
<td>Bi$<em>3$Ni$</em>{0.90}$Fe$_{0.00}$</td>
<td>91.0 9.0 0.0</td>
</tr>
<tr>
<td>Bi$<em>3$Ni$</em>{0.90}$Fe$_{0.10}$</td>
<td>78.0 7.8 14.2</td>
</tr>
</tbody>
</table>
Raman spectroscopy is a powerful tool to detect changes at the microscopic level. Then, the search for specific features in the Raman spectra could shed new light in the effect of iron substitution in Bi$_3$Ni$_{1-x}$Fe$_x$ samples. We probed the samples with different power densities, from 6 to $60 \times 10^4$ W/cm$^2$ (applied power from 2 to 20 mW) at room temperature in order to investigate possible suppression or enlargement of active Raman modes as a function of the laser power density. Different locations on the sample surface were probed in order to assure spectra representability.

Figure 6 shows Raman spectra of Bi$_3$Ni$_{1-x}$Fe$_x$ samples with $x = 0.00$, $x = 0.05$ and $x = 0.10$ obtained at room temperature with an applied power of 10 mW ($30 \times 10^4$ W/cm$^2$). This power had the best signal-to-noise ratio with well resolved Raman peaks. The Raman spectra showed 2 Raman modes at $69 \pm 1$ and $96 \pm 1$ cm$^{-1}$. The line observed in $69$ cm$^{-1}$ is the most prominent, while a weaker band is observed at $96$ cm$^{-1}$. The phonon modes observed in this study show typical Lorentzian line shapes without asymmetry. The two peaks were not identified with any specific displacement mode and to the best of our knowledge, there is no mode identification for this material in the literature. No significant changes were observed in the spectra with Fe doping.

Figure 7. (a) Mapping of Bi$_3$Ni$_{0.95}$Fe$_{0.05}$ sample for a laser power of 10 mW. Measurements were performed in 3 steps spaced by 50 μm starting from the top (1) and (b) the corresponding Raman spectra measured at room temperature.

Magnetization as a function of temperature of Bi$_3$Ni$_{1-x}$Fe$_x$ samples with $x = 0.00$, $x = 0.05$ and $x = 0.10$ is shown in Figure 8. Figure depicts the DC magnetic susceptibility in zero-field-cooled (ZFC) situation in the temperature range 3-5 K and at an applied field $H = 10$ Oe. Superconductivity is observed below a transition temperature $T_c = 4$ K and regardless of iron doping. This is an important aspect of this study and more detailed investigations of the iron doping effects on the intermetallic Bi$_3$Ni$_{1-x}$Fe$_x$ ($0 \leq x \leq 0.10$) superconductor is needed. One important aspect is the coexistence of superconductivity and magnetism for low concentrations of iron$^{17}$.

From the phase diagram of Bi-Fe, Bi$_3$Fe samples may not be formed$^{18}$. In this study, we did not observe any difference in the XRD diffractograms in samples with different Fe
concentrations. SEM showed only small differences in stoichiometry of the Bi$_3$Ni$_{1-x}$Fe$_x$ phase for all Fe concentrations. Also, the Raman spectra were the same for samples with different Fe concentrations, even for the white and gray regions. Therefore, we conclude that Fe completely substitute Ni for all concentrations studied (up to $x = 0.10$).

4. Conclusions

Polycrystalline Bi$_3$Ni$_{1-x}$Fe$_x$ ($0 \leq x \leq 0.10$) superconductor was synthesized by the solid-state reaction method. Samples’ morphology consisted of laminar slab-like crystals. From XRD, it was observed that the main phase corresponds to Bi$_3$Ni$_{1-x}$Fe$_x$ with small quantities of BiNi and Bi as impurities. From SEM observations, two regions were observed. One region is richer in Bi and poorer in Ni and Fe than the other. Raman spectra were obtained and two phonon modes were observed, with no peak shift dependence with Fe doping. It was also observed that Bi$_3$Ni$_{1-x}$Fe$_x$ show superconductivity below a transition temperature $T_c = 4$ K.

5. Acknowledgements

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6. References


