

MAGNETIC AND STRUCTURAL STUDIES OF (Sn, Ni –Sn) SUBSTITUTED BARIUM HEXAFERRITES SYNTHESIZED BY BALL MILLING

ESTUDIOS MAGNÉTICOS Y ESTRUCTURALES DE HEXAFERRITAS DE BARRIO SUSTITUIDAS (Sn, Ni –Sn) SINTETIZADAS POR MOLIENDA DE BOLAS

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RESUMEN: Muestras de $\text{BaFe}_{12-2x}(\text{SnSn})_x\text{O}_{19}$ y $\text{BaFe}_{12-2x}(\text{NiSn})_x\text{O}_{19}$ con composición de $0 \leq x \leq 0.4$ y $0 \leq x \leq 0.3$ respectivamente, fueron procesadas por molienda alta energía. La mezcla $\text{Sn}^{2+}\text{-Sn}^{4+}$ mejoró considerablemente la magnetización de saturación, M_s , (de 60.9 a 66.15 $\text{A}\cdot\text{m}^2/\text{kg}$) y disminuyó rápidamente la coercitividad intrínseca, H_{ci} , (381.1-72.33 kA/m) a valores apropiados para aplicaciones en el registro magnético de alta densidad, con pequeños valores de sustitución. Por otro lado, la mezcla $\text{Ni}^{2+}\text{-Sn}^{4+}$ también disminuyó rápidamente la coercitividad intrínseca (disminución $\sim 75\%$) pero sin mejorar la magnetización de saturación. Las diferencias mostradas en las propiedades magnéticas fueron principalmente debido a la naturaleza magnética del ión divalente y a la presencia de fases secundarias. Mezclas con Sn^{2+} disminuyeron marcadamente la temperatura de Curie ($T_c \sim 21\%$).

PALABRAS CLAVE: Materiales magnéticos, Propiedades magnéticas, Materiales nanocristalinos, Hexaferritas sustituidas.

ABSTRACT: Samples of $\text{BaFe}_{12-2x}(\text{SnSn})_x\text{O}_{19}$ and $\text{BaFe}_{12-2x}(\text{NiSn})_x\text{O}_{19}$ were processed by high energy milling with $0 \leq x \leq 0.4$ and $0 \leq x \leq 0.3$ respectively. $\text{Sn}^{2+}\text{-Sn}^{4+}$ mixture considerably improved the saturation magnetization, M_s , (from 60.9 to 66.15 $\text{A}\cdot\text{m}^2/\text{kg}$) and diminished quickly the intrinsic coercivity, H_{ci} , (381.1-72.33 kA/m) to suitable values for high-density magnetic recording applications, with low substitution values. On

the other hand, the Ni^{2+} - Sn^{4+} mixture also decreased the coercivity rapidly (diminution $\sim 75\%$) however without enhancing the saturation magnetization. The shown differences on magnetic properties were mainly due to both magnetic nature of divalent ion and secondary phase presence. Mixtures with Sn^{2+} as partner ion diminished markedly to T_c ($\sim 21\%$).

KEYWORDS: Magnetic materials, Magnetic properties, Nanocrystalline materials, substituted hexaferrites.

1. INTRODUCTION

At present, the development of microwave communications technology and the need for anti-electromagnetic interference coatings has induced to an intense study of electromagnetic wave absorbing materials in last years [1, 2]. The most studied materials have been ferrites with spinel, garnet and hexagonal structure. Barium hexagonal ferrite,

BaM, is one of the most important hard magnetic materials widely used in many applications. For its high stability, excellent high-frequency response and narrow switching field distribution, BaM has been studied extensively during the last few years. Despite a considerable amount of research published over the past decade related to the magnetic properties and microstructure of substituted barium ferrites, there have been only a few successful breakthroughs regarding to discovery of new compositions, with excellent properties for special applications as high frequency microwave absorbers [3-5].

In order to obtain M-type barium ferrites with improved characteristics and planar anisotropy for applications in the field of high frequency microwave absorbers is necessary to substitute Fe^{3+} by other trivalent ions or cation mixtures [6, 7].

In this study, we compare the effect of two different partner ions on barium hexaferrite magnetic properties, in an attempt to understand both their magnetic behavior and their possible application on high-density magnetic recording and microwave absorption.

2. EXPERIMENT

Substituted hexaferrite powders $\text{BaFe}_{12-2x}(\text{M})_{2x}\text{O}_{19}$ with composition of $0 \leq x \leq 0.3$ and 0

$\leq x \leq 0.4$ were synthesized by high energy milling (where $\text{M} = \text{Ni}^{2+}$ - Sn^{4+} and Sn^{2+} - Sn^{4+}). As raw materials were used BaCO_3 , Fe_2O_3 , NiO , SnO and SnO_2 , all with purity of 98%. The milling process was performed in a Segvari attritor mill using a ball/powder mass ratio of 15 and a Fe/Ba molecular ratio of 10. The starting materials were milled for 28 h in air using 250 ml of benzene to avoid agglomeration of the powders at the mill bottom and to assure active participation of them in milling process. The as-milled powders were annealed in air at 1050°C for 1.5 hours.

Thermo-magnetic measurements were performed to obtain both Curie temperature, T_c , and magnetic susceptibility curves, χ , for all samples using the bridge method in an alternating magnetic field of 421 A/m at 920 Hz. Crystalline phase identification in the samples was performed using an X-pert Phillips diffractometer with $\text{Cu-K}\alpha$ radiation source. The magnetic properties of polycrystalline samples were measured in a Lake Shore 7300 vibrating sample magnetometer at room temperature applying an external magnetic field of 1.2 T. Mössbauer spectroscopy analyses were carried out to study the cationic distribution on hexagonal structure using a spectrometer with conventional constant acceleration mode and $^{57}\text{Co/Rh}$ γ -ray source. Mössbauer spectra were fitted by NORMOS software.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns analyses (Fig. 1) showed the apparition of SnO_2 as secondary phase for $x \geq 0.3$ Sn^{2+} - Sn^{4+} samples. The secondary phase formation occurred presumably for SnO oxidation due to milling conditions, which can be controlled by reducing the starting

oxides quantity (SnO). Magnetoplumbite phase was confirmed for the rest of mixtures; surprisingly no other secondary phases were detected, at least within the errors inherent to X-ray diffractometer.

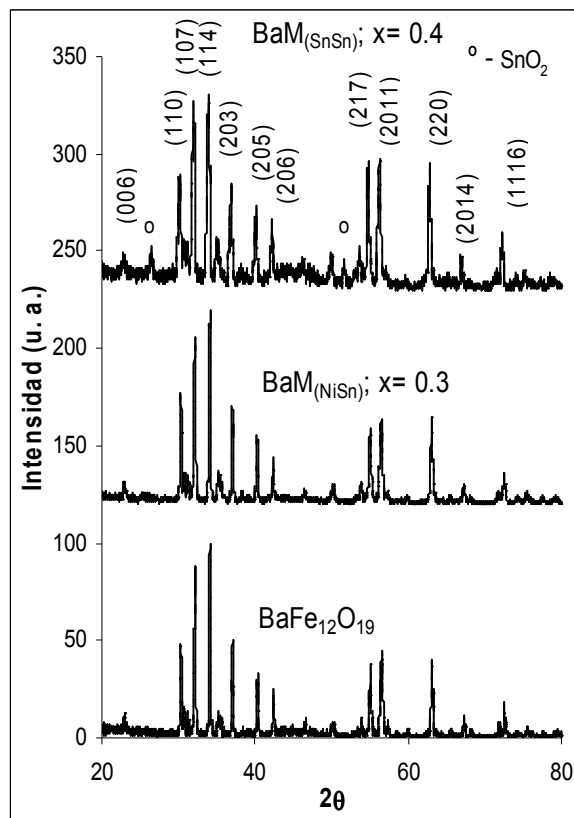


Figure 1. X-ray diffraction patterns of $(\text{Sn, Ni})^{2+}\text{-Sn}^{4+}$ substituted samples for $x = 0.4$ and 0.3 respectively. It can see the nucleation of SnO_2 as secondary phase for SnSn mixture

Mössbauer spectra at room temperature for all analyzed samples are shown in Figure 2. It can be observed that the intensity and shape of the spectra changed as the substitution level increased, indicating that the substitution of iron ions by substituting cations took place.

The realized studies threw that both samples presented similar tendencies to substitute of ion Fe^{3+} namely, both divalent partner ions (Ni^{2+} and Sn^{2+}) possess special preference for octahedral sites ($4f_2$ and $2a$), whilst tetravalent partner ions (Sn^{4+}) prefer to replace iron ions on both bipyramidal ($2b$) and tetrahedral ($4f_1$) sites.

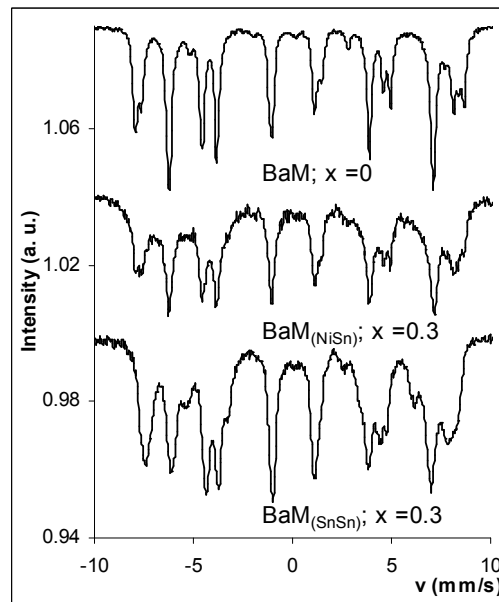


Figure 2. Room temperature ^{57}Fe Mössbauer spectra for $\text{BaM}(\text{Sn, Ni})\text{-Sn}$ mixtures with composition of $x = 0.3$. Note the change in the intensity and broad as the substitution increased as compared to pure magnetoplumbite ($x = 0$)

Nevertheless, it is clear that further Mössbauer studies with ^{119}Sn γ -ray sources would be necessary to determine more exactly the site preferences of the ions. Moreover, to observe the canting evolution on spin structure (change from axial to planar anisotropy), Mössbauer analyses with an external magnetic field applied parallel to γ -ray direction would be of special interest as well.

Thermomagnetic measurements (Fig. 3) were performed to determinate both the dependence of magnetic susceptibility with temperature (χ (T)) and the Curie temperature (T_c). It could be observed how χ was affected for all studied samples, besides; it was possible to detect that mixtures with Sn^{2+} as partner ion diminished markedly to T_c , ($\text{SnSn} \sim 21\%$ as distinct from $\text{NiSn} \sim 1.8\%$) this can be related to the gradually magnetic collinearity break down after replacing iron ions by diamagnetic ions (Sn^{2+}) [8]. NiSn curves also showed the appearance of another peak at ~ 580 °C, which correspond to spinel compound nucleation as secondary phase. This phase is most probably NiFe_2O_4 , which possess a T_c of 585 °C.

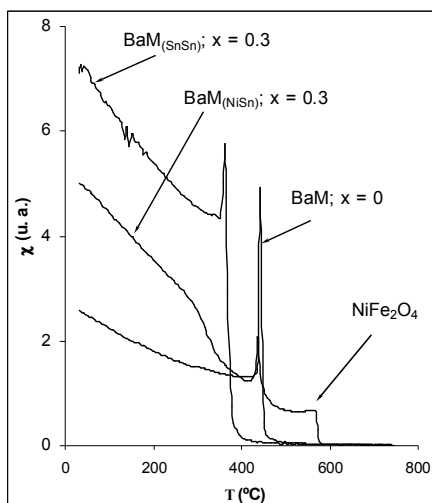


Figure 3. Magnetic Susceptibility temperature dependence studies for BaM(Sn, Ni)-Sn substituted materials. Note the nucleation of Ni spinel (NiFe_2O_4) as secondary phase at $\sim 580^\circ\text{C}$ in BaM(NiSn) sample

The figure 4 shows magnetic properties behavior as a function of substitution for all studied samples. For substituted SnSn sample, it can see how saturation magnetization was enhanced (increase $\sim 9\%$) to reach a maximum at $x = 0.2$, diminishing after. Also it could be observed how M_s for NiSn sample remained almost constant for all substitution range. Taking into account that both mixtures possess similar preferences to replace iron ions into hexagonal structure, therefore, we believe that both the magnetic nature divalent partner ions (Ni^{2+} is magnetic $\sim 2\mu_B$ and Sn^{2+} diamagnetic) and secondary phase nucleation are responsible of M_s behavior.

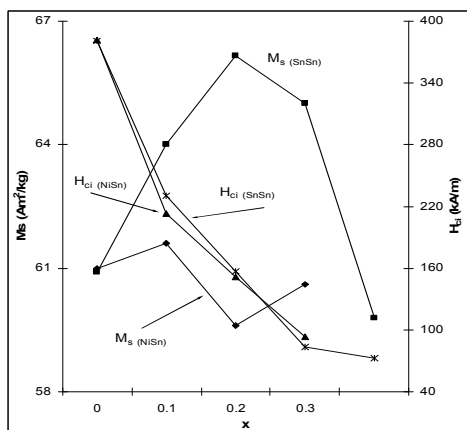


Figure 4. Magnetic properties behavior of all synthesized samples as a function of the substitution

In figure 4, also it can observe the caused effect on intrinsic coercivity, H_{ci} , by all experimented substitution. It can see that H_{ci} suffered a rapid reduction for both studied samples (NiSn and SnSn) with x substitution (drop $\sim 75\%$ and 78% respectively). In addition, observing the obtained results, it can say that the tetravalent Sn^{4+} ion has a special effect on magnetic properties of hexagonal ferrites (increases M_s and diminishes so fast H_{ci} with low substitutions).

4. CONCLUSIONS

Syntheses of two different cationic mixtures were studied, aiming to obtain materials useful for high-density magnetic recording. In this aspect, we can highlight that Sn-Sn mixtures diminished the coercivity (H_{ci}) rapidly to suitable values for high-density magnetic recording applications; increasing at the same time the saturation magnetization (M_s) with low substitution values. Mixtures with Sn^{2+} as partner ion diminished markedly to T_c , (SnSn $\sim 21\%$ as distinct from NiSn $\sim 1.8\%$) this can be related to the gradually magnetic collinearity break down after replacing iron ions by diamagnetic ions (Sn^{2+}), taking as consequence the superexchange interaction decrease. Alternatively, NiSn mixtures showed to be promissory materials for microwave absorption applications.

To determine more exactly the site preferences of substituting ions further Mössbauer studies with ^{119}Sn γ -ray sources would be necessary. Moreover, to observe the canting evolution on spin structure (change from axial to planar anisotropy), Mössbauer analyses with an external magnetic field applied parallel to γ -ray direction would be of special interest as well.

5. ACKNOWLEDGMENTS

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