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ARTICLE

Magnetic and Structural Studies of $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$ Prepared by Ball Milling

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Abstract: Results on structural and magnetic studies of $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$ (where x = 0.2 to 0.6) ferromagnetic powders prepared by mechanical milling are presented. The obtained X-ray diffraction patterns of Zn-Ti substituted $(BaSr)_{0.5}M$ samples showed Magnetoplumbite phase formation for all substituted mixtures; no other secondary phases were detected. Scanning electron microscope analyses reveled that all processed samples possess particle size much below 1 μm and may exhibit promising magnetic and dielectric properties. Magnetic measurements showed that the intrinsic coercivity, H_{ci}, and remanent magnetization, M_r, decreased as the substitution took place, while the saturation magnetization, M_s, remained almost constant (diminution ~ 9%). H_{ci}, decreased from 389.92 down to 171.88 k A/m that represents a 56% drop, whilst M_r registered a fall of ~ 17%.

Key Words: Magnetic Studies, Mössbauer Spectroscopy, Ba-Sr-Hexaferrites, Ball Milling.

Introduction

Intensive work have been done to modify the magnetic parameters of barium or strontium hexaferrite by substitution of Fe^{3+} ions with other cations or cation combinations such as Co-Ti, Zn-Sn, Co-Sn, Ni-Zr, Co-Mo and so on [1-3]. Several methods have been used to modify the structural and magnetic properties of M-type ferrites [1, 3, 4]. The magnetic properties of substituted $Ba_{1-x}Sr_xFe_{12}O_{19}$, where Ba^{2+} gradually substitutes Sr^{2+} ions, have been studied and reported by other researchers [5-7]. These studies show that $Ba_{0.5}Sr_{0.5}Fe_{12}O_{19}$ sample possesses higher Curie temperature, T_C ~ 510 °C, than that of $BaFe_{12}O_{19}$ (502 °C) sample, which increases as Sr concentration increases. In addition, electrical characteristics (AC and DC) of the $Ba_xSr_{1-x}Fe_{12}O_{19}$ compound have been studied [7]. The largest value for the dielectric constant (ε') corresponds to the x = 0.0 sample (ε_r'»1300) and it decreases, as the Ba content increases, to around 100 for x = 1.0. Therefore, it seems interesting to investigate more cationic combination in this ferrite system [8]. Previous studies have shown that Zn-Ti cationic mixture produces materials with suitable characteristics for high-density magnetic recording [9, 10].

This paper reports structural and magnetic properties of the Zn-Ti substituted $(BaSr)_{0.5}M$ -type hexaferrite, prepared by high energy milling.

Experiment

To synthesize $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$; $BaCO_3$, $SrCO_3$, Fe_2O_3, ZnO, and TiO_2 (ACS reagent ~ 98% of purity, Aldrich Co.) were used as starting materials. The raw materials were charged in a Segvari Attritor mill together with several 9-mm steel balls. The powders were milled during 24 hours in air with an angular velocity of 400 rpm and 250 ml of benzene to avoid agglomeration at the mill bottom. The as-milled powders were

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annealed at 1050 ºC with a soaking time of 1.5 h.

To determine the crystalline structure of the prepared specimens, X-ray diffraction and Mössbauer spectroscopy studies were performed in an X' Pert Philips diffractometer using Cu-K_α radiation and a Mössbauer spectrometer with γ-ray source of ^{57}Co embedded in a rhodium matrix, respectively. The magnetic properties at room temperature were measured uzing a Lake Shore 430 vibrating sample magnetometer and applying an external magnetic field up to 954. 9 kA/m. The temperature dependence of the magnetic susceptibility, $\chi(T)$ was obtained using the bridge method in an alternating magnetic field of 421 A/m and 920 Hz. Finally, to obtain information on both morphology and particle size, the $(BaSr)_{0.5}M$ doped samples were observed employing a Philips XL 30 scanning electron microscope (SEM).

Results and Discussions

The X-ray diffraction patterns of Zn-Ti substituted $(BaSr)_{0.5}M$ samples, obtained at different sample preparation stages, are shown in Fig.1. The patterns of all samples (as-milled) after milling for 24 hours show broadened diffraction peaks corresponding to Fe_2O_3 hematite phase. Magnetoplumbite phase was formed for all substituted samples (x = 0 to 0.6) after being annealed at 1050 ºC; no other secondary phases were detected, at least within the errors inherent to this technique.

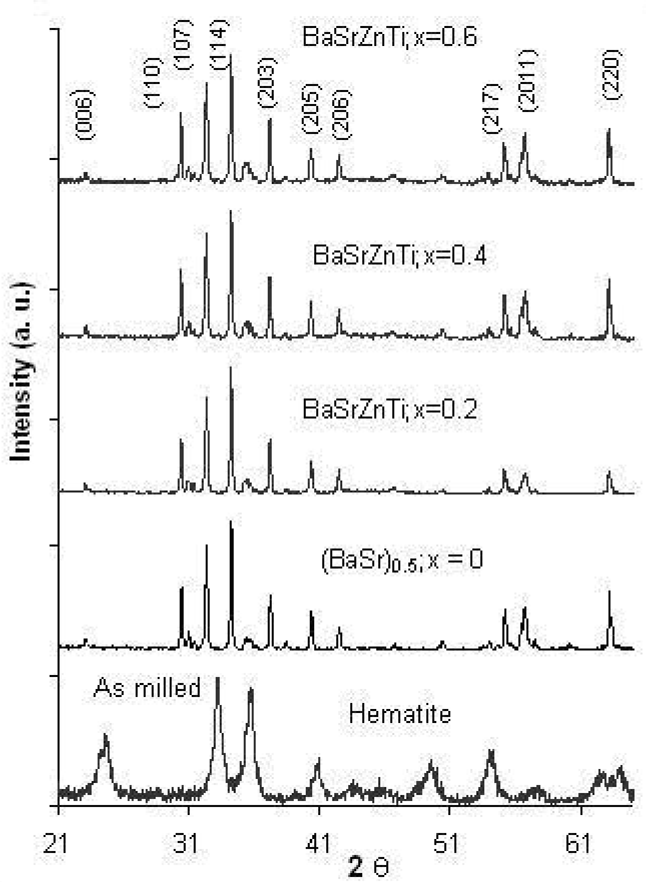

Fig. 1: X-ray diffraction patterns for all prepared samples.

Room temperature Mössbauer spectra for $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$ samples with x = 0.0, 0.2, 0.4 and 0.6 are shown in Fig.2. These measurements revealed that at low substitutions, Ti^{4+} ions substitute Fe^{3+} ions on the $4f_2$ octahedral site, and the Zn^{2+} ions substitute them on the tetrahedral $4f_1$ site. At higher concentrations other iron positions are replaced also, like 2a octahedral sites by Ti^{4+} ions and 2b positions by Zn^{2+} ions [10].

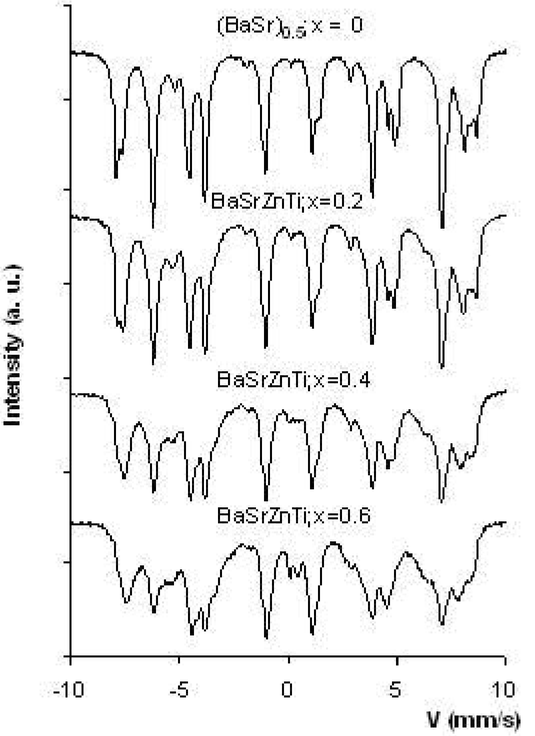

Fig. 2: Mössbauer spectra of Zn-Ti substituted $(BaSr)_{0.5}M$ ferrites.

The results of the temperature dependence of the initial susceptibility of $Ba_{0.5}Sr_{0.5}(ZnTi)_xM$ ferrites is shown in Fig.3. It can be observed, that at room temperature the susceptibility, χ, increases with the substitution level. These curves can be also used as quality test for some preparation techniques. From the sample with x = 0.0 it could be concluded that no other secondary phase was nucleated for all synthesized mixtures. On the other hand, Hopkinson peak appears near Curie point T_C and falls from a relatively high value to near zero. This drop provides a possibility of homogeneity in sample chemical composition. This peak value also gives information about quantity percentage of the ordered single-phase structure with particles smaller than 1μm. In addition, x = 0.0 sample exhibits a curve that roughly approaches the theoretical behavior of hexaferrite initial magnetic susceptibility as a function of temperature. Besides, it could be concluded that T_C for all substituted samples were almost not affected by the increase in x, (diminution ~2%).

The magnetic properties behavior of Zn-Ti-substituted $(BaSr)_{0.5}M$ obtained by vibrating sample magnetometry is shown in Fig.4. Both, the intrinsic coercivity, H_{ci}, and the remanent magnetization, M_r, decreased as the substitution took place, while the saturation magnetization, M_s, remained almost constant (diminution ~ 9%). H_{ci}, decreased from 389.92 down to 171.88 kA/m, which represents a 56% drop, whilst M_r registered a fall of ~ 17%. The fast reduction of H_{ci} is related to the reduction of the magnetocrystalline anisotropy field, H_a, which has been attributed to the cation preference for the bipyramidal site, 2b and octahedral site $4f_2$, which possess the largest contribution to H_a in BaM. On the other hand, the small diminution of M_s and M_r can also be explained by the gradual break down of the magnetic ordering, due to the disappearance of some super exchange interactions when the iron ions are substituted for other diamagnetic or paramagnetic cations.

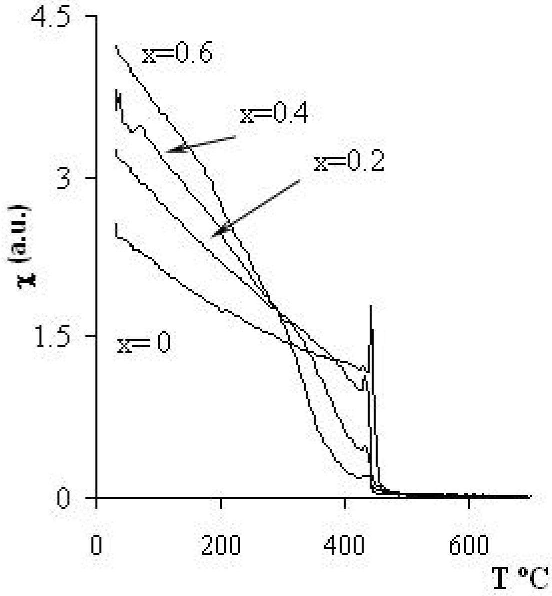

Fig. 3: Temperature dependence of the magnetic susceptibility of $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$.

In Fig.5 the micrographs taken by SEM for the pure $(BaSr)_{0.5}M$ ferrite and x = 0.6 substituted ferrite are shown. It can be seen that all particles of the samples are nearly hexagonal platelet in shape and have a wide spread in particle size. However, it is clear that the particle size is much below 1 μm,

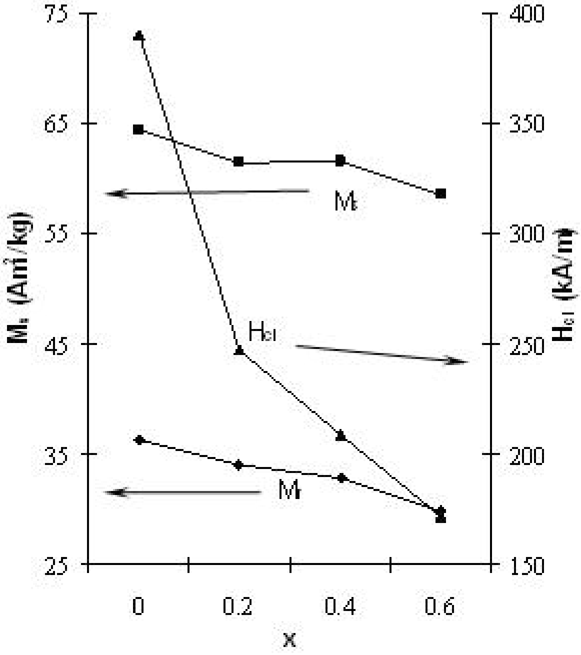

Fig. 4: Magnetic properties behavior of all synthesized samples as the substitution level increased.

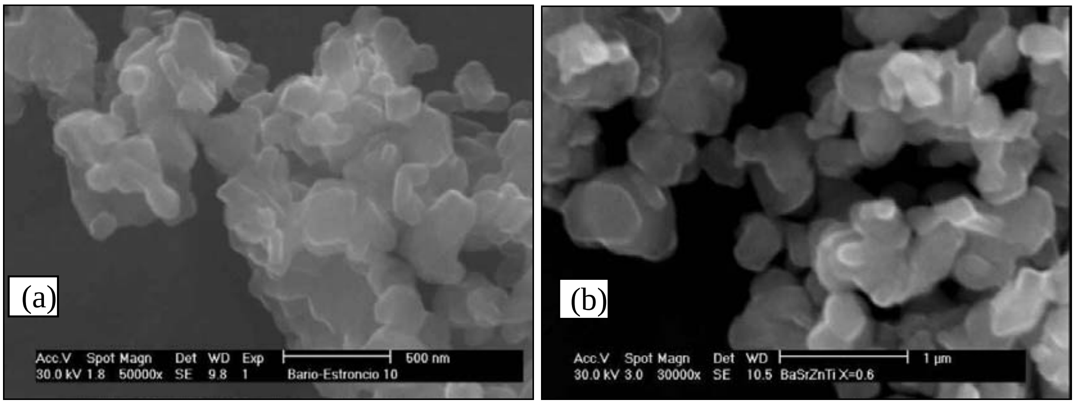

Fig. 5: SEM micrographs show particle size and morphology for samples $Ba_{0.5}Sr_{0.5}(ZnTi)_xFe_{12-2x}O_{19}$. a) x = 0, b) x = 0.6.

Conclusions

This work has shown that it was possible to synthesize $Ba_{0.5}Sr_{0.5}M$ hexaferrite substituted with Zn^{2+} - Ti^{4+} ions by mechanical milling. The magnetic ordering was reduced somewhat (~2%) for all levels of substitution. Changing the substitution ratio x, the coercivity could be easily controlled without a significant reduction of M_s. Magnetic susceptibility measurements have shown that with the increase of x, χ at room temperature increases, which is believed to have a relation with the disappearance of some superexchange interactions. The micrographs of Fig. 5 indicate that the particle size of the samples is much below 1 μm. The studied samples may exhibit promising magnetic and dielectric properties.

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