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CATIONIC DISTRIBUTION IN $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$ HEXAGONAL FERRITES SUITABLE FOR MAGNETIC RECORDING

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Abstract. – The cation distribution in the $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$ compounds has been investigated by means of powder neutron diffraction. The atomic occupancies of the 2a, 4e and $4f_{IV}$ are unambiguously determined while the atomic contents of the 12k and $4f_{VI}$ octahedral positions are strongly delimited. A considerable amount of Co ions occupy the tetrahedral positions thus reducing the effect of these ions as a source of the decrease of the uniaxial anisotropy.

Recent reports on the synthesis and characterization of hexagonal ferrite particles [1-3] have shown that the liquid mix technique may be a valuable method to obtain single domain particles for perpendicular magnetic recording. In order to get particles suitable for magnetic recording it is well known that some Co^{2+} doping is necessary to reduce the intrinsically high uniaxial magnetic anisotropy of $\text{BaFe}_{12}\text{O}_{19}$ [4]. In a recent work [3] we have proved that $\text{Co}^{2+} + \text{Sn}^{4+}$ doping may constitute an interesting alternative to the usual $\text{Co}^{2+} + \text{Ti}^{4+}$ doping scheme because similar decreases of the coercive field may be obtained with a lower substitution rate. We have now investigated by means of powder neutron diffraction and Mössbauer spectroscopy the cation distribution in the $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$ hexagonal ferrites. A study of the isomorphous Ti compounds is in progress for comparison purposes.

The synthesis of the $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$ ($0 \leq x \leq 1.0$) samples used in this investigation was performed by the liquid mix technique as it was described in a previous work [3].

Powder neutron diffraction patterns were recorded at the D2B of the I.L.L. using $\lambda = 1.594 \text{ \AA}$. All spectra were obtained at $T = 520^\circ \text{C}$ in the paramagnetic phase and the diffraction patterns were refined by the Rietveld method [5]. The positional parameters together with occupation factors P_i corresponding to the five sublattices of the M-structure were simultaneously refined.

Details of the refinement procedure will be published elsewhere. Immediately after the first runs it was evident that no Co or Sn substitution takes place in the octahedral 2a and pseudotetrahedral 4e sublattices up to $x = 1.0$, while some substitution occurs in the remaining $4f_{IV}$, $4f_{VI}$ and 12k sublattices. Figure 1 shows the composition dependence of the refined occupation factors assuming $b = b(\text{Fe})$ for these positions. The

Fig. 1. – Refined occupation factors P_i of the different sublattices referred to full Fe occupancy ((x): $4f_{IV}$; (•): $4f_{VI}$; (+): 12k).

observed decrease of these P_i values is indicative of the substitution with Co or Sn ions which have lower scattering lengths. When these occupation factors are converted to atomic occupancies a system of four equations having six variables can be constructed. To solve this system some physical hypothesis are in order. The first hypothesis we have considered is that Sn atoms are not located on the tetrahedral $4f_{IV}$ sublattice. In this way the occupancy rate of Co ions in the tetrahedral site may be immediately found. See figure 2. Because a small amount of the CoFe_2O_4 and $\alpha - \text{Fe}_2\text{O}_3$ oxides were observed as impurities we have not imposed the total Co contents in the M-phase. Instead the Sn contents, was restricted to the nominal values. In this way, we have computed the occupation ratio assuming two limiting situations: i) no Sn atoms are located in the $4f_{VI}$ sublattice, ii) no Sn atoms are located in the 12k sublattice. The results obtained within the first hypothesis are displayed in figure 2a while the second limit led to anomalous Co occupancy in the $4f_{VI}$ sublattice where a change in the slope of the occupation ratio as a function of x was found.

In order to get a physical result where the Co ($4f_{VI}$) occupancy steadily increases with x , we computed the occupancy ratio for several Sn distributions among the

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Fig. 2. - Co substitution percentage in the different sublattices referred to the total occupancy of each position ((x): $4f_{vi}$; (o): $4f_{iv}$; (+): 12 K) assuming that: (a) no Sn atoms are located in the $4f_{vi}$ sublattice, and (b), the Sn occupancy ratio between 12k and $4f_{vi}$ sublattices is 1.2.

12k and $4f_{vi}$ sublattices. We found that the Sn occupation ratio between 12k and $4f_{vi}$ positions must be at least 1.2. The cation distribution resulting from this limit is represented in figure 2b.

We should remark that although the atomic contents of the $4f_{vi}$ and 12k positions may not be completely determined our results allow us to define two strongly stringent limits, as reported in figures 2a and 2b.

It is worth to emphasize that the composition dependence of the mean interatomic distances in these positions are consistent with the ionic radius of the Fe^{3+} , Co^{2+} and Sn^{4+} contents in all the positions.

Finally, we note that in principle the ambiguity remaining in the neutron diffraction analysis could be lifted by using Mössbauer spectroscopy. However, because of strong perturbation of the magnetic spectra induced by the existence of atomic disorder the fitted intensities own an important uncertainty which precluded any further precision in our results.

Summarizing our neutron diffraction study of the $BaFe_{12-2x}Co_xSn_xO_{19}$ series has allowed to ascertain

that two sublattice are fully occupied by Fe ions (2a and 4e) and that the tetrahedral $4f_{iv}$ sublattice is occupied by a non negligible amount of Co^{2+} ions. For the 12k and $4f_{vi}$ sites we have established a narrow interval of possible compositions. This last uncertainty could be probably raised performing saturation magnetization measurements at low temperatures. This study is presently underway.

We would like finally to stress the relevance of our results concerning the macroscopic magnetic properties of the Co-substituted M-type hexagonal ferrites. The most important point is that a considerable amount of Co^{2+} ions occupy the tetrahedral $4f_{iv}$ position thus being ineffective in the reduction the uniaxial magnetic anisotropy. This is also probably the clue for the understanding of the different magnetic behaviour of the Ti and Sn substituted M-type hexagonal ferrites.

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