Influence of La substitutions on the magnetic after-effect in hexaferrites and garnets

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Abstract. Magnetic relaxation has been measured in La-Co substituted M-type Sr hexaferrites and La substituted YIG polycrystalline samples prepared by means of standard ceramic techniques. In the temperature range between 80 and 420 K, the magnetic disaccommodation has been measured. The isochronal disaccommodation spectra show the presence of different relaxation processes. In hexaferrites, the La doping distort the lattice size and the arrangement of cations within the structure, changing the strength of relaxation processes regarding unsubstituted samples. In garnets, substitution rate only modify lattice size, whereas with CO2 atmosphere the formation of secondary perovskite phase is detectable with this technique.

1. Introduction

Hexagonal ferrites have been widely used as permanent magnets owing to their appropriate magnetic properties: big saturation magnetization, large uniaxial anisotropy, and high Curie temperature. In addition, they show promising properties in microwave devices and recording media [1]. There are different stable phases derived from the M-type SrFe12O19. Physical properties needed for different applications can be tailored by choosing the right phase, carrying out adequate cation substitutions and improving the microstructure, by using different synthesis methods. Among the different cation substitutions the addition of rare-earth La3+ and transition Co2+ improve the performance of the permanent magnetic hexagonal ferrites (Hc increase from 275 kA/m to 355 kA/m, i.e. about 25% higher) [2]. YIG are key ferrimagnetic materials for use at high frequencies and their properties can also be tailored. Yttrium substitution for a light RE is known for years, but now the interest is renewed, as La doped YIG exhibit a strong magnetoelectric effect [3].

Regarding magnetic properties, the magnetic after-effect processes have to be taken into account in order to minimize the losses. In addition, the study of this kind of processes provides information about the underlying mechanisms governing the dynamic behavior of Bloch walls [4]. Among the different techniques available, the magnetic disaccommodation measurements are a powerful tool in the detection of this kind of phenomena. It consists in the time variation of the mobility of domain walls after a magnetic shock, and is shown by a temporal evolution of the magnetic permeability after a demagnetization stage, and the relaxation time which characterizes each relaxation process is strongly temperature-dependent. This relaxation phenomenon has been observed firstly in spinel ferrites [4], but is also present in hexaferrites and garnets [5-6]. In this paper we analyze the effect of La substitution on the magnetic disaccommodation in SrM hexaferrites and yttrium iron garnets.
2. Experimental

We have prepared two series of polycrystalline samples of La-Co substituted M-type hexaferrites (details can be found in [7]): one of them with equal substitution of La and Co, i.e. Sr$_{1-x}$La$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ ($x=0.09$ to $0.18$), and other with different amount of them: Sr$_{1-x}$La$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ ($x=0.09$, $y=0.08$; $x=0.13$, $y=0.11$; $x=0.16$, $y=0.13$). Pressed samples were sintered at $1350^\circ$C in air atmosphere, keeping the top temperature for 4 hours, then they were quenched. La doped YIG series Y$_3$La$_{x}$Fe$_{2}$Co$_y$O$_{12}$ ($0<x<0.6$) [6] were prepared in air and CO$_2$ sintering atmospheres at $1420^\circ$C for 5 h.

Magnetic disaccommodation measurements were carried out with a computer aided system based on a LCR bridge, in the $80 \text{ K} < T < 420 \text{ K}$ temperature range. The results have been represented as isochronal spectra, i.e. the relative variation of the initial permeability after sample demagnetization between an initial time $t_1=2 \text{ s}$ and different window times $t_2=4, 8, 16, 32, 64$ and $128 \text{ s}$ in the form

\[
\frac{\mu(t_2,T)-\mu(t_1,T)}{\mu(t_1,T)} \times 100 \%
\]

When the time window ($t_2-t_1$) is of the same order of magnitude that the relaxation time, this curve exhibits a maximum. So, isochronal spectra disclose different after-effect processes in the temperature range tested, and characteristic parameters of the relaxation process, as activation energy, are obtained.

3. Results and discussion

Representative results of the two series of La-Co substituted SrM hexaferrites are presented in Figure 1. Several relaxation processes emerge at temperatures $380 \text{ K}$ (A peak), $300 \text{ K}$ (B), and $165 \text{ K}$ (D) like in pure SrM hexaferrites [5]: B process, with activation energies of $0.84 \text{ eV}$, is caused by anisotropic reorientation of the local symmetry axis due to the jump of a ferrous cation towards a vacancy in the octahedral site $2a$ located in spinel S blocks within the hexagonal lattice. The A peak has a similar origin with increased activation energies ($1 \text{ eV}$) due to the presence of the Sr ion. On the other hand, the D peak is attributed to similar process in the octahedral $4f_2$ sites located in R blocks. These are face-sharing sites so that the energy involved in this process, $0.5 \text{ eV}$, is lower than the corresponding to the B peak. The increase in doping rate in Sr$_{1-x}$La$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ causes a progressive diminution of relaxation processes, especially A and B peaks, and a shift of D process peak temperature to higher values (from $165 \text{ K}$ to $180 \text{ K}$). Mössbauer investigations of La$^{3+}$-Co$^{2+}$ M-type ferrites revealed that most of the Co$^{2+}$ cations enter in the octahedral $2a$ sites [8], then causing the observed diminution of B peak amplitude, and making energetically unfavoured the A process. In addition, local neutrality favors the presence of the divalent ferrous cation in the vicinity of La$^{3+}$ thus enhancing the D process which takes place in face-sharing octahedral $4f_2$ sites. On the other hand, substitution of part of Sr$^{2+}$ (ionic radius 1.27 Å) with La$^{3+}$ (1.61 Å), and Co$^{2+}$ instead Fe$^{3+}$ (0.65 Å and 0.55 Å resp) distort the hexaferrite structure. With this in mind, increased doping rate almost suppresses B peak, due to the small amount of Fe$^{2+}$ in $2a$ sites occupied by Co, and also modifies the D peak in two ways: increasing its activation energy due to lattice distortion and lowering its amplitude, because the unit cell is smaller and then the presence of localized ferrous cations in $4f_2$ sites is less probable in favour of diffusion of cations via lattice vacancies, thus increasing the high temperature process (over $400 \text{ K}$).

Concerning Sr$_{1-x}$La$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ samples, the effect observed with doping rate is similar, i.e. diminution of relaxation amplitudes with increasing doping. We can see that D peak is prominent, and B peak is strongly diminished, even for the lower substitution rate analyzed. As the amount of Co$^{2+}$ is lower than La$^{3+}$ substitution, a higher amount of Fe$^{3+}$ reduces to Fe$^{2+}$ to maintain electrical neutrality. The preference of Co$^{2+}$ for octahedral $2a$ sites promotes the preferential occupation of ferrous cations in octahedral sites in R blocks near La$^{3+}$, thus enhancing the D process and almost suppressing the B process regarding Sr$_{1-x}$La$_x$Fe$_{12-2x}$Co$_x$O$_{19}$ samples. The increased amount of ferrous cations can not enter completely in the $4f_2$ sites due to higher ionic radius of Fe$^{2+}$ (0.61 Å) regarding Fe$^{3+}$ hence increasing also the diffusion processes.
In YIG, characteristic disaccommodation peak II process, centred at 130 K (0.35 eV), is associated with $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ electronic transfer in octahedral sites of the garnet lattice. Ferrous ion is necessary to maintain electrical neutrality due to the existence of oxygen vacancies. The temperature range of this peak, and hence the activation energy lowers with increasing La doping, from 130 K to 120 K, due to the larger size of the unit cell caused by the introduction of the dopant (12.376 Å with $x=0$ to 12.423 Å with $x=0.5$). For La doped YIG sintered in CO$_2$ (Figure 2), the garnet-perovskite transition takes place at a doping rate $x=0.3$. This effect is clearly visible in disaccommodation results for the suppression of YIG process due to the formation of antiferromagnetic perovskite and emergence of III process of magnetite, that appears as secondary phase. However, garnet-perovskite transition does not take place when sintering in air. Thermal dependence of magnetic permeability (not shown) support these conclusions. Low doped samples behaves similary to undoped YIG, and a progressive decrease with increasing substitution rate is observed. Once the garnet-perovskite transition has been reached, the permeability decreases strongly due to the high amount of antiferromagnetic perovskite in the sample. As a conclusion, La doping affects relaxation due to different ionic size in both systems, but has additional characteristic effects in hexaferrites and garnets.

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