An approach to the magnetic disaccommodation in Ti-substituted Ba–W hexaferrites

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The relaxation of the initial permeability has been measured in polycrystalline Ti-doped Ba–W hexaferrites with nominal composition $BaTi_xFe_{18-x}O_{27}$, with x ranging among $x=0$ and 0.3. The samples have been sintered at different temperatures in the $1250\,°C < T < 1350\,°C$ range in a reducing CO_2 atmosphere and rapidly quenched to promote the presence of crystal vacancies. X-ray diffraction spectra reveal the presence of hexaferrite as main phase. In the temperature range between 80 and 500 K, the time decay of the initial permeability after sample demagnetization has been plotted by means of isochronal curves. The isochronal disaccommodation spectra show an increase in the amplitude of the different disaccommodation peaks in substituted samples regarding pure Ba–W hexaferrites. These peaks are centered at 180, 300, and 380 K and they are related to the presence of both ferrous cations and lattice vacancies. The increase of the disaccommodation maxima in Ti-substituted hexaferrites is ascribed to the additional amount of ferrous cations induced by the presence of Ti cations, in order to maintain electrical neutrality. On the other hand, the isochronal spectrum in pure Ba–W shows another relaxation peak at 240 K which almost disappears in substituted hexaferrites, even with the lowest Ti doping analyzed. This behavior is explained in terms of the increasing hindrance to the mechanisms responsible for this ionic relaxation process, owing to the site occupation by the nonmagnetic Ti cations within the hexagonal structure. © *2000 American Institute of Physics.* [S0021-8979(00)23508-1]

I. INTRODUCTION

Barium and strontium hexaferrites have been widely used as permanent magnets owing to their magnetic properties as well as their low manufacturing cost. Many efforts have been made in the last years in order to reduce the coercive field in hexagonal ferrites for its application as magneto-optic or perpendicular magnetic recording media. It has been found that the most useful substitutions are Co and Ti or Co and Sn.[1,2] As a consequence of the substitutions the material becomes magnetically softer and magnetic relaxation phenomena have to be taken into account.[3] The magnetic disaccommodation measurements are a powerful tool in the detection of these kind of phenomena. It consists of 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. This relaxation phenomenon has been observed in spinel ferrites,[4] but is also present in hexaferrites.[5] Its origin has been attributed to both the rearrangement and the diffusion of anisotropic point defects (i.e., lattice vacancies, interstitials) within the Bloch walls, and the relaxation time which characterizes each relaxation process is strongly temperature dependent. In addition, it has been previously shown that the introduction of titanium in the magnetite structure promotes marked changes in terms of magnetic relaxation, even with

very low Ti content.[4] In this article we present a preliminary note on the disaccommodation in Ti substituted W-phase barium hexaferrites.

II. EXPERIMENT

For this study, we have prepared a series of polycrystalline samples with nominal composition $BaTi_xFe_{18-x}O_{27}$ with x ranging among $x=0$ and 0.3. The mixtures were prepared with high purity starting elements: α-Fe_2O_3, $BaCO_3$, and TiO_2, mixed in the appropriate molar ratio for 1 h in an agate mortar. The mixtures were prefired at $950\,°C$ for 12 h, ground, and pressed in a cylindrical die. Samples with 5 mm in diameter and 15 mm in length were sintered in CO_2 atmosphere at sintering temperatures in the $1250\,°C < T < 1350\,°C$ range. X-ray diffraction (XRD) spectra reveal the presence of hexaferrite as main phase. Magnetic disaccommodation measurements were carried out with a computer aided system based on a LCR bridge,[6] in the $80\,K \leqslant T \leqslant 500\,K$ temperature range. The results have been represented as isochronal curves, i.e., the relative variation of the initial permeability after sample demagnetization between an initial time $t_1 = 2$ s and different window times $t_2 = 4, 8, 16, 32, 64,$ and 128 s in the form

$$\frac{\mu(t_1,T) - \mu(t_2,T)}{\mu(t_1,T)}(\%). \qquad (1)$$

When the time window $(t_2 - t_1)$ is of the same order of magnitude as the relaxation time at a specified temperature, this

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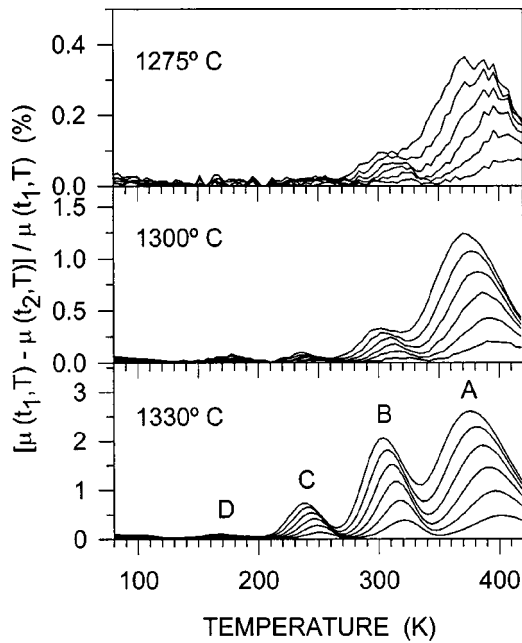[a]Electronic mail: pabloher@ee.uva.es

FIG. 1. Isochronal spectra of $BaFe_{18}O_{27}(Fe_2W)$ hexaferrite samples sintered in CO_2 at different temperatures. The isochronal curves are formed by using the Eq. (1) with $t_1 = 2$ s and $t_2 = 4$, 8, 16, 32, 64, and 128 s (curves from bottom to top in each graph).

FIG. 2. Isochronal spectra of $BaTi_{0.1}Fe_{17.9}O_{27}$ hexaferrite samples sintered in CO_2 at different temperatures, with t_1 and t_2 values as in Fig. 1.

curve exhibits a maximum. The demagnetization stage is achieved by using a linearly decreasing ac magnetic field.

III. RESULTS AND DISCUSSION

In Fig. 1 the isochronal spectra of the pure Fe_2W hexaferrite samples sintered at different temperatures is shown. It can be noted that different disaccommodation processes emerge at sintering temperatures above 1275 °C. The temperatures where these peaks have their maxima, for the higher time window isochronal curve tested, are 380, 300, 240, and 180 K (respectively, A, B, C, and D processes). It is noteworthy that the amplitudes of the processes raise with the sintering temperature, especially the C process.

In the Figs. 2 and 3 the corresponding isochronal spectra obtained for samples with initial composition $x = 0.1$ and 0.3 are shown. There are several differences regarding pure BaW hexaferrites: (i) The amplitude of the disaccommodation peaks is higher in substituted samples; (ii) The 240 K peak (C) is not present at sintering temperatures down to 1330 °C and is not present at all in $x = 0.3$ samples, whereas in pure BaW appears at 1300 °C with higher amplitude than in substituted hexaferrites. (iii) The D peak is enhanced in substituted samples, but its amplitude does not seem to be dependent on the Ti content. In addition, it should be noted that the amplitude of the B peak increases with Ti content, at the same sintering temperature.

It is well known that the magnetic disaccommodation in cubic ferrites is very dependent on the presence of both ferrous cations and lattice vacancies. Keeping in mind that the W-type hexaferrite contains Fe^{2+} cations, and that the hexagonal and cubic close packed structures have some similarities in terms of interstitial sites, it is feasible to think that magnetic aftereffect phenomena can take place in hexagonal
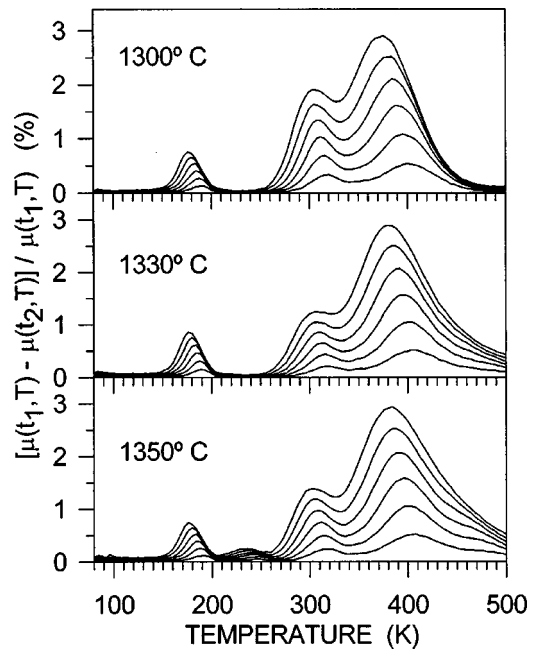
ferrites. In addition, it is noteworthy that x-ray analysis does not show the presence of magnetite in our samples, and hence the possibility of a spinel-like secondary phase as responsible for the disaccommodation processes observed have to be ruled out. The different disaccommodation processes observed have to be ascribed to similar underlying mechanisms responsible for the magnetic aftereffects in spinel ferrites within the hexagonal lattice.

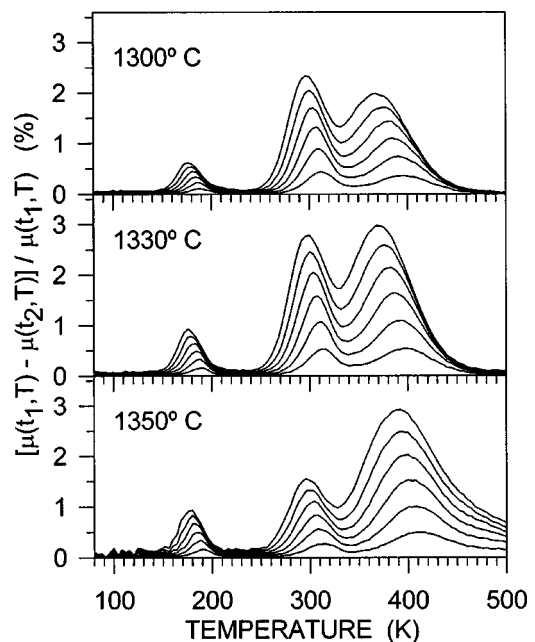The W compound is built up with hexagonal (R) and spinel (S) blocks, in the stacking sequence RSSR*S*S*,

FIG. 3. Isochronal spectra of $BaTi_{0.3}Fe_{17.7}O_{27}$ hexaferrite samples sintered in CO_2 at different temperatures, with t_1 and t_2 values as in Figs. 1 and 2.

with the* blocks turned $180°$ around the c axis. In this framework the B process is similar to the well known III peak in magnetite, i.e., the anisotropic reorientation of the local symmetry axis of a vacancy, by means of the jump of a neighbor ferrous cation, which take place in octahedral $4f$ sites located in the S block.[5] The A process has a similar origin with increased activation energy owing to the presence of a Ba ion. C and D process are ascribed to similar orientational processes in bipyramidal trigonal ($2d$) and octahedral ($4f_{VI}$) sites in the R blocks. When the sintering temperature is raised, the partial pressure of oxygen increases and the vacancy content in the sample is higher, and this effect causes the amplitudes of the different disaccommodation peaks to be higher.

On the other hand, and regarding pure BaW, the introduction of Ti cations induce an increment of Fe^{2+} in order to maintain electrical neutrality,[7] and hence the disaccommodation processes, especially the D process, are favored by this extra amount of ferrous cations, leading to an overall increment of the amplitudes of disaccommodation peaks.

In order to explain the differences observed with pure BaW, the sites occupied by Ti cations should be taken into account. It has been suggested that titanium enters in octahedral face-sharing $4f_{VI}$ and bipyramidal trigonal $2d$, located in R blocks.[8] Thus, the processes associated with the spinel structure, the 300 and 380 K peaks, which can take place within the hexagonal structure with two consecutive S blocks, are not affected by Ti substitution. On the other hand, taking into account that the Fe^{2+} cations seem to occupy the octahedral $4f_{VI}$ sites,[7] the D process is favored, whereas the occupation of bipyramidal trigonal $2b$ site by Ti^{4+} cations promotes the progressive hindrance to the mechanism responsible for the C process.

As a conclusion of this approach, we have shown that the introduction of Ti in W-type hexaferrites in order to decrease the coercive field leads to an overall increment in the disaccommodation spectra observed, and that even small additions of Ti in the hexagonal structure considerably affects the magnetic aftereffect regarding the unsubstituted compound.

[1] X. Batlle, X. Obradors, J. Rodríguez-Carvajal, M. Pernet, V. Cabañas, and M. Vallet, J. Appl. Phys. **70**, 1614 (1991).

[2] F. Sandiumenge, B. Martínez, X. Battle, S. Gali, and X. Obradors, J. Appl. Phys. **72**, 4608 (1992).

[3] Y. Kawai, V. A. M. Brabers, Z. Simsa, and J. H. J. Dalderop, J. Magn. Magn. Mater. **196/197**, 314 (1999).

[4] L. Torres, F. Walz, K. Bendimya, C. de Francisco, and H. Kronmüller, Phys. Status Solidi A **161**, 289 (1997).

[5] P. Hernández-Gómez, K. Hisatake, C. de Francisco, J. M. Muñoz, O. Alejos, C. Torres, and I. Matsubara, J. Magn. Soc. Jpn. **23**, 2134 (1999).

[6] C. de Francisco, J. Iñiguez, J. M. Muñoz, and J. Ayala, IEEE Trans. Magn. **23**, 1866 (1987).

[7] V. A. M. Brabers, A. A. E. Stevens, J. H. J. Dalderop, and Z. Simsa, J. Magn. Magn. Mater. **196/197**, 312 (1999).

[8] Z. Simsa, S. Lego, R. Gerber, and E. Pollert, J. Magn. Magn. Mater. **140–144**, 2103 (1995).