JOURNAL OF MATERIALS SCIENCE 25 (1990) 2765–2770

Magnetic and Mössbauer study of rare-earth-substituted M-, W- and X-type hexagonal ferrites

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The effects of substitution of Ba^{2+} ions for some trivalent rare-earth ions on the magnetic properties and phase formation of M-, W- and X-type hexaferrites are studied. The compounds considered were: $Ba_{1-x}RE_{x/2}Na_{x/2}Fe_{12}O_{19}$ with RE = gadolinium, lanthanum, lutetium, samarium and $0.0 \leqslant x \leqslant 0.3$; $Ba_{0.9}La_{0.05}Na_{0.05}Zn_2Fe_{16}O_{27}$ and $Ba_{1.9}La_{0.05}Na_{0.05}Zn_2Fe_{28}O_{46}$. The samples were prepared by standard ceramic procedures and have been investigated by thermomagnetic analysis, X-ray diffraction, Mössbauer spectroscopy, scanning electron microscope and magnetic measurements. Monophasic $BaRE_{x/2}$–M compounds were found for $0.0 \leqslant x < 0.2$ giving an indication of the solubility range of the rare-earth (RE) atoms in this phase. The intrinsic magnetic properties and the coercive field are lowered with the exception of the lanthanum-substituted hexaferrite. No significant differences in the phase formation and magnetic properties were observed for the W- and X-type hexaferrites.

1. Introduction

Hexagonal ferrites are a large family of ferrimagnetic oxides with singular and useful properties. The crystal structure of the different known types of hexagonal ferrites (M, W, X, Y, Z and U types) is very complex and can be described as a superposition of those named R, S and T blocks. Depending on their number and sequence, as well as the starting chemical composition, different intrinsic magnetic properties result. Among these materials, M-type hexaferrites ($BaFe_{12}O_{19}$) are the most relevant because they are the basis of the current ceramic permanent magnet industry and, recently, have been considered for potential applications in perpendicular magnetic recording media and microwave devices [1–3]. Owing to their intrinsic magnetic properties, W- and X-type hexaferrites are also of prospective interest for their potential applications [4–8]. However, at present there are still some difficulties in obtaining suitable magnetic properties for practical uses.

M-type hexaferrites have been extensively studied and many efforts have been devoted to improving their magnetic properties by partial substitution of iron with other diamagnetic or paramagnetic cations [9–13]. The effects of the rare-earth (RE) elements on the magnetic properties and microstructure of these materials have been given less attention; nevertheless, recently some papers have appeared on this subject [14–17]. By considering the ion radius of Fe^{3+}, Ba^{2+} and RE^{3+}, the replacement of barium for the RE elements can in principle be considered.

The latter introduces a renewed interest in the investigation of hexagonal ferrites. It is of further interest to evaluate new phenomena such as the superexchange interactions between rare-earth and iron ions; changes in the magnetocrystalline anisotropy and magnetic order, due to the proximity of barium ions to the 2b bipyramidal site occupied by Fe^{3+} ions, which play a relevant role in both properties; changes in the reaction kinetics; the effects on the morphology and grain size of the final products.

The present investigation addresses a preliminary evaluation of the consequences of barium substitution for RE^{3+} = gadolinium, lanthanum, lutetium and samarium ions in M-type hexaferrites and barium substitution for La^{3+} in W- and X-type hexaferrites. Charge compensation has been obtained by introducing Na^+ ions, in such a way that the chemical formula can be expressed as $Ba_{1-x}RE_{x/2}Na_{x/2}Fe_{12}O_{19}$ with RE = lanthanum, lutetium, gadolinium, samarium and $0.0 \leqslant x \leqslant 0.3$; $Ba_{1-x}La_{x/2}Na_{x/2}Zn_2Fe_{16}O_{28}$ and $Ba_{2-x}La_{x/2}Na_{x/2}Zn_2Fe_{28}O_{46}$ with $x = 0, 0.1$. In the following phase formation, the morphological grain characteristics and the main magnetic properties are also reported and discussed.

2. Experimental procedures

Polycrystalline samples with the above nominal

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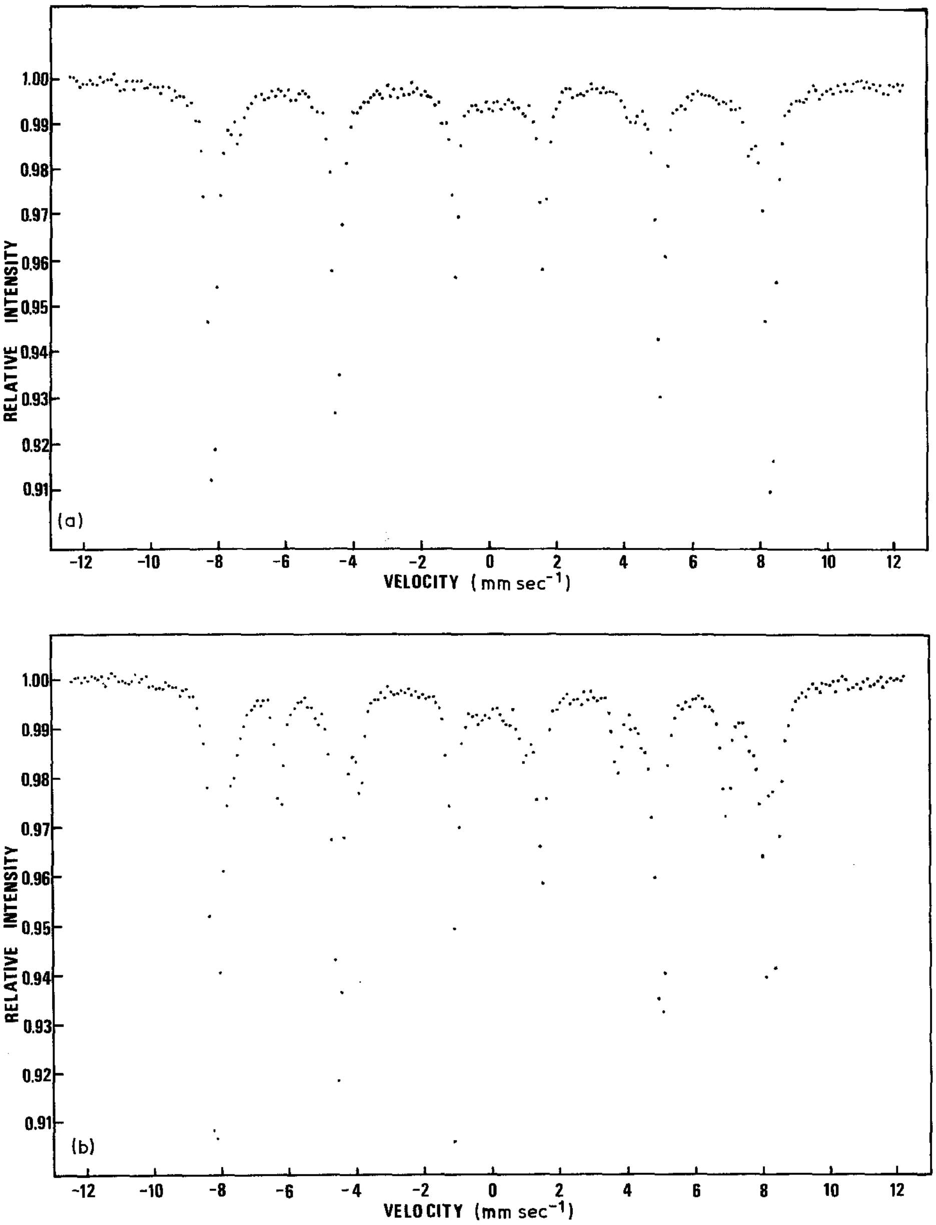

Figure 1 Room-temperature Mössbauer spectra for $Ba_{0.7}Gd_{0.15}Na_{0.15}Fe_{12}O_{19}$ samples heated at (a) 630; (b) 730° C for 48 h.

composition were prepared by standard ceramic methods. Stoichiometric amounts of iron oxide, barium and zinc carbonates were mixed and ground for 4 h in a planetary ball mill under ethanol. The green powder was pressed into tablets and then subjected to different heat treatments in air to study the reaction kinetic and to reach sample monophasicity. The time and temperature of the heat treatments will be specified in the text.

Mössbauer measurements were performed using an Elscint AME-30A Mössbauer spectrometer in constant acceleration mode and transmission geometry; the source (Co^{57} in Rh matrix) and the absorber were maintained at room temperature. Saturation magnetization (σ_s) and intrinsic coercive field ($_iH_c$) were determined by using a PAR 155 vibrating sample magnetometer with a maximum applied field of 19.3 kOe. The anisotropy field (H_a) was determined by means of the singular point detection technique (SPD) [18]. The thermomagnetic analysis (TMA) was used to verify the magnetic phases present and to determine the Curie temperature (T_c). Particle size and morphology were determined by using a Cambridge 250 scanning electron microscope (SEM). X-ray diffraction (XRD) was performed on powdered samples with a Philips PW 1050/25 diffractometer employing CoK_α radiation.

3. Results and discussion

3.1. Rare-earth-substituted M-type barium ferrite ($BaRE_{x/2}$–M)

Figure 1 shows the Mössbauer spectrum of gadolinium-substituted samples ($x = 0.3$) heated at 630 and 730° C, respectively, for 48 h. The spectra can be interpreted as the superposition of $BaFe_2O_4$ and remanent α-Fe_2O_3, showing that in the early stages of the solid-state reaction, the compounds present are the same as those observed for the pure barium hexaferrite [19]. To determine whether the $REFeO_3$ perovskite is present at higher temperatures, we prepared some samples with a high rare-earth concentration ($x = 0.7$), which were annealed at 1100° C for 2 h. The corresponding Mössbauer spectra show a superposition of $REFeO_3$ and α-Fe_2O_3 plus a small amount of Ba–M compound; this suggests that at high temperatures the perovskite also reacts to form the hexaferrite.

In Fig. 2, the Mössbauer spectra obtained for

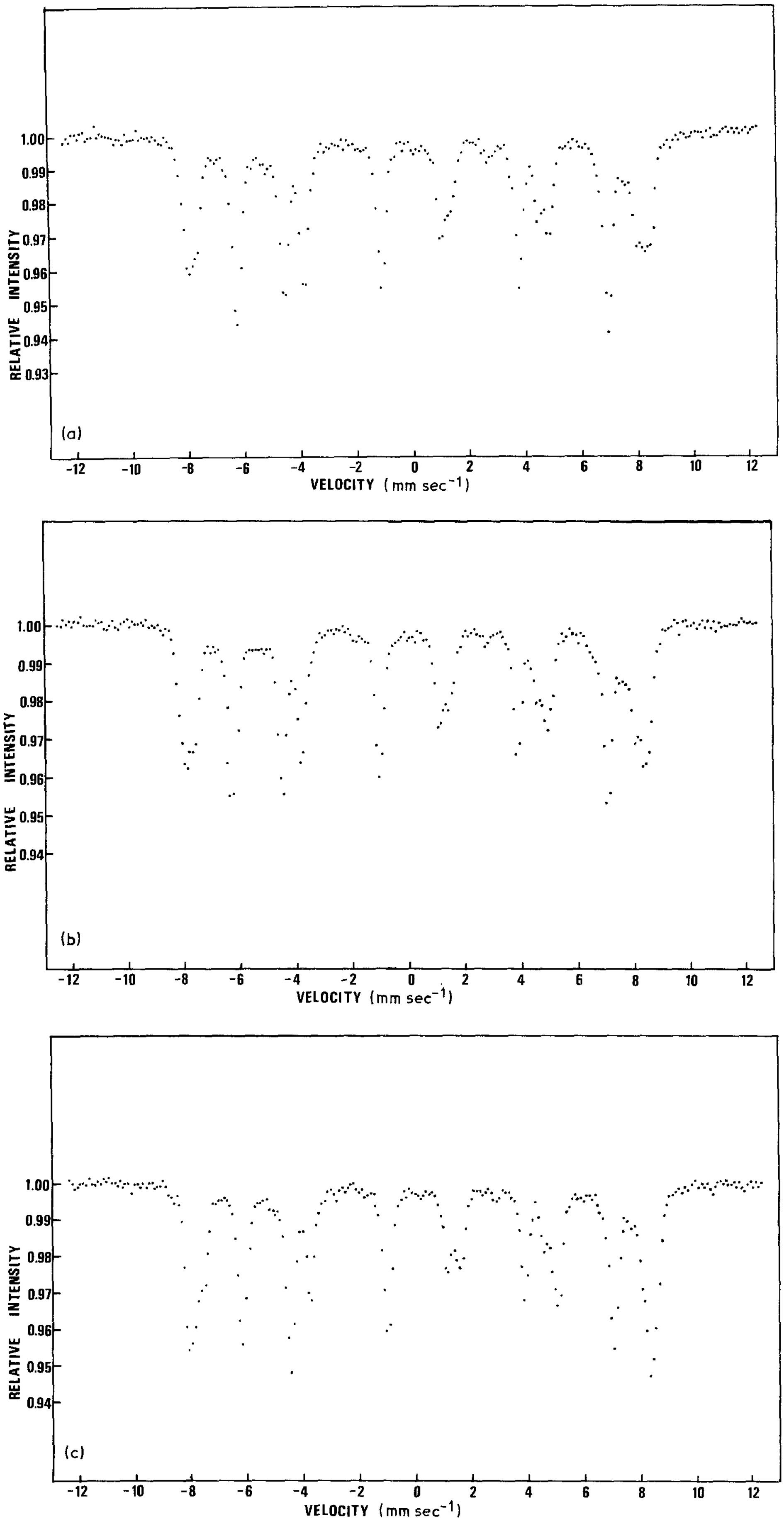

Figure 2 Room-temperature Mössbauer spectra for $Ba_{1-x}Gd_{x/2}Na_{x/2}Fe_{12}O_{19}$ samples heated at 1300° C for 6 h. x = (a) 0.1; (b) 0.2; (c) 0.3.

samples with different gadolinium concentrations ($0.1 \leqslant x \leqslant 0.3$) are reported. The spectra have been interpreted following the scheme adopted in the literature for M-type hexagonal ferrite [20]. As can be seen, the main change for $x = 0.1$ is a small reduction of the hyperfine field of the f_2 sites. This result could be understood taking into account that the Gd^{3+} and Na^+ ions are introduced in the R-blocks of the structure and the nearest sites to this position are the 2b, f_2 and 12k, respectively. If we compare this spectrum

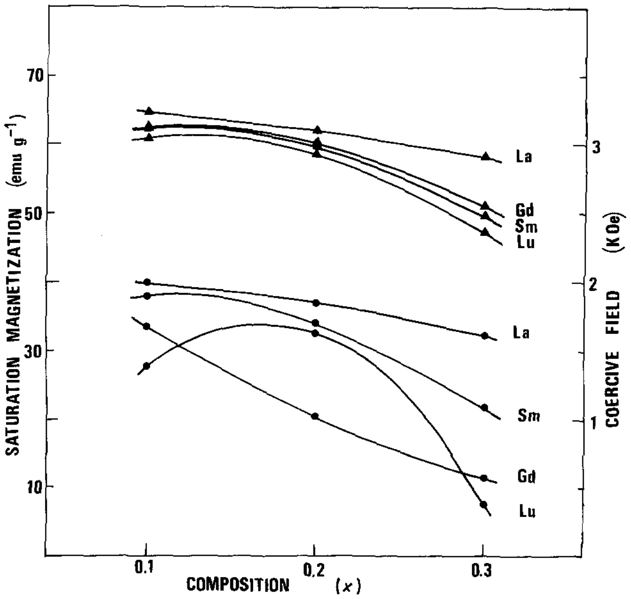

Figure 3 Saturation magnetization (σ_s, ▲) and coercive field ($_iH_c$, ●) against x for $Ba_{1-x}RE_{x/2}Na_{x/2}Fe_{12}O_{19}$ (RE = gadolinium, lanthanum, lutetium, samarium) heated at 1300° C for 6 h.

with the corresponding ones for $x = 0.2$ and 0.3, a change appears in the relative intensity of the extreme peaks ($V = -8.1$ and $-6.3\,\mathrm{mm\,sec^{-1}}$, respectively) suggesting that other phases are segregated. We suggest that these phases are $REFeO_3$ and α-Fe_2O_3.

The dependence of the σ_s and $_iH_c$ as a function of rare-earth concentration for samples treated at 1300° C for 6 h is reported in Fig. 3. The magnetic properties of all samples for $x = 0.1$ are summarized in Table I. The H_a and T_c values of all samples are slightly lower than that of Ba–M pure hexaferrite. This small difference can be understood if we take into account that with the introduction of RE^{3+} ions, it is possible to modify the superexchange interactions owing to the strong spin-orbital interaction of the rare-earth elements, and also considering the smaller ion radius in comparison with the barium ions. For a rare-earth addition higher than $x = 0.1$, H_a and T_c values remain practically constant; these data suggest that the solubility limit of rare-earth ions in the structure is lower than that $x = 0.2$. From the TMA curves a single magnetic phase is detected, therefore the further decrease of σ_s with the rare-earth addition ($x > 0.1$) should be connected with the appearance of non-magnetic phases. The Mössbauer spectra presented above for gadolinium-substituted ferrite also support this view.

Figures 4a–c show SEM micrographs of pure Ba–M and $Ba(La,Lu)_{x/2}$–M (with $x = 0.1$ and 0.2) heat-treated at 1300° C for 6 h. The increase in particle size was hindered by addition of La^{3+} and Na^+ ions, remaining in the range of 3 to 6 μm.

3.2. Lanthanum-substituted W- and X-type hexaferrites ($BaLa_{x/2}$-W, $BaLa_{x/2}$-X)

Taking into account the results obtained for BaRE–M compounds, we prepared $BaLa_{x/2}$–W and $BaLa_{x/2}$–X hexagonal ferrites with a relatively low rare-earth concentration ($x = 0.1$). Nevertheless, a detailed study considering higher rare-earth concentrations is being performed in order to establish the solubility limit in these compounds. To obtain information on intermediate phases occurring in the solid-state reaction for these systems, the samples were heated for 6 h at different temperatures ranging from 1100 to 1400° C.

TABLE I Room temperature values of σ_s, H_a, T_c and $_iH_c$ for $BaRE_{x/2}$–M samples with $x = 0.1$, heated at 1300° C for 6 h

RE–M	σ_s (emu g^{-1})	H_a (kOe)	T_c (° C)	$_iH_c$ (kOe)
M-pure	67.4	17.9	450	0.70
Gadolinium	63.0	15.9	445	1.69
Lanthanum	65.0	15.9	445	2.00
Lutetium	61.4	16.0	440	1.49
Samarium	62.9	17.5	448	1.93

By TMA and Mössbauer measurements, the phases detected at lower temperatures were the same as those for non-substituted hexaferrites: pure Ba–M, $ZnFe_2O_4$ and $LaFeO_3$. The BaLa–M compound was not observed. The monophasic $BaLa_{x/2}$–W and $BaLa_{x/2}$–X hexaferrites were obtained by heating at 1300 and 1400° C, respectively.

Figure 5 reports the TMA curves for $BaZn_2$–W and $BaLa_{x/2}$–W hexaferrites heated at 1400° C for 6 h; as can be seen at this temperature, decomposition of W-type compounds into two magnetic phases takes place. The decomposition products are X-type hexaferrites and a second magnetic phase not yet identified. In the case of the $BaLa_{x/2}$–W system, the Curie temperature is higher than a non-substituted one (T_c = 275 and 223° C, respectively) which could be evidence that lanthanum and/or sodium ions are present in this magnetic phase.

The saturation magnetization of $BaZn_2$–W hexagonal ferrites annealed at 1300° C for different times is systematically lower by approximately 5% than for corresponding lanthanum-substituted compounds (see Fig. 5, insert). This small variation in σ_s admits two interpretations: (i) a decrease of magnetization of octahedral sublattices in the R block with respect to octahedral sublattices of the S block, due to the presence of rare-earth ions in the former; (ii) an acceleration of the kinetic reaction due to the presence of the rare-earth- or sodium-intermediate compounds. These suggestions require further confirmation. The $_iH_c$ in both materials is very low and does not change with lanthanum addition in the concentration range studied.

Figs 6a and b report Mössbauer spectra measured at room temperature for $BaLa_{x/2}$–W and $BaLa_{x/2}$–X, respectively. They are in good qualitative agreement with those reported earlier for non-doped compounds.

Table II reports the main magnetic properties of $BaLa_{x/2}$–W and $BaLa_{x/2}$–X hexaferrites with a low lanthanum content ($x = 0.1$).

TABLE II Room temperature values of σ_s, H_a, T_c and $_iH_c$ for $BaLa_{x/2}$–W/$BaLa_{x/2}$–X together with the values of $BaZn_2$–W and BaZn–X pure hexaferrites

Samples	σ_s (emu g^{-1})	H_a (kOe)	T_c (° C)	$_iH_c$ (Oe)
$BaZn_2$–W	72.2	11.5	370	100
$BaLa_{x/2}$–W	76.0	11.9	345	100
BaZn–X	75.8	12.4	430	100
$BaLa_{x/2}$–X	79.7	12.6	400	100

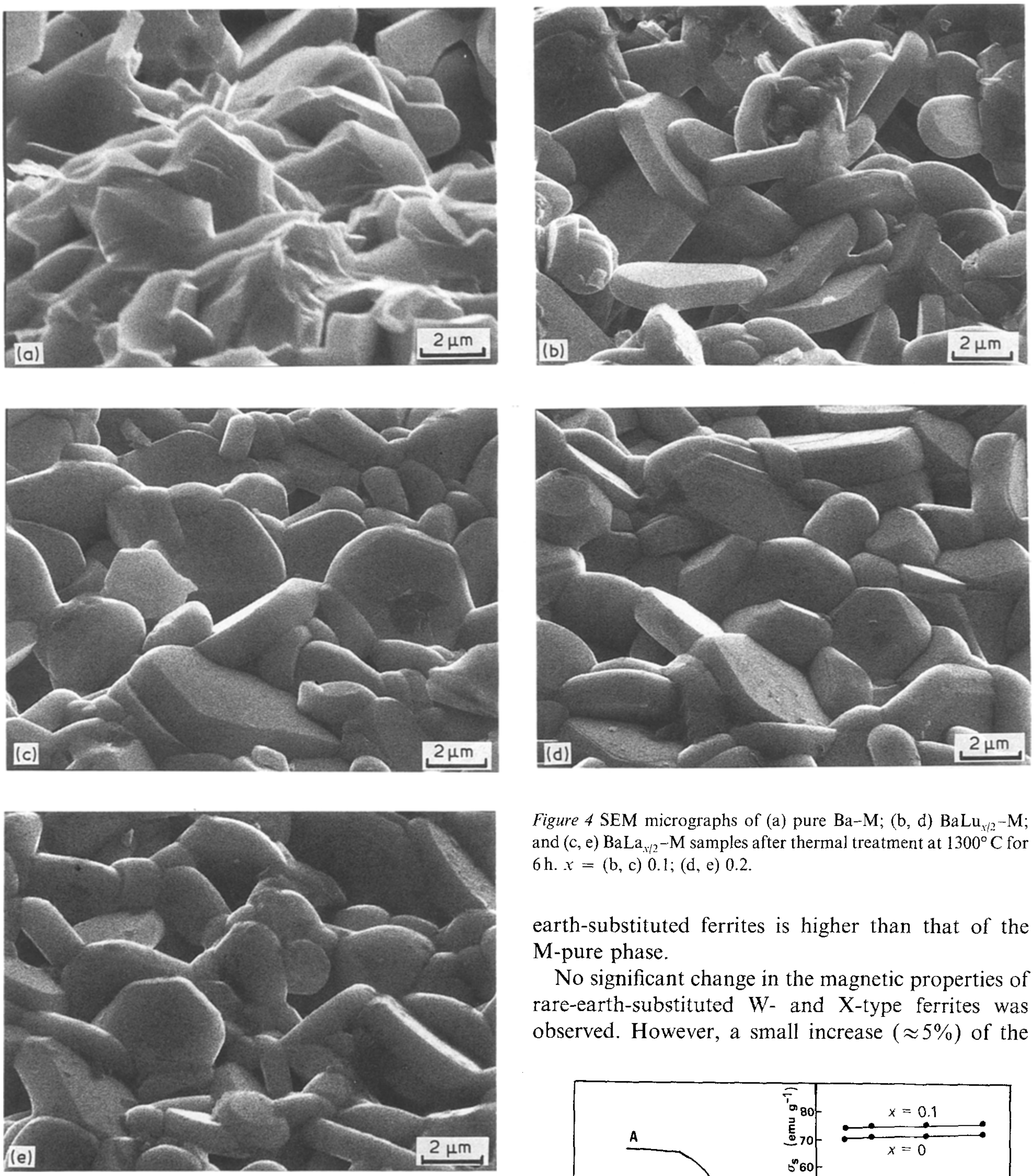

Figure 4 SEM micrographs of (a) pure Ba–M; (b, d) $BaLu_{x/2}$–M; and (c, e) $BaLa_{x/2}$–M samples after thermal treatment at 1300° C for 6 h. x = (b, c) 0.1; (d, e) 0.2.

4. Conclusions

M-, W- and X-type rare-earth-substituted hexaferrites have been prepared by standard ceramic procedures. In addition to $BaFe_2O_4$ and α-Fe_2O_3, the $REFeO_3$ perovskite was also detected in the phase formation rare-earth-substituted system; this compound participates in the reaction of formation of the M-type hexaferrite. Our results suggest that the solubility limit of rare-earth ions in M-type barium ferrite is lower than $x = 0.2$. Although the magnetic properties do not change remarkably, a little decrease within the solubility limit range of the intrinsic saturation magnetization, Curie temperature and anisotropy field was observed. A further decrease in σ_s for higher rare-earth content might be attributed to the segregation of other phases. Under the same preparation conditions (1300° C for 6 h) the $_iH_c$ values of rare-earth-substituted ferrites is higher than that of the M-pure phase.

No significant change in the magnetic properties of rare-earth-substituted W- and X-type ferrites was observed. However, a small increase ($\approx$5%) of the

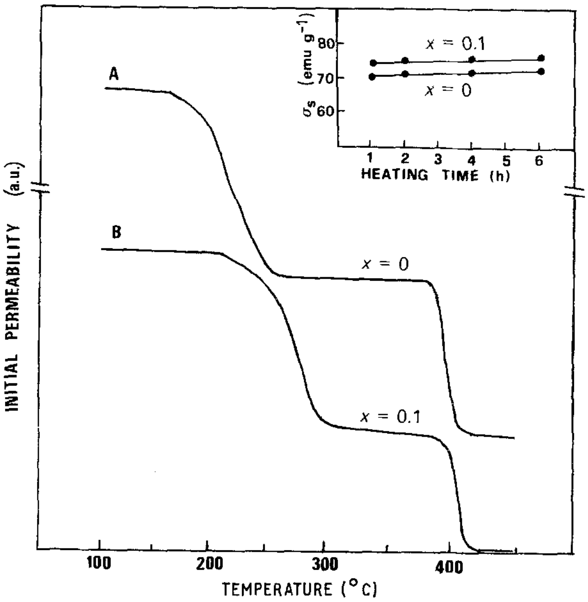

Figure 5 TMA curves for pure W and $BaLa_{x/2}$–W ($x = 0.1$) hexaferrites heated at 1400° C for 6 h. The dependence of σ_s against annealing time at 1300° C for pure W and $BaLa_{x/2}$–W ($x = 0.1$) hexaferrites is shown in the insert.

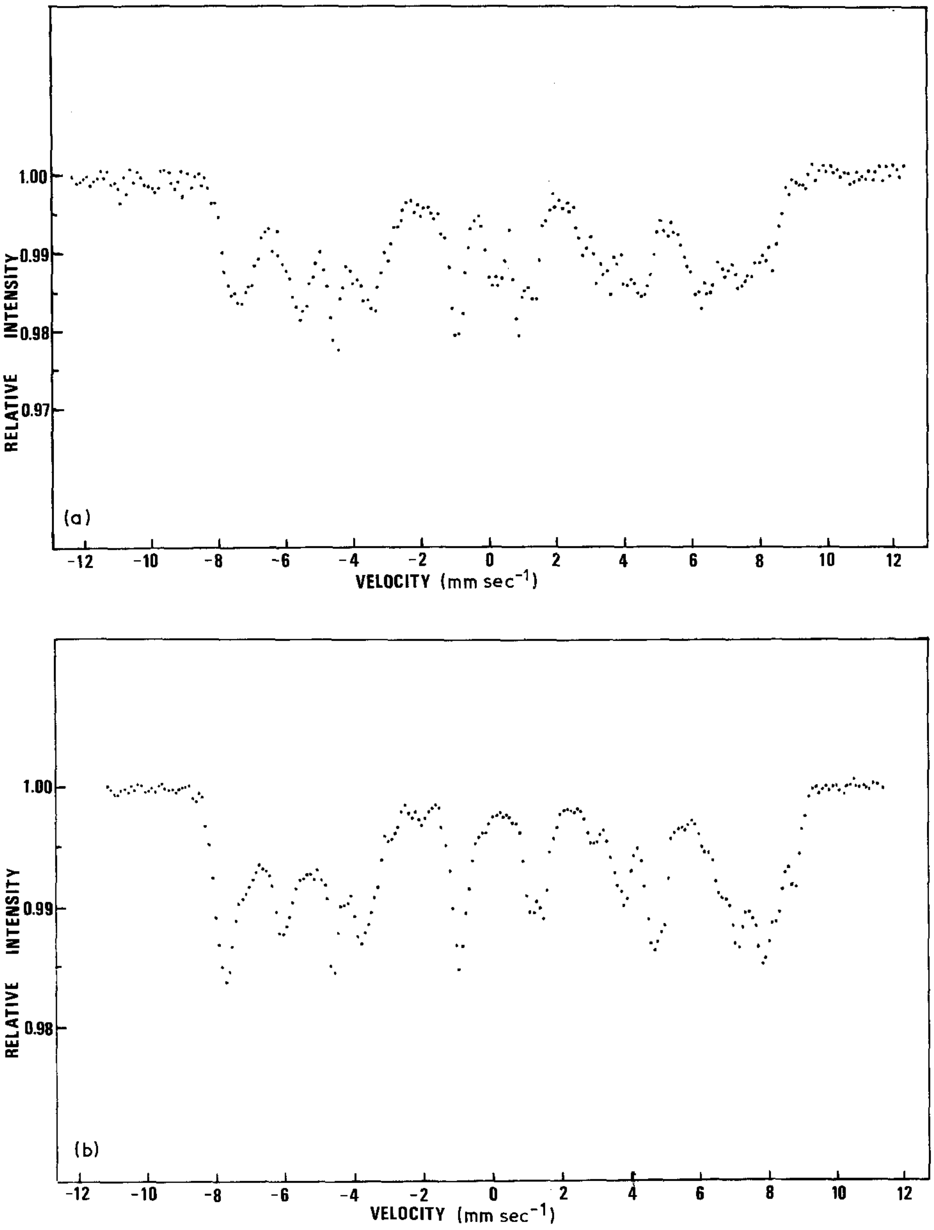

Figure 6 Room-temperature Mössbauer spectra measured for $BaLa_{x/2}$-W and $BaLa_{x/2}$-X compounds heated at (a) 1300; (b) 1400° C for 6 h, respectively.

saturation magnetization in $BaLa_{x/2}$-W hexaferrites was measured. At 1400° C, the decomposition of W-type into two magnetic phases takes place. The high heating temperature, necessary for obtaining the rare-earth-substituted compounds, leads to a very rapid grain growth which is responsible for the low coercive field. Our results indicate that the solubility limit in these compounds has not yet been reached.

Acknowledgements

We would like to thank Dr G. Salviati for SEM micrographs. This work has been partially supported by the International Centre for Theoretical Physics, Trieste.

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Received 14 March
and accepted 16 August 1989