

La–Zn Substituted Hexaferrites Prepared by Chemical Method

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Abstract La–Zn substituted M-type Ba hexaferrite powders were prepared by sol-gel (Mx) and organometallic precursor (Sk) methods with Fe/Ba ratio of 11.6 and 10.8, respectively. The compositions $(\text{LaZn})_x\text{Ba}_{1-x}\text{Fe}_{12-x}\text{O}_{19}$ with $0.0 \leq x \leq 0.6$ were annealed at $975^\circ\text{C}/2$ h. The cationic site preferences of nonmagnetic La^{3+} instead of Ba^{2+} ions and Zn^{2+} instead of Fe^{3+} ions were determined by Mössbauer spectroscopy. The La^{3+} ions substitute the large Ba^{2+} ions at 2a site and for $x \geq 0.4$ also at $4f_2$ site. The nearly all Zn^{2+} ions are placed at the $4f_1$ sites. The thermomagnetic analysis of $\chi(\vartheta)$ confirms that only the small substitutions for $x \leq 0.4$ can be taken as a single-phase hexaferrites. The coercivity H_c almost does not change at $x = 0.2$ for (Mx) samples and further decrease up to $x = 0.6$. For (Sk) samples at substitution $x = 0.2$ the values of H_c are decreasing and at higher x the values nearly do not change. The Curie points, T_c , slowly decrease with x for both (Mx) and (Sk) samples.

Key words ferrites-hexagonal · magnetic recording · Mössbauer effect.

1. Introduction

The substituted Ba hexaferrites are potential candidates for recording media because of their mechanical hardness and chemical stability. In order to improve the

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fundamental magnetic properties of hexaferrite, many studies have been carried out on synthesis methods and cationic substitutions of divalent or multivalent ions and of their mixture. In M-type hexaferrite the iron ions are positioned on five non-equivalent sites 2a, 12k and 4f₂ octahedral, 4f₁ tetrahedral and 2b bipyramidal sites. In the magnetically ordered state in Ba ferrite the 12k, 2a and 2b sites have their spins aligned parallel to each other in the crystallographic *c*-axis, whereas those of 4f₂ and 4f₁, point into the opposite direction. The magnetic properties of the substituted hexaferrites strongly depend on the electronic configuration of the substituting cations. It is known, that more electronegative ions prefer octahedral coordination [1]. The electronegativity of substituted ions La³⁺, Zn²⁺ is 1.10 and 1.65, respectively. According to the ligand field [2], ions with d¹, d², d³ and d⁴ orbitals prefer tetrahedral and ions with d⁶, d⁷, d⁸ and d⁹ orbitals occupy octahedral positions mainly. Ions with d⁰, d⁵, d¹⁰ orbitals have no site preference. The tendency to occupy a particular site depends also on the ionic radii of the ions and their partner cations.

The investigations have been performed covering two aspects of preparations, which are Fe/Ba ratio and heat treatment [3–5]. At the sol-gel preparation of Ba ferrite, when the Ba/Fe is higher than the 11.5, nonmagnetic BaFe₂O₄ is presented [6]. In the previous work [7] by the precursor method a Fe/Ba ratio of 10.8 were used. Different compounds as starting materials have different solubilities in different aqueous media, so that the range of Fe/Ba values found yielding single-phase materials, could be related to these aspects. The optimum Fe/Ba ratio depends on the raw materials used and the processing procedure [6]. The substitution Ba²⁺ by La³⁺ ions is associated with a valence change of Fe³⁺ to Fe²⁺ at 2a or 4f₂ site [8]. A suitable content of La–Zn substitution can reduce the value of $\Delta H_c/\Delta T$ near room temperature [9]. La–Zn substitutions show clearly their positive effect on $J_s - m$. The coercivity H_c decreases much slower, it changes from 464 to 224 kA/m, where $0 \leq x \leq 0.6$ [3].

The presented investigation reports on the magnetic properties and determination of the crystallographic site of La–Zn substitutions. For the preparation of the samples (Mx) by sol-gel method with traditional evaporation drying procedure and (Sk) by modified organometallic precursor method with alcohol drying were employed.

2. Experimental

Samples of (LaZn)_xBa_{1-x}Fe_{12-x}O₁₉ (Mx) with $0.0 \leq x \leq 0.6$ were prepared by sol-gel way [3]. Fe(NO₃)₃·9H₂O, BaCO₃, ZnCl₂ and La(NO₃)₃·6H₂O and citric acid were used as starting materials with a high purity of 99.99%. A Fe/Ba ratio of 11.6 was used. The obtained powders were annealed at 975°C for 2 h.

Samples of (LaZn)_xBa_{1-x}Fe_{12-x}O₁₉ (Sk) with $0.0 \leq x \leq 0.6$ were prepared by organometallic precursor way [5]. Fe(NO₃)₃·9H₂O, Ba(OH)₂·8H₂O, La(NO₃)₃·6H₂O, further ZnO dissolved in HNO₃, and citric acid were used as the starting materials, all of 99% purity. In this case a Fe/Ba ratio of 10.8 was used. The samples were annealed at temperatures of 700 and 975°C for 2 h in a muffle furnace.

The magnetic properties were studied according to [10], using a vibrating sample magnetometer with a maximum external magnetic field up to 540 kA/m. The phase constitution was analyzed by Mössbauer spectroscopy using a conventional constant acceleration equipment with source of ⁵⁷Co in Rh matrix. The temperature dependencies of the magnetic susceptibility $\chi(\vartheta)$ were measured by the bridge method

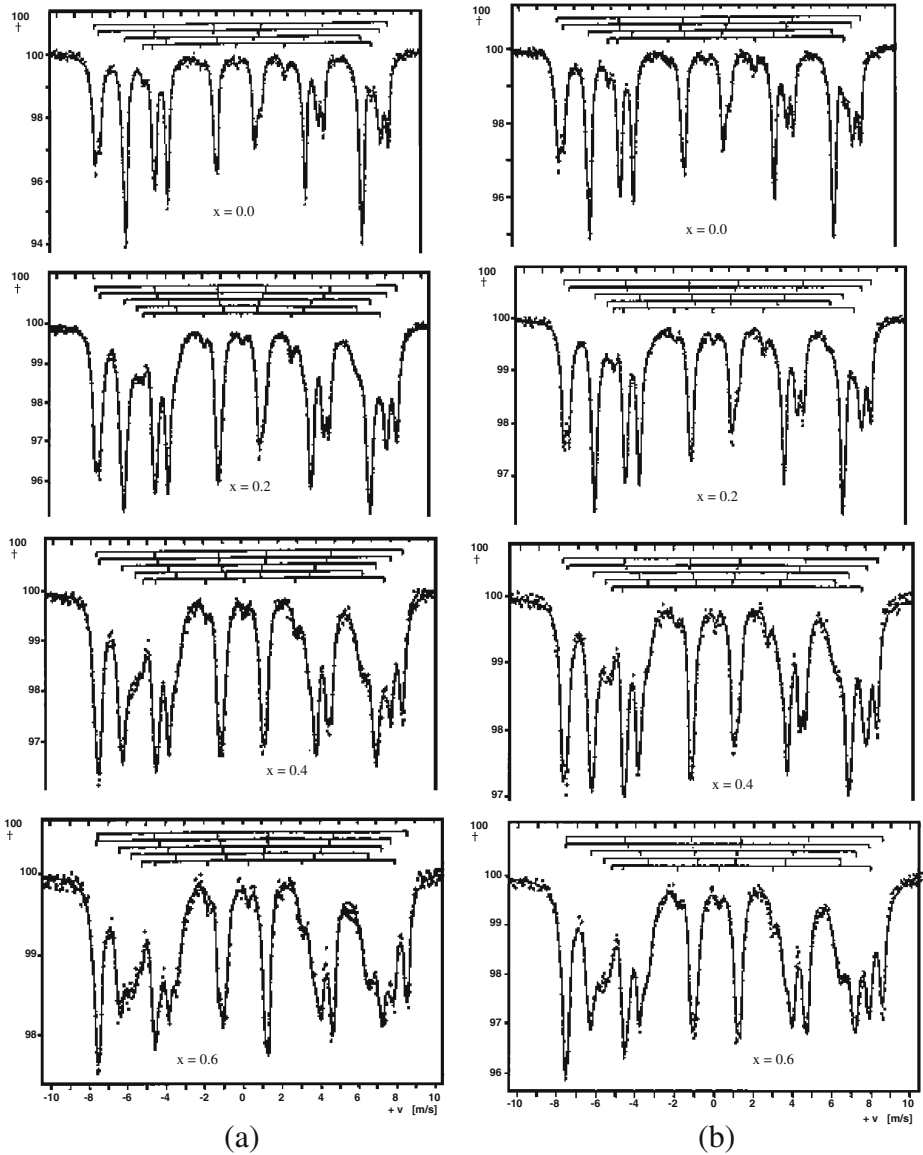


Figure 1 The room temperature Mössbauer spectra for La-Zn substituted BaM, for **a:** (Mx) and **b:** (Sk) samples, for $0.0 \leq x \leq 0.6$.

according to [11]. A Philips XL 30 scanning electron microscope (SEM) was used to obtain data for microstructural characteristics.

3. Results and discussion

The room temperature Mössbauer spectra of La-Zn substituted BaM samples prepared by sol-gel method (Mx) with $x = 0.0, 0.2, 0.4$ and 0.6 are shown in Figure 1a

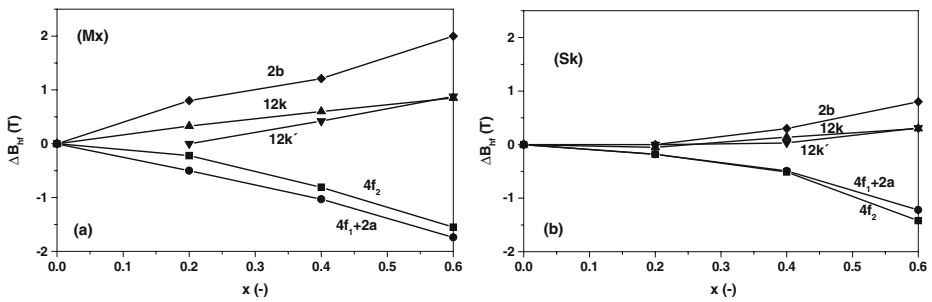


Figure 2 ΔB_{hf} vs. x , for La–Zn substituted BaM, for **a:** (Mx) and **b:** (Sk) samples.

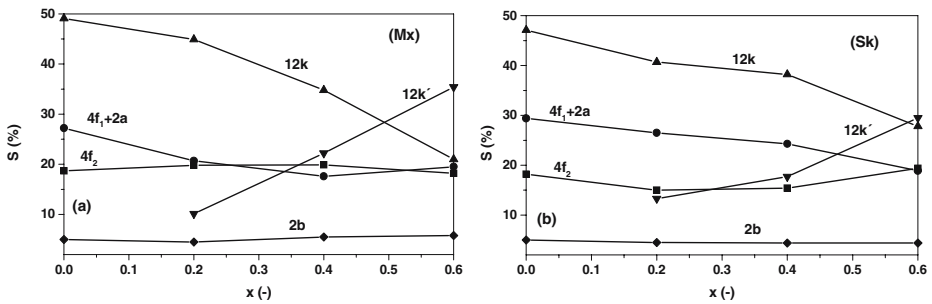


Figure 3 The relative areas S (%) vs. x , for La–Zn substituted BaM, for **a:** (Mx) and **b:** (Sk) samples.

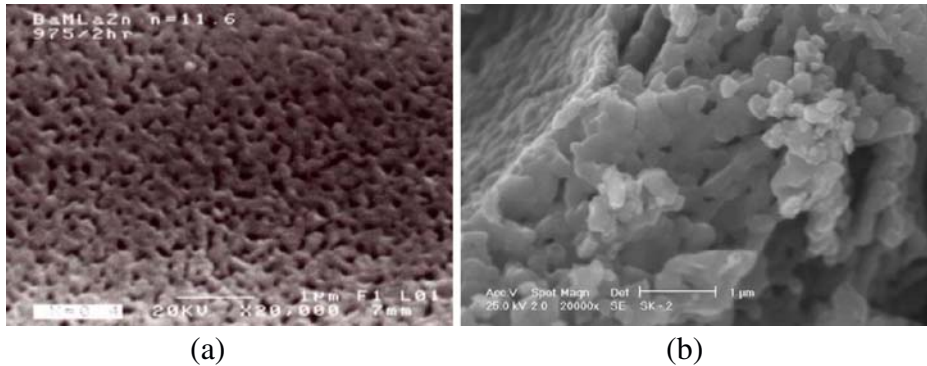
and same composed samples prepared by precursor method (Sk) are in Figure 1b. The spectra were fitted with four sextets corresponding to $4f_2$, $4f_1 + 2a$, $12k$ and $2b$, for $x = 0.0$. The hyperfine parameters for $2a$ and $4f_1$ sites are nearly equal, so that subpatterns could not be resolved. The substitutions of La–Zn ions from 0.2 up to 0.6 on the Fe^{3+} sites cause the appearance of five different magnetic surroundings and the $12k$ position is broadened. This position splits into two sublattices, one representing the ions with three nearest magnetic neighbours in the $4f_1$ site and other, $12k'$ with two neighbours in the $4f_1$ site whereby its value B_{hf} is the smallest at about 36 T [5, 12]. The variations of local hyperfine fields ΔB_{hf} (T) and of the relative areas S (%) as a function of x for both (Mx) and (Sk) samples are shown in Figures 2 and 3. It can be seen clearly that diamagnetic La^{3+} and Zn^{2+} ions show remarkable preferences for the sites $4f_1 + 2a$, $4f_2$ and also $12k$ for sample (Mx), as it can be seen in Figure 2a. The same site preferences are also shown in Figure 2b for the samples (Sk), but slightly more are occupied the $4f_2$ rather than $4f_1 + 2a$ sites.

There is agreement with [8], where La^{3+} is associated with a valence change of Fe^{3+} to Fe^{2+} at $2a$ or $4f_2$ site and nearly all Zn ions are placed at the tetrahedral $4f_1$ site. This position has a negative contribution to magnetic polarisation because substitution of Fe^{3+} ion with spin-down by non-magnetic Zn^{2+} ions, increase resultant values of J_{s-m} .

Sauer [13] found, that in La–Zn the expected Fe^{2+} should reside on the $2a$ sites. At higher concentrations ($x \geq 0.6$) we detect strong reduction of the quadrupole splitting QS (mm/s) in the $4f_1 + 2a$ sites, and the relative area S (%) for $12k'$ position

Table I Magnetic properties of La-Zn substituted BaM

$x(-)$		J_{s-m} (10^{-6} T m ³ kg ⁻¹)	J_{s-r} (10^{-6} T m ³ kg ⁻¹)	H_c (kA/m)	$\Delta H_c/\Delta T$ (kA/m ² °C)
0.0	Sol-gel	66.11	28.59	400	0.40
0.2		73.14	34.95	395	0.35
0.4		80.83	41.41	370	0.35
0.6		81.16	41.58	325	0.26
0.0	Precursor	68.85	37.07	375	0.60
0.2		93.83	48.07	330	0.46
0.4		76.27	39.19	340	0.32
0.6		74.85	38.98	340	0.40

**Figure 4** The micrograph of the La-Zn substituted BaM, for $x = 0.4$, for **a:** (Mx) and **b:** (Sk) samples.

increases, whilst that decreases for 12k for both (Mx) and (Sk) samples, as is shown in Figure 3a, b.

The magnetic properties of La-Zn (Mx) and (Sk) samples with $0.0 \leq x \leq 0.6$, measured at room temperature are summarized in Table I. The results of the specific magnetic polarisation J_{s-m} and J_{s-r} show the positive effect of the La-Zn substitution on these values, with concentration rate in (Mx) samples. The coercivity H_c decreases mid-slowly, it varies from 400 to 325 kA/m, where x changes from 0.0 to 0.6. The H_a values are strongly dependent on contents of the La³⁺ ions [8]. For (Sk) samples J_{s-m} , J_{s-r} expressively increase for $x = 0.2$; further at higher substitution the values are decreasing. The coercivity H_c at $x = 0.2$ decreases, at $x = 0.4$ slightly increases or it does not change. It can be seen, that the best values of J_{s-m} , J_{s-r} and of H_c are achieved at $x = 0.2$ for (Sk) samples. The values of temperature coefficient of coercivity $\Delta H_c/\Delta T$, defined in [8] are shown in Table I. The La-Zn (Sk) samples have positive values of $\Delta H_c/\Delta T$, which are slightly higher than those of the La-Zn (Mx) samples.

Micrographs taken by SEM of La-Zn (Mx) and (Sk) samples with $x = 0.4$ are in Figure 4a, b. It was found [3] that, La-Zn substitution leads to 'D' values clearly of about 40 nm and 't' decreases to about 25 nm up to $x = 0.4$, the aspect ratio (D/t) varies between 2.3 and 3.2. The La-Zn substitution yields a homogeneous microstructure and finer crystalline size in (Mx) samples, than those in (Sk) samples. Cell

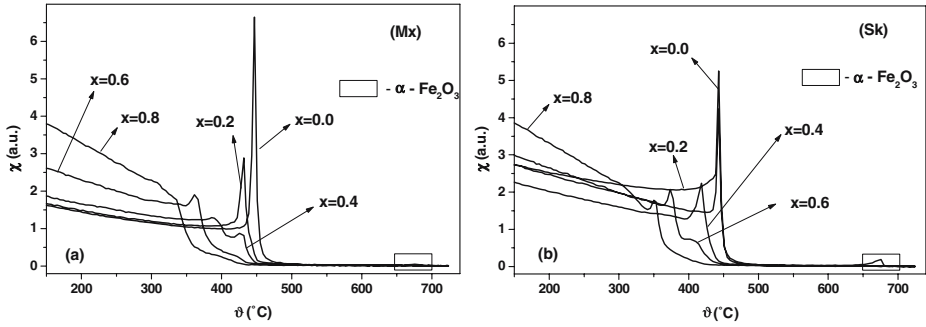


Figure 5 The $\chi(\vartheta)$ dependencies for La–Zn substituted BaM, for **a:** (Mx) and for **b:** (Sk) samples.

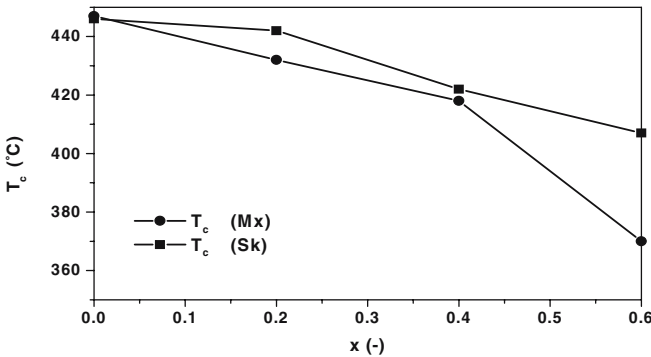


Figure 6 The Curie temperature dependencies of concentration rate for La–Zn substituted BaM samples.

parameters examination show that c -axis decreased markedly and a -axis decrease for $x < 0.4$, whilst an increase are observed for $x > 0.4$. According to [9] a - and c -axes decreased with x . These discrepancies might be related to way of the processing.

When the substitutions are of $x \leq 0.4$, the samples form single phase M-type hexagonal ferrite, what was confirmed by the measurements of the magnetic susceptibility. The $\chi(\vartheta)$ dependencies for La–Zn substituted (Mx) and (Sk) samples are shown in Figure 5a, b.

It can be seen that at room temperature, χ increases with the substitution level. In the vicinity of the Curie temperature T_c , a sharp Hopkinson peak occurs for $x = 0.0$ and for $x = 0.2$ at (Mx) samples. At $x \geq 0.6$ there are multiphase systems. The (Sk) samples have Hopkinson peak continuously up to $x = 0.4$. There is presently single-phase system with homogeneous microstructure. The samples with $x \geq 0.6$ were detected as unstable multiphase systems [14]. Here was occurrence of the hematite phase that was confirmed by Mössbauer spectroscopy measurements. For example, for $x = 0.8$, the composition contained also secondary hematite phase, (α - Fe_2O_3) with the relative area of 12.2% for (Mx) and of 33.8% for (Sk) samples further the hexaferrite phase. The T_c decreases linearly with increasing La–Zn substitutions, by only about of 15% for (Mx) samples and of 7% for (Sk) samples, Figure 6.

4. Conclusions

The magnetic analysis of La–Zn substituted M-type Ba ferrites prepared by the sol-gel method showed better J_{s-m} , J_{s-r} and H_c than those prepared by the precursor method. The J_{s-m} , J_{s-r} increase for (Mx) samples up to $x = 0.4$ and then slowly at higher substitutions. The La–Zn substituted (Sk) samples have J_{s-m} , J_{s-r} values increasing only up to $x = 0.2$, then their values decreases at $x \geq 0.4$ and further are almost not changing. By La–Zn ions is probably more substituted 2a site than those of $4f_1$ and of $4f_2$ sites. We found, that Zn^{2+} occupies the $4f_1$ sites, which have negative contribution to magnetic polarisation, what might be confirmed by slight increase of J_{s-m} and J_{s-r} at small x . The H_c as a function of x , slowly decreases at both substitutions. The expressive decrease of H_c at $x = 0.2$ for (Sk) sample confirmed, that substitutions of La^{3+} ions for Ba^{2+} ions is associated with a valence change of Fe^{3+} to Fe^{2+} ion at 2a or $4f_2$ site.

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