INFLUENCE OF SUBSTITUTION ON BARIUM FERRITE PROPERTIES

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Summary BaFe_{12-x}Zn_xSn_xO_{19} M-type compounds processed by citrate precursor method with substitution level 0.0 ≤ x ≤ 0.6 were studied. Mössbauer spectroscopy and thermomagnetic analysis were used to investigate the magnetic-crystalline structure of these hexaferrites. Correlofield intensity H_c, specific saturation magnetic polarization J_{ms} and compensation magnetic polarization J_{comp}, of ferrite powder specimens were measured. A large change of the coercivity H_c from 330 kA/m (x = 0.0) to the 88 kA/m (x = 0.6) was reached as a function of the substitution x. These changes are caused by reorientation of the Fe^3+ ions within the crystalline lattice. Sn^2+ ions replace Fe^3+ ions on 2b and slightly 2a+4f sites, while Ni^2+ ions occupy 4f and 12k sites and Zn^2+ ions strongly prefer 4f sites.

1. INTRODUCTION

The M-type substituted Ba hexaferrites are a promising media for high-density magnetic recording due to their better performance compared with other materials [1, 2]. In addition, substituted hexaferrites are suitable for use as high-frequency wave absorbers (1 - 50 GHz), where they compete with the spinel compounds [3].

The regular barium hexaferrite has the crystal structure of the mineral magnetoplumbite, Fig. 1. The dimension of the unit cell a = b = 0.588 nm and c = 2.22 nm. The basic structure of the unit cell is built up by ten layers of oxygen ions, which are formed by a close packing of cubic or hexagonal stacked layers alternately. One O^2- ion is replaced by Ba in every fifth layer (Fig. 1). The crystal structure can be divided into several blocks. The S - block contains two oxygen layers forming a spinel structure, where the R - block is a three-layer block containing the layer with the Ba ion. The whole structure can be symbolically described RSR'S', where the R' and S' - blocks are built up by a rotation of 180° around the hexagonal c - axis. The Fe^3+ ions occupy five different interstitial sites within the basic structure. Three sites named 12k, 2a and 4f have an octahedral coordination, one site 4f has a tetrahedral coordination and the 2b site has a five-fold (hexahedral) coordination. In addition, 4f and 4f' spins are configured down, whereas contribution of the other three sites to the magnetic polarization is positive. Therefore, each magnetic sublattice has a specific contribution to the total magnetic moment and to the crystalline anisotropy of BaM. The number in the expression of the different sites indicates the number of Fe^3+ ions per unit cell. Non - substituted barium hexaferrite has a ferrimagnetic structure with a Curie temperature T_C = 450°C [4].

The way of the properties modification of the ferrite is to substitute the Ba^2+ or Fe^3+ cations to reduce the high magneectrocrystalline anisotropy of M-type hexaferrite. This procedure yields decreasing of the coercivity H_c, while the saturation magnetisation J_{ms} remains high. Suitable value of H_c for high-density magnetic recording media is 150 – 240 kA/m [5].

Recently, many workers focused their studies on Co-Sn [6], Ni-Sn [3, 7], Zn-Sn [8] and Ti-Sn [9] substituted Ba ferrite particles prepared by attrition milling, citrate precursor, chemical co-precipitation and sol-gel methods. The Zn-Sn substituted BaM ferrite nanoparticles exhibit interesting magnetic properties; the magnetization J_{ms} has a smooth maximum at low substitutions and the coercivity H_c changes strongly with substitutions [10].

4. CONCLUSION

Magnetic and magnetocrystalline structure of BaFe_{12-x}Zn_xSn_xO_{19}, M_x = (Zn, Ti, Sn) or La^3+ ions and M_x = (Co, Ni, Zn) ions synthesized by precursors were determined experimentally. Mössbauer studies show that preference occupancy of various metal ion combinations were found. Zn^2+, Sn^2+, less Co^3+, Zn^2+ ions strongly prefer 2b and then 4f(2a) sites. The La^3+, Ti^4+ and Ni^2+ ions prefer to enter the 4f sites and slightly 12k sites. The Zn^2+ ions also strongly prefer 4f sites. It is possible to control the value of H_c by the substitution, which is interesting from the point of view for perpendicular magnetic recording.

The highest dependence on H_c have Sn^2+ ions from 4- valence and Zn^2+ ions from 2-valence group. The highest change of H_c was achieved with Sn^2+, Ni^2+ couple as a combination of a these groups.

Acknowledgement

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Fig. 1. Unit cell of barium hexaferrite based on two cells of BaFe_{12}O_{19} and the spin orientation of the Fe^3+ ions at different sites.

The aim of the presented work is the study of magneto-crystalline structure and magnetic properties of Ni-Sn and Zn-Sn substituted Ba ferrite particles. Mössbauer spectroscopy, thermomagnetic analysis and magnetic measurements were used for investigation.

2. EXPERIMENT

High-purity Ba(OH)_{2}, 4H_{2}O, Fe(NO)_3, 9H_{2}O, SnCl_2, H_2O, Zn(CH_3COO)_2, 4H_2O or Ni(NO)_3, 9H_2O were used as raw materials. The Ba/Fe ratio of 10.8 was chosen. An aqueous solution was prepared by dissolving Fe(NO)_3, 9H_{2}O in deionized water, the amount of the iron ion was determined by spectrophotometrically. From this, iron hydroxide was precipitated by adding a concentrated ammonia solution drop by drop under a constant stirring. A second solution was prepared by dissolving...
citric acid in deionised water along with the other reagents (Ba(OH)₂, 8H₂O, Ni(NO₃)₂·9H₂O, SnCl₂·H₂O, ZnCl₂·(CO₂)₂·H₂O). Both solutions were mixed together and an additional small amount of ethylene glycol was added to obtain an amorphous phase after dehydration. The solvent was removed by introducing the solution in the excessive amount of the alcohol during one hour. The finely divided precipitate was heated at 80°C for 30 min, then it was filtered and dried in the vacuum oven. Next, the amorphous citrate precursor was decomposed at 300°C for 5 hours. Finally, the powdered samples were annealed at the temperature 1050°C for 2 hours.

3. RESULTS AND DISCUSSION

Four sextets corresponding to 4f, 2a4f₁, 12k and 2b sites were found in the Mössbauer spectra of the pure Ba hexaferrite taken at room temperature (Fig. 2a). The spectra of substituted Ba ferrite (Fig. 2b, c) were fitted according to [12].

The Mössbauer spectra were recorded using the source ⁵⁷Co in Rh matrix with constant acceleration at the room temperature. The temperature dependences of the magnetic susceptibility \(\chi(T)\) and the Curie temperature \(T_C\) were measured using the bridge method in an alternating magnetic field of 360 A/m and 920 Hz [11]. These dependences are very sensitive to phase composition of the specimen. They also give a good information about impurities and they detect majority of failings during ferrite preparation. The samples were heated up to 730°C at a constant rate of 4°C/min during the \(\chi(T)\) measurement. The Mössbauer spectra and the \(\chi(T)\) dependences were used to determine the crystalline phases and the magnetic and chemical stability of the powdered samples. Measurement of the specific saturation magnetic polarization \(J_{sat}\), remanence magnetic polarization \(J_{r}\), and coercivity \(H_c\) was performed using the vibrating sample magnetometer with an external magnetic field of 540 kA/m.

The Ni²⁺ ions would shift to octahedral 12k and 4f₁ sites, Sn⁴⁺ ions to bipyrimal 2b and spinel block 2a+4f₁ sites, whereas Zn²⁺ enter 4f₁ sites. In all ferrites containing Ni²⁺ ions, Ni⁴⁺ is found to occupy octahedral site, since it has large site preference energy for symmetric octahedral site, which is 20 kcal/mol higher compared to site preference energy for tetrahedral site [13]. As it can be seen in Fig. 3a, b, a negative \(\Delta H\) slope from \(x = 0.0\) to 0.6 beside 12k position was observed. These changes of slope can be related to the variation in the lattice volume and grain growth [14].

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The intensity of each sextet is directly proportional to the number of iron ions in that site. The substitution of a part of Fe⁴⁺ by Zn²⁺, Ni⁴⁺ and Sn⁴⁺ ions lead to changes in the exchange interactions between the magnetic sublattices and to the appearance of new positions of the iron ions. Therefore, the 12k sites can split into two non-equivalent subpatterns 12k and 12k’ with increasing \(x\). The relative area of 12k’ increases at the expense of the disturbed 12k sites.

Fig. 3. \(\Delta H\) vs. \(x\) of substituted Ba ferrites.

The behaviour of the magnetic properties (Ni,Zn)-substituted Ba ferrites is summarised in Table 1. The magnetic properties directly depend on the electronic configuration, electronegativity and ionic radii of the dopant cations and on their preference to occupy different Fe⁴⁺ sublattices of the magnetoplumbite structure [3]. Both the coercivity \(H_c\) and the specific remanence magnetic polarization \(J_{r}\), except the substitution \(x = 0.2\), decreased with the substitution level \(x\). \(J_{r}\) slightly increased up to \(x = 0.4\) for both substitutions. \(H_c\) decreased from 330 kA/m down to approximately 70 kA/m, which represents 75% drop. The decrease of \(H_c\) is related to the reduction of the magneto-crystalline anisotropy field \(H_a\) which is

<table>
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<tr>
<th>(x)</th>
<th>(J_{sat}) (10⁻⁸ Tm⁻¹ kg⁻¹)</th>
<th>(J_{r}) (10⁻⁸ Tm⁻¹ kg⁻¹)</th>
<th>(H_c) (kA/m)</th>
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<tr>
<td>0.0</td>
<td>73.5</td>
<td>39.1</td>
<td>330</td>
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<td>0.2</td>
<td>84.0</td>
<td>39.3</td>
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<tr>
<td>0.4</td>
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<th>$J_{rem}$ (10$^{-7}$ Tm$^3$ kg$^{-1}$)</th>
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<tr>
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<td>90.8</td>
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Fig. 3. $\Delta B_{\downarrow}$ vs. $x$ of substituted Ba ferrites.

Fig. 4. Temperature dependences of magnetic susceptibility for BaFe$_{0.72}$Ni$_{0.06}$Zn$_{0.2}$O$_{19}$.
attributed to the preference of the Se\textsuperscript{2-} ions for the 2b sites. Vincent et al. (15) show that the uniaxial magnetic anisotropy for Zn-Sn mixtures becomes planar at lower substitutions (x < 0.4).

4. CONCLUSIONS

Ni-Sn and Zn-Sn substituted Ba hexaferrites were synthesized by citrate precursor method changing the substitution level x. The coercivity H\textsubscript{c} could be easily controlled without a significant reduction of J\textsubscript{m} at the bipyramidal 2b and slightly on tetrahedral 4f\textsubscript{1} sites, while the Ni\textsuperscript{2+} ions preferred octahedral 4f\textsubscript{2} and 2a+4f\textsubscript{2} sites at low and high substitutions respectively. Zn\textsuperscript{2+} ions strongly preferred the 4f\textsubscript{1} sites. The drop of M\textsubscript{Pr} is caused by the substitution of non-equivalent Fe\textsuperscript{3+} positions. The 12k site splits into two sublattices 12k and 12k' with the substitution of different ions. This may be the results of changes of the neighbours of the Fe\textsuperscript{3+} ions on 12k site, when substitutions take place at hexagonal blocks. J\textsubscript{m} reached maximum at x = 0.4 probably due to the substitutions Sn\textsuperscript{2+} into 4f\textsubscript{1} and less magnetic ions Ni\textsuperscript{2+} on 4f\textsubscript{2} sites. Zn-Sn substitution effectively decreased particle size and coercivity H\textsubscript{c}, while the value J\textsubscript{m} remains constant.

Acknowledgement

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Analysis of acoustic spectra reflecting ion transport processes in glassy electrolytes

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Summary

The investigation of acoustic spectra in ion conductive glasses with different composition can reflect the basic features of the relaxation and transport processes of the mobile ions. It was found that the temperature responses of all acoustic spectra are very similar and the relaxation peaks associated with ion transport depend on the glass composition. Experimental and theoretical aspects of acoustic attenuation measurements in ion conductive glasses of the system Cu-CdBr-Cu\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5} are reviewed. Theoretical studies of acoustic spectra due to the ionic hopping motion and relaxation processes connected with the mobility of Cu\textsuperscript{2+} ions are compared with experimental results and some attempts to fit the acoustic attenuation spectra are accomplished.

Abstrakt

Studium akustických spektier v ionových vôdnych skliech rozličného složení môže počúvať na základe čír storitelných a transportných procesov polovodných ionov. Je známe, že teplom závislé vzhľadom akustických spektier sú velmi podobné a poskytujú relativne maximálnu súvisiaciu s transportom ionov v ionových vôdnych skliech závislú na chemickom složení sklie. So zreteľom na experimentálnu a teoretickú aspektu bol skúmaný akustický útvar v ionových vôdnych skliech systém Cu-CdBr-CuO-P\textsubscript{2}O\textsubscript{5}. Výsledky teoretického štúdia akustických spektier ionových prelukovým pohybom a relaxačných procesov spojených s pohybom Cu\textsuperscript{2+} ionov vôdnych skliech sú porovnávané s experimentálnymi výsledkami a sú vyzývané pokusy štvorčie akustické spektier.

1. INTRODUCTION

It is known that the investigation of acoustic spectra of ion glasses can reflect the basic features of the relaxation and transport mechanisms of the mobile ions. The acoustic attenuation measurement seems to be a useful technique for nondestructive investigation of transport mechanisms in conductive glasses and compared to the electrical ones they have even some advantages as high sensitivity, the absence of the measuring time and so on [1,2]. Acoustical measurements made over a wide range of frequencies and temperatures can characterize different relaxation processes according to the corresponding transport mechanisms due to a strong acousto-ionic interaction.

The ion transport properties of many ion conducting glasses, melts and crystals are similar [3]. Ion conductive glasses have common structural characteristic that includes a highly ordered, immobile framework complemented by a highly disordered interstitial sublattice in which carriers are randomly distributed and in which the number of equivalent sites is greater than the number of available ions to fill them. These low potential sites that comprise the carrier sublattice must be sufficiently interlinked to provide continuous transport paths necessary for optimal movement of ions [4]. In glassy electrolytes, the mobile ions encounter different kinds of site and ionic hopping motion and relaxation processes connected with charge mobility so that modified jump relaxation model can be used for transport mechanisms description [5].

The conductivity of glasses is affected not only by the type of conductive ions, but also strongly depends on „glass forming“ oxide. Phosphate glasses containing Cu\textsuperscript{2+} conductive ions are good ionic conductors with room temperature conductivity of the order 10\textsuperscript{-4} S/cm. The highest conductivity has been recorded in systems containing large fractions of cuprous halides, such as Cu or CuBr [6].

In this contribution we present theoretical description of experimental results obtained by acoustic investigation of the set of glasses prepared in the system Cu-CdBr-Cu\textsubscript{2}O-P\textsubscript{2}O\textsubscript{5} with the purpose to study ion transport mechanisms in these ion conductive glasses and to find the role of cuprous halides producing Cu\textsuperscript{2+} ions.

2. THEORETICAL MODELS

The formal theory of all relaxation processes is similar. A comparison between the electric and acoustic response functions may give useful insights into the dynamic behaviour of ion conducting glasses. In practice, the experimental data are obtained in the frequency domain, while the experimental data of acoustic attenuation are usually available in a narrow frequency region and over a wide temperature range. It is well known that the frequency dependent conductivity of ionic glasses is extremely informative and that there have not been systematic comparative studies of mechanical and electrical processes in the same glasses. Moreover, in many electrical investigations, the data have not