DETERMINATION OF MAGNETOCRYSTALLINE STRUCTURE OF SUBSTITUTED IRON OXIDES

Vladimír Jančárik* — Mária Papánová** — Anna Grusková** — Darina Kevická** — Jozef Sláma*

Application of thermomagnetic analysis for finding of optimum synthesis of single-phase ferrites is presented. Measurement of temperature dependence of magnetic susceptibility \(\chi(\vartheta)\), Mössbauer spectroscopy, and other magnetic analysis methods were used for determination of the structural parameters and phase composition of different iron oxides. Advantages and drawbacks of the thermomagnetic analysis besides other methods are pointed out.

Keywords: iron oxides, initial susceptibility, Mössbauer spectroscopy, Curie temperature

1 INTRODUCTION

Measurement of temperature dependence of magnetic susceptibility \(\chi(\vartheta)\) [1] is a proper method for analysis various kinds of magnetic materials in many cases. It can be used for iron oxides (\(\gamma\)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), \(\alpha\)-Fe\(_2\)O\(_3\)) [2], ferrites with spinel structure – (MnZn)Fe\(_2\)O\(_4\), (NiZn)Fe\(_2\)O\(_4\) [3] and/or hexagonal structure – BaFe\(_{12}\)O\(_{19}\) with various substituents [4, 5, 6]. The shape of \(\chi(\vartheta)\) curve is very sensitive to crystalline and magnetic phase structure, as well as chemical composition and stability where other measurements are not suitable. This technique is more sensitive to impurities of low content than Mössbauer spectroscopy and X-ray diffraction.

Ferro- and ferrimagnetics fall to the paramagnetic state at Curie temperature \(T_C\). The \(\chi(\vartheta)\) dependence exhibits drop to a value near zero at \(T_C\). Curie temperature is given by the chemical composition mainly. However, it can be difficult to determine \(T_C\) when the ferrite material is of multiphase composition.

Mössbauer spectroscopy as supplementary method [7] is used for determination of the structural parameters and phase composition of different substituted iron oxides. The identification of crystalline phases is carried out by X-ray diffraction [4].

Advantages, drawbacks and especially possible misleading results of thermomagnetic analysis are pointed out.

2 EXPERIMENTAL

The substituted iron oxides Ba(NiSn)\(_{x}\)Fe\(_{12-2x}\)O\(_{19}\), with substitution level \(x = 0.0 – 0.3\) named (Sk) were prepared by citrate precursor method with an initial Fe/Ba ratio of 10:8 according to the method described in [8]. The samples named (Mx) were processed by a mechanical alloying [4] with an initial Fe/Ba ratio of 10 and 250 ml of benzene to avoid agglomeration of the powder particles at the bottom of mill. The ferrite specimens prepared by both methods were annealed at 1050°C for 1.5 hour.

The temperature dependencies of the magnetic susceptibility \(\chi(\vartheta)\) has been measured by a bridge method, in the alternating magnetic field of 360A/m and 920 Hz. The specimens were heated up to 730°C at a constant rate of 4°C/min. The Curie temperature \(T_C\) was determined by the Hopkinson’s peaks in \(\chi(\vartheta)\) curves. The susceptibility is given in arbitrary units and is related to the same amount of specimen (1 mg) in all cases.

The Mössbauer spectra were obtained using the conventional constant acceleration source \(^{57}\)Co in Rh matrix at the room temperature. The spectra were fitted using the NORMOS software package.

The X-ray diffraction was carried out by X' Pert Philips diffractometer using Cu-K\(_{\alpha}\) radiation.

The specific magnetic saturation polarization \(J_{sat}\) and remanent polarization \(J_{r}\) and the coercivity \(H_c\) were determined using the vibrating sample magnetometer (VSM) with an external magnetic field of 540 kA/m at various temperatures.

3 RESULTS AND DISCUSSION

Influence of the substitution level \(x\) on \(\chi(\vartheta)\) dependencies is shown in Fig. 1. Presence of various phases in (Mx) Ni-Sn substituted ferrites is shown for all values of \(x\) (Fig. 1a). On the other hand, (Sk) ferrites prepared by other procedure exhibits \(\chi(\vartheta)\) dependence of simple shape, only sharp Hopkinson’s peaks appeared in the vicinity of the Curie temperature (Fig. 1b).

The temperature dependencies of the magnetic susceptibility \(\chi(\vartheta)\) of pure BaFe\(_{12}\)O\(_{19}\) ferrite (i.e. with \(x = 0\)) specimens (Mx) and (Sk) are in Fig. 2a. A sharp Hopkinson’s peak appeared for single phase M type hexaferrite in the vicinity of the Curie temperature in both specimens. The \(\chi(\vartheta)\) curves (Fig. 2b) of Ni-Sn substituted Ba ferrites (Sk) show a single-phase structure for \(x = 0.3\), whereas multiple drops were found at \(\chi(\vartheta)\) curves of (Mx) specimens at \(x = 0.3\). It reveals their multiphase composition.

The complex system is stable, no change in \(\chi(\vartheta)\) curves were found due to the heating cycle during the measurement (up to 730°C), which was repeated three times in an air environment.
It can be difficult to determine the Curie temperature from $\chi(\theta)$ dependencies in the case of multi-phase composition of the specimen. When the components of the specimen have different temperatures at which they drop from magnetic order, the $\chi(\theta)$ exhibits partial drops or Hopkinson’s peaks. Measured values of the dependence are approximated by natural cubic splines. In the case of partial drops, the Curie temperature is determined by the position of point of inflexion. If the Hopkinson’s peak appears near the drop, the Curie temperature can be found by its position. Three interesting regions can be found at $\chi(\theta)$ curves of the (Mx) specimen ($x = 0.3$).

- It is difficult to conclude anything from the soft drop around the temperature 320°C. It can be caused by presence of the iron oxide ($\gamma - Fe_2O_3$) or Ni-Sn substituted iron oxides.
- The sharp peak at 445°C for (Mx) specimen with value close to $T_C$ of pure Ba ferrite, whereas $T_C = 410°C$ is for (Sk) specimen with Ni-Sn substitution ($x = 0.3$).
- The drop around 580°C can correspond to nickel ferrite ($NiFe_2O_4$) with spinel structure or magnetite ($Fe_3O_4$), both with $T_C \sim 585°C$. Accurate determination of this secondary phase may be accomplished by our database of reference specimens. However, the thermomagnetic analysis evidently showed that mechanical alloying (Mx) is not optimum way of preparation in this case, secondary phase occurred in Ni-Sn substituted Ba ferrites. On the other hand, the citrate precursor method (Sk) was found by thermomagnetic analysis be optimum for single-phase ferrite preparation.

The Mössbauer spectroscopy was used for comparison of presented results of thermomagnetic analysis.

**Fig. 1.** The dependencies of $\chi(\theta)$ of Ni-Sn substituted Ba ferrites with $x = 0.0$ up to 0.3, for (Mx) (a) and (Sk) (b) specimens.

**Fig. 2.** Dependence $\chi(\theta)$ for pure Ba ferrite (a) and Ni-Sn substituted Ba ferrite, $x = 0.3$ (b).

Mössbauer spectra measured at room temperature for (Mx) specimens, $x = 0.0$ and 0.3, are in Fig. 3. The spectrum was analysed in terms of five Zeeman sextets for $x = 0.0$ (Fig. 3a), which corresponds with five different Fe$^{3+}$ sites (4f$_2$, 2a, 4f$_1$, 12k, 2b) in the hexagonal structure. Ni-Sn substitution ($x = 0.3$) on the Fe$^{3+}$ sites causes appearance of other magnetic surroundings and the 12k position is broadened.

**Fig. 3.** Mössbauer spectra for (Mx) substituted Ba ferrite, $x = 0.0$ (a) and 0.3 (b).
This position splits into two sublattices:

- 12k site representing ions with three nearest magnetic neighbours in the 4f₁ site in hexagonal structure
- 12k with two neighbours in the 4f₁ site, its value \( B_{12k} \approx 36T \) is the smallest [8, 9].

Since NiFe₂O₄ was not identified by XRD, one may assume that the volume fraction of this spinel is low. Mössbauer spectra were taken at 460°C and 520°C to identify magnetic phases above 450°C for substituted Ba ferrites (Mx). Single doublet was found for both these temperatures which showed that no magnetic order is present in the material. Thermomagnetic analysis evidently shows presence of the magnetic order in this case (Fig. 2b).

The Mössbauer spectrum for (Mx) specimen \( x = 0.3 \) (Fig. 3b) was fitted by seven positions of Fe³⁺ ions. Compared with five sextets for pure Ba ferrite, there is (B) site \( (B_{12k} \approx 45T) \) present in addition. It can presumably be attributed to octahedral (B) sublattice of magnetite Fe₂O₄. Tetrahedral (A) sublattice of the magnetite can be included in 4f₁ position. The rise of relative areas \( S(\%) \) of 4f₁ position (Fig. 4) indicates increasing of spinel block of hexagonal structure, it can also be attributed to the presence of NiFe₂O₄ besides Fe₂O₄ in complex system.

The analysis of the X – ray diffraction patterns for (Mx) specimen with \( x = 0.0 \) and 0.3 is in Fig. 5. This pattern revealed that only the hexaferrite phase was present for \( x = 0.3 \), no secondary phases were detected.

**Fig. 4.** The variation of the relative areas \( S(\%) \) vs. \( x \) for (Mx) specimens.

**Fig. 5.** X – ray diffraction patterns for spectra for (Mx) substituted Ba ferrite, \( x = 0.0 \) (a) and 0.3 (b).

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**Fig. 6.** The \( B(H) \) curves measured at different temperatures. The inset shows a remanent ferromagnetic phase.

**Table 1.** Magnetic properties of substituted Ba ferrites.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( J_{c1} ) (10⁻⁶Tm³kg⁻¹)</th>
<th>( J_{c2} ) (10⁻⁶Tm³kg⁻¹)</th>
<th>( H_{c1} ) (kA/m)</th>
<th>( T_{c1} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 (Mx)</td>
<td>75.7</td>
<td>38.7</td>
<td>370</td>
<td>443</td>
</tr>
<tr>
<td>0.1 (Mx)</td>
<td>80.2</td>
<td>41.2</td>
<td>220</td>
<td>442</td>
</tr>
<tr>
<td>0.2 (Mx)</td>
<td>84.5</td>
<td>40.9</td>
<td>153</td>
<td>438</td>
</tr>
<tr>
<td>0.3 (Mx)</td>
<td>83.6</td>
<td>36.3</td>
<td>100</td>
<td>436</td>
</tr>
<tr>
<td>0.0 (Sk)</td>
<td>73.6</td>
<td>39.1</td>
<td>330</td>
<td>447</td>
</tr>
<tr>
<td>0.1 (Sk)</td>
<td>78.2</td>
<td>42.4</td>
<td>302</td>
<td>426</td>
</tr>
<tr>
<td>0.2 (Sk)</td>
<td>84.0</td>
<td>39.3</td>
<td>189</td>
<td>410</td>
</tr>
<tr>
<td>0.3 (Sk)</td>
<td>80.0</td>
<td>37.0</td>
<td>146</td>
<td>399</td>
</tr>
</tbody>
</table>
The coercivity $H_c$ fell from 370 down to 100 kA/m with the Ni-Sn substitution for (Mx) samples. The strong fall of $H_c$ (drop by \textasciitilde72\%) for (Mx) samples at higher substitutions was probably caused the presence of two phases, hexagonal and spinel ferrite. The reduction of $H_c$ of (Sk) specimens from 330 kA/m to 146 kA/m was less than that found in the case of (Mx) specimens possibly by different presence of the Sn$^{4+}$ ions in the 2b and 4f$_1$ sites and Ni$^{2+}$ ions in 4f$_2$ and 12k sites.

The ordering temperatures $T_c$ decreased with the substitution level. The linear decreasing of the Curie temperature with $x$ for (Sk) samples is related to weakening of the superexchange interaction of the Ni-Sn substitution. Slight decreasing for (Mx) specimens is a consequence of the presence of other phases in complex system.

4 CONCLUSIONS

Thermomagnetic analysis is very sensitive to phase composition of ferrites. It was used for investigation of substituted M – type barium hexaferites. $\chi(\vartheta)$ dependencies are very sensitive to phase and chemical composition of the specimen. Software for analysis of $\chi(\vartheta)$ dependence was built to determine Curie temperature. It can be done by several ways depending on the shape of the $\chi(\vartheta)$ curve. Deep information about the iron oxides can be brought by $\chi(\vartheta)$ measurements together with Mössbauer spectroscopy and X - ray diffraction analysis.

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REFERENCES


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