1 INTRODUCTION

Strontium (Sr) and barium (Ba) M-type hexaferrites (SrFe$_{12}$O$_{19}$) and (BaFe$_{12}$O$_{19}$) are extensively used as hard magnetic materials due to their relatively high coercivity. Hexaferrites have high anisotropy field ($H_a = 1.353$ MA.m$^{-1}$) compared to other hard magnetic materials. They are convenient for permanent magnets, high-density magnetic and magneto-optical recording with higher signal-to-noise ratio. Other possible application is for microwave circuits because of their high resistivity and permittivity at high frequency. Their preparation is relatively cheap, they exhibit corrosion resistance and good chemical stability [1]. Theoretical value of coercive field $J_H = 533.169$ kAm$^{-1}$ was estimated for Ba ferrite [2] and critical size of single-domain insulated spherical particles was predicted to 0.5 μm [3].

Ferrites with particle size around 1 μm can be produced by standard ceramic technology. Ba ferrites with average particle size approx. 0.1 μm can be obtained by heating treatment of chemically coprecipitated precursor. Such particles are near single-domain size. Therefore the coercivity can be considerably higher – typically 437 – 477 kAm$^{-1}$ than of those prepared by ceramic method. The particles are relatively free of defects and hence the possibility of the inverse nucleation centres formation is reduced. The coercivity $J_H = 510$ kAm$^{-1}$ near to theoretical limit has been reported when a chemical etching by HCl was performed [4]. It can be explained by considering that the acid preferentially reduces the surface defects and the edges of the grains. It reduces the surface demagnetising fields i.e. reduces nucleation of closing domains.

Hexagonal ferrites can be prepared by various processing techniques, especially by ceramic [3, 5], various wet methods [1, 2, 4] and [6-10] or mecanochemical processing [11]. Following preparation methods were used for samples analysed in this paper – ceramic method, citrate precursor method and low-temperature combustion synthesis. Three methods were used for evaluation of properties of the prepared ferrites – measurement of the temperature dependence of magnetic susceptibility, measurement of magnetization characteristics (hysteresis loops) using the vibration magnetometer and Mössbauer spectroscopy.

Measurement of the temperature dependence of magnetic susceptibility $\chi(T)$ was used as main method of analysis.
Fig. 1. Temperature dependences of saturation polarization \( J_s(T) \) (a) and initial susceptibility \( \chi(T) \) (b) of strontium ferrite.

All particles are magnetically stable (blocked) at temperature \( T < T_c \). Probably at the temperature \( T_c \) the content of superparamagnetic particles increase in our case. The critical volume \( V_s \) of superparamagnetic particles at zero field \( H \) may be determined by a thermodynamic balance relationship

\[
kT = J_s(T) H_s(T) V_s(T).
\]

A mixture of both types of particles – stable and superparamagnetic – arise at the temperature \( T > T_c \). Susceptibility increases when changing from the stable to the superparamagnetic state and the \( \chi(T) \) dependence exhibits a sharp Hopkinson peak at the temperature \( T_{pk} \). At this temperature, major part of particles is superparamagnetic and \( H_s \) approaches zero, so the height of the Hopkinson peak is several times larger than the value of \( \chi(T) \) in the local minimum at \( T_c \). At the Curie temperature \( T_C \) the susceptibility strongly decreases to zero because spontaneous magnetization vanishes \( (J_s \to 0) \) and the system becomes to be paramagnetic.

Several ways are commonly used for finding Curie temperature \( T_C \) from the \( \chi(T) \) dependence:

(a) Temperature responding to the point of inflexion.
(b) Temperature responding to the cross-section of tangents to \( \chi(T) \) dependence at point of inflexion with the temperature axis.
(c) Temperature responding to the Hopkinson’s peak, if any.
(d) Temperature at which the susceptibility value is almost zero.

Automated system was used for measurement of temperature dependence \( \chi(T) \) of the initial susceptibility [12]. Software was created for processing of the measured curves. Attention was focused on unambiguous algorithm of Curie temperature determination from point of inflexion mainly. It is important in order to make the results comparable between various samples.

The point of inflexion is found by a numerical procedure in case (a). Measured points of the \( \chi(T) \) curve are fitted by natural cubic splines around the expected Curie temperature and the temperature at which

\[
\frac{\partial^2 \chi(T)}{\partial T^2} = 0
\]

is found. Because this condition is usually valid at several points within the analysed region, the point it taken into account at which the slope is maximum

\[
\frac{\partial \chi(T)}{\partial T} \rightarrow \text{max}.
\]

The results (a) and (b) are almost the same because the \( \chi(T) \) dependence is usually steep near Curie temperature and the difference can be less than measurement uncertainty and inhomogeneity of sample temperature. However, Curie temperatures found by this way are comparable only if the shape of the analysed curves are of similar shape around the drop. When the ferrite sample contains more phases and several drops appear in the \( \chi(T) \) dependence, point of inflexion for each drop brings adequate information about corresponding magnetic phases. The results obtained by the procedure (d) are usually too uncertain.

2.2 Methods of ferrite preparation

Two steps are necessary for preparation of hexagonal ferrite. In the first step, homogeneous mixture is prepared from the raw starting materials strontium - or barium - and iron-inorganic compounds by pre-sintering. In the second step, the calcinate is treated by heating to achieve ordered ferrite structure.

The ceramic method is widely used for preparation of \( M \)-type hexaferrites. The drawback of the ceramic method is the necessity of the high-temperature annealing to build the hexagonal structure in the solid solution (in our case \( 1320 \, ^\circ\text{C}/2\text{h} \)). This processing yields large-size ferrite particles (approximately 10 \( \mu \)m) improper for our application.

Water solution of the raw strontium or barium and iron salts with organic solution is used for preparation of the ferrite by wet method. The homogeneity of the liquid solution is better than mechanically milled mixture in ceramic method, therefore the lower temperature is necessary to build the homogeneous ferrite powder with magnetoplumbite structure.

Two ways of ferrite preparation from gel was used in our case – cumulative annealing and low-temperature auto-combustion.

The raw mixture containing strontium or barium and iron soluble in water nitrates and citric acid was dehydrated. Solvent was removed from citrate complex by pouring the solution into excessive amount of alcohol and then the amorphous citrate precursor was decomposed. The product was then cumulatively annealed, only the temperatures 700 \( ^\circ\text{C} \) and 1050 \( ^\circ\text{C} \) was enough to build the hexagonal structure. In our conditions, only small amount of the ferrite (tens of grams) was possible to prepare by this method. Therefore, low-temperature auto-combustion method was used for preparation of higher amount of hexaferrite (up to 1 kg). Glycine was used as organic component in the amorphous precursor. It burns at low temperature and no solid residues remain after the combustion process. Annealing at 750 \( ^\circ\text{C} \) was sufficient to reach or-
order hexagonal structure in the ferrites prepared by this method.

3 RESULTS AND DISCUSSION

Temperature dependences of magnetic susceptibility $\chi(T)$ of Sr ferrite (SrF) and Ba ferrite (BaF) samples prepared by ceramic method are in Fig. 2.

![Fig. 2. Temperature dependences of $\chi(T)$ of Sr and Ba ferrite samples, prepared ceramic method, annealed at 1320°C/2h.](image)

These dependences exhibit strong drop at temperature 450 °C with small indication of Hopkinson’s peak. Curie point at the temperature 459 °C for Sr ferrite and 453 °C for Ba ferrite were determined. Particles of Ba and Sr ferrites prepared by the ceramic technology are large and multi-domain, which is caused by large annealing temperature (1320 °C/2h). It implies small coercive field $H_C$ (below 100 kAm$^{-1}$) as shown in Tab. 1 and also higher value of the susceptibility $\chi$ at room temperature. $\chi(T)$ dependences of Sr and Ba ferrite samples were prepared by citrate precursor method with the cumulatively annealing up to 1050°C/2h are in Fig. 3.

![Fig. 3. Temperature dependences of $\chi(T)$ of Sr and Ba ferrite samples, prepared citrate precursor method, annealed at 1050 °C/2h.](image)

They correspond to the single-phase composition with local minimum and the expressive Hopkinson’s peaks are at the temperature 457 °C (SrF) and 450 °C (BaF). Such behavior is due to occurrence of the ordered single-phase structure with particles smaller than 1 µm. It is proved by relatively high value of $H_C$ (Tab. 1).

$\chi(T)$ dependences of Sr hexaferrite samples prepared by the combustion synthesis are in Fig. 4. Immediately after the first step a mixture of the iron oxides arose, containing the maghematized magnetite mainly (a). After the annealing at 750 °C/3h, uniform particles with hexagonal structure appear, as indicated by excessive Hopkinson’s peak at temperature 455 °C (b). Composition of this annealed sample was verified by Mössbauer spectrum (Fig. 5). It was resolved as superposition of subspectra (4f$_1$, 2a, 4f$_1$, 12k and 2b) [13]. The relative areas $S(\%)$ of all subspectra (14.1 %, 9.9 %, 21.4 %, 48.3 % and 6.3 %) show the ordered magnetic structure of Sr ferrite.

In the case of small ferrite particles with the size below 1 µm they can be assumed as non-interacting uniaxial, single-domain and disordered. According to the Stoner-Wohlfarth theory, the intrinsic coercivity $H_C$ resulting from coherent rotation of magnetization can be then estimated for by the formula

$$H_C = C \left( \frac{2K}{J_S} - N \cdot J_S \right),$$

where $K_1$ and $N$ are the first anisotropy constant and demagnetization factor of particles, $C$ is dimensionless constant of material. In such case, the value of coercivity is high and susceptibility is low as proved by the measurements.

![Fig. 4. Temperature dependences of $\chi(T)$ of Sr ferrite prepared by combustion synthesis without annealing (a), annealed at 750°C/3h (b).](image)

The values of specific saturation and remanent magnetic polarization ($J_{s-m}$ and $J_{s-r}$) and of coercivity $H_C$ of SrF and BaF prepared by ceramic method (1), citrate precursor (2) and combustion synthesis (3) are in Tab. 1. They were measured by vibrating magnetometer [14]. The maximum values of $J_{s-m}$ and $J_{s-r}$ are for SrF and BaF (2) and maximum value of $H_C$ is for SrF (3). The grain size of samples (1) was approx. 10 µm, samples (2) and (3) below 1 µm.

Coercive field $H_C$ of samples prepared by citrate precursor method was by 33 % (SrF) and 11 % (BaF) less than of heat-treated chemically co-precipitated ferrites.
(particle size 0.1 μm). [2]. However, \( H_C \) of the Sr ferrite prepared by low-temperature combustion synthesis and then annealed was less by 8.9 %. Such value is less by 25 % only than the theoretical value.

**Fig. 5.** Mössbauer spectrum for Sr ferrite sample prepared combustion synthesis, annealed at 750°C/3h.

**Table 1.** Magnetic properties of Sr and Ba ferrites prepared various methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( J_m ) (mT cm(^{-2}))</th>
<th>( J_r ) (mT cm(^{-2}))</th>
<th>( H_C ) (kA m(^{-1}))</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF (1)</td>
<td>1320°C/2h</td>
<td>73.32</td>
<td>91.87</td>
<td>4f</td>
</tr>
<tr>
<td>BaF (1)</td>
<td>1320°C/2h</td>
<td>71.98</td>
<td>42.85</td>
<td>4f</td>
</tr>
<tr>
<td>SrF (2)</td>
<td>1050°C/2h</td>
<td>89.86</td>
<td>52.05</td>
<td>4f</td>
</tr>
<tr>
<td>BaF (2)</td>
<td>1050°C/2h</td>
<td>67.73</td>
<td>24.01</td>
<td>4f</td>
</tr>
<tr>
<td>SrF (3)</td>
<td>750°C/3h</td>
<td>67.73</td>
<td>24.01</td>
<td>4f</td>
</tr>
<tr>
<td>BaF (3)</td>
<td>1050°C/2h</td>
<td>67.73</td>
<td>24.01</td>
<td>4f</td>
</tr>
</tbody>
</table>

Note: \( H_m = 755 \text{ kA.m}^{-1} \); (1) ceramic method, (2) citrate precursor, (3) combustion synthesis

4 CONCLUSIONS

Temperature dependence of magnetic susceptibility was used as a method of hexagonal ferrites properties evaluation. It can bring good information about the magnetic phase composition. Because susceptibility is dependent on magnetization process of the particles, it is influences by ferrite particles shape, size and anisotropy.

Annealing 750°C/3h was enough to achieve ordered hexagonal structure of Sr and Ba ferrite samples prepared by the low-temperature combustion synthesis.

High coercivity and excessive Hopkinson peak appear with monodomain particles of size below 1 μm.

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REFERENCES


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