Synthesis and Structure Characterisation of Micro- and Nanocrystalline Powders of Dy$_{1-x}$R$_x$FeO$_3$ (R = La, Pr, Nd, Sm, Gd)

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This work deals with the study of the phase and crystal structure behaviour of new micro- and nanocrystalline ferrites Dy$_{1-x}$R$_x$FeO$_3$ obtained by solid state reactions (R = La, Pr) and sol–gel citrate (R = Nd, Sm, Gd) techniques. It was established that all synthesized samples adopt orthorhombic perovskite structure isotypic with GdFeO$_3$. Unit cell dimensions and atomic coordinates of the mixed rare earth ferrites derived by full profile Rietveld refinement technique agree well with the data of the “pure” DyFeO$_3$ and RFeO$_3$ compounds, thus proving formation of continuous solid solutions Dy$_{1-x}$R$_x$FeO$_3$ in the DyFeO$_3$–RFeO$_3$ systems (R = La, Pr, Nd, Sm, Gd). Peculiarity of the Dy$_{1-x}$La$_x$FeO$_3$ series is the lattice parameters crossover and formation of dimensionally tetragonal structure at $x \approx 0.97$.

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1. Introduction

Complex oxides with perovskite structure RFeO$_3$, where R are rare earth elements, represent an important class of functional materials. RFeO$_3$ compounds are used in thermoelectric devices, solid oxide fuel cells [1], as membranes for gases separation, sensory materials and catalysts [2–4], as magnetic and multiferroics materials [5, 6]. Complementary, the interest to the rare earth ferrites is stimulated by their specific fundamental physical properties and interesting high temperature magnetic behaviour, namely, spin-reorientation phenomena and the para- to antiferromagnetic transition which occur in RFeO$_3$ series at 620–750 K [7–9]. Just recently interesting phenomena of magnetoelastic coupling were detected in SmFeO$_3$ and some solid solutions based on them [10, 11]. Recently, versatile and gigantic magnetoelastic phenomena have been found for a single crystal of DyFeO$_3$ [12]. It was revealed that application of magnetic field along the c axis induces a multiferroic phase with magnetization and electric polarization both along the c axis. In this respect, several mixed DyFeO$_3$-based systems, such as Dy$_{1-x}$La$_x$FeO$_3$ [13], Dy$_{1-x}$Pr$_x$FeO$_3$ [14, 15], Dy$_{1-x}$Ho$_x$FeO$_3$ [16], Dy$_{1-x}$Er$_x$FeO$_3$ [17] and Dy$_{1-x}$Tm$_x$FeO$_3$ [18] were studied in the last decade. However, no structural parameters were reported for the majority of Dy$_{1-x}$R$_x$FeO$_3$ systems. The aim of the present work is a study of crystal structure behaviour of new micro- and nanocrystalline ferrites Dy$_{1-x}$R$_x$FeO$_3$ (R = La, Pr, Nd, Sm, Gd) obtained by solid state and sol–gel citrate techniques.

2. Experimental

New mixed orthoferrites Dy$_{1-x}$R$_x$FeO$_3$ (R = La, Pr, Nd, Sm, Gd) were obtained by two different methods. The samples containing La and Pr were synthesized by solid state reactions technique according to the following reaction schemes:

\[
(1 - x)\text{Dy}_2\text{O}_3 + x\text{La}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Dy}_{1-x}\text{La}_x\text{Fe}_3\text{O}_9,
\]

\[
3(1 - x)\text{Dy}_2\text{O}_3 + x\text{Pr}_{6}\text{O}_{11} + 3\text{Fe}_2\text{O}_3 \rightarrow 6\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_3\text{O}_9 + x\text{O}_2↑.
\]

Stoichiometric amounts of precursor oxides La$_2$O$_3$, Pr$_6$O$_{11}$, Dy$_2$O$_3$ and Fe$_2$O$_3$ were ball-milled in ethanol for 4 h, dried, and heat treated in alundum crucibles in air at 1473 K for 80 h. As obtained products were repeatedly heat treated in air subsequently at 1673 K for 25 h and at 1773 K for 25 h, after that slowly cooled to the room temperature (RT). For preparation of nanocrystalline powders of Dy$_{0.5}$R$_{0.5}$FeO$_3$ (R = Nd, Sm, Gd) a low-temperature sol–gel citrate method was used. Rare earth oxides Dy$_2$O$_3$, Sm$_2$O$_3$ and Gd$_2$O$_3$ as well as Nd(NO$_3$)$_2$ · 6H$_2$O and Fe(NO$_3$)$_2$ · 9H$_2$O were used as an initial reagents. Neodymium and iron nitrates were dissolved in distilled water, whereas nitrate solutions of Dy,
Sm, and Gd were prepared by dissolving of corresponding oxides in HNO₃. Appropriate amounts of corresponding solutions were mixed on magnetic stirring for 30 min, after that water solution of citric acid (CA) and ethyleneglycol (EG) were sequentially added to the reaction mixture under continuous stirring. The molar ratio of reagents was \( n(Dy^{3+}) : n(R^{3+}) : n(Fe^{3+}) : n(CC) : n(EG) = 0.5 : 0.5 : 1 : 2 : 1 \) (R = Nd, Sm, Gd). As prepared solutions were gelled at 373–393 K for 4 h after that heat treated sequentially at 573 K and 723 K for 1 h. The foamy product obtained was finally calcined at 1273 K for 2 h. In such a way single phase nanocrystalline powders of Dy₀.₅R₀.₅FeO₃ were obtained with average grain size of 86–300 nm.

X-ray powder diffraction technique (Huber imaging plate Guinier camera G670, Cu K\( \alpha_1 \) radiation, \( \lambda = 1.54056 \) Å) was used for the phase and structural characterization of the samples at room temperature. Structural parameters, average crystallite size of the powders (\( D, [\text{nm}] \)) and microstresses (\( \langle \epsilon \rangle = \langle \Delta d / d \rangle, [%] \)) of the samples were derived from the experimental diffractograms by using full profile Rietveld refinement technique applying WinCSD program package [19]. The morphology of sol–gel derived Dy₀.₅R₀.₅FeO₃ (R = Nd, Sm, Gd) series was investigated by means of Hitachi SU-70 scanning electron microscope.

3. Results and discussion

X-ray powder diffraction examination revealed that Dy₁₋ₓRₓFeO₃ (R = La, Pr) samples synthesized by solid state method adopt orthorhombic perovskite structure isotypic with GdFeO₃. No traces of foreign phases were detected. Refinement of crystal structures in space group \( Pbnm \) by using full profile Rietveld method shows excellent agreement between the experimental X-ray powder diffraction pattern (red dots) and calculated pattern (blue line) (Fig. 1) thus proving a phase purity and crystal structure of the samples.

![Graphical results of the Rietveld refinement of Dy₀.₅Nd₀.₅FeO₃ structures, obtained by sol–gel citrate method and SEM pictures of these materials (insets).](image1)

Examination of X-ray diffraction patterns of sol–gel derived Dy₀.₅R₀.₅FeO₃ (R = Nd, Sm, Gd) materials revealed that even short-term heat treatment at 1273 K for 2 h led to formation of pure perovskite structure. Graphical results of the Rietveld refinement of as-obtained Dy₀.₅R₀.₅FeO₃ materials are presented in Fig. 2. Detectable peak broadening in the XRD patterns indicate nanoscale grains size of sol–gel derived specimens. Indeed, evaluation of microstructural parameters of the Dy₀.₅Nd₀.₅FeO₃, Dy₀.₅Sm₀.₅FeO₃, and Dy₀.₅Gd₀.₅FeO₃ samples from the analysis of the XRD profile broadening by full profile Rietveld technique, lead to the average grain size \( D_{ave} = 86, 121, 316 \) nm and microstrains...
The lattice parameters, coordinates and displacement parameters of atoms in Dy$_{1-x}$RE$_x$FeO$_3$ (R = La, Pr, Nd, Sm, Gd) structures.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Parameters</th>
<th>Dy$<em>{0.7}$La$</em>{0.3}$FeO$_3$</th>
<th>Dy$<em>{0.4}$La$</em>{0.6}$FeO$_3$</th>
<th>Dy$<em>{0.5}$Pr$</em>{0.5}$FeO$_3$</th>
<th>Dy$<em>{0.5}$Nd$</em>{0.5}$FeO$_3$</th>
<th>Dy$<em>{0.5}$Sm$</em>{0.5}$FeO$_3$</th>
<th>Dy$<em>{0.5}$Gd$</em>{0.5}$FeO$_3$</th>
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<tbody>
<tr>
<td>a [Å]</td>
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<td>5.5323(4)</td>
<td>5.3955(3)</td>
<td>5.3805(2)</td>
<td>5.3490(1)</td>
<td>5.3258(5)</td>
<td></td>
</tr>
<tr>
<td>b [Å]</td>
<td>5.5929(3)</td>
<td>5.5653(4)</td>
<td>5.5921(3)</td>
<td>5.5874(2)</td>
<td>5.5904(1)</td>
<td>5.5984(6)</td>
<td></td>
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<tr>
<td>c [Å]</td>
<td>7.025(4)</td>
<td>7.8324(6)</td>
<td>7.7082(4)</td>
<td>7.6944(3)</td>
<td>7.6612(2)</td>
<td>7.6439(7)</td>
<td></td>
</tr>
<tr>
<td>V [Å$^3$]</td>
<td>231.13(4)</td>
<td>241.07(6)</td>
<td>232.57(4)</td>
<td>231.31(3)</td>
<td>229.09(2)</td>
<td>227.91(7)</td>
<td></td>
</tr>
</tbody>
</table>

Refined structural parameters of all micro- and nanocrystalline Dy$_{1-x}$RE$_x$FeO$_3$ samples synthesized, as well as corresponding residuals are presented in Table I.

Fig. 3. Concentration dependences of unit cell dimensions of Dy$_{1-x}$La$_x$FeO$_3$. Orthorhombic lattice parameters and unit cell volume are normalized to the perovskite ones as follows: $a_p = a_0/\sqrt{2}$, $b_p = b_0/\sqrt{2}$, $c_p = c_0/2$, $V_p = V_0/4$. The dashed lines are polynomial fits: $a_p(x) = 3.750 + 0.16x + 0.02x^2$; $b_p = 3.958 - 0.01x - 0.015x^2$; $c_p = 3.8118 + 0.119x - 0.002x^2$; $V_p = 56.58 + 4.5x + 0.1x^2$.

Structural parameters of the mixed Dy$_{1-x}$RE$_x$FeO$_3$ ferrites obtained agree well with the data for the “pure” RFeO$_3$ compounds, thus proving formation of continuous solid solutions with orthorhombic perovskite structure in the DyFeO$_3$–RFeO$_3$ (R = La, Pr, Nd, Sm, Gd) systems. Peculiarity of the Dy$_{1-x}$La$_x$FeO$_3$ series is the lattice parameters crossover and formation of dimensionally tetragonal structures at $x = 0.97$ (Fig. 3). Such strongly anisotropic behaviour of the unit cell dimensions, which was also recently observed in the related in La$_{1-x}$Sm$_x$FeO$_3$ series [20], is explained by crystal structure peculiarities of the end members of the systems. In spite of being isostuctural, DyFeO$_3$ and LaFeO$_3$ show different order of the perovskite cell parameters: $b_p > c_p > a_p$ and $b_p > a_p > c_p$, respectively. As a result, a crossover of $a_p$- and $c_p$-parameters occurs in Dy$_{1-x}$RE$_x$FeO$_3$ system. Similar phenomena were earlier observed in the related cobaltite-ferrites RCo$_{1-x}$Fe$_x$O$_3$ [21, 22], as well as among isostuctural rare earth perovskites R$_{1-x}$R$_x$Al(Ga)O$_3$ [23, 24], in which end members of the systems possess different relations of the unit cell dimensions.

Figure 4 demonstrates evolution of the lattice parameters and unit cell volumes in Dy$_{0.5}$RE$_{0.5}$FeO$_3$ series versus ionic radii of rare earth cations. The perovskite lattice parameters show anisotropic convergent behaviour: the
a- and c-parameters increases with increasing R-cation radii, whereas b-parameter decreases (Fig. 4). However, the unit cell volumes in Dy$_{1-x}$R$_x$FeO$_3$ series increases almost linearly according to the Vegard rule. This observation indicates statistical distribution of dysprosium and rare earth species over positions of A-cations in Dy$_{1-x}$R$_x$FeO$_3$ perovskite structures.

![Graph showing unit cell parameters vs. R-cation radius](image)

Fig. 4. Dependences of the unit cell parameters versus of average R-cation radii. The values indicated by asterisks are calculated from polynomial fits of the data presented in Fig. 3.

4. Conclusions

Series of micro- and nanocrystalline powders of Dy$_{1-x}$R$_x$FeO$_3$ were obtained by solid state reactions in air at 1773 K (R = La, Pr) and by a wet sol–gel citrate route at 1273 K (R = Nd, Sm, Gd). In comparison with a traditional energy-consuming high-temperature ceramic technique, the low-temperature sol–gel citrate method is very promising tool for a synthesis of the phase pure fine powders of mixed perovskite ferrites. Both micro- and nanocrystalline series of the samples synthesized adopt orthorhombically distorted perovskite structure isotypic with GdFeO$_3$. Obtained structural parameters of Dy$_{1-x}$R$_x$FeO$_3$ ferrites prove the formation of continuous solid solutions in DyFeO$_3$–RFeO$_3$ (R = La, Pr, Nd, Sm, Gd) pseudobinary systems. Peculiarity of Dy$_{1-x}$La$_x$FeO$_3$ solid solution is divergence behaviour of unit cells dimensions with increasing lanthanum content and crossover of the a and c perovskite lattice parameters at $x \approx 0.97$.

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References


