Synthesis and Structure Characterisation of Micro- and Nanocrystalline Powders of $Dy_{1-x}R_xFeO_3$ (R = La, Pr, Nd, Sm, Gd)

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The interest in the rare earth ferrites and their solid solutions is stimulated by their unique properties, such as high electrical conductivity, specific magnetic properties including spin reorientation phenomena, as well as significant electrochemical and catalytic activity. These materials have been found diverse technological applications, such as electrode materials for SOFC, HT multiferroics, dielectric, catalysts, sensory materials, etc.

New mixed orthoferrites $Dy_{1-x}R_xFeO_3$ were obtained by two different methods. The samples containing La and Pr were obtained by traditional solid state synthesis in air at the temperatures 1673–1773 K. For a 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_2O_3, Sm_2O_3 and Gd_2O_3 as well as $Nd(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ 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 HNO_3. 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 head 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 $Dy_{0.5}R_{0.5}FeO_3$ were obtained with average grain size of 86–300 nm.

Structural parameters of all mixed $Dy_{1-x}R_xFeO_3$ 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 $Dy_{1-x}La_xFeO_3$ series is the lattice parameters crossover and formation of dimensionally tetragonal structures at $x \approx 0.97$. The lattice parameters of $Dy_{1-x}R_xFeO_3$ show anisotropic convergent behaviour: the a- and c-parameters increases with increasing R-cation radii, whereas b-parameter decreases (Figure). However, the unit cell volumes in $Dy_{1-x}R_xFeO_3$ series increases almost linearly with according to the Vegard's rule.

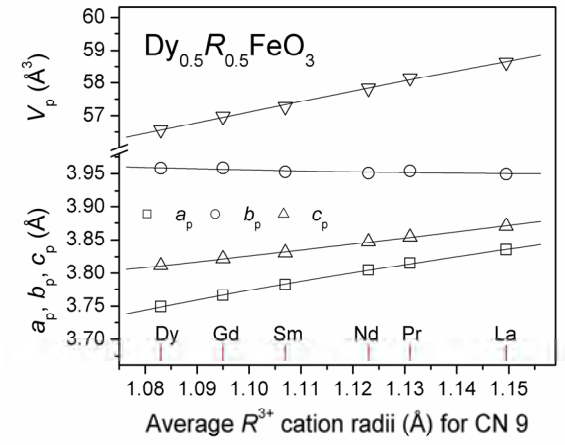

Figure. Unit cell dimensions of $Dy_{0.5}R_{0.5}FeO_3$ series *vs* average R-cation radii. Lattice parameters and unit cell volume of the orthorhombic cell are normalized to the perovskite ones as follows: $a_p = a_o/\sqrt{2}$, $b_p = b_o/\sqrt{2}$, $c_p = c_o/2$, $V_p = V_o/4$.

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