

## FA2-MS14-P04

**Thermal annealing effect on cation inversion and particle size of Zn-ferrite.** B. Antic<sup>a</sup>, A. Kremenovic<sup>b</sup>, J. Blanus<sup>a</sup>, L. Bessais<sup>c</sup>, E. S. Bozin<sup>d</sup>. <sup>a</sup>The "Vinča" Institute, Belgrade, Serbia. <sup>b</sup>University of Belgrade, Belgrade, Serbia. <sup>c</sup>Institut de Chimie et Matériaux Paris Est, Paris, France. <sup>d</sup>Columbia University, New York, USA.

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The crystal structure and microstructure analysis of Zn-ferrite, as-prepared sample (S1) as well as annealed at 400 °C (S2) and 500 °C (S3) are carried out by two methods: PDF (pair distribution function) in direct space and Rietveld refinement in reciprocal space, using synchrotron x-ray powder diffraction data. Some deviations between Rietveld and PDF results are found in the values of lattice parameter, in which case those derived from PDF can be considered as more reliable. It is interesting to note that the best agreement in lattice parameter is achieved for as-prepared sample S1. The occupation number of Zn ions at the A site is determined by Rietveld refinement, showing the change of Zn ion occupation ratio over A and B sites. The results show that bulk sample resembles a normal spinel structure, while there is about 25% of inversion found in S1. Thus, from one metastable structure with of 25% of Fe<sup>3+</sup> at tetrahedral sites in the space group  $Fd\bar{3}m$  for S1 and S2 sample, a jump in cation distribution is achieved through sample annealing at 500 °C and then a stable distribution with Zn<sup>2+</sup> exclusively at tetrahedral sites is obtained.

The microstructure analysis of S1, S2 and S3 sample is performed by using TCH approximation of pseudo-Voigt function to describe the peak shape and Ni powder standard to determine the instrumental line broadening. The particle size and microstrain are refined using isotropic (spherical) particle shape model and isotropic microstrain (random defects distribution), which provide satisfactory agreement with experimental data. Particle size values are further compared to those obtained from PDF analysis. The notable agreement for annealed samples S2 and S3 is found, however, there is a discrepancy in particle size obtained for S1 sample. Smaller particle size obtained from Rietveld refinement could be due to a higher degree of disorder in particle shell region of S1, thus diminishing the coherent scattering domain approximately to the particle core and reducing the scattering from shell region to amorphous-like background. On the other hand, PDF is not affected by these limitations and can provide more accurate information on microstructure parameters in highly disordered systems, for which Rietveld refinement operates at its limits.

The effect of particle size on coercivity, saturation magnetization and freezing temperature will be shown. Results of dc magnetization measurements suggest a picture of ferrite nanoparticles with inter-particle interactions. Within core/shell model nanoparticles are structured of ordered core and disordered crystalline or amorphous shell with different thicknesses. Absence of hysteresis loop shift and high field irreversibility both point to smaller magnetic contribution of shell region. Also, the absence of saturation in magnetic hysteresis is the additional evidence of shell existence, which is in agreement with results of PDF structure analysis.

**Keywords:** nanoparticles, microstructure analysis, cation distribution

## FA2-MS14-P05

**Crystal structure behaviour prediction in the RAlO<sub>3</sub>-R'AlO<sub>3</sub> system.** Tetyana Basyuk<sup>a</sup>, Sergiy Fedeev<sup>a</sup>, Vasyl Berezovets<sup>b</sup>, Dmytro Trots<sup>c</sup>, Stefan Hoffmann<sup>d</sup>, Rainer Niewa<sup>c</sup>, Leonid Vasylechko<sup>a</sup>.

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Perovskite-like compounds have widely technological applications, which initiated a numerous crystal structure investigation. The point at issue of present work is phase and structure behaviour of solid solutions in the PrAlO<sub>3</sub>- and LaAlO<sub>3</sub>-based systems.

In the LaAlO<sub>3</sub>-RAlO<sub>3</sub> (R=Pr, Nd) and PrAlO<sub>3</sub>-NdAlO<sub>3</sub> systems, continuous solid solutions with rhombohedral structure are formed at room temperature. Two type of solid solutions with rhombohedral (*R-3c*) and orthorhombic (*Pbnm*) structures exist in the LaAlO<sub>3</sub>-RAlO<sub>3</sub> and PrAlO<sub>3</sub>-RAlO<sub>3</sub> systems, starting from R = Sm. In addition, third kind of solid solutions having orthorhombic *Imma* structure has been found in the PrAlO<sub>3</sub>-RAlO<sub>3</sub> system with Tb-Tm and Y. Exceptional behaviour among R<sub>1-x</sub>R'<sub>x</sub>AlO<sub>3</sub> solid solutions show some Ce-containing compositions, which adopt tetragonal structure at ambient temperature [1]. Immiscibility gaps of different extensions exist between different perovskite phases in the RAlO<sub>3</sub>-R'AlO<sub>3</sub> systems.

La<sub>1-x</sub>R<sub>x</sub>AlO<sub>3</sub> solid solutions with R=Pr, Ce and Nd undergo high-temperature phase transition from a rhombohedral to the cubic structure, whereas two HT transformation *R-3c* ↔ *Pm-3m* and *Pbmn* ↔ *R-3c* are observed in the La(Pr)AlO<sub>3</sub>-RAlO<sub>3</sub> systems with R=Sm-Tb. Both HT transformations are induced by a structural deformation and its temperatures rise with decreasing Pr(La) content. Low-temperature (LT) phase transformations, which are involved by electronic effects, has been detected only in the Pr- and Ce-containing systems.

In the present study the temperatures of HT phase transformations occurred in RAlO<sub>3</sub>-R'AlO<sub>3</sub> systems has been parametrised as a function of average R-cation radius and structure parameters, such as perovskite cell volume and lattice parameter ratios. Both experimental and literature data for more than 30 compositions of solid solutions R<sub>1-x</sub>R'<sub>x</sub>AlO<sub>3</sub>, as well as for the "pure" RAlO<sub>3</sub> compounds were analyzed.

It is shown, that dependences of transition temperature on rare earth content, R-cation radius and structure parameters can be used for a prediction of crystal structure and phase transitions of rare earth aluminates with various compositions in a wide temperature range.

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[1] Vasylechko L., Senyshyn A., Bismayer U., *Handbook on the Physics and Chemistry of Rare Earths*. 2009, 39, 113.

**Keywords:** rare-earth elements, crystal structures, phase transitions