

s8.m28.p12 **Nano-Dimensional Twins as the Manifestation of the Nano-Structuredness of $Ba_{1-x}La_xF_{2+x}$ and $Ca_{1-x}La_xF_{2+x}$ Crystals.** B. Sobolev^a, P. Herrero^b, S. Maksimov^c, A. Avilov^a, ^aInstitute of Crystallography RAS, ^bInstitute of Material Science, Madrid, Spain, ^cMoscow Institute of Electronic Technology. E-mail: msec2003@ns.crys.ras.ru

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Properties of non-stoichiometry crystals $M_{1-x}R_xF_{2+x}$, ($M = Ba, Ca, R$ - rare-earth metals) are explained on the basis of the idea of nano-dimensional volumes vary in composition (nano-structuredness). Twinning has been observed in $Ca_8Tm_5F_{31}$ crystals [2]. Inclusions of the Ca_2RF_7 and $Ca_8R_5F_{31}$ ordering phases have been revealed in $Ca_{0.95}R_{0.05}F_{2.05}$ ($R = Y, Yb$) by the electron diffraction [3]. Objects with the moiré contrast are seen in electron micrographs of $Ba_{1-x}Lu_xF_{2+x}$ [4] and $Ba_{1-x}La_xF_{2+x}$ [5] with the CaF_2 structure. Non-matrix reflections correspond to these objects in local electron diffraction patterns, and they have been described as defect volumes (DV) of unknown structure [5]. We try to identify DV in this work. Ion radii difference of Ba^{2+} and La^{3+} is maximal among $M_{1-x}La_xF_{2+x}$ compounds, that simplifies an identification of reflections belonging to volumes of different compositions, but their atomic scattering amplitudes are practically equal, that excludes an observation of composition variations with the help of the z-contrast. In $Ca_{1-x}La_xF_{2+x}$ differences of scattering amplitudes of Ca and La allow to use the z-contrast, and $Ca_{1-x}La_xF_{2+x}$ crystals form another group of studied objects. $Ba_{0.69}La_{0.31}F_{2.31}$, $Ba_{0.75}La_{0.25}F_{2.25}$, $Ba_{0.35}La_{0.65}F_{2.35}$, $Ca_{0.85}La_{0.15}F_{2.15}$, $Ca_{0.95}La_{0.05}F_{2.05}$ have been grown by the crystallization from a melt. $Ba_{1-x}La_xF_{2+x}$ were studied in as-grown and annealed (at 1173 K and 1132 K) states. $Ca_{0.35}La_{0.65}F_{2.35}$ was studied in as-grown and annealed (at 1280 K) states. Other $Ca_{1-x}La_xF_{2+x}$ were studied after annealing at 1280 K. Visible density of DV in $Ba_{1-x}La_xF_{2+x}$ is two orders more after annealing than before it. Although a few anomalies are observed in electron diffraction patterns [6], DV have been identified as twins [5]. This DV nature is confirmed by: *i.* appearance of non-matrix reflections when an orientation of the object deviates from the exact [111] projection (as a result of the capture of reflections of the twin Laue zones), and their disappearance in the exact [111] projection. *ii.* variations of non-matrix reflection nets when projections are changed, *iii.* positions of non-matrix reflections in [111], [011], [255], [114] projections, etc. Increasing twin density during annealing means their deformation origin as a result of relaxation of misfit strains between volumes of different compositions and generation of the $1/6\langle 211 \rangle$ dislocations, but signs of composition stratification in $Ba_{1-x}La_xF_{2+x}$ have not been revealed. However these signs are observed in all $Ca_{1-x}La_xF_{2+x}$, wherein twin density grows also during annealing, although less intensive than in $Ba_{1-x}La_xF_{2+x}$, and wherein nano-twins adjoin with inclusions of a phase with a lattice derivative from the tisonite lattice. Existence of nano-dimensional deformation twins can be considered as the manifestation of the nano-structuredness.

- [1] B.P.Sobolev *et al. Crystallogr. Rep.*, 2002, Vol.47, 201-212
- [2] P.P.Fedorov *et al. J. Solid State Chem.*, 1974, v.9, 368-374
- [3] O. Greis, Habilitation Thesis, University of Heidelberg, West Germany, 1980
- [4] R.Munoz *et al.* 29th Reunion bienal Soc. Espanola de Microscopia, Murcia, Spain, Proc., 1999, 317 - 318
- [5] S.K. Maksimov *et al. JTP Letters* (in press).
- [6] A.S. Avilov *et al.* (in this proceedings)

s8.m28.p13 **Vacancy Distribution in Maghemite.** E. Sváb¹, Gy. Mészáros¹, Z. Somogyvári¹, K. Krezhov², I. Sajó³, F. Bourée⁴, I. Dézsi⁵, Cs. Fetzter⁵ and Á. Gombkötő⁵, ¹Research Institute for Solid State Physics and Optics, 1525 Budapest, POB 49, Hungary, ²Institute for Nuclear Research and Nuclear Energy, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria, ³Institute of Chemistry, 1525 Budapest, POB 17, Hungary, ⁴Laboratoire Léon Brillouin, CEA/Saclay, 91191 Gif-sur-Yvette, France, ⁵Research Institute for Particle and Nuclear Physics, 1525 Budapest POB 49, Hungary. E-mail: zs@szfki.hu

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Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) serves as the subject of many recent studies on nanomagnetism. However, there have been only few attempts to correlate its microstructure with the size/shape of the grains.

The structure of $\gamma\text{-Fe}_2\text{O}_3$ is closely related to that of magnetite (Fe_3O_4 , inverse spinel, s.g. $Fd\bar{3}m$), but the network of iron atoms is partially depleted containing only ferric ions. The vacancies are dominantly distributed on the octahedral sites, and their basic ordering can be described in s.g. $P4_332$. Eventually, a more complex ordering has been observed, and s.g. $P4_12_12$ was found to identify the lattice symmetry [1], but the detailed structural description has not yet been provided.

We have undertaken a systematic study for the quantitative analysis of maghemite with different shape/size grains, focusing our interest on vacancy distribution. Samples of needle shaped (240nm×30nm), and spherical (17nm and 28nm) grains were prepared by soft chemistry. In order to verify the only presence of Fe^{3+} , charge state Mössbauer measurements were performed. The spectra showed six characteristic lines indicating the lack of Fe^{2+} cations and supported the $\gamma\text{-Fe}_2\text{O}_3$ structure.

Neutron- and X-ray diffraction patterns measured on acicular maghemite have shown several sharp extra peaks in addition to the basic spinel reflections, while such type of extra peaks were not observed for the two other samples.

For the needle shaped $\gamma\text{-Fe}_2\text{O}_3$ sample - from multiprofile Rietveld analysis - we have concluded, that the ordering of vacancies results in the formation of an approximately tripled unit cell with space group $P4_12_12$ even at this small particle size. For the spherical grain sized samples the best fit was obtained by a model, based on random vacancy distribution on the octahedral cation sites. Preliminary results of this work have been reported in [2,3].

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- [1] N. Shmakov, G.N.Kryukova, S.V. Tsibula, A.I. Chuvilin, L.P. Solovyeva, *J. Appl. Cryst.* **28**, 141-145 (1995)
- [2] Z. Somogyvári, E. Sváb, Gy. Mészáros, K. Krezhov, I. Nedkov, I. Sajó, F. Bourée, *Applied Physics A74* [Suppl.], S1077-S1079 (2002)
- [3] Z. Somogyvári, E.Sváb, Gy. Mészáros, K. Krezhov, P. Konstantinov, T. Ungár, J. Gubicza, *Materials Science Forum* 378-381, 771-776 (2001)