P11.01.10

Acta Cryst. (2008). A**64**, C510

Twinning in the adamantine-like quaternary calcogenide Li_2ZnSnS_4; A crystallographic detective story

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Li_2ZnSnS_4 is a diamond-like semiconductor (DLS) material which is of interest as a host structure for the creation of potentially interesting magnetic and photovoltaic materials. The crystal structure of the compound was predicted to adopt the wurtz-stannite structure with all atoms possessing tetrahedral geometries. Initial studies indicated that the structure was disordered but, upon closer examination this "disorder" violated many basic chemical principles. The structure was reevaluated and the apparent "disorder" problem was the result of pseudo-merohedral twinning. The twinning masqueraded as "static disorder". The final result was that the crystal crystallized in the non-centrosymmetric space group *P*n which is a subgroup of the predicted *P*mn2_1. The resulting structure was chemically reasonable and the refinement converged with R_{all} = 1.61 %.

Keywords: diamond-like semiconductor, twinning, wurtz-stannite

P11.03.11

Acta Cryst. (2008). A**64**, C510

Nanoscale structural inhomogeneity at the phase boundary in $Nd_{1-x}Sr_xMnO_3$

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Strongly correlated electron systems are materials with a tremendous amount of application potential for a new electronics. The reason comes from the fact that the physical properties change dramatically by application of external stimuli such as magnetic field, hydrostatic pressure and electric field. The changes arise from a close interplay among spin, charge, and orbital degrees of freedom. Colossal magnetoresistive perovskite manganites, which show a large variety of intriguing phenomena, have made a great contribution to understand the strongly correlated electron systems. The orbital degree of freedom has a critical role to play in the magnetoelectric properties. Moreover, the orbital orderings have an intense effect on the crystal structures through an innate electron-lattice interaction, i.e., Jahn-Teller effect. This indicates the crystal structure analyses can decide the orbital ordering states. Recently, a large magnetoresistance was discovered at the phase boundary of A-type and C-type antiferromagnetic phases in $Nd_{1-x}Sr_xMnO_3$ crystals. We will report that nanoscale structure exists in the orbital ordered phase in the vicinity of the phase boundary, by the combination of transmission electron microscopy and synchrotron X-ray diffraction. The diffraction studies revealed that the nanoscale structure is an orbital disordered state. The electron micrographs show the direct evidence for the presence of the nanoscale structure. This phase is characterized by a nanoscale inhomogeneity but is not a phase separation which has been the much-discussed subject of the colossal magnetoresistance effect.

Keywords: magnetic perovskite materials, magnetic materials, electron microscopy, Lorentz

P11.06.12

Acta Cryst. (2008). A**64**, C510

Crystal structure and magnetic properties of complex oxides $Mg_{4-x}Ni_xNb_2O_9$, x=0-4

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In the $Mg_{4-x}Ni_xNb_2O_9$ (x=0-4) system two ranges of solid solution have been found. One of the solid solutions has a corundum related structure type (space group *P-3c*1); the second one adopts the II-$Ni_4Nb_2O_9$ structure type (space group *Pbcn*). Two samples, $Mg_3NiNb_2O_9$ and $MgNi_3Nb_2O_9$, from the first and the second range respectively, have been selected for a detailed crystal structure and microstructure investigation. The unit cell constants and atomic positions have been determined and refined using neutron powder diffraction data. Structures of $Mg_3NiNb_2O_9$ and $MgNi_3Nb_2O_9$ can be described as layers of hexagonally close packed oxygen atoms with 2/3 of the octahedral sites occupied by metal atoms. In the case of $Mg_3NiNb_2O_9$, cations fill the octahedral sites forming honey-comb pattern. In the case of $MgNi_3Nb_2O_9$, the metal layer with honey-comb pattern alternates two metal layers with chain pattern. Electron diffraction and high resolution transmission electron microscopy from $MgNi_3Nb_2O_9$ crystals identify the presence of planar defects and the intergrowth of several (structurally related) phases, which appear due to rotational staking faults between chain corundum layers. The extent and frequency of these defects suggest the possibility to obtain new modifications of corundum related compounds. The magnetic susceptibility of $Mg_3NiNb_2O_9$, measured in the temperature range T = 2-300 K, shows no indications of magnetic ordering at low temperatures, while for $MgNi_3Nb_2O_9$ there is a magnetic ordering at temperatures below 45.5K. This work was supported by Belgium Science Policy, by the Council for Grants of the President of the Russian Federation for Support of Young Scientists (grant no. MK 84.2007.3) and for Support of Leading Scientific Schools (grant no. NSh − 1170.2008.3).

Keywords: niobates, neutron powder diffraction, electron microscopy

P11.06.13

Acta Cryst. (2008). A**64**, C510−511

RXMS study of non-collinear spin structure of $BaFe_{10}CoTiO_{19}$

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Barium hexaferrite $BaFe_{12}O_{19}$ is ferrimagnetic and has the strong uniaxial magnetic anisotropy. Substitution of some Fe ions by non-magnetic ions results the reduction of the axial anisotropy along the c axis and it makes the substituted Barium-ferrite an attractive material. Our group has reported in the previous paper that we succeeded to observe a magnetic satellite reflection of $BaCoTiFe_{10}O_{19}$ at Fe K edge [1]. The observation verified that the Fe K edge can excite resonantly but indirectly the 3d state of iron and the magnetic resonant enhancement is sufficiently large to study the magnetic order of Fe compounds. In this study we have investigated the magnetic anisotropy change due to the substitution of $BaCoTiFe_{10}O_{19}$ by XMCD and RXMS method at Fe K edge. RXMS experiments were carried out at the BL-3A/6C of Photon Factory. X-rays were circularly-polarized by a transmitted-type phase retarder. Diffraction profiles were measured at wavelengths of λ = 1.7406 and 1.7390 Å. Low-temperature experiments at T = 100 K were performed with the Oxford Cryostream Cooler. The magnetic structure can be determined based on the difference between observed and calculated asymmetry ratios. The observed asymmetrical ratio ΔR_{obs} was obtained for 32 Bragg reflections through the RXMS measurements. The ΔR_{calc} was estimated from the crystal structure factors related to charge, anomalous, magnetic and resonant magnetic scattering terms, based on the structural model. The canting angles of spins were estimated with residual factors of $\Sigma(\Delta R_{obs} - \Delta R_{calc})^2$. The non-collinear spin structure of $BaCoTiFe_{10}O_{19}$ and magnetic anisotropy change due to the substitution will be disscussed.

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Keywords: doped ferrites, magnetic structures, X-ray resonant scattering

P11.06.14

Acta Cryst. (2008). A**64**, C511

Evidence of heterogeneous nucleation of $Nd_2Fe_{14}B$ upon crystallisation of Nd-Fe-B melt-spun ribbons

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This work studies the crystallisation behaviour of melt-spun $Nd_5Fe74B_{18}Cr_3$ nanocomposite magnets. Previous studies [1, 2] showed that the formation of $Nd_2Fe_{14}B$ can be promoted by flash annealing. Our study suggests that an orientation relationship exists between the $Nd_2Fe_{14}B$ and t-Fe_3B. An example of this is shown in Fig. 1. Several other interfaces were examined to consolidate our finding that the orientation relationship of <110>t-Fe_3B//<110>$Nd_2Fe_{14}B$ exists in the flash annealed ribbon. A similar orientation relationship was previously reported by Tomida et al. [3]. Our work confirms that $Nd_2Fe_{14}B$ forms via heterogeneous nucleation and that its orientation is related to t-Fe_3B.

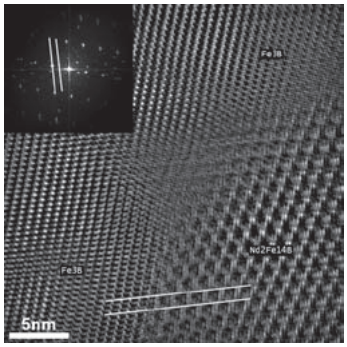

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Fig. 1: A Fourier-filtered high resolution TEM image of adjacent $Nd_2Fe_{14}B$ and t-Fe_3B grains in a nanocrystallised melt-spun Nd-Fe-B ribbon.

Keywords: nucleation and crystal growth mechanisms, nanocrystalline materials, amorphous crystalline transition

P11.06.15

Acta Cryst. (2008). A**64**, C511

Resonant X-ray scattering study on the cation distribution of $BaTiAFe_{10}O_{19}$ (A=Mn,Co)

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The site occupancy of Ti, Mn, Fe and Co ions among five independent Fe sites of M-type barium hexaferrites has been determined by the resonant x-ray scattering method, which uses the difference in anomalus scattering factor f' and is a useful tool to determine the site occupancy among the atoms having similar atomic numbers. The magnetic anisotropy of the end-member $BaFe_{12}O_{19}$ becomes suitable for perpendicular magnetic recording and microwave absorbers when it is optimized by substituting Fe^{3+} ions for several magnetic and/or non-magnetic ions. The hexagonal ferrite structure has tetrahedral $4f_1$, bipyramidal 2b, and octahedral 2a, $4f_2$ and 12k sites. It is reported that the ordering temperature and saturation magnetization are different between types of doping atom and the magneto-crystalline anisotropy may be correlated to the substitution on the bipyramidal site. Thus, it is important to determine the site occupancy of such ions as Ti, Mn and Co for the M-type barium ferrites. Single crystals of $BaTiCoFe_{10}O_{19}$ and $BaTiMnFe_{10}O_{19}$ ferrites were synthesized to cool slowly the powder crystals for 10 days from T = 1623 K. Conventional and synchrotron x-ray diffraction experiments were carried out using Rigaku AFC-7R and PF-BL10A four-circle diffractometers, respectively. The structural parameters of $BaTiAFe_{10}O_{19}$ (A=Mn, Co) were determined using the Mo Kα data by a full-matrix least-squares software, RADY. The site occupancy of Fe and Co ions was determined with the anomalous scattering effects at wavelengths of λ = 1.7480 and 1.6132 Å, while that of Ti ions was determined based on the data set measured with Mo Kα radiation. The relationship between the occupancy parameters and structural characteristics will be discussed.

Keywords: ferrites, resonant scattering, cation distribution