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A compositionally and displacively disordered, Bi-based pyrochlore phase found in a range of ternary  $\text{Bi}_2\text{O}_3\text{-M}^{2+}\text{-Nb}_2\text{O}_5$  systems has been the subject of much recent interest as a result of its relatively low sintering temperatures and often excellent dielectric properties, including electric field tuneability. In this study, two such  $A_2B_2\text{O}(1)_6\text{O}(2)_1$  pyrochlore type phases of stoichiometry  $(\text{Bi}_{0.825}\text{Ni}_{0.125}\text{O}_{0.05})_2(\text{Ni}_{0.25}\text{Nb}_{0.75})_2\text{O}_7$  (BNN) and  $(\text{Bi}_{0.835}\text{Mg}_{0.085}\text{O}_{0.08})_2(\text{Mg}_{0.235}\text{Nb}_{0.765})_2\text{O}_7$  (BMN) have been synthesized via solid-state reaction. Their average as well as their local structure have been investigated by means of Rietveld refinement of neutron powder diffraction data combined with an study of structured diffuse intensity via electron diffraction. The refined average structures of both phases show large amplitude Atomic Displacement Parameters (ADP's) for the atoms occupying the *A* and O(2) sites of the ideal pyrochlore structure. A disordered model, involving splitting of the  $\text{Bi}^{3+}/\text{M}^{2+}$  atoms on the *A*-site from the 16*d* to the 96*h* and of the O(1) atoms from the 8*b* on to the 32*e* positions was found to significantly improve the average structure refinements as well as substantially reduce the refined *A*-site ADP's. A highly structured characteristic diffuse intensity distribution was found in electron diffraction patterns of both phases and was partially interpreted in terms of large amplitude rotations of the O(2)*A*<sub>2</sub> tetrahedral framework,  $\beta$ -cristobalite-type sub-structure of the ideal pyrochlore structure. The BNN and BMN show relatively high dielectric permittivities at room temperature and at 1MHz, 116 and 151 respectively. Their dielectric loss tangents under the same conditions were also very good *i.e.* as low as 0.00065 and 0.00042.

Keywords: bismuth compounds, local structure, dielectric properties

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### Structural study of Co-doped zinc aluminate

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Zinc aluminate,  $\text{ZnAl}_2\text{O}_4$ , is a wide-band-gap semiconductor transparent for light wavelengths greater than 320 nm [1]. When doped with  $\text{Co}^{2+}$ ,  $\text{Mn}^{3+}$  or rare-earth ions it exhibits luminescence and can be used as a cathodoluminescent material [2].  $\text{ZnAl}_2\text{O}_4$  possesses a spinel structure, the space group Fd-3m. Its unit cell contains 32 oxygen atoms in cubic close packing, 16 octahedral sites occupied by Al cations and 8 tetrahedral sites occupied by Zn cations [3]. Powder samples of gahnite doped with 0-100 at% Co (on account of Zn) were prepared by a sol-gel technique and additionally annealed at 800°C for 2 h. Structural changes due to Co incorporation in zinc aluminate lattice were studied by XRD and crystal structures were refined by the Rietveld method. The XRD patterns revealed that the samples had spinel type structure. Lattice parameter *a* for undoped  $\text{ZnAl}_2\text{O}_4$  agreed well with the literature data [3]. In doped samples it increased with Co-doping level. Considering the ionic radii for 4-coordinated  $\text{Zn}^{2+}$  (0.060 nm), 4-coordinated  $\text{Co}^{2+}$  (0.058 nm), 6-coordinated  $\text{Al}^{3+}$  (0.0535 nm) and 6-coordinated  $\text{Co}^{2+}$  (0.065 nm) it follows that the unit cell expansion on Co-doping could be induced by cobalt substitution for octahedral aluminum. However, all prepared samples were blue powders which indicated that some amount of  $\text{Co}^{2+}$  should be present in tetrahedral sites (substituting for Zn), but

not influencing the general trend of lattice expansion. The Rietveld structure refinement confirmed such Co-doping mechanism.

1. K. E. Sickfaus and J. M. Wills, *J. Am. Ceram. Soc.* 82 (1998) 3279.
2. G. Müller, *Electroluminescence II*, Semiconductor and Semimetal, Academic Press (2002).
3. P. Fischer, *Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie* 124 (1967) 275.ü

Keywords: co-doped  $\text{ZnAl}_2\text{O}_4$ , X-ray powder diffraction, Rietveld structure refinement

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### Effect of tin level on microstructure of tin-doped indium oxide

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Tin-doped  $\text{In}_2\text{O}_3$  (ITO) is a transparent conductive oxide [1]. Its electrical and optical properties are associated with microstructure as well as with the preparation methods [2]. Both  $\text{In}_2\text{O}_3$  and ITO crystallize in a cubic bixbyite-type structure [3]. Recently, a detailed structural study of ITO has been reported [4]. Powder ITO samples with Sn doping level up to 12.3 at% were prepared by a sol-gel technique from  $\text{InCl}_3$  and  $\text{SnCl}_4$ . The samples were examined by XRD and TEM. Diffraction lines were broadened. The line broadening increased with Sn content. Analysis of line broadening was performed in the Rietveld structure refinement by the PANalytical X'Pert HighScore Plus program. Silicon powder was used as a size-strain standard. Crystallite sizes decreased from 25.5 to 16.8 nm, while strain increased from 0.112 to 0.369 %, as Sn level increased from 0 to 12.3 at%. The interplanar distances, *d*, in the samples determined by the selected area electron diffraction (SAED) agreed with XRD data. SAED showed that the observed regions appear to be nanocrystalline with a bixbyite-type structure, giving a strong evidence on incorporation of Sn in the starting structure of  $\text{In}_2\text{O}_3$ . TEM studies proved that ITO samples contained nanosized particles/grains. The grains had nearly spherical shape at lower tin level, while at higher level (>8 at%) they were elongated. The crystallite sizes determined by TEM well agreed with those obtained from XRD. HRTEM gave an additional insight into ITO microstructure.

1. K. L. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* 102 (1983) 1.
2. Y. Shigesato, D. C. Paine, *Thin Solid Films* 238 (1994) 44.
3. M. Marezio, *Acta Cryst.* 20 (1966) 723.
4. J. Popovic, E. Tkalcec, B. Grzeta, C. Goebbert, V. Ksenofontov, M. Takeda, *Z. Kristallogr. Suppl.* 26 (2007) 489.

Keywords: Sn-doped  $\text{In}_2\text{O}_3$ , X-ray diffraction, transmission electron microscopy

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### Crystal structure and site occupancy of boron in synthetic high-pressure spinel $\text{MgAl}_{2-x}\text{B}_x\text{O}_4$

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Single crystals of  $MgAl_{2-x}B_xO_4$  ( $x = 0.11$  and  $0.13$ ) spinel were synthesized under 11 GPa and 1873-1273 K using a large volume split sphere-type multi-anvil apparatus. These crystals were ascertained to satisfy the systematic absence of space group  $Fd\bar{3}m$  from precession photographs. Crystal structure refinements were carried to determine the site occupancy of cations and Debye-Waller factors in spinel structure. The R factors for  $x = 0.11$  and  $x = 0.13$  were 2.97 % and 2.52 %, respectively. Based on the site preference refinements and observed bond length of each site, the chemical formula of the B-bearing spinels are  $(Mg_{0.62}, Al_{0.38})[Mg_{0.60}, Al_{1.29}, B_{0.11}]O_4$  and  $(Mg_{0.63}, Al_{0.37})[Mg_{0.63}, Al_{1.24}, B_{0.13}]O_4$ , respectively. All  $B^{3+}$  occupy the octahedral site in the synthetic B-bearing spinels. These results are very important; the small B ion does not occupy the small tetrahedral site, but it occupies the large octahedral site. When we compare the  $MgAl_2O_4$  spinel end-member, disorder which can also be detected by Debye-Waller factors is largely increased with boron contents. The large octahedral site in normal  $MgAl_2O_4$  spinel is preferred by smaller Al ion than larger Mg ion. Moreover, the smallest B ion gives priority to the octahedral site most in the Mg-Al-B system. The peculiar site preference depends greatly on the host  $MgAl_2O_4$  spinel structure with high symmetry. Such a feature is not observed in olivine structure of the Mg-Al-B system.

Keywords: spinel, high pressure, powder and single crystal diffraction

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#### Magnetic and structural investigations of nanocrystalline nickel ferrite $NiFe_2O_4$

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Nickel ferrite is an important high frequency magnetic material due to its ultrahigh resistivity. Nanoparticles of  $NiFe_2O_4$  ferrite have been synthesized by the chemical co-precipitation of the amorphous metal hydroxides (under controlled pH values). The prepared powders have been sintered at 800°C. Room temperature X-ray measurements of the prepared samples of  $NiFe_2O_4$  reveal the production of single cubic phase with average particle size of about 30 nm. The lattice parameters, the oxygen position and the cation distribution have been determined by using Rietveld analysis. The results of Mossbauer Effect spectroscopy (ME) and the Vibrating Sample Magnetometer (VSM) indicate the correlation between the magnetic properties and the nanocrystallinity of the investigated nickel ferrite.

Keywords: nanoparticles, ferrites, magnetization

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#### X-ray structural study of intercalation compound $M_xTiS_2$ ( $M=Ni, Co$ )

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Transition-metal intercalated titanium disulfides  $M_xTiS_2$  have various structures and characteristic physical properties depending on the kind or composition of intercalated atoms M. It is reported that long-range ordered structure, short-range ordered structure and staging structure of intercalated atoms appear in  $M_xTiS_2$ . However, there are few detailed structural studies of  $Ni_xTiS_2$  and  $Co_xTiS_2$  until now. Single and polycrystalline crystals of  $Ni_xTiS_2$  and  $Co_xTiS_2$  were grown in evacuated silica tubes by chemical vapor transport method using iodine as a transport gas. M compositions x were determined by electron probe micro analysis (EPMA). Both superlattice reflections and diffuse scattering, depending on x, were observed by electron diffraction and single-crystal X-ray diffraction methods. X-ray intensity data were collected at room temperature with the use of an automatic four-circle diffractometer. Crystal structure refinements and electron density distribution analysis by maximum entropy method of  $Ni_xTiS_2$  and  $Co_xTiS_2$  were performed. Intercalated atoms occupy octahedral sites and tetrahedral sites in the van der Waals gap. Lattice parameter of the compounds was decreasing with increasing the intercalated M atoms. The covalent electron exists between Ti, M and S atoms. Further, order-disorder transition phenomena of intercalated atoms were observed by high temperature *in-situ* powder X-ray diffraction and differential scanning calorimetry (DSC) measurements.

Keywords: intercalation compounds, sulfides, crystal structures

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#### A synchrotron powder diffraction study for luminescent materials

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The crystal structure of some luminescent materials were solved *ab initio* from synchrotron powder data without preliminary knowledge of the chemical formula. The time resolved luminescence and concentration quenching behavior for the phosphors were also examined. Each deconvoluted Gaussian peak in the emission spectra was assigned to its corresponding crystallographic site with the assistance of density functional theory (DFT) calculations. The thermal stability and the color purity were also discussed from the crystallographic analysis.

Keywords: luminescence, *ab initio* structure determination, synchrotron