Australia, E-mail：bnguyen@rsc.anu.edu.au

A compositionally and displacively disordered, Bi-based pyrochlore phase found in a range of ternary Bi_2O_3-$M^{2+}O$-Nb_2O_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 $A_2B_2O(1)_6O(2)_1$ pyrochlore type phases of stoichiometry $(Bi_{0.825}Ni_{0.125}\square_{0.05})_2(Ni_{0.25}Nb_{0.75})_2O_7$ (BNN) and $(Bi_{0.835}Mg_{0.085}\square_{0.08})_2(Mg_{0.235}Nb_{0.765})_2O_7$ (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 Bi^{3+}/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_2 tetrahedral framework, β-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

Jasminka Popovic[1], Emilija Tkalcec[2], Biserka Grzeta[1], Stanislav Kurajica[2]

[1]Rudjer Boskovic Institute, Division of Materials Physics, Bijenicka 54, Zagreb, Croatia, HR-10000, Croatia (Hrvatska), [2]Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 20, HR-10000 Zagreb, Croatia (Hrvatska), E-mail：jpopovic@irb.hr

Zinc aluminate, $ZnAl_2O_4$, is a wide-band-gap semiconductor transparent for light wavelengths greater that 320 nm [1]. When doped with Co^{2+}, Mn^{3+} or rare-earth ions it exhibits luminescence and can be used as a cathodoluminescent material [2]. $ZnAl_2O_4$ 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℃ 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 $ZnAl_2O_4$ agreed well with the literature data [3]. In doped samples it increased with Co-doping level. Considering the ionic radii for 4-coordinated Zn^{2+} (0.060 nm), 4-coordinated Co^{2+} (0.058 nm), 6-coordinated Al^{3+} (0.0535 nm) and 6-coordinated 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 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 $ZnAl_2O_4$, X-ray powder diffraction, Rietveld structure refinement

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

Biserka Grzeta[1], Jasminka Popovic[1], Emilija Tkalcec[2], Andjelka M. Tonejc[3], Mirjana Bijelic[3]

[1]Rudjer Boskovic Institute, Division of Materials Physics, Bijenicka cesta 54, P.O. Box 180, Zagreb, HR-10002, Croatia (Hrvatska), [2]Faculty of Chemical Engineering and Technology, University of Zagreb, Marulicev trg 20, Zagreb, HR-10000, Croatia (Hrvatska), [3]Faculty of Science, University of Zagreb, Bijenicka cesta 32, Zagreb, HR-10000, Croatia (Hrvatska), E-mail：grzeta@irb.hr

Tin-doped In_2O_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 In_2O_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 $InCl_3$ and $SnCl_4$. 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 In_2O_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 In_2O_3, X-ray diffraction, transmission electron microscopy

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Crystal structure and site occupancy of boron in synthetic high-pressure spinel $MgAl_{2-x}B_xO_4$

Shunsuke Sakai[1], Kazumasa Sugiyama[1], Akira Yoshiasa[2],