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Keywords: mesoporous materials, adsorption, charge density

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Nanoporous metal phosphates with photoluminescence property

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For the past two decades, research about metal silicate and phosphate with microporous structure has always played an important role in the field of materials chemistry due to their wide application potential from traditional catalyst, molecular sieve and ion exchange to recently developed low-k materials and zeolitic dye laser. In recent years, we have discovered several gallium phosphates containing transition metal with pore size around 1 nm and intriguing photoluminescence property. For example, 24-member ring NTHU-11 and the first organo-metallo phosphates NTHU-2,2 can emit blue light when excited with UV light. The photoluminescence phenomenon is a new property of nanoporous metal phosphate with emission mechanism apparently different from that of existing inorganic phosphor since the later is doped with metal activator or added with sensitizer in host lattice in order to illuminate. At present, the photoluminescence property of nanoporous metal phosphate is substantiated. Besides blue light, zinc gallophosphate that can emit yellow light or even white light have been synthesized. In this presentation, we are going to present a series of nanoporous gallophosphates and zinc gallophosphates via the synthetic strategy of employing the large 4,4'-trimethylenedipyridine (tmdp) amine as a template. Their structures will be described and photoluminescence property will be examined.

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Keywords: metal phosphate, photoluminescence, nanoporous

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Crystal growth, structure and physical properties of $Ln(\text{CuGa})_{13}$ compounds ($Ln = \text{La-Nd, Eu}$)

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Single crystals of $Ln(\text{CuGa})_{13}$ ($Ln = \text{La-Nd, Eu}$) compounds have been synthesized by flux-growth methods and characterized by single

crystal X-ray diffraction. $Ln(\text{CuGa})_{13}$ ($Ln = \text{La-Nd, Eu}$), which are isostructural to NaZn_{13} , crystallize in the cubic $Fm-3c$ (No. 226) space group, with $Z = 8$ and lattice parameters $a \sim 11.8 \text{ \AA}$. Magnetic susceptibility data show paramagnetic behavior down to 2 K for Ce, Pr, Nd, and Eu compound, respectively. Metallic behavior is observed below 300 K for each compound. A large positive magnetoresistance up to 154 % at 9 T is also observed for $\text{Pr}(\text{CuGa})_{13}$. The structure, magnetic, heat capacity and transport properties of these compounds will be presented and compared to $Ln(\text{CuGa})_{12}$ ($Ln = \text{Y, Gd-Er, Yb}$) family of compounds.

Keywords: magnetism, magnetoresistance, flux growth

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Structure and magnetic properties of a iron(III) spin crossover complex

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New complex, $[\text{Fe}(\text{3-OMe-salMen})_2]_2[\text{Ni}(\text{mnt})_2]\text{CH}_3\text{CN}$, (3-OMe-salMen=2-([2-(methyl-amino)ethyl]imino)methyl)-3-methoxyphenol; mnt=maleonitriledithiolate) is synthesized and characterized. (at 298 K, triclinic $P-1$, cell parameters $a = 9.402(2)$, $b = 10.476(2)$, $c = 16.636(3) \text{ \AA}$, $\alpha = 87.17(3)$, $\beta = 77.38(3)$ and $\gamma = 75.21(3)^\circ$. The Fe (III) is an octahedrally coordinated (N_4O_2) by two tridentate ligand. The bond lengths of Fe-N and Fe-O suggests the Fe(III) is in a low spin (LS) state configuration. From the thermally dependent magnetic measurements, the title complex is in the LS state ($S=1/2$) at temperature range of 5~350K. As the temperature higher than 350 K, the compound becomes at HS state (high spin, $S=5/2$) based on the magnetic data. According to the TGA, the spin transition may be due to the removal of the solvent molecule of CH_3CN . The non-solvated species then displays a gradual spin transition between HS and LS with $T_{1/2}$ of 290K. When the non-solvated compound was treated with water vapor, the magnetic property of this hydrated sample appears to have different spin transition temperature at 122K. It is known that solvent molecules sometimes do play important roles in the spin transition; the title complex did show different spin transition behaviors in the presence of CH_3CN or of water as a solvent; the one with acetonitrile prefers in LS at room temperature, however the non-solvated one is in HS at room temperature. With the presence of water, a spin transition occurs at lower temperature. The process of removing and retaking solvent molecule is reversible by referring to powder pattern and magnetic measurements. The structure and magnetic relationship, especially in the presence or absence of solvent molecules, is currently under investigation.

Keywords: spin crossover, iron (III), reversible

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The local structure & dielectric properties of the cubic pyrochlore $\text{Bi}_{1.67}\text{M}_{0.75}\text{Nb}_{1.5}\text{O}_7$ ($\text{M}=\text{Mg}$ and Ni)

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A compositionally and displacively disordered, Bi-based pyrochlore phase found in a range of ternary $\text{Bi}_2\text{O}_3\text{-M}^{2+}\text{O-Nb}_2\text{O}_5$ 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 $A_2\text{B}_2\text{O}(1)_6\text{O}(2)_1$ 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*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

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Zinc aluminate, ZnAl_2O_4 , is a wide-band-gap semiconductor transparent for light wavelengths greater than 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°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 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.

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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

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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.

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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 $\text{MgAl}_{2-x}\text{B}_x\text{O}_4$

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