

**P08.14.142***Acta Cryst.* (2008). A64, C462**Jahn-Teller distortions in mixed crystals,  $[\text{Cu}_x\text{Mn}_{1-x}(\text{H}_2\text{O})_4(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2](\text{H}_2\text{O})_2$** Gligor Jovanovski<sup>1,2</sup>, Pance Naumov<sup>1,3</sup>

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The structure of the isomorphous tetraaquabis(saccharinate)metal(II) dihydrates was employed as structurally flexible coordination framework capable of sustaining large internal distortions to study the competitive inclusion of Jahn-Teller (JT) distorted  $d^9$  ions,  $[\text{Cu}(\text{H}_2\text{O})_4(\text{sac})_2]^{2+}$ , and undistorted  $d^5$  ions,  $[\text{Mn}(\text{H}_2\text{O})_4(\text{sac})_2]^{2+}$ , in a series of mixed crystals of composition  $[\text{Cu}_x\text{Mn}_{1-x}(\text{H}_2\text{O})_4(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2](\text{H}_2\text{O})_2$ , under thermodynamically controlled conditions (sac = saccharinate anion,  $\text{C}_7\text{H}_4\text{NO}_3\text{S}^-$ ). Probing of the metal content of the solid phase showed a two-regime inclusion profile: increasing of the ratio of the distorted cation relative to the undistorted one in the solution phase of up to about 35% results in linear dependence and preferred inclusion of the former with maximum concentration of 100% in the crystal, and complete exclusion of the undistorted ion above that point. A mixed crystal with highest copper ratio of 63% was obtained from solution with 25% copper, which under the  $P2_1/c$  crystal symmetry corresponds to sustainable integrity of the undistorted lattice by substitution of up to 2/3 of its sites. This stability limit shows that four out of six sites around each  $[\text{Mn}(\text{H}_2\text{O})_4(\text{sac})_2]^{2+}$  ion can be substituted by distorted  $[\text{Cu}(\text{H}_2\text{O})_4(\text{sac})_2]^{2+}$  guests under conditions of thermodynamically controlled, statistically averaged exchange. The undistorted ion is tolerant toward inclusion of the strongly distorted guests, whereas the distorted ion is exclusive toward the undistorted ion. Along with the expectation from the JT theory, structural refinement of seven crystals, including a mixed crystal with composition of  $[\text{Cu}_{0.126}\text{Mn}_{0.874}(\text{H}_2\text{O})_4(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2](\text{H}_2\text{O})_2$ , showed that metal-ligand distances are significantly affected by the metal substitution.

Keywords: copper and manganese saccharinates, solid solutions, Jahn-Teller distortions

**P08.14.143***Acta Cryst.* (2008). A64, C462**Evolution of phonon spectra and elastic constants from graphene to graphite**

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We present a unified theory of the phonon dispersions and elastic properties of graphene, graphite and graphene multilayer systems. Starting from a fifth-nearest neighbor force constants model derived from full in-plane phonon dispersions of graphite [Mohr et al., Phys. Rev. B 76, 035439 (2007)] we use Born's long wavelength method to calculate the tension and bending coefficients of graphene. Extending the model by interplanar interactions, we study the phonon dispersions and the elastic constants of graphite and the phonon spectra of graphene multilayers. We find that the inner displacement terms due to sublattice shifts between inequivalent C atoms are quantitatively important in determining the elasto-mechanical properties of graphene but not of graphite. We investigate the

evolution from graphene to graphite by studying the increase of the  $wB2g1(N)$  rigid planes optical mode as a function of the number of layers  $N$ . At  $N = 10$  the graphite value  $wB2g1$  127  $\text{cm}^{-1}$  is practically reached near  $N = 15$ .

Keywords: graphene, graphite, phonons, elastic constants

**P08.14.144***Acta Cryst.* (2008). A64, C462**Lattice strain tuning in  $\text{SrTiO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  films by inverse piezoelectric effect of PMN-PT wafer**Alexandr A. Levin<sup>1</sup>, Hartmut Stoecker<sup>1</sup>, Stephan Ritter<sup>1</sup>, Torsten Weissbach<sup>1</sup>, Orkidia Bilani-Zeneli<sup>2</sup>, Dirk C. Meyer<sup>1</sup>

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Due to properties favorable for technical applications, ferroic nanometer film composites with perovskite-related structures have received great attention. In this report, the results of an *in-situ* X-Ray Diffraction (XRD) investigation under the influence of a static electric field are presented for 30 nm...100 nm  $\text{SrTiO}_3$  (STO; cubic perovskite; paraelectric)/30 nm  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO; trigonal perovskite-related lattice; ferromagnetic) film composites grown on a (001)  $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$ -28%  $\text{PbTiO}_3$  (PMN-PT; pseudo-cubic rhombohedral perovskite; relaxor ferroelectric (RFE) with high piezoelectric properties) wafer. XRD reflection profiles ( $\text{Cu-K}\alpha$ ) of the 001, 002 and 013 PMN-PT (corresponding to attenuation depths of 500 nm, 1000 nm and 1300 nm, resp.) as well as 002 LSMO (pseudo-cubic indexing) and 002 and 013 STO were recorded for every stage of electric field strength  $E$ . The lattice strain  $s(E)$  dependence obtained for the bulk of the PMN-PT substrate exhibited a butterfly-like low-hysteresis shape, which is typical for a RFE. The piezoelectric lattice strain of the substrate induced strain in the films. Initially, for the sample with 30 nm STO film, the near-surface PMN-PT region and films showed a wide smoothed asymmetrical  $s(E)$ . After extended electric field processing, the sample exhibited a low  $s(E)$  hysteresis similar to bulk PMN-PT. In contrast, the sample with 100 nm STO film exhibited a  $s(E)$  response closer to the bulk material at all stages. The differences in the  $s(E)$  behavior of the STO/LSMO film composite structure with different thickness of the top STO film are discussed. A conclusion is drawn that the strained state of the 30 nm...100 nm STO/30 nm LSMO films can be effectively controlled by the inverse piezoelectric effect of the PMN-PT substrate.

Keywords: X-ray diffraction, ferroics, strain

**P08.14.145***Acta Cryst.* (2008). A64, C462-463**Coupling between magnetic and dielectric properties in a triangular lattice antiferromagnet  $\text{CuCrO}_2$** Kenta Kimura<sup>1</sup>, Hiroyuki Nakamura<sup>1</sup>, Kenya Ohgushi<sup>2</sup>, Tsuyoshi Kimura<sup>1</sup>

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Coupling between magnetic and dielectric properties has been attracting much attention in the past few years. Recent experimental

and theoretical studies revealed that noncollinear spiral spin structures breaking the spatial inversion symmetry often make the system ferroelectric. A 120° structure which is the classical ground state in a Heisenberg triangular lattice antiferromagnet (TLA) also breaks the inversion symmetry, being another candidate for inducing ferroelectricity. To test this prediction, we investigated magnetic and dielectric properties of a typical TLA  $\text{CuCrO}_2$  showing the 120° structure with easy axis anisotropy [1]. Single crystals of  $\text{CuCrO}_2$  were successfully grown by a flux method. Temperature profile of the magnetic susceptibility shows an anomaly at  $T_N \approx 24.5\text{K}$ , due to the ordering into the 120° structure. Dielectric constant perpendicular to the  $c$  axis shows a sharp peak near  $T_N$ . In addition, spontaneous polarization perpendicular to the  $c$  axis emerges below  $T_N$ . The sign reversal of spontaneous polarization by applying electric field is also observed below  $T_N$ . These results ensure the emergence of ferroelectricity induced by 120° structure in  $\text{CuCrO}_2$ . Furthermore, the ferroelectric property is affected by an application of magnetic fields. In the presentation, we show detailed experimental results, and discuss the coupling between the magnetic and dielectric properties in the TLA  $\text{CuCrO}_2$ .

[1] H. Kadowaki, H. Kikuchi and Y. Ajiro, *J. Phys.: Condens. Matter* 2, 4485 (1990)

Keywords: strongly correlated systems, magnetoelectricity, magnetic frustration

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#### Location of proton in proton conducting perovskite oxides $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ and $\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{2.9}$

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Some oxides with perovskite structure have high proton conductivity of  $10^{-2}$  -  $10^{-3}$   $\text{Scm}^{-1}$ . However, the locations of proton, the proton conduction path, and the thermodynamic properties have not been clarified yet. In the present study, the location of proton and the lattice vibrations have been studied by neutron diffraction and heat capacity measurements. The samples of a proton conducting mixed perovskite oxide  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$  and a simple perovskite oxide  $\text{BaZr}_{0.8}\text{Sc}_{0.2}\text{O}_{2.9}$  were synthesized by a method of solid-state reaction. The neutron diffraction experiments were performed using HRPD at JAEA for the deuterated and dried samples. All the neutron diffraction peaks of the deuterated samples are shifted to lower angles comparing with the dried samples. This attributes to the expansion of the lattice due to the introduction of oxide and deuterium ions into the dry samples. The location of deuterium was analyzed by Rietveld method and maximum entropy method (MEM). The MEM shows that deuterium exists at 96j site in  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ , which leans to the Ca/Nb mixed site, and 12h site in  $\text{Zr}_{0.8}\text{Sc}_{0.2}\text{O}_{2.9}$ , which is similar to that of the other simple perovskite-type proton conductors. The shift of OD groups slightly toward the opposite side of deuterium was observed in both compounds. The location of proton was discussed comparing with the results of *ab-initio* structure calculations. The results of heat capacity measurements are also discussed in terms of the change of the lattice vibrations due to the introduction of oxide and hydrogen ions.

Keywords: neutron diffraction, proton conductivity, *ab-initio* calculations

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#### Solution SAXS and NMR on the domain orientation and binding of the components of human BCKD complex

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The mammalian mitochondrial branched-chain- $\alpha$ -ketoacid dehydrogenase (BCKD) complex, containing E1, E2, and E3 subunits, catalyzes the oxidative decarboxylation of branched-chain- $\alpha$ -ketoacids derived from leucine, isoleucine, and valine, hence, gives rise to branched-chain acyl-CoAs. The transacylase subunit (E2) of BCKD complex carries three independently folded domains linked together by flexible loops: the hbLBD (a.a. 1-84), hbSBD (a.a. 104-152), and C-terminal inner-core domain hbICD (aa.168-395). Both hbLBD and hbSBD domains play central roles in substrate channeling and substrate recognition, which functions relate closely to their structures and relative orientations in the BCKD complex. With solution NMR, we have extracted the individual structures of hbLBD and hbSBD domains, respectively. Whereas the tertiary structure of the full di-domain hbDD (aa. 1-168), consisting of hbLBD, hbSBD, and the linker region, in a linear-like arrangement, is resolved for the first time by solution small angle X-ray scattering (SAXS) with the rigid body refinement, based on the two structures of hbLBD and hbSBD individually determined by NMR. Furthermore, SAXS profiles measured for the E1 component before and after its binding to the hbDD, imply that hbLBD is less confined than hbSBD, in the binding. The result helps in differentiating the two interaction modes of hbDD-E1 and hbDD-E3 in the BCKD complex.

Keywords: SAXS, protein complex structure, NMR

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#### Crystal and local structural studies of superionic conductor cubic CuI

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Crystalline superionic conductor of copper iodide (CuI) with cubic symmetry has been studied by time-of-flight (TOF) neutron powder diffraction in  $\gamma$ -phase (300 K) and  $\alpha$ -phase (773 K). Crystal structure of the both phases were examined by the Rietveld method combined with maximum entropy method (MEM) technique using single-atom and split-atom structural models with the F-43m ( $\gamma$ -phase) and Fm-3m ( $\alpha$ -phase) symmetry, respectively. Local structure analyses were also carried out by employing pair distribution function (PDF) and the reverse Monte Carlo (RMC) techniques to model the disorder of the mobile copper ions. The crystal structure analysis revealed