a different conditions and studied by X-ray diffraction.

The $(Na_{0.5}La_{0.5})MoO_4$ with $|\Delta r_{(Na\text{-}La)}|=r_{Na}-r_R=0.02$Å (r-ionic radius) has the scheelite structure (sp. gr. $I4_1/a$), in contrast to the $(Na_{0.5}Gd_{0.5})WO_4$ ($|\Delta r_{(Na\text{-}Gd)}|=0.13$Å) and $(Na,Gd,Yb)WO_4$ ($r_{Na}>r_{Gd}>r_{Yb}$) with the pseudo-tetragonal superstructure unit cell with double parameters. The non-annealed (growth in Ar) and annealed by 1000ºC for 4 days in air crystals of $(Na_{0.500}La_{0.445}Ce_{0.05}Er_{0.005})MoO_4$ nominal composition have "enantiomorphic" structures. The annealed by 1000ºC for 24 h in air crystal of $(Na_{0.500}La_{0.295}Ce_{0.20}Er_{0.005})MoO_4$ has the scheelite structure. A statistical distribution of oxygen on two sites of structure of non-annealed (growth in $99\%N_2+1\%O_2$) and annealed by 700ºC for 100 h in air of these crystals was found.

Keywords: sheelite, structure, properties

P.08.14.19

Acta Cryst. (2005). A**61**, C345

Lattice Parameters Measurements of $YBa_2Cu_3O_{7-\delta}$ Superconductors Prepared under Various Forming Pressures using X-ray Diffraction Technique

Hafiz Homeida, *Accademy of Medical Science and Technology, Khartoum, Sudan.* E-mail: hafizhomeida@yahoo.com

The effect of pressure on the critical temperature T_c is studied for $YBa_2\ Cu_3\ O_{7-\delta}$ compounds prepared under various forming pressures. A systematic decrease in lattice parameters is observed with forming pressure. Resistivity measurements show an increase of the onset temperature T_{cO} with forming pressure. A value of $dT_{cO}/dP \approx (0.070 \pm 0.010) \times 10^{-8}$ K/Pa is determined. A new mechanism based on the variation of the interlayer tunneling integral $t_\perp$ is used to analyse the experiment results.

Keywords: superconductors, lattice, parameters

P.08.14.20

Acta Cryst. (2005). A**61**, C345

On a New Wave Type Generated in Deforming Metal Crystals

Svetlana A. Barannikova, Lev B. Zuev, *Institute of Strength Physics and Materials Science, SB RAS, Tomsk, Russia.* E-mail: bsa@ispms.tsc.ru

Quasi-static deformation was studied on tensile fcc, bcc and hcp single crystals by holographic technique. It iahs been found that slow wave processes are generated in the deforming material. These involve concerted motion and temporal evolution of local flow nuclei whose nature is defined by micro-scale self-organization mechanisms.

The wave pattern type is determined for a given flow stage by work hardening law $\theta(\varepsilon)$, where $\theta=G^{-1}\cdot d\sigma/d\varepsilon$ is the work hardening coefficient; G, the shear modulus; σ, the plastic flow stress and ε, the deformation. The waves are characterized by wavelength $5\leq\lambda\leq10$mm propagation rate $10^{-5}\leq V\leq10^{-4}$m/s and frequency $10^{-3}\leq\omega\leq10^{-2}$Hz. The waves are found to exhibit the following regular features: wave rate $V=\Xi/\theta$, where $\Xi=const\approx10^{-7}$m/s; quadratic dispersion law $\omega(k)=1+k^2$ and a concurrent decreases in the entropy of material by wave generation $\Delta S<0$.

These can be likened to quasi-particles whose mass as calculated from the de Broglie equation for all the monocrystals tested $m=h/V\approx1.5$amu and dimensionless mass $\mu=m/A$ (A is the respective metal's atomic mass) are found to grow with the number of electrons n per metal unit cell as $\mu=\mu_0+\kappa n$.

Thus it is contended that by plastic flow slow waves would be generated spontaneously in a single metallic crystal, which is regarded as a complex thermodynamically open system. The nature of these wave processes and their role on plastic deformation are discussed.

Keywords: plasticity, wavelength, entropy

P.08.14.21

Acta Cryst. (2005). A**61**, C345

Structure and Magnetic Properties of 3-substituted-5-(2-pyridyl) Pyrazole Metal(II) Complexes

Lai-Chin Wu[a], Gene-Hsiang Lee[a], Yun Chi[c], Chih-Chieh Wang[b], Yu Wang[a], [a]*Department of Chemistry, National Taiwan University, Taipei, Taiwan.* [b]*Department of Chemistry, Soochow University, Taipei, Taiwan.* [c]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan.* E-mail: d92223012@ntu.edu.tw

Five substituted pyridyl-pyrazole metal(II) complexes, $[Fe(Hpp\text{-}But)_3(X)_2]$, $X=ClO_4^-$ (***1***), BF_4^- (***2***), $[Co(Hpp\text{-}But)_3(ClO_4)_2]$ (***3***), *cis*-$[Fe(Hpp\text{-}\phi)_2(NCS)_2]$ (***4***) and *trans*-$[Fe(Hpp\text{-}\phi)_2(NCS)_2]\cdot(H_2O)_2$ (***5***), were synthesized. Molecular and crystal structures of these complexes were investigated by single crystal structure analysis. The comparison in molecular structures between these complexes will be presented. The magnetic properties were studied by SQUID magnetometer.

Complex (***1***) and (***2***), with t-Butyl substituted group, are spin-crossover compounds. Complex (***1***) is a gradual but completed spin transition from RT to 200K. The Fe $L_{2,3}$-edge of iron(II) of (***1***) and (***2***) X-ray absorption spectroscopy are studied using synchrotron radiation. The apparent change due to HS-LS transition will be presented in coordination geometry around Fe and in Fe core electron excitation. However, compound (***4***) and (***5***), with substituted phenyl group, show no spin transition phenomenon within the temperature range studied. The relationship between structure and magnetic properties will be discussed.

Keywords: structure-magnetism relationships, spin crossover, magnetism

P.08.14.22

Acta Cryst. (2005). A**61**, C345

X-ray Absorption Studies of Fe-btr Spin Crossover Complexes

Yen-Chen Lin[a], Sébastien Pillet[b], I-Jui Hsu[a], Yu Wang[a], [a]*National Taiwan University, Taipei, Taiwan.* [b]*Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, UniVersité Henri Poincaré, UMR CNRS 7036, 54506 VandoeuVre les Nancy, France.* E-mail: sirius8@gmail.com

The aim of this work is to take the advantage of the X-ray absorption spectroscopy to get insight into the evolution of electronic configuration in HS and LS states of the specific absorption atoms at various temperatures and also in the LIESST state. Three Fe spin crossover complexes, (**1**) $Fe(btr)_2(NCS)_2\cdot H_2O$[1], (**2**) $Fe(btr)_3(ClO_4)_2$[2] and a Co doped $Fe_xCo_{1-x}(btr)_2(NCS)_2\cdot H_2O$[3] (**3**) were chosen to be studied. With temperature changing **1** shows an abrupt spin transition with a hysteresis of 25K ($T_{1/2}\downarrow = 119.8$K and $T_{1/2}\uparrow = 145.1$K) while **2** was found to behave as a two-step spin crossover complex.

K-edge absorption spectra of **1** and **3** were collected in both RT (HS) and 16K (LS) and also after irradiating by a laser light of 532 nm. The existence of the HS-2 after irradiation in both **1** and **3** is varified by Fe K-edge spectra. However, spin transition only occurs at Fe site not at Co site, though they should be situated on the same site.

Fe L-edge spectra of **2** illustrate a two-step spin transition; one is abrupt and the other one is gradual, which is consistent with the results reported earlier.

[1] Vreugdenhil W., et al., *Polyhedron*, 1990, **9**, 2971. [2] Garcia Y., et al., *Inorg. Chem.*,1999, **38**, 4663. [3] Martin J. P., et al., *Inorg. Chem.*, 1994, **33**, 6325. [4] Hannay C., et al., *Inorg. Chem.*, 1997, **36**, 5580. [5] Pillet S., et al., *Eur. Phys. J. B*, 2004, **38**, 541.

Keywords: spin-crossover, X-ray absorption, Fe(II) complexes

P.08.14.23

Acta Cryst. (2005). A**61**, C345-C346

Change of Structure and Properties of System WC-Ti at Mechanical Activation

Victor Ilyasov[a], Anatoly Ryzhkin[a], T. Grigorieva[b], N. Lyakhov[b], S. Tsybulya[c], [a]*Department of Physics, Don State Technical University, Rostov-on-Don.* [b]*Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk.* [c]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia.* E-mail: viily@mail.ru

Tungsten carbide is one of the most interesting representatives carbides transition of metals of maximum groups, which can have as cubic, and hexagonal crystallographic modification. In particular, cubic WC with structure as NaCl has rather wide area homogeneity on carbon and has high temperature melting, hardness and durability, and also propensity to formation double carbides with transitive 3d-metals. The data about peculiarities of the chemical bonding and changes in then electronic structure of the cubic WC at partial replacement of tungsten atoms by titanium atoms in the published literature has not enough for understanding of laws of formation properties of system "WC-Ti". Therefore in the given work the electronic structure and character of chemical bonding in carbide systems WC, $W_{1-x}Ti_xC$ is theoretically investigated. Recently presence lattice as C-, and W-vacancies in WC is shown. At mechanical activation in ball mill of powders WC and Ti, the size of a grain of which makes size about 1…5 micron, it is possible to expect solid-solid of reaction. Our estimations, carried out on basis of quantum-mechanical accounts of their electronic structure, show, that the mechanical properties of the given system can grow. The samples are investigated XRD by a method, analysis of areas coherent dispersion is carried out which are called to supervise changes of structure and properties during mechanical activation. Complex research of crystal and electronic structures of the given system allows to understand the laws of formation of physical properties of new materials.

Keywords: structure-physical properties relationships, tungsten compounds, X-ray powder diffractometry

P.08.14.24

Acta Cryst. (2005). A**61**, C346

Search for Polarons in $Li_{1-5x}Nb_{1-4x}O_{3-y}$. Structural Investigation of the Defect Structure in Thermally Reduced Single Crystals

Jürg Schefer[a], Dominik Schaniel[b], Theo Woike[b], Manfred Wöhlecke[c], Mirco Imlauf[c], [a]*Laboratory for Neutron Scattering, ETH Zürich & PSI, CH-5232 Villigen PSI, Switzerland.* [b]*Institut für Mineralogie, University at Cologne, DE-50674 Köln, Germany.* [c]*Fachbereich Physik, University of Osnabrück, DE-49069 Osnabrück, Germany.* E-mail: Jurg.Schefer@psi.ch

In the search for new complex materials for optical data storage, a main effect to understand is the refraction index. A bigger refraction index separarates the holograms more in space, therefore allowing a higher hologram density in the material. Interesting materials for both, application and basic understanding, are for example $LiNbO_3$, $LiTaO_3$ [1] and sodiumnitroprusside, $Na_2[Fe(CN)_5NO)]2H_2O$ [2].

$Li_{1-5x}Nb_{1-4x}O_{3-y}$ is a widely used material. We are introducing polarons by removing oxygen in order to tune the refraction index. Neutron single crystal diffraction (TriCS, SINQ) has been used in order to determine the structural changes, mostly the determination of the removed oxygen. The results are needed in order to calculate the polaron density. We report on the defect structure of single crystals exposed to vacuum for 24h at 800°C.

[1] Strehlow W.H., et al., *J. Opt. Soc.*, 1974, **64**, 543. [2] Schaniel D., Schefer J., Delley B., Imlau M., Woike Th., *Phys. Rev. B*, 2002, **68**, 104108.

Keywords: optical materials, neutron diffraction, polarons

P.08.14.25

Acta Cryst. (2005). A**61**, C346

Structural Origin of the low Superconducting Anisotropy of Bi,Pb-2212 Crystals

Roman E. Gladyshevskii[a], Nicolas Musolino[b], René Flükiger[b], [a]*Ivan Franko Natl. University of Lviv, Ukraine.* [b]*University of Geneva, Switzerland.* E-mail: Roman.Gladyshevskii@franko.lviv.ua

Systematic investigations were performed with the aim to improve the properties of $Bi_2Sr_2CaCu_2O_8$. The structure of Bi-2212 is modulated, the atom arrangement in the BiO layers changing from square meshes (rocksalt-type) to chains with a given periodicity. Due to the insertion of additional O atoms, the actual composition of these layers is Bi_9O_{10} ($Bi_2O_{2.22}$ per formula unit, leading to a total oxygen content per formula unit 8.22). This deviation from electroneutrality, which is partially compensated for by the presence of Bi^{3+} in the Ca layers, is a crucial parameter for the existence of the superconducting phase. By replacing part of the cations in Bi-2212 by chemically similar cations in a lower oxidation state it is possible to keep the same electron concentration, while removing the additional O atoms, thus suppressing the structural modulation. This was achieved by substituting ~22% of Bi^{3+} by Pb^{2+}. The arrangement of atoms in the BiO layers in modulation-free Bi,Pb-2212 can be considered as distorted rocksalt-type. The cell parameter along the stacking direction is slightly larger for Bi,Pb-2212 than for the Pb-free phase. However, the distance between the two Bi layers is decreased by 0.13 Å, which is in agreement with the fact that these layers are no longer corrugated but planar. The superconducting anisotropy of the Pb-doped crystals was found to be reduced with respect to undoped ones. Consequently, modulation-free Bi,Pb-2212 has an enhanced irreversibility field and a lower relaxation rate than in modulated Bi-2212.

Keywords: high-T_c superconductor, modulated structure, structure-property relationship

P.08.14.26

Acta Cryst. (2005). A**61**, C346

Structure Investigation of Pure and Cr Doped Li_3VO_4

Doretta Capsoni[a], V. Massarotti[a], M. Bini[a], P. Mustarelli[a], C.B. Azzoni[b], P. Galinetto[b], M.C. Mozzati[b], G. Chiodelli[c], [a]*Department of Physical Chemistry "M. Rolla", University of Pavia.* [b]*CNISM - Department of Physics "A. Volta", University of Pavia, Italy,* [c]*CNR-IENI, Pavia.* E-mail: capsoni@unipv.it

Li_3VO_4 finds applications in the fields of optics, electrochemistry (ionic conduction) and electronics. The RT βII form is orthorhombic (S.G. $Pmn2_1$) with LiO_4 tetrahedra larger and more distorted than VO_4 ones; empty sites exist allowing the Li^+ cation migration. Other polymorphs were revealed by increasing temperature up to the melting point. Our study deals with the effect of chromium doping (up to 10% of the V-cationic fraction) on the structure of Li_3VO_4. The structural investigation was carried out by means of XRD, μ-Raman, EPR and ^7Li and ^{51}V MAS-NMR. To study the thermal stability of the solid solutions also HT XRD measurements were performed. XRD and μ-Raman analyses point out that Cr ions can easily substitute on the cationic sites of Li_3VO_4 without evidence of impurity phases. The host crystal structure does not depend on Cr-doping, neither at RT nor at HT. The EPR spectra put into evidence the presence of Cr^{3+} and Cr^{5+}. The combined analysis of EPR and ^7Li and ^{51}V MAS-NMR signals allows us to detect that Cr^{5+} and Cr^{3+} substitute on V^{5+} and Li^+ site respectively. The Cr^{3+} presence on Li site is also compatible with Rietveld refinements and Raman results: such substitution requires vacancies formation on Li sublattice, so increasing the ionic conductivity of the material as demonstrated also by our impedance spectroscopy and thermoelectric power measurements.

Keywords: ionic materials, vanadium compounds, occupancy

P.08.14.27

Acta Cryst. (2005). A**61**, C346-C347

Structures of *C.perfringens* α-toxin mutant, T74I, that Affects its Activity

Sebastien Vachieri[1], Graeme Clarke[2], David S. Moss[1], Richard William Titball[1], Ajit Basak[1], [1]*School of Crystallography, Birkbeck College, London WC1E 7HX, UK.* [2]*DSTL, Porton Down, Salisbury, Wiltshire SP4 0JQ, UK.* E-mail: s.vachieri@mail.cryst.bbk.ac.uk

The α-toxin of *Clostridium perfringens* is the major virulence determinant produced by the bacterium associated with gas gangrene in man. The toxin is a Zn^{+2} dependent, Ca^{+2} activated phospholipase C (PLC), is haemolytic and able to interact with membrane-packed phospholipids. The ability to interact with eukaryotic cell membranes distinguishes the α-toxin from related enzymes, such as *C. bifermentans* and *B. cereus* PLC.

Several crystal structures of this enzyme from different Clostridial strains and sources have showed the structure is composed of two, an α-helical (N-terminal) and a β-sandwich (C-terminal) domains.

A site directed mutagensis study revealed that the substitution of a single residue, Thr74 with Ile (T74I), resulted in the loss of haemolytic, phospholipase C and the sphingomyelinase activities by 1/250 fold to that of wild enzyme. We have determined the crystal structure of T74I mutant in two different crystal forms, $C222_1$ and $P4_32_12$ to1.9Å and 3.2Å resolution respectively. The crystal contains a monomer, in $C222_1$ structure, and a trimer in $P4_32_12$ structure, in the asymmetric unit of their unit cell. The overall topologies of the mutant structures are very similar, but have conformational differences in the mutant containing 60-90 loop, which is one of the proposed membrane interacting loops. We will compare the structures of T74I mutant with other α-toxin structures and relate the differences to the