

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). A61, 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<sup>a</sup>, Dominik Schaniel<sup>b</sup>, Theo Woike<sup>b</sup>, Manfred Wöhlecke<sup>c</sup>, Mirco Imlauf<sup>c</sup>, <sup>a</sup>Laboratory for Neutron Scattering, ETH Zürich & PSI, CH-5232 Villigen PSI, Switzerland. <sup>b</sup>Institut für Mineralogie, University at Cologne, DE-50674 Köln, Germany. <sup>c</sup>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 separates 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,  $Na_2[Fe(CN)_5NO] \cdot 2H_2O$  [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). A61, C346

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

Roman E. Gladyshevskii<sup>a</sup>, Nicolas Musolino<sup>b</sup>, René Flükiger<sup>b</sup>, <sup>a</sup>Ivan Franko Natl. University of Lviv, Ukraine. <sup>b</sup>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). A61, C346

#### Structure Investigation of Pure and Cr Doped $Li_3VO_4$

Doretta Capsoni<sup>a</sup>, V. Massarotti<sup>a</sup>, M. Bini<sup>a</sup>, P. Mustarelli<sup>a</sup>, C.B. Azzoni<sup>b</sup>, P. Galinetto<sup>b</sup>, M.C. Mozzati<sup>b</sup>, G. Chioldelli<sup>c</sup>, <sup>a</sup>Department of Physical Chemistry "M. Rolla", University of Pavia. <sup>b</sup>CNISM - Department of Physics "A. Volta", University of Pavia, Italy. <sup>c</sup>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  $\beta$ II form is orthorhombic (S.G. Pmn2<sub>1</sub>) 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,  $\mu$ -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  $\mu$ -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). A61, C346-C347

#### Structures of *C.perfringens* $\alpha$ -toxin mutant, T74I, that Affects its Activity

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

The  $\alpha$ -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  $\alpha$ -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  $\alpha$ -helical (N-terminal) and a  $\beta$ -sandwich (C-terminal) domains.

A site directed mutagenesis 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<sub>1</sub> and P4<sub>3</sub>2<sub>1</sub> to 1.9Å and 3.2Å resolution respectively. The crystal contains a monomer, in C222<sub>1</sub> structure, and a trimer in P4<sub>3</sub>2<sub>1</sub> 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  $\alpha$ -toxin structures and relate the differences to the

loss/reduction of its haemolytic, phospholipase C and sphingomyelinase activity.

**Keywords:** bacterial toxins, crystal structures, site-directed mutant

**P.08.14.28**

*Acta Cryst.* (2005). A61, C347

**An Improved Method for Calculating Ligand Solid Angles**

Ilija A. Guzei, *University of Wisconsin-Madison, Madison, WI 53706, USA.* E-mail: iguzei@chem.wisc.edu

A new approach has been developed to numerically calculate solid angles of the ligands in organometallic complexes. The novelty of the method is in using atomic radii corresponding to the distance where the Morse potential becomes zero, rather than in using the "typical" atomic van der Waals radii corresponding to the minimum of the Morse function. The calculated values include the ligand solid angles, the corresponding cone angles (rather than Tolman cone angles), the ligand special overlaps, ligand overshadowing, and the molecular solid angle. In addition, the calculated solid and cone angles are normalized to a Metal-Ligand distance of 2.28 Å to allow facile comparison of ligand steric demands in complexes of different metals with different compositions of coordination spheres. The new approach has been implemented in the program Solid-G and solid angles parameters with standard deviations have been computed for most common ligands such as cyclopentadienyl and tri-substituted phosphines. The new approach allows to evaluate the conformational flexibility of the ligands.

**Keywords:** solid angle, organometallic complexes, ligands

**P.08.14.29**

*Acta Cryst.* (2005). A61, C347

**The Perpendicular Magnetic Anisotropy Effect and the Directional Structure Ordering of CrPt<sub>3</sub> the Epitaxial Films**

Chih-Hao Lee<sup>a,b</sup>, Ming-Zhe Lin<sup>a</sup>, Yeng-Heng Huang<sup>a</sup>, Kuan-Li Yu<sup>a,c</sup>, J. C. A. Huang<sup>d</sup>, G.W. Chen<sup>d</sup>, <sup>a</sup>*Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan.* <sup>b</sup>*Nuclear Science and Technology Development center, National Tsing Hua University, Hsinchu.* <sup>c</sup>*National Synchrotron Radiation Research Center, Hsinchu, Taiwan.* <sup>d</sup>*Department of Physics, National Cheng-Kung University, Tainan, Taiwan.* E-mail: chlee@mx.nthu.edu.tw

The epitaxial cubic symmetric CrPt<sub>3</sub> films exhibit a perpendicular magnetic anisotropy (PMA) with large Kerr rotation angles. In order to understand the PMA effect of such a cubic CrPt<sub>3</sub> thin film, the directional chemical order parameters S and polarization dependent x-ray absorption fine spectroscopy (XAFS) were measured in both in-plane and plane-normal directions. The best PMA effect can be found when the plane normal order parameter is largest while the in-plane one is still low. At the same time, Cr-Cr bond-distances have slight distortion by XAFS analysis. This anisotropic directional long range chemical order might be due to the anisotropic interdiffusion and the compound formation between the Cr and Pt layer. For a short-range order analysis, the PMA effect might be attributed to the difference of the Cr-Cr bond-distance between plane-normal and in-plane directions.

**Keywords:** ordering, magnetic properties, CrPt alloy

**P.08.14.30**

*Acta Cryst.* (2005). A61, C347

**Distribution of Sr Ions in Tungstenbronze-type-like (Ba<sub>1-x</sub>Sr<sub>x</sub>)<sub>6-3x</sub>R<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> (R = Sm, Nd) Solid Solutions**

Masafumi Suzuki<sup>a</sup>, Hitoshi Ohsato<sup>a</sup>, <sup>a</sup>*Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Japan.* E-mail: 16415075@stn.nitech.ac.jp

Tungstenbronze-type-like (Ba<sub>1-x</sub>Sr<sub>x</sub>)<sub>6-3x</sub>R<sub>8+2x</sub>Ti<sub>18</sub>O<sub>54</sub> (R = rare earth) solid solution is one of the microwave dielectric materials. The crystal data is as follows: orthorhombic, *Pbnm* (No. 62), *a* ≈ 12, *b* ≈ 22, *c* ≈ 7 Å and *Z* = 2. The crystal structure of the solid solution is composed of two kinds of large cation sites: four pentagonal sites with Ba ions and ten rhombic sites with Ba, Sr and R ions in the framework

formed by TiO<sub>6</sub> octahedron.

These single crystals for R = Sm and Nd system were synthesized by conventional cooling method and FZ method, respectively. The X-ray diffraction data were obtained by a diffractometer with imaging plate (Rigaku; R-AXIS RAPID). Structural parameters were refined by full-matrix least-squares (RADY) [1].

All Sr ions occupied rhombic sites. Especially, one rhombic sites had more amount of Sr ions as compared with another rhombic sites in both of the R = Sm and Nd system. These solid solutions have relationship between distribution of cations and microwave dielectric properties [2]. Therefore, improvement of these properties with increasing composition *x* is lead by substituting Sr ions for Ba ions.

[1] Sasaki S., *XL Report, ESS, State University of New York*, 1982, 1–17. [2] Ohsato H., *J. Eur. Ceram. Soc.*, 2001, **21**, 2703–2711.

**Keywords:** tungsten bronze, microwave absorption material, structure-properties relationship in solids

**P.08.14.31**

*Acta Cryst.* (2005). A61, C347

**Structural Investigation of Cyclamic Acid and Related Cyclamates**

Ivan Leban<sup>a</sup>, Darja Rudan-Tasic<sup>b</sup>, Cveto Klofutar<sup>b</sup>, <sup>a</sup>*Faculty of Chemistry and Chemical Technology.* <sup>b</sup>*Biotechnical Faculty, University of Ljubljana, P.O. Box 537, SI-1231 Ljubljana, Slovenia.* E-mail: ivan.leban@uni-lj.si

There exist extensive studies on structure-taste relationship for the artificial sweetening agents, like sucralose (600 times sweeter than sucrose), saccharin (300), acesulfame-K (200) aspartame (180), and cyclamates (30). In order to perceive the sweetness, molecules must activate receptor sites in taste-bud proteins on the tongue. The activation is believed to take place when a molecule of suitable shape has a characteristic functional distribution. According to some theories, there are three essential structural components of a sweeter molecule, oriented in a triangular fashion. More elaborated theories on sweetness are given in an overview [1].

Because the shape of the molecule with the potential sweetness is important and the X-ray structural data for cyclamic acid (cyclohexylsulfamic acid) and cyclamates are not available, the following crystal structures were determined: cyclamic acid, sodium cyclamate, potassium cyclamate, ammonium cyclamate, rubidium cyclamate, caesium cyclamate, tetraethylammonium cyclamate, tetrapropylammonium cyclamate, tetrapentylammonium cyclamate and guanidinium cyclamate.

The financial support of the Ministry of Education and Sport, Republic of Slovenia through grant P1-0175-05 is gratefully acknowledged.

[1] Ellis J.W., *J. Chem. Educ.*, 1995, **72**, 671-675.

**Keywords:** X-ray structure, artificial sweetener, cyclamates

**P.08.14.32**

*Acta Cryst.* (2005). A61, C347-C348

**Structure and Microwave Dielectric Properties on ALa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A=Ba, Sr and Ca)**

Hitoshi Ohsato, Yusuke Tohdo, Ken-ichi Kakimoto, *Material Science and Engineering, Nagoya institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan.* E-mail: ohsato.hitoshi@nitech.ac.jp

Developments of microwave dielectrics for base station are desirable because of increasing amount of cellular phone. The materials are expected to have high quality factor (*Q*) and high dielectric constant ( $\epsilon_r$ ). We have reported a candidate of homologous compounds Sr-doped BaLa<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> with high *Q* of 46000GHz, high  $\epsilon_r$  of 46, and a temperature coefficient of resonant frequency  $\tau_f$  of -11 ppm/°C. On the other hand the  $\tau_f$  can be improved to near zero: 1.3 ppm/°C with high  $\epsilon_r$  of 44 and *Q* of 47000 GHz by substituting Al ions. And when Ba ions are substituted by Sr, it also shows good: *Q* of 46220 GHz,  $\epsilon_r$  = 43.7, and  $\tau_f$  = -8.4 ppm/°C. The crystal data of Ba-system are as follows: crystal system: trigonal, space group: *P*  $\bar{3}c1$ , and lattice constants: *a* = 5.609 Å, *c* = 22.648 Å. This crystal structure belongs to hexagonal layered perovskite-type structure. The packing