computational investigation of the relationship between the resolution efficiency of ephedrine (E) as a resolving agent for 2-phenylpropionic (hydratropic) acid (PP) and the physical properties of the diastereomeric salt pairs E***R***PP and E***S***PP. The crystal structure of the least soluble salt (E***R***PP) and a polymorph of the most soluble salt (E***S***PP form IV) have been determined by low temperature single crystal X-ray diffraction and E***S***PP form II by powder X-ray diffraction (PXRD). Two further polymorphs and a hydrate of E***S***PP have been identified by infrared spectroscopy and PXRD. Differential scanning calorimetry with thermogravimetric analysis was used to determine the relative stability of the salt pairs and polymorphs. HPLC and solubility measurements have been used to measure the resolution efficiency of E***R***PP and the most stable polymorph (form I) of E***S***PP.

The experimental crystal structures reveal that the resolution efficiency is affected by the competition between intra- and intermolecular interactions, as in the most stable salt (E***R***PP), the ephedrine forms an intramolecular N-H···O interaction, in addition to having different intermolecular hydrogen bonding motif to both E***S***PP polymorphs. CrystalOptimizer [2] has been used to calculate the lattice energy, $E_{latt}=U_{inter}+\Delta E_{intra}$, the balance between the intramolecular energy penalty, ΔE_{intra}, for distortions of the ions within the crystal, and the intermolecular lattice energy, $U_{inter.}$ The experimental work on this system shows both the challenges to, and potential benefits of, computational assessment of resolving agents.

[1] H. Caner, E. Groner, L. Levy, I. Agranat, *Drug Discovery Today.* **2004**, *9 (3)*, 105-110. [2] P.G. Karametzanis, S.L. Price, *J.Chem.Theor.Comp.* **2006**, *2 (4)*, 1184-1199.

Keywords: chirality, resolution, computation

MS32.P04

Acta Cryst. (2011) A**67,** C439

Microstructure evolution in MgF_2 and ZnO doped LAS Glass-Ceramics

Chih-Hao Lee,[a,b] Yu-Han Wu,[a] Kuo-Chuan Hsu,[c] *[a]Department of Engineering and System Science, National Tsing Hua University, Hsinchu. [b]National Synchrotron Radiation Research Center, Hsinchu. [c]Ta Hsiang Containers Ind. Co., Ltd., Hsin Pu, Hsinchu (Taiwan).* E-mail: chlee@mx.nthu.edu.tw

The microstructure evolution, including glassy phase separation, crystallization and phase transformation plays the most important role in practical mechanical property and application of lithium aluminosilicate (LAS) glass-ceramic materials. The main goal of this study is to demonstrate the correlations among phase development, microstructure, thermal expansion coefficient and mechanical strength associated with the content of MgF_2 and ZnO with commercial-like recipes. In this work, the result of flexural strength of LAS glass-ceramics strongly depends on the concentration of additives, MgF_2 and ZnO. When about 6% ZnO are added, the strength of a sample increases from about 62 MPa to 78 MPa. However, MgF_2 bearing samples accompany with a ~50% decreased in flexural strength. This is because the morphology, phase composition and transformation temperature are changed via doping. X-ray powder diffraction (XRD) results shows that the main phase follows the regular way, hexagonal β-quartz solid solution formed at lower temperature and transform to tetragonal β-spodumene solid solution at higher temperature. The transformation temperature of β-quartz solid solution to β-spodumene solid solution is lowered for several tens of degrees when the ZnO or MgF_2 is doped. It might be due to the weakening effect of silicate network by these additives. Also, various secondary phases, such as $ZrTiO_4$, and spinel of zinc and magnesium are usually precipitated at higher temperatures for samples with higher content of MgF_2. In addition, X-ray absorption near edge structure (XANES) feature is also used to certify the existence of some minor phases and the structural role of the doped elements. The significant change in XANES features of Zn K-edge indicates that Zn ions are usually involved in the crystallization process for samples doped with > 1% ZnO. Zn^{2+} ions might substitute Li^+ site in the main crystalline phase. This substitution phenomenon results in the formation of secondary phases. Thermal expansion mismatch from the microstructure non-uniformity is responsible for the strength drop of MgF_2 bearing samples.

Keywords: glass-ceramic, XANES, X-ray diffraction

MS32.P05

Acta Cryst. (2011) A**67,** C439

Evolution of the microstructure of bimetallic valves

Pavel Kodess, German Teterin, Boris Kodess, *ISC&E- VNIIMS , Aurora, CO.* E-mail: bnk27@hotmail.com

New our casting methods using heightened pressure of inert gas allow to obtain complex-form products from a variety of combination traditional and new high-temperature materials (G. Teterin at al. 1996). Distribution of the alloy components as well as phase composition across the valve section was obtained by means of energy-dispersive analysis and X-ray diffraction. The difference X-ray method has been used to investigate the evolution of the phase composition and microstructural characteristics of highly effective bimetallic engine valves. The head of the valves is made of Ti or Ti-Al, and the main rod is made of different materials. Bragg angle and the width of Bragg intensity profiles of reflection of high and low order for the phases were measured. The assessment of the change in the microstructure of the strain level at the predominant phase has been made on the basis of data of the angular dependence of the width of the Bragg reflection. As a reference standard of an instrument shape of reflections SRM 660 (LaB6) is used. Reliability and composition of the joining of head and stem was investigated by various method also. Hardness measurements were undertaken using 15-g, 50-g and 100-g loads using Micromet-2001 and PMT-3 testers. After casting the head of the valve it has a tetragonal gamma-phase and hexagonal alpha-phase; the ratio of the phases changes during the subsequent thermal treatment, and as a result the mechanical properties of the valve head become better. It should be noted that it is necessary to perform the control over the rod junction area because during some processing modes the martensitic beta-phase could appear, which can reduce the fracture toughness of the material and lead to a higher level of strain and as a result may appear some kind of micro-cracks in the junction of the valve. The exhaust valve were tested as a part of engine under the real-life condition of operation. It has been suggested the model described the processes

Keywords: strain-stress, phase composition, casting methods

MS32.P06

Acta Cryst. (2011) A**67,** C439-C440

Analytical methodology for the quantification of respirable crystalline silica (RCS) in occupational environments using a CIP 10-R sampler

Mª Pilar Gómez-Tena, Eulalia Zumaquero, Mª Jesús Ibáñez, Alberto Escrig, Eliseo Monfort. *Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE). Universitat Jaume I. Castellón. (Spain).* E-mail: pilar.gomez@itc.uji.es

The classification, in 1997, by the International Agency for Research on Cancer (IARC) of certain forms of respirable crystalline silica (RCS) [1] as a category 1 carcinogen has led to the revision of a number of aspects relating to occupational protection against free silica. Thus, in 2003, the European Commission addressed the harmonisation of RCS exposure limits, proposing a value of 0.05 mg/m^3 as daily occupational exposure limit, which is 50% of the value currently in force in Spain. The reduction of the RCS occupational exposure limits makes it necessary to use increasingly sensitive analysis methodologies.

In this study, different analysis methodologies [2] were reviewed and a new methodology is proposed, using CIP 10-R personal samplers [3] and polyurethane foams, which allow the captured amount of powder to be increased with a flow rate up to 10 L/min, thus improving the detection and quantification limits.

The new methodology was validated in accordance with quality standard UNE-EN ISO/IEC 17025.

The proposed new methodology, using a CIP 10-R sampler, provides acceptable recovery and repeatability values. The methodology enables the detection limits attained by current methodologies (cyclone-type personal samplers with a 2 L/min flow rate) to be reduced to one fifth

The certified reference materials used to determine the traceability of the method were standard powders BCR-66 and SRM 1878a, and the standard powder deposited on filters SRM 2551-2557.

[1] The measurement of the exposure of workers to respirable crystalline silica (RCS) and the work of the international standard organisation (ISO). Working group TC146/SC2/WG7 Silica. P.R. Stacey IOHA **2005** [2] W.J, Miles, *American Industrial Hygiene Association Journal*, **1999**, *60 (3)*, 396-402. [3] T. Lee, S. Won Kim, W. P. Chisholm, J. Slaven, M. Harper. *Ann. Occup. Hyg*., **2010**, *54 (6),* 697–709.

Keywords: respirable crystalline silica (RCS), CIP 10-R, analytical methodology

MS32.P07

Acta Cryst. (2011) A**67,** C440

An study of the evolution of the NSA fertilizers with humidity

Jose Montejo-Bernardo, Santiago García-Granda, Alfonso Fernández-González, *Departament of Physical and Analytical Chemistry. University of Oviedo-CINN. Asturias (Spain).* E-mail: montejojose@uniovi.es

NSA fertilizers are formed mainly by the 2AN·AS and 3AN·AS double salts (AN: ammonium nitrate; AS: ammonium sulphate) [1], mixed in a determined range of percentages. But it is known that the 3AN·AS salt is meta-stable and evolves into the 2AN·AS salt [2]. Even though it is known that the evolution is catalyzed by the presence of humidity in the environment, this effect was not studied in deep.

In this work we analyze the evolution of the 3AN·AS salt in different humidity conditions in the presence of free AS salt. We analyze also the evolution of mixtures of AS and AN, in different proportions and in different humilities conditions. This work is an extension of a previous work, started sometime ago [3].

Results show the influence of the humidity conditions, the presence of free AS, the time of the experiment, and the initial amount of both double salts in the samples.

Analyses were made using XRPD data collected in an Agilent Nova diffractometer, with a CCD area detectors, and Rietveld fit. Acknowledgements: Spanish MICINN (MAT2006-01997, MAT2010-15094 and CSD2006-015, Consolider Ingenio 2010, “Factoría de Cristalización”) financial support and FEDER funding is acknowledged.

[1] J.M. Montejo-Bernardo, S. García-Granda, A. Fernández-González. *Acta Cryst. B*. **2010**. *66*, 358-365. [2] T. Y. Ling, C. K. Chan. *Environ. Sci. Technol*. **2007**, *41*, 8077-8083. [3] J.M. Montejo-Bernardo, S. García-Granda. *Book of abstract of the 2nd MISCA* **2010,** 126. Oviedo (Asturias, Spain).

Keywords: fertilizer, phase evolution, XRPD area detector

MS33.P01

Acta Cryst. (2011) A**67,** C440-C441

Crystalline structure identification by TEM with Microdiffraction, PED and CBED

Loïc Patout,[a] Jean-Sébastien Merot,[a] Giuseppe Pavia,[b] Gerd Benner,[b] Harald Niebel,[b] [a]*Laboratoire d'Etudes des Microstructures, Office Nationale des Etudes et Recherches en Aérospatiale, ONERA, Châtillon (France)*, [b]*Carl Zeiss NTS, Oberkochen (Germany).* E-mail: loic.patout@onera.fr

Microdiffration and Convergent Beam Electron Diffraction (CBED) are two techniques used in TEM to identify respectively the space and the point group of a crystal. One of the interests is to work with a small beam to overcome problems regularly met with the selected area diffraction such as the curvatures, faults and thicknesses variations.

Microdiffraction requires a slightly convergent beam with a nanometers probe size and this approach enables the Ewald sphere to probe several strata of the reciprocal lattice. Thus, when the sample is perfectly oriented in a zone axis, Microdiffraction patterns give access to ideal symmetries (position and intensity of diffracted beams), the gaps and the differences of periodicity between the Zero and the First Order Laue Zone. From this method, the space group of a crystalline sample is determined by identifying the Bravais lattice, the presence of glide mirrors and helicoidals axes depicted on some mains patterns [1].

Nevertheless, electron diffraction patterns are highly affected by dynamical effects due to the strong interaction of electrons with matter. Precession Electron Diffraction (PED) is a recent technique perfectly adapted to obtain more kinematical diffraction patterns by using a rocking beam illumination. Diffraction patterns obtained with a de-scanned precession of the incident beam contain as well more reflections and this allows to identify surely and easily the Bravais lattice and the glide mirrors [2].

CBED used with the Buxton or Tanaka (multibeam) methods allows to appreciate the symmetries inside the diffracted and incident disks of a slightly away from a perfect zone axis pattern. By comparing it with simulated patterns, the identification of the point group is then possible [3].

Both techniques were used to identify the space group $P6_3/mmc$ and the point group mmm of Ti_3SiC_2 and $TiSi_2$ respectively, two crystalline phases found by microanalysis (EELS, EDX and STEM HAADF). On one hand, CBED was very useful to find the point group mmm in working with only one zone axis. On the other hand, the space group Fddd has been determined in the same zone axis by Microdiffraction and PED.

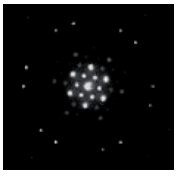

Fig.1: Microdiffraction

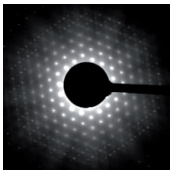

Fig.2: Precession

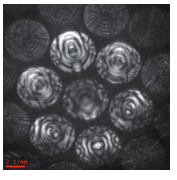

Fig.3: CBED Multibeam