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**Keywords: high pressure, neutron diffraction, amorphous ice**

**P.20.07.1**

*Acta Cryst*. (2005). A**61**, C469

**High-Temperature X-ray Study of Zn-substituted $Cu_2V_2O_7$**

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A room temperature X-ray study has been performed on the Zn-substituted β-$Cu_2V_2O_7$ [1, 2], however no study of the $Cu_2V_2O_7$ - $Zn_2V_2O_7$ solid solutions has been yet done under high temperature *in situ*. Such studies are important as there are two known polymorphs of $Zn_2V_2O_7$ and three polymorphs of $Cu_2V_2O_7$, both high-temperature modifications (β'-$Zn_2V_2O_7$ [3] and β'-$Cu_2V_2O_7$ [4]) are not retained on quenching at a practicable rate.

High-temperature X-ray analysis of the $Cu_{2-x}Zn_xV_2O_7$ solid solutions ($0 \le x \le 0.7$) was carried out in the temperature range of 25°-770°C *in situ*. With substitution of Cu by Zn temperatures of the α→β' and β→β' phase transitions decreased, and both phase transitions changed their features and character in comparison with pure $Cu_2V_2O_7$.

As the main difference between the β'-$Cu_2V_2O_7$ and β-$Cu_2V_2O_7$ structures involves the V-O-V angle in the $[V_2O_7]^{4-}$ groups decreasing sharply upon quenching, a concentration dependence of structural parameters for both Zn-substituted structures was established and probable cause for the β'↔β phase transition was given.

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**Keywords: vanadates, structural transitions, temperature**

**P.20.07.2**

*Acta Cryst*. (2005). A**61**, C469

**A Furnace for *in situ* Time Resolved Diffraction with Gas Flow**

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The understanding of chemical reactions has become a major challenge in the development of new materials and processes, and the improvement of existing industrial processes. *In situ* time resolved diffraction is one obvious solution, and the use of synchrotron sources coupled with outstanding detectors such as RAPID2 [1] allows the collection of refinable patterns in times as short as 1s [2].

In order to observe the reactions in different non-ambient conditions, we designed a furnace able to perform classical temperature dependent experiments, but also allowing a gas to flow through the capillary. This unique design is highly interesting, especially for the study of reactions occurring in the presence of oxidative or reductive conditions (e.g. catalysis). The use of this device and of a synchrotron source was already proven and we were able to observe an oxidation occurring in less than 20s! [3].

The furnace designed for these experiments is slimmer than the length of the capillary, and can reach temperatures up to 950°C. A rotating seal is used for the gas insertion (alternatively it can be connected to a vacuum line). It is fixed on the goniometer allowing the spinning of the capillary. The gas is collected at the other side of the furnace and can be study with a gas analyzer.

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**Keywords: *in situ* diffraction, time-resolved, red-ox reactions**

**P.20.08.1**

*Acta Cryst*. (2005). A**61**, C469

**A Parametric Approach to Single Crystal Diffraction Data Analysis**

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Snapshots of molecular crystal structures using single crystal diffraction at a single temperature yield a determination that is sufficient for many purposes. However, for systems that are undergoing change, characterisation of the structure at a series of temperatures is vital. There has been a recent increase in the number of such variable temperature studies being undertaken; however, measurements have been traditionally performed at rather few temperatures. There is relatively little evidence to date of single crystal diffraction studies involving the exploitation of data sets of an evolving molecular structure at many temperatures (say, for example, 50-100) in the more parametrically challenging regime.

We have been developing novel ideas regarding both experimental protocol and data analysis which could maximise the information content available from laboratory single crystal X-ray diffraction data. The basic idea behind the approach is that, when analysing variable temperature data, one is not examining sets of unrelated parameters at individual different temperatures, but the evolution of the fundamental parameters throughout the whole experimental period. One can thus treat the data as an ensemble and, by defining the temperature evolution of a parameter by a suitable function, fit all the data simultaneously to a single continuously evolving structural model. The approach will be outlined and selected examples of its application given.

**Keywords: data analysis, refinement methods, structure analysis**

**P.20.09.1**

*Acta Cryst*. (2005). A**61**, C469

**A Combined Raman-X-ray Powder Diffraction Study at Non-ambient Condition**

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Raman spectroscopy can often help to overcome the well-known limitations of X-Ray Powder Diffraction (XRPD) alone by providing additional information on samples containing light elements and/or disordered moieties and/or amorphous phases. We designed and carried out a combined Raman-XRPD *in situ* experiment to exploit the complementarities of the two techniques in investigating the kinetics of a transformation occurring in the solid state at non-ambient conditions. The experimental setup was tested on a simple solid-state to solid-state transformation, consisting in a phase transition occurring at 330K to octakis(isobutyl)-octasilsesquioxane. The crystal structure of the RT phase was solved by single crystal X-Ray diffraction [1], whereas the high temperature (HT) phase was only recently discovered by some of us. The *ab initio* solution of the high T crystal structure was hampered by the poorness of the 330 K XRPD pattern. Monitoring the transformation simultaneously using the Raman technique combined to XRPD allowed a full structural characterization of the HT phase and in particular:

i) to understand that the phase transition was strongly correlated to the features of the isobutyl moieties;

ii) to monitor the possible radiation damage;

iii) to carefully check the temperature of the system (exploiting the Stokes/anti-Stokes ratio of the Raman bands).

[1] Bassindale, et al., *Dalton Trans.*, 2003, 2945.

**Keywords: powder diffraction under non-ambient condition, Raman spectroscopy, kinetics**