

21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

the effects of deuteration on the transition temperature; and the structure of ammonia at ~5 GPa where the neutron data reveal a lower symmetry than expected. Examples of this work will be presented.

PS-21.01.09 DATA COLLECTION AND ANALYSIS TECHNIQUES FOR ACCURATE NEUTRON POWDER-DIFFRACTION STUDIES ABOVE 10 GPa. By J.S.Loveday*, R.M.Wilson and R.J.Nelmes, Department of Physics, The University of Edinburgh, UK; J.M.Besson, S.Klotz and G.Hamel, Physique des Milieux Condensés (CNRS), Université Paris VI, France; and S.Hull, ISIS Facility, Rutherford Appleton Laboratory, UK.

The use of a pressure cell in a neutron powder diffraction experiment creates a number of problems for accurate data collection. The development of the Paris-Edinburgh opposed-anvil cell at the UK pulsed-neutron source, ISIS, for powder-diffraction studies to 10 GPa and above, has thus required careful attention to the neutron-scattering aspects of the experimental techniques.

The anvil design, the shielding geometry and the materials used have been optimised to give the best possible signal-to-background taking into account the sources of the background scattering and the energy of the neutrons involved. Finite-element calculations have been developed, and tested, to correct for the effects of attenuation by the pressure-cell materials. In the case of the sintered-diamond anvils, used to achieve the highest pressures, the attenuation corrections also have to include the effects of Bragg edges due to diffraction by the (polycrystalline) anvils. And it is frequently necessary to apply corrections for preferred-orientation effects in the samples.

Residual non-sample scattering and/or inadequate corrections for attenuation and preferred-orientation effects can bias refined structural parameters in all types of high-pressure set-up. Examples of these problems will be shown, and the current procedures for accurate structure refinement will be presented.

PS-21.01.10 SYNCHROTRON DIFFRACTION ON Fe AND Au IN THE RANGE UP TO 1.1 Mbar IN NOVEL MODULAR HYDRAULIC DIAMOND SQUEEZER. By G. Will and Chr. Höffner, Mineralogical Institute, University Bonn, Poppelsdorfer Schloß, 5300 Bonn 1, Germany.

We report measurements on gold and iron measured with synchrotron radiation at DORIS/HASYLAB, Hamburg, in a diamond anvil squeezer at pressures up to 1.1 Mbar. By the method of profile analysis and profile fitting with a new program HFIT developed in this laboratory we could separate overlapping peaks yielding very reliable data for the d -values. These were then used to

calculate lattice constants and volumes as a function of pressure. This technique of profile fitting will be reported. It is mandatory when doing synchrotron experiments at extended pressures where many overlapping peaks are present, most of them not even coming from the sample in question. In addition the background is non-monotonous in general and requires additional care.

In total we have performed about 100 experiments. The experimental data have been fitted by the Birch-equation as well as by the Murnaghan-equation. The results are used to calculate the compressibility parameters K_0 and K'_0 .

Further on we have developed a new diamond squeezer driven by a hydraulic oil pressure system. The cell is a modular system and the diamond setting can be used in an anvil lever system as well. The oil driven pressure cell allows us to vary the pressure in synchrotron experiments without entering the radiation area. This is very important for synchrotron experiments, because of the radiation hazards and the time consuming access to the experiments.

PS-21.01.11 THE STRUCTURAL BEHAVIOUR OF COPPER IODIDE AT ELEVATED TEMPERATURES AND PRESSURES. S. Hull* and D.A.Keen, ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, United Kingdom.

In common with the other group Ib halides, copper(I) iodide (CuI) has been widely investigated owing to the superionic behaviour it displays at elevated temperatures (1). Despite its simple zincblende structure, several aspects of the structural modifications associated with the onset of thermally induced disorder are still the subject of debate in the literature. We have recently addressed these topics, using powder neutron diffraction techniques.

The structure of β -CuI, stable between ~640K and ~670K has been determined in $P\bar{3}m1$, with Cu^+ disordered over tetrahedral interstices in an essentially close-packed hexagonal anion sublattice. We find no evidence for cation occupancy of the octahedral voids as reported previously (2). Detailed investigations as a function of temperature through the $\gamma \rightarrow \beta \rightarrow \alpha$ transitions demonstrate the gradual evolution of Cu^+ disorder on the available tetrahedral sites in each phase. The preference for tetrahedral co-ordination of the cations is supported by measurements made at ambient temperature and elevated pressures. At $p=16.3$ kbar CuI transforms to a rhombohedral structure which possesses $R\bar{3}m$ symmetry and at $p=42$ kbar to a tetragonal phase. The latter appears isostructural with the 'intermediate' phase of AgI, stable between 2.8kbar and 3.8kbar. This has the anti-litharge structure, $P4/nmm$ (3), so that both high pressure forms can be considered as different geometrical arrangements of tetrahedrally co-ordinated Cu^+ within slightly distorted cubic close-packed anion sublattices.

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PS-21.01.12 ANISOTROPIC THERMAL EXPANSION CHARACTERISTICS OF $\text{SrZr}_4(\text{PO}_4)_6$ - $\text{KZr}_2(\text{PO}_4)_3$ SYSTEM CERAMIC MATERIALS BY X-RAY DIFFRACTION. By Chang-lin Kuo*, Rong-fa Guo, Yue-hong Huang and Hui-ming Chen, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, P.R.China.

Some of the compounds in strontium (potassium) zirconium phosphate silicate system are kinds of ceramic materials having ultralow-thermal expansion and high-thermal shock-resistant properties (S.Y. Limaye, Patent, 1990: WO 90 12,766). These compounds normally crystallize in the hexagonal crystal system, and are characterized by only two principal thermal expansion coefficients, parallel and normal to the c or Z axis.

An accurate value of the lattice parameter of the compounds in $\text{SrZr}_4(\text{PO}_4)_6$ - $\text{KZr}_2(\text{PO}_4)_3$ system have been determined at different temperatures, ranging from 293 to 1300 K, by X-ray powder diffraction. Unit-cell dimensions of seven compositions [$\text{K}_{2x}\text{Sr}_{1-x}\text{Zr}_4(\text{PO}_4)_6$, $x=0,0.2,0.4,0.5,0.6,0.8,1.0$] at each temperature were obtained by the method of least-squares based on the measurement of 8-16 unambiguously indexed reflections recorded in the 2θ angle region 80 to 120° using a Rigaku-Denki high-temperature stage mounted on a 12 kW rotating anode X-ray generator with Cu K_α radiation ($\lambda_{\text{CuK}\alpha} = 1.540598\text{Å}$). The lattice parameters were found to vary non-linearly with temperature and the dependence has been expressed by the third-order polynomial relations of the form:

$$a_T = a_0 + a_1T + a_2T^2 + a_3T^3 \quad (T \text{ in K})$$

Least-squares fit of the experimental data has led to the analytical expression results. For example, the lattice parameters of $\text{SrZr}_4(\text{PO}_4)_6$ are as follows

$$a = 8.6825 + 1.9725 \times 10^{-5}T - 1.0953 \times 10^{-9}T^2 + 2.4105 \times 10^{-12}T^3$$

$$c = 23.4016 - 3.8332 \times 10^{-5}T + 1.0007 \times 10^{-7}T^2 - 3.0210 \times 10^{-11}T^3$$

The data have been used to evaluate the coefficients of thermal expansion at various temperatures. The temperature dependence of the coefficient of expansion can be represented by the equation

$$\alpha_a = 2.2703 \times 10^{-6} - 2.5213 \times 10^{-10}T + 8.3232 \times 10^{-13}T^2$$

$$\alpha_c = -1.6382 \times 10^{-6} + 8.5536 \times 10^{-9}T - 3.8734 \times 10^{-12}T^2$$

The relative percent thermal linear expansions are

$$\left(\frac{\Delta L}{L_0}\right)_a = -0.0679 + 2.2703 \times 10^{-4}T - 1.261 \times 10^{-8}T^2 + 2.774 \times 10^{-11}T^3$$

$$\left(\frac{\Delta L}{L_0}\right)_c = 0.0145 - 1.6382 \times 10^{-4}T + 4.277 \times 10^{-7}T^2 - 1.291 \times 10^{-10}T^3$$

The thermal expansion coefficients of all seven compositions were determined. Two principal thermal expansion coefficients of the compounds $X \leq 0.5$ above room temperature are positive, but for $X \geq 0.8$, they are negative. However, for compound

$\text{K}_{1.2}\text{Sr}_{0.4}\text{Zr}_4(\text{PO}_4)_6$ ($X=0.6$), one coefficient α_a is positive, and the other one α_c is negative. Therefore, the average thermal expansion of the bulk material of the compound $X=0.6$ is lower than that of the other compositions. The measuring thermal expansion coefficients (all $\times 10^{-6}/^\circ\text{C}$) of different composition compounds by dilatometers method at temperature 700 K are: $X=0.2, \alpha=2.65$; $X=0.4, \alpha=1.74$; $X=0.6, \alpha=-0.16$; $X=0.8, \alpha=-5.02$. These results agree with the conclusion obtained from the X-ray diffraction method.

PS-21.01.13
 THE EQUATION-OF-STATE OF PdD_x AT HIGH PRESSURE AND A HYDROSTATIC REGION IN THE DIAMOND ANVIL CELL

Ji-an Xu

Institute of Earth Sciences, Academia Sinica, P.O. Box 1-55, Nankang, Taipei, Taiwan, China

ABSTRACT

The lattice constants of PdD_x were measured by X-ray diffraction in a diamond anvil cell up to average 111 GPa with peak pressure about 144 GPa. Results fitted to a Murnaghan equation for PdD_x yield values for the bulk moduli K_0 and its pressure dependence K_0' of 198.5 GPa and 5.09, respectively. In addition, the R_1 - R_2 splitting in the ruby fluorescence indicates the existence of a small hydrostatic region (about 1 micrometer) in the center of the culet surface of a diamond anvil.