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

PS-21.03.15 THE FERROELECTRIC PHASE TRANSITION IN LIGHTLY DOPED BARIUM TITANATE: By C.N.W. Darlington, School of Physics, University of Birmingham, Birmingham, U.K. and R.J. Cernik, Daresbury Laboratory, Warrington, U.K.

The ferroelectric phase transition in lightly-doped barium titanate at 130°C has been studied using the diffractometer on last 9.1, SRS, Daresbury in high-resolution mode. The concentration of dopant was typically 0.3 mole % with both barium and titanium being replaced. In all cases the transition was smeared out, with the discontinuity unobservable. We find that, when the valency of the dopant is different from that of the ion it replaces, the value of a critical exponent indicates that the system behaves as a "soft" i.e. pure barium titanate, plus point-like impurity. Imperfections with a higher valency than the replaced ion are electrically screened, while those with lower valency are not. However, no difference in behaviour between these was detectable. All impurities studied caused the low-temperature phase to form locally at temperatures above the transition temperature of the pure material, yet lowered the temperature at which the overall symmetry became tetragonal. This is interpreted as inhibition of phonon softening of the low-temperature form by small clusters. Solid solutions e.g. (bismuth, strontium) titanate behave differently; clearly one cannot consider strotium as an impurity in a barium-rich solid solution.

PS-21.03.16 THE PHASE SEQUENCE OF Ca4[Al2O7](CrO4)2; By R. Meier*, W. Degmemeier, S. Doyle, H. Hahn-Meier-Institut, Glienicker Str. 100, D-1000 Berlin 39, Mineralogisches-Petrographisches Institut, Universitaet Kiel, D-2300 Kiel. Hasylab, DESY, Notkestr. 85, D-2000 Hamburg 52.

Ca4[Al2O7](CrO4)2 in short notation CaCrz, is a member of the aluminosilicate family (Degmemeier, Phys. Chem. Min. 15, 419, 1985) a simple to complex host-guest interactions in this cage structure, all end members show one or more, in general, ferroic phase transition. Three of them were found for CaCrz at high temperatures. The only structural information available for CaCrz was that the room-temperature phase shows a 3.2.1 modulation. Therefore, we focussed our attention on CaCrz and started investigations such as temperature-dependent X-ray powder and single crystal diffraction.

In order to follow the lattice parameters of CaCrz with increasing temperature, an X-ray powder experiment was performed at the diffractometer at beamline B2 at Hasylab using the furnace described by Arnold (Materials Sci. Soc. 79-82, 445, 1997). All three known phase transitions could be identified by anomalies in the variation of lattice parameters. We found an additional anomaly at about 500K, which is a further, new phase transition. A re-examination of DTA curves confirmed this transition and led us to the assumption of still another transition at 46K. This transition should be verified in a forthcoming experiment. Consequently the proposed phase sequence of CaCrz is:

Phase# 1 2 3 4 5 6
<483K<456K<464K<560K<610K<690K

Each phase is summarized above by two letters. The first one is about the crystal system: orthorhombic, tetragonal, cubic. The second is about the modulation: monoclinic, triclinic, rhombohedral. For both informations, too, be established. Transition temperatures between phases are given.

The crystal symmetries have been determined from the splitting of the main reflections (formerly cubic reflections of phase 6, ferroelastic phase transitions) in the X-ray powder diffraction experiment. We tried to verify all phases in a single crystal X-ray precession experiment with a Huber healing device. Until now, we have not been able to identify phases 4 and 5. There is evidence that phase 5 which has been found in the powder diffraction experiment at Hasylab is incompletely modulated.

At the conference we will present in detail the results of the temperature dependent X-ray powder and single crystal experiments.

PS-21.03.17 PHASE TRANSITIONS OF Na2SO4 AND STRUC-TURE REFINEMENTS AT SEVERAL TEMPERATURES, By S.E. Rasnussen* and J.-E. Jorgensen, Department of Chemistry, University of Aarhus, Denmark.

Sodium sulphate, Na2SO4, has been reported to exist in five polymorphs forms labelled I-V and structure analyses and thermal analysis have been reported on most of the polymorphs. Na2SO4 has been investigated in the system by differential thermal analysis, DTA, and differential scanning calorimetry, DSC, and by X-ray powder diffraction at several temperatures in order to examine the Na2SO4 system with one and the same batch of material in one and the same laboratory by two independent methods.

Guinier transmission techniques were applied both with film methods and with diffractionometer methods. The X-ray results confirm the existence of the crystaline phases labelled I, II, III, and V, whereas the phase IV whose existence in the temperature range 458-514K was alleged by Brode, G.E. and Ginacote, W.F. (1972), J. Phys. Chem. 76, 737-743. on the basis of calorimetric data does not appear to have a powder diagram which confirms the independent existence of this phase. The DSC measurements do, however, indicate the existence of a slight thermal effect near 500K.

Rietveld refinements have been carried out on the structures of I and III at several temperatures and of V at room temperature. The structure of II which exists in a narrow temperature interval around 220±5°C is presently being investigated.

Heats of reactions have been measured for the transitions: I-II, II-III and III-I. The transition I-II has been found to be reversible whereas the other transitions are not.


The goal of this paper is to summarize together the results yielded by neutron diffraction and inelastic neutron scattering to characterize the phase transitions with the temperature observed in the organometallic compound UC2CNCl2. It is a part of the thesis of P. Raison to be published in Molecular Physics.

We have used neutron diffraction technique on single crystal sample to examine the symmetry of the unit cell of the organometallic compound UC2CNCl2 as a function of temperature below 300K. Two phase transitions occur. The first, at 245K, results in a change of space group but the monoclinic symmetry is retained (P21/n → Pn1); the second, at 78K, results in the material becoming triclinic. The crystallographic work is important because to compare observed and calculated values of structure factors, we need a great number of reliable observations together with difficult calculation of complicated models. We show that at 300K, it is not possible with the diffraction alone to determine whether the structure is statistically or dynamically distributed.