

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

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and then sharply falls down owing to the escape of the gases contained in the pitchblende. The sample phase composition after the heating to 900°C represents the mixture of the following uranium oxides:  $UO_2$  ( $a = 5.438 \pm 0.028 \text{ \AA}$ ), orthorhombic  $U_2O_5$  and  $U_3O_8$ , hexagonal  $U_3O_8$  and  $UO_3$ .

**PS-21.03.28 PHASE TRANSITIONS IN  $Li_xV_2O_5$ .** By H. Katzke and W. Depmeier, Inst. f. Mineralogie, Universität Kiel, D-W 2300 Kiel, Germany.

The quasi two-dimensional layer compound  $V_2O_5$  is one of the most extensively investigated compounds for the development of solid state batteries working at ambient temperature.

The electrochemical intercalation of  $Li^+$ -ions into the van der Waals-gaps of  $V_2O_5$  has been studied *in situ* under ambient conditions in aqueous  $Li^+$ -solutions. The results differ in several aspects from those of chemical or thermal intercalation. A series of electron transfer rate controlled isomorphous phase transitions could be detected, and a new orthorhombic vanadium bronze  $\zeta$ - $Li_xV_2O_5$  identified.

A theoretical model is based on repulsive O...O-interactions and helps to explain the observed shortening of the a-axes. A unified reaction-pathway diagram for electrochemical, chemical and thermal intercalation is presented, as well as a group-subgroup diagram connecting the various phases.

**PS-21.03.29 Low-temperature structural study and phase transitions in superionic conductor tetramethylammonium trichlorogermanate(II),  $N(CH_3)_4GeCl_3$ .** K. Fütterer<sup>1</sup>, W. Depmeier<sup>2</sup>, <sup>1</sup>Institut für Mineralogie und Kristallographie, TU Berlin, D-W-1000 Berlin 12, Germany; <sup>2</sup>Mineralogisch-Petrographisches Institut, Univ. Kiel, D-W-2300 Kiel 1, Germany

Tetramethylammonium trichlorogermanate(II),  $N(CH_3)_4GeCl_3$ , (TGC) is orthorhombic at ambient conditions, with space group  $Pna2_1$  and lattice parameters  $13.07 \times 8.89 \times 9.12 \text{ \AA}^3$ . The room-temperature crystal structure of TGC ( $\gamma$ -phase) has been determined (Depmeier, Möller, Klaska, Acta Cryst. 1980, B36, 803). DSC measurements revealed three phase transitions at 424K, 204K and 176K, respectively (Möller, PhD-thesis, Univ. Konstanz 1980). At 424K the compound undergoes a phase transition to a cubic, ionic conducting ( $\alpha$ -)phase,  $a = 6.552 \text{ \AA}$ , with a change of the electrical conductivity at  $T_c$  of 6 orders of magnitude.

This contribution reports structural studies on the two low-temperature phase transitions at 204K ( $\gamma$ - to  $\delta$ -phase) and 176K ( $\delta$ - to  $\epsilon$ -phase). Guinier powder and single crystal x-ray experiments were carried out, which clearly confirm the occurrence of two phase transitions, matching the transition temperatures observed by DSC within 5K.

Precession photographs of ( $h; k; 0,1,2$ ) and ( $0,1,2; k; l$ ) reciprocal lattice planes (indices refer to the orthorhombic room temperature lattice) were recorded at 183K and 158K. The exposures strongly suggest the occurrence of an incommensurately modulated phase (IC phase) between 200K and 170K, with  $q=0.145 \cdot b^*$ . Satellite reflections up to fourth order are observed, some of them being even more intense than the corresponding main reflections. No satellite reflections are observed in the  $hk0$ -plane, which points to a transverse modulation wave with the polarization vector perpendicular to the  $a,b$ -plane. A temperature dependent study of the  $\gamma$ - and the  $\delta$ -phase on a four-circle diffractometer is under work.

Possible structural models of the  $\delta$ - and  $\epsilon$ -phase will be discussed as well as the temperature dependent behaviour of the modulation wave vector and the modulation amplitude.

**PS-21.03.30 LOW TEMPERATURE PHASE TRANSITION IN AN ALUMINATE SODALITE.** By X. Hu, Hahn-Meitner-Institute Berlin and W. Depmeier<sup>\*</sup>, University Kiel, Germany.

Subject of this work is the aluminate sodalite  $Sr_8[Al_{12}O_{24}](SO_4)_2$ , abbreviated to SAS. It shows at least one phase transition at a temperature far below room temperature ( $T_c = 135K$ ), actually the first low temperature phase transition observed in the family of aluminate sodalites so far. Electron diffraction studies revealed an incommensurately modulated phase below the phase transition temperature (Hu 1992). There is also evidence for a lock-in phase transition at about 40K.

Aluminate sodalites possess a typical framework structure with non-framework guest species. Both the framework itself and the guest species are charged. Thus, there are strong Coulomb interactions between guests and host and between the two different guests. In the case of SAS the dominant interactions are described as follows:

- (i) repulsive interaction between framework oxygens and oxygens of the cage anion  $SO_4^{2-}$ ,
  - (ii) attractive interaction between cage cations and framework oxygens, and
  - (iii) attractive interaction between the cage cations and cage anions.
- Other interactions are possible, but less dominant.

We will present results characterizing the low temperature phase transition and speculate about the factors leading to this transition in SAS.

### References:

Hu, X. (1992). PhD Thesis. TU Berlin.

**PS-21.03.31 STUDY OF PHASE TRANSITIONS IN  $LiNbO_3$  CRYSTAL BY MEANS ELASTIC SCATTERING OF LIGHT.** By S.V. Ivanova and I.I. Naumova. Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, Moscow 117924, Russia.

Lithium niobate ( $LiNbO_3$ ) crystal at the room