ESRF	Experiment title: Study of the modulated phase of the $K_2Mo_xW_{(1-x)}O_4$ $(0 < x < 1)$ compounds as a function of temperature	**Experiment number**:
Beamline: BM1B	**Date of experiment**: from: 06/03/2002 to: 10/03/2002	**Date of report**: 18/12/2002
Shifts: 8	**Local contact(s):** Wouter Van Beek	*Received at ESRF:*

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Experimental

High temperature X-ray powder diffraction experiments were carried out in the SNBL High Resolution Powder Beamline BM1B in the following compounds: K_2MoO_4, $K_2Mo_{0.5}W_{0.5}O_4$ and K_2WO_4. We used radiation with λ=0.5 Å. The sealed high temperature oven with quartz window was mounted in the beamline and its temperature controller was tested. It was possible to achieve and to stabilize all the temperatures required for the experiments but in general we observed a systematically overshooting during the heating in the total investigated temperature range (300 K ≤ T ≤ 930 K). In order to minimize the overshooting and to achieve the set point temperature as fast as possible, P.I.D. parameters have been optimized for different temperature set points (see the oven book note for more details). Capillaries of 0.4mm of diameter were filled with a dry powder of each compound just before the beginning of the experiment. The capillaries were not sealed allowing the water exchange between the samples and the oven environment during the data collection. Different kinds of scanning were done in each sample (*Table 1*) in two series of heating-cooling cycles (RT → 800 K → 373 K → 800 K → RT After the first series of measurements we observe an abnormally high background at the low angles. The overall data background was considerably reduced by placing an additional peace of WC close to the oven window forming a kind of low angle beam stop. At the very end a diffraction pattern of the empty oven was also taken. The “experimental” background (empty oven + WC peaks) was fitted using a polynomial function and subtract from each diffraction pattern.

	Scanning range (°)	Speed (°)	Counting time (s)
1	6.4 ≤ 2θ ≤ 10.2 12.9 ≤ 2θ ≤ 16.2	0.04	1
2	3.0 ≤ 2θ ≤ 30	0.004	1
3	3.0 ≤ 2θ ≤ 13 13 ≤ 2θ ≤ 23 23 ≤ 2θ ≤ 30	0.003	1 2 4

Table 1: Different kinds of scanning performed during the investigations of the $K_2Mo_xW_{(1-x)}O_4$ $(0< x <1)$ structures in the High Resolution Powder Beamline BM1B.

For the investigated compounds the presence, intensity and shape of diffraction peaks were used to determine the phase evolution with temperature. In the mixed $K_2Mo_{0.5}W_{0.5}O_4$ compound additional scans around $8.8^o \leq 2\theta \leq 9.2^o$ with speed of 0.002^o/s were done in the last cooling cycle.

Results

The compounds K_2MoO_4 and K_2WO_4 are isomorphic with monoclinic symmetry *C2/m* (Z=4) at room temperature (Gatehouse & Leverett, 1969 and Koster *et al.*, 1969) and hexagonal symmetry $P6_3/mmc$ (Z=2) at high temperature (van den Akker *et al.*, 1970). Previous results report the existence of a modulated orthorhombic intermediary phase in both compounds. In this phase the modulation vector ***q*** lies in the basal plane of the high temperature hexagonal symmetry. The modulated phase is incommensurate with $0.29 < q < 0.30$ between 593 K and 733 K for K_2MoO_4 and commensurate with $q = 1/4$ from 643 K up to 733 K for K_2WO_4 (Tuinstra & van den Berg, 1983). The modulation was assumed to be a periodic change in the orientation of the tetrahedral anion $\{XO_4\}^{2-}$ (van den Berg, Tuinstra & Warczewski, 1973).

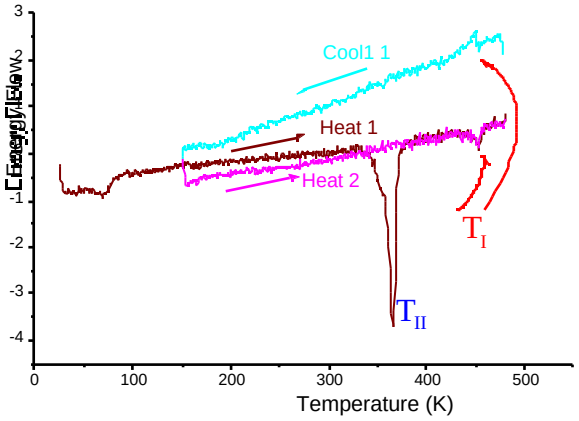

Figure 1 - DSC scanning.

Mixed $K_2Mo_xW_{(1-x)}O_4$ compounds have been successfully synthesised by solid state reaction for seven different compositions (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1). Differential Scanning Calorimetry thermograms have shown two distinct behaviours when comparing the first heating process with subsequent ones (*Figure 1*). Two phase transition temperatures could unambiguously be determined. The higher phase transition temperature T_I is independent of the crystal composition and the lower temperature T_{II} decreases with increasing x; the obtained values of T_I and T_{II} for the pure compounds (x = 0 and 1) are in agreement with those found in literature. The first transition at temperature T_{II} seems to be related to H_2O loss. The existence of both the hydrated and the anhydrous forms of the crystal is evidenced in the X-ray powder diffraction results when comparing the diffraction pattern obtained in successive heating-

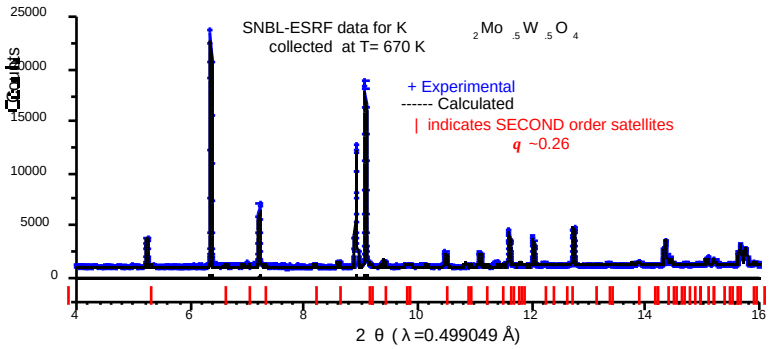

Figure 2 - Diffraction pattern obtained in successive heating-cooling cycles. Evidence of symmetry change

cooling cycles (*Figure 2*). Semi-empirical crystal structure analysis of the K_2MoO_4, K_2WO_4 and $K_2Mo_{0.5}W_{0.5}O_4$ has shown that the anhydrous phase diffraction data can be fitted using a presumable orthorhombic unit cell, twice as big (Z=8) as the original hydrated one. Attempts to refine a model for the crystal structure in this phase are in progress. In the presumable modulated phase, the strongest satellites are of 2nd order. The * in *Figure 3* indicates the most important ones. As can be seen, the intensity of the satellite reflections increases with decreasing temperature. Data have been fit to *Cmcm (0 q 0)* symmetry but no model for the structure can be proposed yet. Further investigations are in progress; it is intended to check the possibility for the anhydrous form to be a superstructure with *q* equal to 0.5.

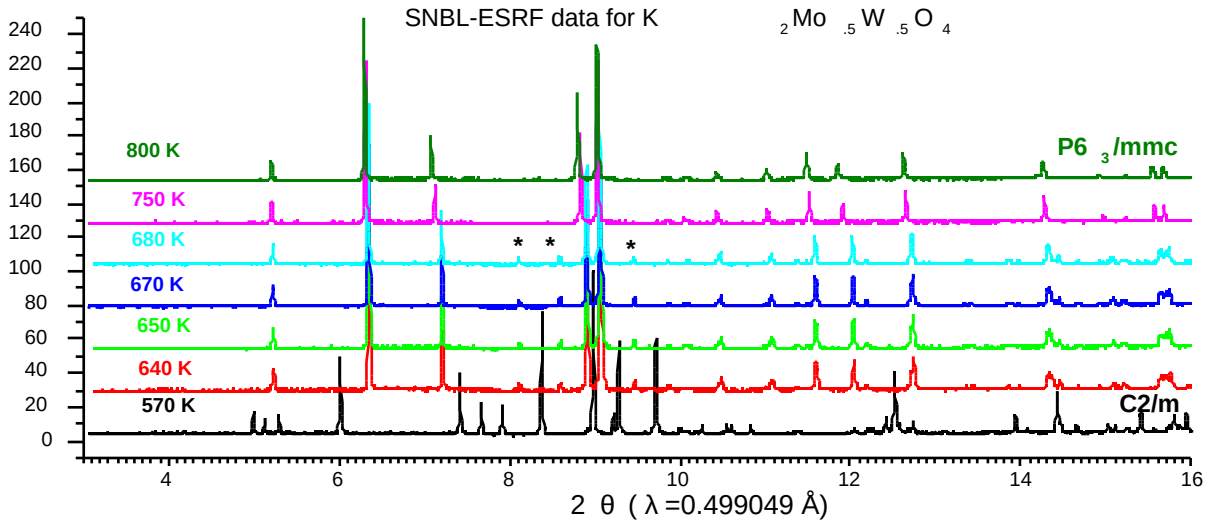

Figure 3 - Diffraction pattern for the $K_2Mo_{0.5}W_{0.5}O_4$ at different temperatures

Conclusions

Despite the initial problems with operation of high temperature oven a good data set could be obtained. The experiments with mixed $K_2Mo_xW_{(1-x)}O_4$ compounds using SNBL High Resolution Powder Beamline confirmed previous results and clearly evidenced the existence of the satellite reflections in the high temperature phase and that the room temperature phase is dependent of the thermal history of the sample. The data is currently been analysed in order to determine new models for the crystal structure in the modulated phase.

References

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