ESRF	**Experiment title:** Phase transition of K_2TaF_7 above 730 C.	**Experiment number**: 01-02-915
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Report:

The compound K_2TaF_7 (K-salt) is one of the components of the melts used for electrodeposition of pure tantalum metal, which has a lot of interesting properties leading to its wide applications in industry. Because K_2TaF_7 is used in molten-salt applications, knowledge of the structural changes during heating below the melting temperature is desirable in order to propose reliable model of solid–liquid phase transitions. There are several ambiguities in the interpretation of the endothermic effects observable within 680-800^{o}C, i.e. close to its melting point. In our study of the phase transitions of β-K_2TaF_7 by DSC (Differential Scanning Calorimetry) within 680-800^{o}C three thermal features have been identified and the corresponding enthalpy changes calculated. As the understanding of the structural changes during heating to the temperatures close to the melting point is not only essential for analysis of electrochemical processes, but also is a prerequisite for building of accurate models of solid-liquid phase transitions, we proposed in situ HT powder diffraction study of phase transitions of K_2TaF_7 within 730 – 800 ^{o}C. In the case of a solid-solid phase transforms it was assumed to obtain basic crystallographic information on the respective phases and to solve their structures from powder diffraction data.

Prior to data collection the wavelength of the incident radiation was refined to 0.69775 Å and the 2D detector was calibrated using LaB_6.

A powder of K_2TaF_7 was filled in a sapphire capillary which oscillated (typically for 60^o) during data collection. A single snap was taken in 120s. Capillaries were be heated by a hot-air blower, the temperature at the samples was, in addition to the built-in thermocouple, measured by the thermocouples installed below and above the capillaries. Voltages at these

thermocouples were sampled by an A/D converter installed and controlled by an external computer belonging to the team. The first patterns collected at 200 and 250°C, respectively, corresponded to those of the α-phase. Further heating up to 600°C showed, in line with the expectations, presence of the β-phase. Heating to 700-740°C has however brought the patterns of crystalline phase (phases), which could not be directly interpreted. The overall picture has further changed at T>740°C, when a new phase, whose diffraction pattern was noticeably different from that of the β-phase, started to dominate. The shape of the pattern did not change until 900°C (i.e. above the expected melting temperature), when heating was interrupted. Furthermore, the character of the pattern did not change even after cooling, i.e. the process was, in contrast to our expectations, irreversible.

A post experiment data treatment revealed that the patterns collected within 600-740°C most probably correspond to mixtures. In contrast, the patterns collected within 760-900°C, were recognized to fairly correspond to the pattern of $K_6Ta_{10.8}O_{30}$ phase and not to any unknown phases of K_2TaF_7. Interestingly, while the $K_6Ta_{10.8}O_{30}$ phase was previously synthesized by a solid state reaction from the oxides [1], in our case the compound must have been formed by a reaction of K_2TaF_7 with oxygen from air. Such ~~a solid state of~~ reaction ~~of K_2TaF_7~~ has however not been documented before. As our most recent DSC experiments triggered by these results showed, that while heating up to the temperature of melting under inert gases K_2TaF_7 was not chemically changed, we plan propose a new experiment with a capillary purged by inert gas during heating

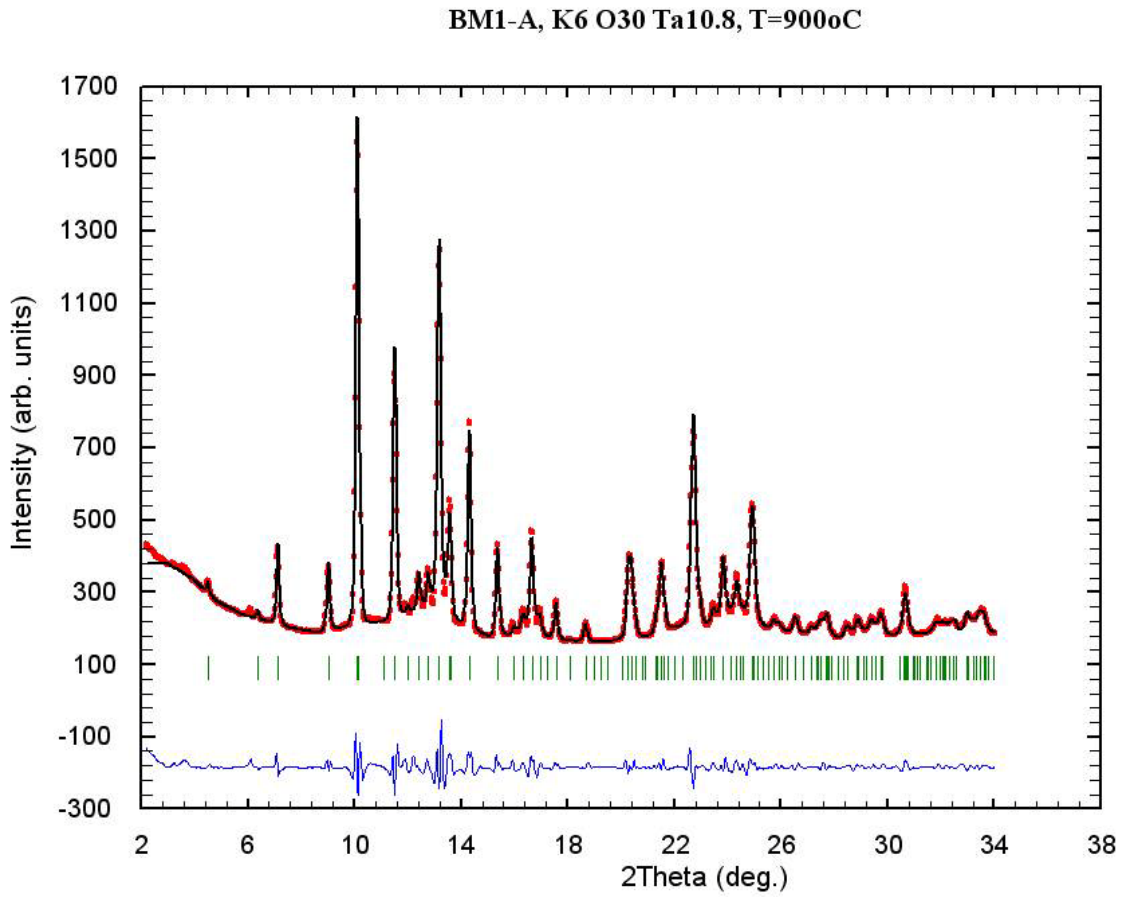

Fig.1 LeBail fit of the of $K_6Ta_{10.8}O_{30}$ phase obtained during the experiments. The space group is *P*4/*mbm*, the lattice parameters are a=12.5364 Å, c=3.944 Å.

1. A.A. Awadalla, B.M.Gatehouse (1978) J. Solid State Chem. **23** 349-355.