	Experiment title: Crystal structure of K_2TaF_7 between600^o and 800^{o}C	**Experiment number**: HS-3321
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Shifts:6	**Local contact(s)**: Dr. Michela BRUNELLI	*Received at ESRF:*

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Report:

Physicochemical properties of melts of certain inorganic salts such as low density, moderate viscosity, and high electric conductivity predetermine their usage in the field of electrochemistry. In order to analyze electrochemical processes the knowledge of the structure of melt is crucial. In the more complex cases the knowledge of the structural changes during heating before melting is also required to facilitate suggesting a more accurate model of solid-liquid phase transition. K_2TaF_7 is one of the components of the melts for electrodeposition of pure tantalum metal, which has many of interesting properties leading to its wide applications in industry. The aim of the project is to find the phase composition at several temperatures below the melting point. From the information on phase composition physical background of the thermal effects recognized in DSC experiment will be deduced. In case of solid-solid transformation it is assumed to obtain basic crystallographic information on the respective phases.

Inasmuch as absorption of Pt-K_2TaF_7 is rather large, a first set of measurements was performed in a quartz rather than Pt capillary. The rationale behind such a decision was to get temperature variation of the lattice parameters prior to data collection in a Pt capillary. The powder diffraction patterns were collected at seven temperatures: 200, 300, 400, 500, 600, 650 and 720^{o}C while heating and at 300 and RT while cooling (using incident X-ray beam with wavelength λ=0.85023 Å). Samples were heated by hot air blower mounted perpendicularly with respect to the capillary. The pattern collected at T=200^{o}C was identified as α-K_2TaF_7 [1], while those taken at 300-400^{o}C corresponded to pure β-K_2TaF_7 [2]. The major phase in the pattern collected at 400^{o}C was still β-K_2TaF_7, but traces of unknown phase also appeared. The patterns obtained at 500, 600, 650 and 720^{o}C, respectively, did not correspond to either of known K_2TaF_7 polymorphs. Because

the capillary was sealed by flame to keep stable reaction conditions and no effects within at least within the temperature range 500-650°C were detected by DSC, we could expect solid state reaction of β-K_2TaF_7 and SiO_2 giving solid solutions. Elemental analysis of reaction product by EDX has given ambiguous results due to overlap of Si(K) and Ta(L) peaks. Analysis of these compounds will be a subject of further study.
Data from the sample contained in a Pt capillary were collected at RT, 240 and 720°C (using incident X-ray beam with wavelength λ=0.39823 Å). Usable angular range was upper limited due to larger Debye-Waller factor to 15 degrees. The contributions of two Pt peaks dominating the range were manually erased from the data sets prior to any calculations. Despite a rather limited 2Θ range the analysis of the diffraction patterns was straightforward. The patterns collected at T=240 and 720°C corresponded to pure β-K_2TaF_7 (Fig.1). Calculations of structural data are in progress.

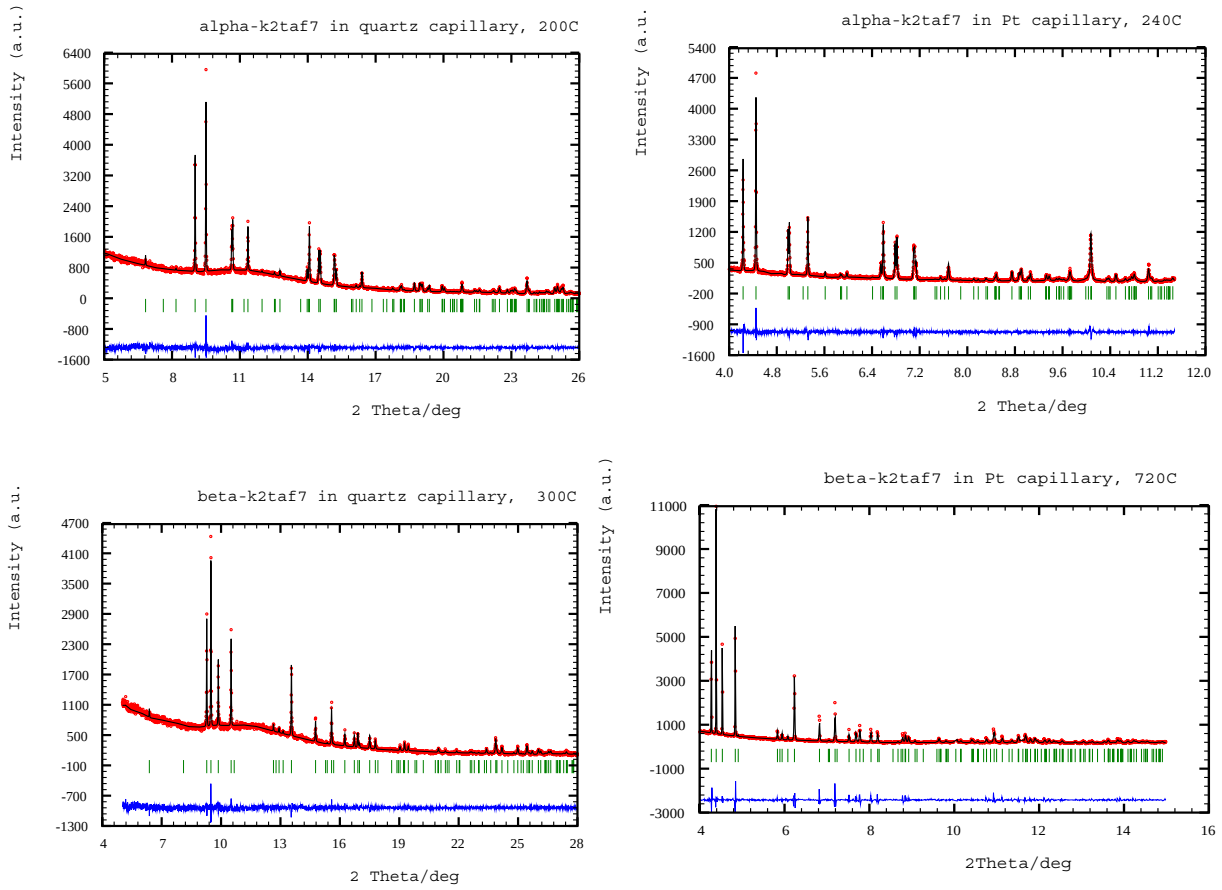

Fig.1. LeBail fit to the data collected at T=200, 240, 300 and 720°C in quartz and Pt capillaries.

Our experiment has confirmed that it is possible to collect usable diffraction data even in highly-absorbing Pt capillary. The main outcome of the experiment is that it has shown, that at temperature of 720°C the compound is still well-crystalline β-modification. This finding can shed more light on previous thermodynamic experiments and encourage planning of further experiments in the temperature range 710°C <T<800°C. Such experiments can help to identify possible phase transition to (yet) hypothetical γ-form.

[1] Torardi, C.C., Brixner, L.H. & Blasse, G. (1987). *J. Solid. State Chem.* **67**, 21-25.
[2] Langer, V., Smrcok, L., Boca, M. (2006) *Acta Cryst.* E**62**, i91-i93