Contribution ID: **23** Type: **Poster**

Synchrotron X-ray diffraction study of novel orthovanadates, $Ca_{10.5-x}TM_x(VO_4)_7$, in broad temperature range

Thursday, 8 September 2022 19:35 (20 minutes)

Calcium orthovanadates and orthophosphates substituted with various cations attract researchers'attention because of opportunity of their application in various fields, especially in optoelectronics, biomedicine and in chemistry in connection with their catalytic properties. Parent compounds $Ca_3(XO_4)_2$, X = V or P, are known to crystallize in R3c space group. The unsubstituted $Ca_3(XO_4)_2$ crystals can be modified by replacing a small fraction (typically up to ~10%) of Ca atoms by other ones, of valences from +1 to +4, without a change of structure, forming novel materials of modified properties; for the case of a divalent transition metal (TM) substituent, their formula is routinely written as $Ca_{10.5-x}TM_x(VO_4)_7$. The structure of such substituted crystals is similar to that of whitilockite related material. Their complex structure including five independent sites (M1-M5) for Ca (and substituting) cations, with polyhedra arranged according to an unusual columnar architecture. Understanding of site occupation preference by transition metal atoms is one of main issue for consideration of such compounds.
Thermal expansion Studies regarding transition metal substituted to $-Ca_3(PO_4)_2$ (β-TCP) or $Ca_3(VO_4)_2$ (TCV) have not been reported, neither for orthovanadates nor orthophosphates except for $Ca_{10}Co_{0.5}(VO_4)_7$ and $Ca_{10}Cu_{0.5}(VO_4)_7$ [1]. The phenomenon of thermal expansion has been studied only for some whitlockite related materials incorporating monovalent and/or trivalent substituents, for instance $Ca_9Y(VO_4)_7$ [2], $Ca_{9.33}K_{2.33}(VO_4)_7$ [3], $Ca_9Gd(VO_4)_7$, and $Ca_{10}K(VO_4)_7$ [4]. Most of these results have been obtained by dilatometric methods.
In this presentation, the structure of whitlockite related TCV oxide is studied at non-ambient temperatures. The high resolution X-ray powder diffraction experiments were performed at ID22 at ESRF. In addition, the structural properties of novel calcium orthovandates, $Ca_3(VO_4)_2$, with Ca atoms partially substituted by transition metal (TM^{2+}), investigated at room and non-ambient temperature based on powder diffraction measurements.
Inspection of the non-ambient-temperature diffraction patterns indicated that the structure does not change with temperature, as confirmed by the Rietveld refinements, the sample maintained the trigonal structure (R3c space group) in the temperature range studied, 4 –1173 K,. This observation is in line with the high temperature Raman scattering studies for TCV (performed in temperature range 298 - 1483 K); the only ferroelectric-paraelectric phase transition is reported to occur at a considerably higher temperature, Tc = 1383 K [5]. In this work, the lattice parameters and unit cell volume of $Ca_{10.5-x}TM_x(VO_4)_7$ are determined as function of temperatures. Moreover, the Rietveld analysis allowed for investigation of temperature variation of both, the site preference of the substituting transition metal atoms and the interatomic distances.

We are grateful to the Polish Ministry of Education and Science for financing the access to ESRF, decision number: 2021 / WK / 11.

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Session Classification: List of posters presented during the conference