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Effect of cationic substitution on structural properties of $Ca_3(VO_4)_2$ orthovanadates

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Orthovanadates have attracted significant research attention due to their potential applications across various fields, including optoelectronics, biomedicine, and catalysis. Calcium orthovanadate ($Ca_3(VO_4)_2$) is known to crystallize in *R*3*c* space group[1]. The structure of natural and synthetic compounds of this family is complex and constructed in a way allowing for various substitutions, with two columnar building units. As the structure supposes five cationic sites (M1-M5) where various substituents can be located at various site, at low or high concentration (up to 10% in specific cases), the determination of structure requires refinement of the occupancies at all these sites.

In this presentation, we explore the structural properties of calcium orthovanadates, specifically $Ca_{10.5-x}TM_x(VO_4)_7$ (x=0-1), where some of the calcium ions have been partially replaced by transition metal ions. We investigate these properties at both, room temperature and non-ambient conditions, through X-ray diffraction measurements[2-4]. High-resolution X- ray powder diffraction experiments were conducted at the ID22 beamline at ESRF. The solubility limit was determined for three sets of samples. The EXAFS results align with the XRD findings regarding the presence of a transition metal at the M5 site. The study of diffraction patterns at non-ambient temperatures indicates that the structure remains unchanged with temperature varying from 4 K to 1100 K, as confirmed by Rietveld refinements. In this work, we determine the unit cell size and atomic positions of $Ca_{10.5-x}TM_x(VO_4)_7$ as functions of temperature. Additionally, we calculate the thermal expansion coefficient for these materials in relation to temperature using various models

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