Structural properties of $Ca_{10.5-x}TM_x(VO_4)_7$ orthovanadates: XRD study at ambient and non ambient

H.S .Rahimi Mosafer[1*], W. Paszkowicz[1], R. Minikayev[1], M Berkowski[1], C. Martin[2], A. Fitch[3]

[1] *Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, 02-668 , Warsaw, Poland*

[2] *Laboratoire CRISMAT, Normandie Université, ENSICAEN, UNICAEN, CNRS, 14050 Caen, France*

[3] *European Synchrotron Radiation Facility, 71 avenue des Martyrs, Grenoble 38000,France*

** Corresponding author email: rahimi@ifpan.edu.pl*

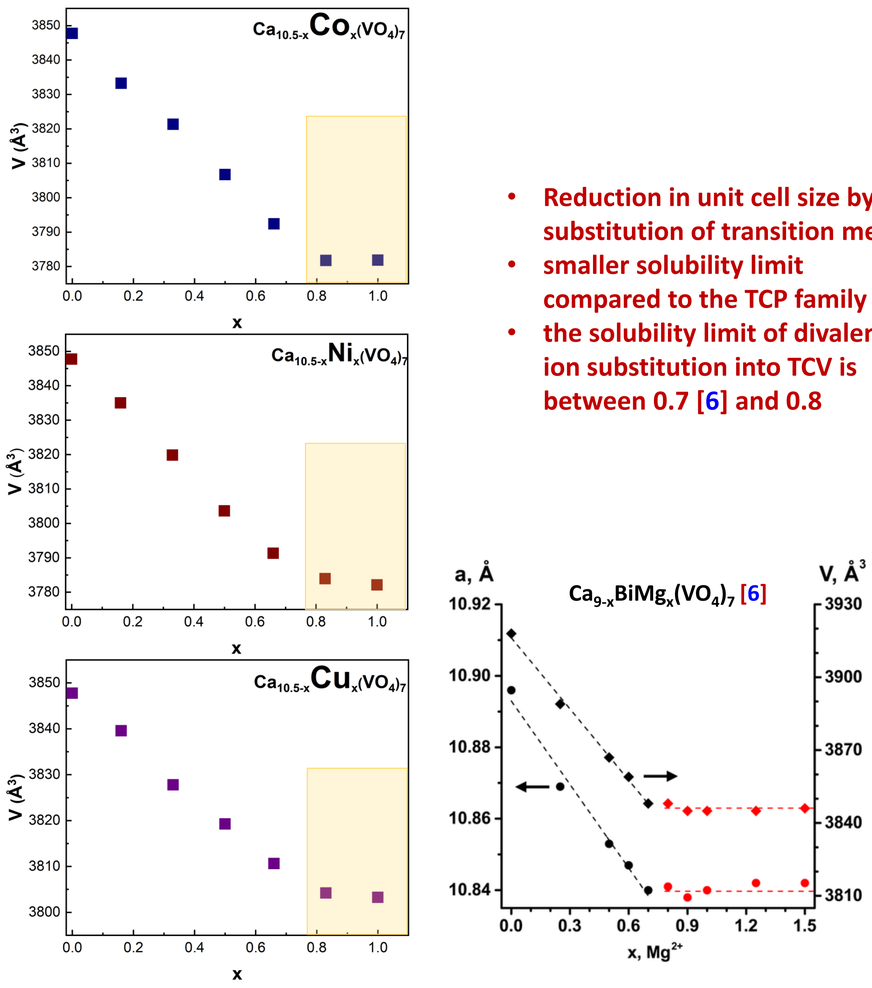
Introduction

- Calcium orthovanadate $Ca_3(XO_4)_2$, X = P or V, is known to crystallize in *R*3*c* space group with structure similar to that of whitlockite mineral, $Ca_{18}(Mg, Fe)_2(PO_4)_{12}(PO_3OH)_2$ [1].
- In $Ca_3(VO_4)_2$ a small fraction of Ca atoms can be replaced by other ones, of valences from +1 to +4, without a change of structure [2].
- In the $Ca_3(VO_4)_2$ (TCV), as in all other whitlockite related compounds, there are five inequivalent Ca sites, named M1(18b -Wyckoff position), M2 (18b), M3 (18b), M4 (6a) and M5 (6a). M4 is half occupied which is justified by theoretical calculation [3].
- This complicated structure can be described as being composed of only two building units, namely, columns named A and B of difference atomic arrangement and composition [4].

Experiment

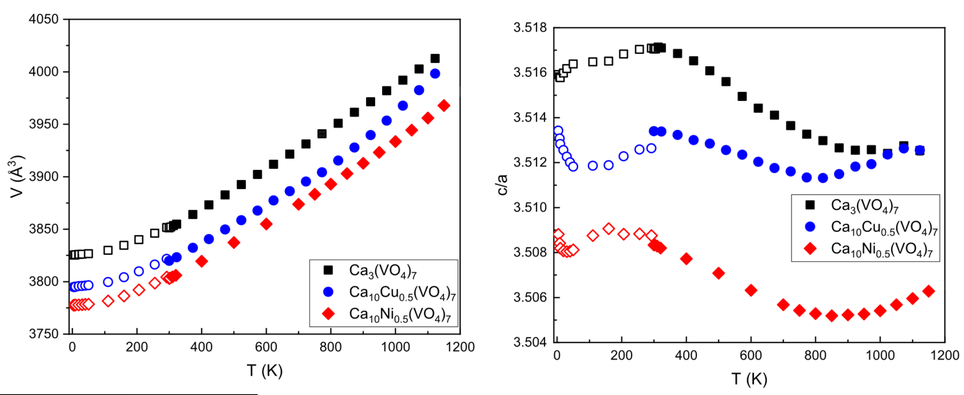
The polycrystalline material was prepared by the solid state reaction of cobalt/copper and vanadium oxides and calcium carbonate.
Powder diffraction measurement were performed by Philips X'Pert Pro Alpha1 diffractometer with Bragg Brentano geometry and CuKα_1 radiation. PXRD Data were collected at room temperature over the range of 9°-160°(2θ) with step of 0.0167°.
Crystal structures of obtained compounds were refined by the Rietveld method using the Fullprof software.
Low temperature powder diffraction measurements were performed by high-resolution X-ray powder diffraction at the ID22 beamline at the European Synchrotron Radiation Facility (ESRF) in the temperature range 4(1)–292(1) K using a helium cryostat. XRPD patterns were measured from a fine powder of samples sealed in a 0.5 mm diameter borosilicate glass capillary.
High temperature powder diffraction measurements were also performed by high-resolution X-ray powder diffraction at the ID22 beamline at the ESRF in the temperature range 300(1) - 1200(1) K using a hot-air blower for two selected samples. XRD patterns were measured from a fine powder of samples sealed in a 0.7 mm
diameter capillary.

Unit cell size

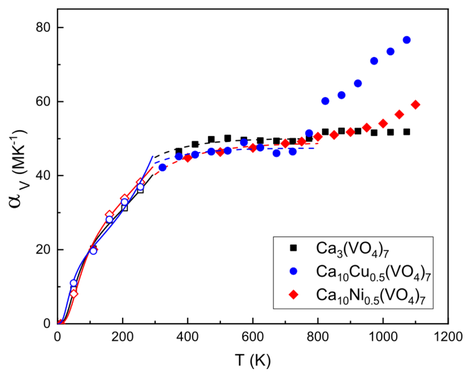


- **Reduction in unit cell size by substitution of transition metal**
- **smaller solubility limit compared to the TCP family [5]**
- **the solubility limit of divalent ion substitution into TCV is between 0.7 [6] and 0.8**

Unit cell size & thermal expansion

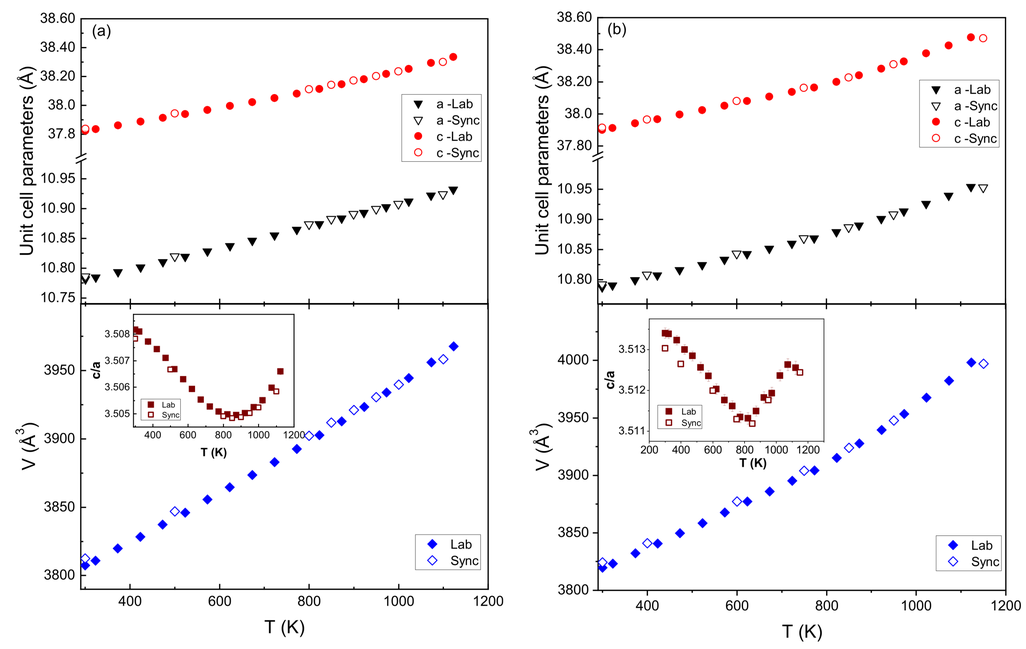


sample	θ_D (K)
$Ca_{10.5}(VO_4)_7$	264(2)
$Ca_{10}Ni_{0.5}(VO_4)_7$	331(1)
$Ca_{10}Ni_{0.5}(VO_4)_7$	177(1)



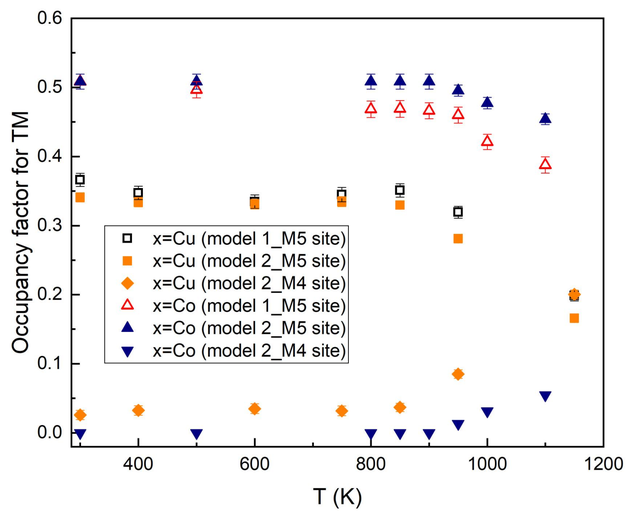
- **The values of volumetric thermal expansion coefficients from room temperature up to approximately 800–900 K do not change significantly for all compounds.**

Synchrotron data at high temperature



- **The behavior of unit cell size is in good agreement with laboratory data for these two samples.**

Structure modifications at high temperature



- **The occupancy remains stable up to 850 K, but above this, the M5 site occupancy decreases, suggesting some transition metals shift to other sites.**
- **According to the final model (model 2), both M4 and M5 sites are the most probable joint hosts for the TM ions. The occupancy of TM ions at M5 decreases and M4 increases gradually by raising the temperature.**

Conclusions

- Phase analysis of $Ca_{10.5-x}TM_x(VO_4)_7$ has shown that samples crystalize in *R*3*c* space group. Diffraction peaks are assigned to whitlockite-β-$Ca_3(PO_4)_2$ structure type.
- One notable characteristic of these compounds is smaller solubility limit compared to the β-$Ca_3(PO_4)_2$ family
- The structures of $Ca_{10.5-x}TM_x(VO_4)_7$ remain stable over the entire temperature range (4-1150 K), with no signs of phase transition and decomposition.
- The M4 and M5 site are preferable sites for Cu ions above inflection temperature

References

[1] A. Gopal and C. Calvo, Nature, vol. 238, p. 37, 1972.
[2] G. Renaudin et al., Materials (Basel)., vol. 10, no. 1, pp. 1–22, 2017.
[3] E. E. Jay et al., J. Solid State Chem., vol. 183, 2261–2267, 2010.
[4] B. Dickens et al., J. Solid State Chem., vol. 10, 232–248, 1974.
[5] K. Spaeth et al.. *J. Solid State Chem.* 285, 121225 ,2020.
[6] N. G. Dorbakov et al, J. Am. Ceram. Soc., 101, 4011–4022,2018

Acknowledgements

The access to ESRF was financed by the Polish Ministry of Education and Science decision number 2021/WK/11.