

Modeling of Site Occupation for Novel Orthovanadates, $\text{Ca}_{10}\text{TM}_{0.5}(\text{VO}_4)_7$ (TM = Co, Ni, Cu)

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Introduction

Calcium orthovanadate $\text{Ca}_3(\text{XO}_4)_2$, X = P or V, is known to crystallize in $R3c$ space group with structure similar to that of whitlockite mineral, $\text{Ca}_{18}\text{Mg}_2(\text{PO}_4)_{12}(\text{PO}_3\text{OH})_2$ [1]. In $\text{Ca}_3(\text{XO}_4)_2$ a small fraction of Ca atoms can be replaced by other ones, of valences from +1 to +4, without a change of structure [2]. Cobalt-containing tricalcium phosphate ceramics may be purposed for bone tissue regeneration with improved angiogenic capacity [3]. Catalytic behavior of $\text{Ca}_{10.5-5-x}\text{Cu}_x(\text{PO}_4)_7$ was studied by Benaraf et al. [4]. In this study, we investigate the structural properties of $\text{Ca}_{10}\text{TM}_{0.5}(\text{VO}_4)_7$ where TM are cobalt, nickel and copper. The insight of the structural properties of these materials, not reported until now, is therefore helpful for their full understanding and characterization.

General info

In the 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 [5]. The vanadium atoms locate in three different V1 (6a), V2 (18b) and V3 (18b) sites with tetrahedral coordination. 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 [6]. As the structure supposes five cationic sites where various substituents can be located at different site, at low or high concentration, the determination of structure requires refinement of the occupancies at all these sites. This task uses to meet difficulties arising as a function of the scattering factors of the contributing atoms. Because of large unit cell, modeling by first principle is a bit difficult but recently, structural properties of whitlockite related material based on quantum chemical calculation were done in ref. 7. It leads to generation of information such as occupancy of M sites by substitution ions.

Experiment

Solid solution of new materials, $\text{Ca}_{10}\text{TM}_{0.5}(\text{VO}_4)_7$ where TM = Co, Ni, Cu were synthesized by solid state reaction. Copper (Cobalt) and vanadium oxide with calcium carbonate mixed in stoichiometric proportion and formed into pellet. By 3 steps of 6h this pellet calcined. The temperature for the first step was 1000 °C and for other 2 step was 900 °C.

Powder diffraction measurement was performed by Philips X'Pert Pro Alpha1 diffractometer with Bragg-Brentano geometry and $\text{CuK}\alpha_1$ radiation. PXRD Data were collected at room temperature over the range of 9°-160°(2 θ) with step of 0.0167°.

The crystal structure refinement of the synthesized sample was made by employing the Rietveld method using XRD data. The refinement procedure is based on the minimization of the weighted, squared differences between the observed and calculated intensities at every step in the diffraction pattern. The minimization was carried out using the reliability index parameters.

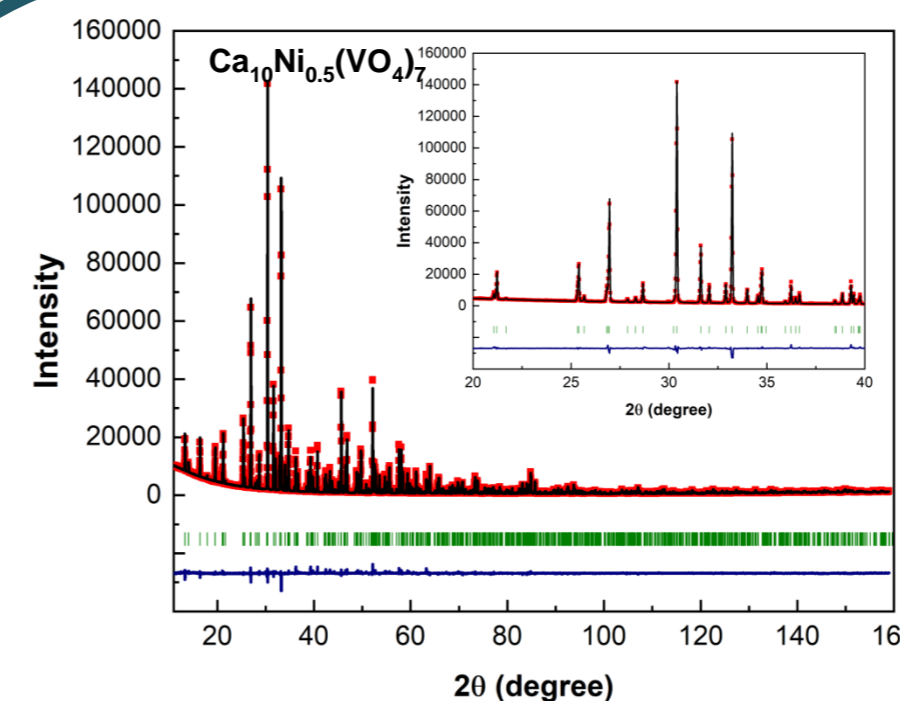


Fig. 1. Rietveld refinement for $\text{Ca}_{10}\text{Ni}_{0.5}(\text{VO}_4)_7$

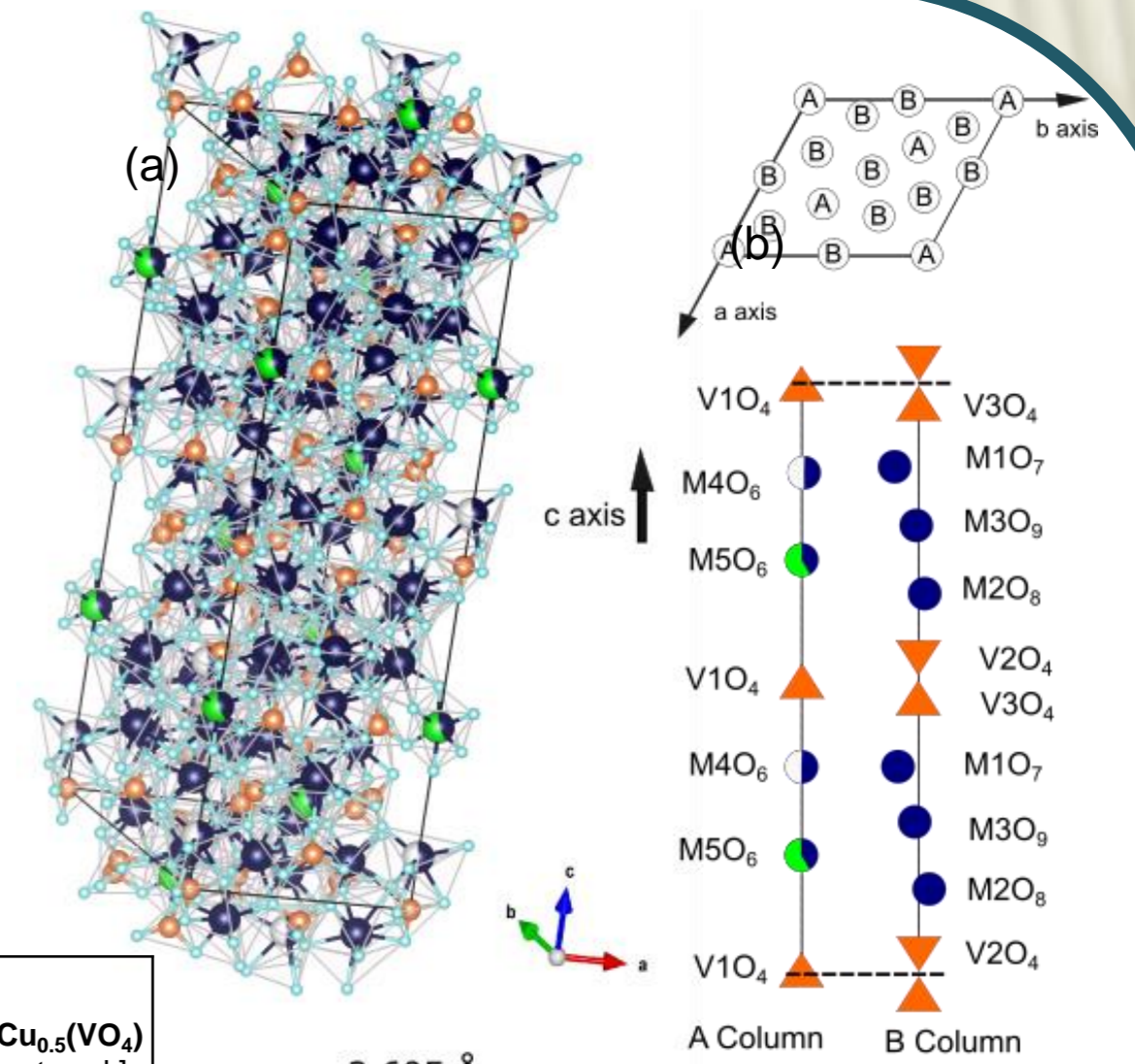


Table 1. structure parameters of various samples

samples	$\text{Ca}_{10.5}(\text{VO}_4)_7$ [8]	$\text{Ca}_{10}\text{Co}_{0.5}(\text{VO}_4)_7$ [present work]	$\text{Ca}_{10}\text{Ni}_{0.5}(\text{VO}_4)_7$ [present work]	$\text{Ca}_{10}\text{Cu}_{0.5}(\text{VO}_4)_7$ [present work]
a (Å)	10.810(2)	10.78013(6)	10.77732(3)	10.78703(7)
c (Å)	38.0290(1)	37.81961(23)	37.81334(10)	37.89954(28)
v (Å ³)	3848.5	3806.660	3803.633	3819.164
c/a	3.51795	3.50827	3.50860	3.51343

Fig. 2. Unit cell (a), crystal structure model of $\text{Ca}_{10}\text{Co}_{0.5}(\text{VO}_4)_7$. The layout of A and B columns and columns composition (b), First nearest coordination around M1-M5 and minimum (dashed arrow) and maximum (solid arrow) distances of M-O for $\text{a}_{10}\text{Co}_{0.5}(\text{VO}_4)_7$ are shown (c).

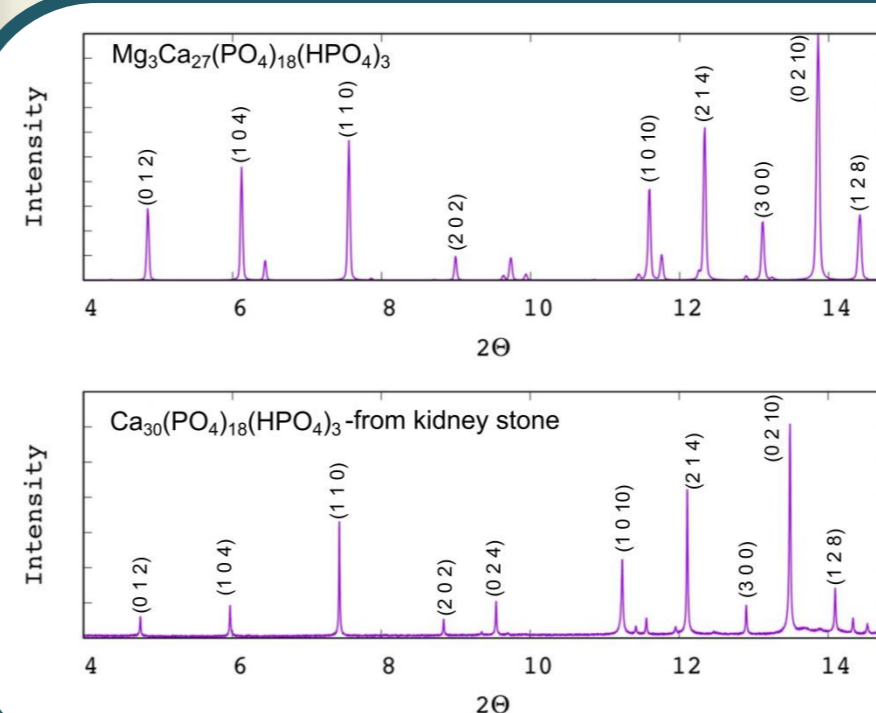


Fig. 3. Comparison theoretical X-ray diffraction pattern of $\text{Mg}_3\text{Ca}_{27}(\text{PO}_4)_{18}(\text{HPO}_4)_3$ from DFT calculation with experimental diffraction patterns of $\text{Ca}_{30}(\text{PO}_4)_{18}(\text{HPO}_4)_3$ from a kidney stone. This is modified figure from [7].

Results

- Phase analysis of $\text{Ca}_{10}\text{TM}_{0.5}(\text{VO}_4)_7$ has shown that samples crystallize in $R3c$ group. Diffraction peaks are assigned to those of whitlockite-type materials.
- The starting model for refinement of these material was $\text{Ca}_{1.5}\text{Sr}_{1.5}(\text{VO}_4)_7$ [9].
- Lattice parameters decrease by substitution of TM [TM = Co, Ni, Cu].
- The ideal stoichiometric TM/(TM + Ca) ratio in the unit cell is 4.76%. These refinements bring 5.58% for cobalt sample, 4.20% for nickel sample and 4.10% for copper sample.
- Structural refinement was performed, assuming various variants of occupancy, according to different possible variants of site occupation.
- Among the five available Ca sites, only M5 is found to be occupied by the transition metal, this finding is in line with observation for related phosphates [10]. This results is consistence with DFT calculation of Mg site occupation which is substitute to calcium orthovanadates [7].
- Transition metals enter to column A (for this column, one of building blocks is the M5-centered polyhedron) and column B is without any change.
- M5 site exhibits octahedral geometry with two set of bond distances. Mean Ca-O bond length on M5 sits are short (2.308 Å) as compared to Ca-O (2.404 Å) [9]. Partial substitution of cobalt, nickel and copper induce more shrinking of this bond, 2.192 Å, 2.189 Å and 2.245 Å due to smaller radius of these three cations (Co-O 2.13 Å and Cu-O 1.97 Å [11]).

References

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