



**UNIMORE**  
UNIVERSITÀ DEGLI STUDI DI  
MODENA E REGGIO EMILIA

Dipartimento di Scienze Fisiche,  
Informatiche e Matematiche



## FIM-S3 SEMINAR

# Crystal chemistry of whitlockite-type materials

Wednesday September 4<sup>th</sup>, 2024 – 15.00 (sharp)

S3 Seminar Room, 3<sup>rd</sup> Floor, Physics building

Remote link: [Teams](#)

## Speaker

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## Abstract

Whitlockite mineral,  $\text{Ca}_9(\text{MgFe})(\text{PO}_4)_6\text{PO}_3\text{OH}$  and some other hydrated and (mostly extraterrestrial) chemically-related anhydrous minerals, such as merrillite,  $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ , exhibit a close structural relation with  $\text{Ca}_3(\text{XO}_4)_2$ ,  $\text{X} = \text{P}, \text{V}$  or  $\text{As}$ . Mg-substituted variant,  $\text{Ca}_{9.5}\text{Mg}(\text{PO}_4)_7$ , is a minor component of living organisms (in scaffold and teeth) and in microcalcifications connected with human diseases, like breast cancer and arteriosclerosis. The whitlockite-type minerals form the cerite supergroup, whereas the synthetic materials of this structure build a quite large family, with members differing by chemical composition and site occupation. Virtually all these oxides crystallize in  $R3c$  space group (the hexagonal cell size is described by  $a \sim 11 \text{ \AA}$  and  $c \sim 38 \text{ \AA}$ ). At existing five inequivalent Ca sites, they can accommodate a high amount of dopants (frequently, up to  $\sim 10\%$  of the Ca content). Natural minerals contain Na, Mg, Fe and Y substituents at Ca sites, whereas the synthetic ones can include these and also many other iso- or aliovalent dopant ions. Substitutional or occupational disorder is observed for these materials. The doped structures can be substitutionally ordered (e.g. for Mg dopant) or disordered (e.g. for rare-earth dopants). Synthetic variants are described e.g. as  $\text{Ca}_{10}\text{M}^{1+}(\text{XO}_4)_7$ ,  $\text{Ca}_{9.5}\text{M}^{2+}(\text{XO}_4)_7$ ,  $\text{Ca}_9\text{M}^{3+}(\text{XO}_4)_7$ . These formulae differ due to the charge-balance condition. Usually (but with exceptions) the substituent content ranges from 0 to about 10% in respect to Ca. The opportunity of diverse doping opens the possibility of tuning of physical properties. A tentative systematics of synthetic whitlockite-related orthophosphates and orthovanadates and some other crystalline materials illustrates the wealth of available chemical compositions. The natural and synthetic crystals of whitlockite family are based mostly on  $\text{Ca}_3(\text{XO}_4)_2$  with a part of cations substituted by dopant ion(s) residing at specific crystallographic sites. Some XRD experiments performed for doped synthetic  $\text{Ca}_3(\text{XO}_4)_2$  samples demonstrate the existence of earlier not reported orthovanadates of this family. The proposed compositional systematics is expected to be useful in design of such materials exhibiting desired structural and physical properties, being suitable for consideration of their application in optoelectronic or other fields. When considered series of substitutions by univalent ions, one observed a variation of unit cell volume with ionic size. Such dependence tends to be linear, if the substituents reside at a single crystallographic site. Also dual substitutions have been studied and they are found to exhibit similar behavior. The flexibility in doping and the resulting opportunity of tuning the crystal characteristics suggest that the meaning of the whitlockite-family materials may increase in future.

Host: Rita Magri

In collaboration with

