

Impact of dopant type (Tm, Co, and Mn) and doping method on the local and statistical structure of framework whitlockite-type $\text{Ca}_3(\text{VO}_4)_2$ crystals. New crystal-chemical effects.

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The whitlockite-type compounds have a structure favorable for the introduction of dopant ions, which led to the implementation or enhancement of functional properties. The use of different doping methods can significantly affect the concentration and structural location of activator ions in the crystal matrix, and hence the properties of the material. This was the motivation for the work. The main research methods are X-ray structural analysis (diffractometers and synchrotron, room temperature and 100 K; *statistical structure*) and X-ray absorption spectroscopy (synchrotron; *local structure*).

In the idealized whitlockite structure $\text{Ca}_3(\text{PO}_4)_2$ (space group $R3c$, $Z = 18$) with the composition $(\text{Ca}_{18}\text{Ca}_{218}\text{Ca}_{318})(\text{P}_{18}\text{P}_{218})\text{O}_{144}$, Ca1 and Ca3 atoms are located in two-capped trigonal prisms (CN = 8; CN is a coordination number) and Ca2 atoms form mono-capped trigonal prisms (CN = 7), P1 and P2 atoms being in tetrahedra (CN = 4). In the whitlockite-type structure $\text{Ca}_3(\text{VO}_4)_2$ (CVO; space group $R3c$, $Z = 21$) with the composition $[\text{Ca}_{18}\text{Ca}_{218}\text{Ca}_{318}\text{Ca}_{46}(\text{Ca}_{52.65})(\text{Ca}_{5A0.35})](\text{V}_{18}\text{V}_{218}\text{V}_{36})\text{O}_{168}$, there are additional sites in the framework channels: Ca4 and Ca5A (octahedra; CN = 6), Ca5 (tetrahedron; CN = 4), Ca5 + Ca5A (distorted octahedron; CN = 6), and V3 (trigonal pyramid; CN = 3 + 1).

Dopant ions (up to 1.0 wt%) introduced into the melt (Czochralski method) over CVO stoichiometry are distributed over the Ca3 and Ca4 (light-green CVO:Tm and green CVO:Mn crystals) as well as Ca5 + Ca5A (CVO:Mn) crystallographic sites. The dopant ions form specific local environments: in the CVO:Tm structure, CN $\text{Tm}^{3+} = 7$ (octahedral coordination by O^{2-} ions with one additional O atom) and CN $\text{V}^{5+} = 4.4$; in the CVO:Mn structure, CN $\text{Mn}^{3+} = 6$ (an elongated octahedron is a tetragonal bipyramid; Jahn-Teller effect) and CN $\text{V}^{5+} = 4$. Air annealing of CVO:Mn crystals promotes the appearance of yellow-orange crystals with Mn^{4+} and $\text{Mn}^{(3+\delta)+}$ ions having octahedral coordination in the Ca3 and Ca5 sites in the structures of the lower and upper parts of the crystal boule, respectively.

High-temperature diffusion annealing of CVO crystal with the presence of Mn_2O_3 solid phase (blue-green CVO: Mn_2O_3) increases the number of sites (Ca2, Ca3, Ca4) occupied by a greater number of $\text{Mn}^{(2+\delta)+}$ ions with variable formal charge and tetrahedral local environment. Similar annealing of CVO with the Co_3O_4 solid phase (violet CVO: Co_3O_4) leads to the appearance of Co^{2+} ions, which, unlike CVO: Mn_2O_3 , partially replace the Ca^{2+} ions in the Ca2, Ca3, Ca4, Ca5, and Ca5A crystallographic sites.

The bands revealed on the absorption spectra were assigned to Tm, Co, and Mn ions having different formal charges and different local environments in the CVO structure.

Keywords: crystal growth; doping; transition metals; frame structure; local structure

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