

# Crystal chemistry of synthetic mukhinite, V-analogue of clinozoisite, on the join $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ - $\text{Ca}_2\text{Al}_2\text{VSi}_3\text{O}_{12}(\text{OH})$

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This is the first report of the crystal structure of mukhinite, V-analogue clinozoisite, on the join  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ - $\text{Ca}_2\text{Al}_2\text{V}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$  synthesized at 1.5 GPa and 800 °C (Run 20). The study was performed to clarify the distribution of  $\text{V}^{3+}$  among structurally independent octahedral M1, M2 and M3 sites, and the effect of  $\text{V}^{3+}$  on the crystal structure. Although epidote-supergroup minerals occur widely in low- to medium-grade metamorphic mafic rocks, and hydrothermally altered rocks, clinozoisite- and allanite-subgroup minerals rich in  $\text{V}^{3+}$  are not common, and have been reported from restricted localities. Mukhinite from the Tashelginskoye iron ore deposit, southwestern Siberia, having the composition of  $\text{Ca}_{2.0}(\text{Al}_{2.1}\text{V}_{0.8}\text{Fe}_{0.1})\text{Si}_{3.1}\text{O}_{12}(\text{OH})$  has been regarded as a  $\text{V}^{3+}$ -analogue of clinozoisite (Shepel and Karpenko 1969). However, its crystal structure and  $\text{V}^{3+}$  distribution among octahedra have not been investigated. Several syntheses and/or phase-equilibrium studies on clinozoisite-subgroup minerals have been performed. To the best of our knowledge, there has been no investigation of synthetic V-bearing epidote-supergroup minerals.

Syntheses were performed under the conditions of 1.2-1.5 GPa and 600-800 °C, and run duration 89-261 hours. Mukhinite and  $\text{V}^{3+}$ -bearing clinozoisite (Czo) in all run products are associated with zoisite (Zo), and also coexist with V-bearing phases such as vanadomalayaite, goldmanite, V-oxides and unidentified Ca-Al-bearing vanadates. Czo and Zo were distinguished by using Raman spectra. As the result of submicroscopic texture observation by TEM, Zo in Run 19 product often contain Czo lamellae with several nm thickness, and they have epitaxial relationship as  $\text{Zo}[010]//\text{Cz}[010]$ . Czo and Zo in Run 20 product are generally separated, but in a few cases, they contact each other at boundaries. However, the phases in Run 20 do not have an epitaxial relationship, and Zo intergrowth with Czo is not observed. Mukhinite and  $\text{V}^{3+}$ -bearing clinozoisite crystallized in the Run 20 product show a compositional gap between 0.33-0.74 V atoms per formula unit (apfu), and the V content attains 1.14 apfu. The co-existence of low  $\text{V}^{3+}$ - and high  $\text{V}^{3+}$ -clinozoisites indicates the presence of a miscibility gap at 1.5 GPa and 800 °C. Two mukhinite crystals with 0.75 and 0.83  $\text{V}^{3+}$  apfu were used for X-ray single-crystal structure analysis (hereafter, labelled as 20d and 20k). Structure refinements of the 20d and 20k crystals converged to  $R_1$  values of 4.20% and 3.33%, respectively. The unit-cell parameters are  $a = 8.8995(2)$ ,  $b = 5.6299(1)$ ,  $c = 10.1532(2)$  Å,  $\beta = 115.327(1)^\circ$ , and  $V = 459.81(2)$  Å<sup>3</sup> for 20d, and  $a = 8.8999(1)$ ,  $b = 5.6357(1)$ ,  $c = 10.1499(1)$  Å,  $\beta = 115.306(1)^\circ$ , and  $V = 460.24(2)$  Å<sup>3</sup> for 20k. The resulting  $\text{V}^{3+}$  occupancies among the octahedral sites of 20d and 20k are  $^{\text{M1}}(\text{Al}_{0.894(6)}\text{V}_{0.106})^{\text{M2}}(\text{Al}_{0.976(6)}\text{V}_{0.024})^{\text{M3}}(\text{V}_{0.621(6)}\text{Al}_{0.379})$  and  $^{\text{M1}}(\text{Al}_{0.868(4)}\text{V}_{0.132})^{\text{M2}}(\text{Al}_{0.957(4)}\text{V}_{0.043})^{\text{M3}}(\text{V}_{0.652(2)}\text{Al}_{0.348})$ , respectively. Site preference of  $\text{V}^{3+}$  at the octahedral sites is  $\text{M3} > \text{M1} > \text{M2}$  as that of  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$ . The intracrystalline partition coefficient of  $\text{V}^{3+}$  and  $\text{Al}^{3+}$  between the M1 and M3 sites,  $K_D = (\text{V}^{3+}/\text{Al})^{\text{M1}}/(\text{V}^{3+}/\text{Al})^{\text{M3}}$ , is 0.07-0.08, which is greater than those of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  (0.03-0.05) and of  $\text{Mn}^{3+}$  and  $\text{Al}^{3+}$  (0.04-0.06). Variations of the unit-cell parameters are strongly related to the variations of the M3-Oi and M1-Oi distances. The unit-cell volumes of mukhinites are similar to those of  $\text{Ca}_2(\text{Al},\text{Fe}^{3+})_3\text{Si}_3\text{O}_{12}(\text{OH})$ -epidote. However, it is noticed that the *a*-dimension is longer, and the *c*-dimensions shorter. The *b* angles of the mukhinites are also different from those of epidotes, but similar to those of  $\text{Cr}^{3+}$ -clinozoisite. Although the behavior of  $\text{V}^{3+}$  and its effect on the epidote-type structure are expected to be similar to those in the case of  $\text{Fe}^{3+}$  due to their similar ionic radii, some structural

variations cannot be explained only in terms of the similarity of ionic radii between  $V^{3+}$  and  $Fe^{3+}$ .

Keywords: mukhinite, clinozoisite, synthesis, crystal chemistry, Raman spectroscopy, TEM