

SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

**Crystal chemistry of spinels in the system  $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$ - $\text{Mg}_2\text{VO}_4$**

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**ABSTRACT**

Eight spinel single-crystal samples belonging to the spinel sensu stricto-magnesiocoulsonite series ( $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$ ) were synthesized and crystal-chemically characterized by X-ray diffraction, electron microprobe and optical absorption spectroscopy. Site populations show that the tetrahedrally coordinated site (T) is populated by Mg and minor Al for the spinel sensu stricto compositions, and only by Mg for the magnesiocoulsonite compositions, while the octahedrally coordinated site (M) is populated by Al,  $\text{V}^{3+}$ , minor Mg, and very minor amounts of  $\text{V}^{4+}$ . The latter occurs in appreciable amounts in the Al-free magnesium vanadate spinel,  $^{\text{T}}(\text{Mg})^{\text{M}}(\text{Mg}_{0.26}\text{V}_{1.48}^{3+}\text{V}_{0.26}^{4+})\text{O}_4$ , showing the presence of the inverse spinel  $\text{VMg}_2\text{O}_4$ . The studied samples are characterized by substitution of  $\text{Al}^{3+}$  for  $\text{V}^{3+}$  and  $(\text{Mg}^{2+}+\text{V}^{4+})$  for  $2\text{V}^{3+}$  described in the system  $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$ - $\text{VMg}_2\text{O}_4$ .

The present data in conjunction with data from the literature provide a basis for quantitative analyses of two solid-solution series  $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2^{3+}\text{O}_4$  and  $\text{MgV}_2^{3+}\text{O}_4$ - $\text{V}^{4+}\text{Mg}_2\text{O}_4$ . Unit-cell parameter increases with increasing  $\text{V}^{3+}$  along the series  $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$  (8.085–8.432 Å), but only slightly increases with increasing  $\text{V}^{3+}$  along the series  $\text{VMg}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$  (8.386–8.432 Å). Although a solid solution could be expected between the  $\text{MgAl}_2\text{O}_4$  and  $\text{VMg}_2\text{O}_4$  end-members, no evidence was found. Amounts of  $\text{V}^{4+}$  are nearly insignificant in all synthetic Al-bearing vanadate spinels, but are appreciable in Al-free vanadate spinel.

An interesting observation of the present study is that despite the observed complete solid-solution along the  $\text{MgAl}_2\text{O}_4$ - $\text{MgV}_2\text{O}_4$  and  $\text{MgV}_2\text{O}_4$ - $\text{VMg}_2\text{O}_4$  series, the spinel structure seems to be unable to stabilize  $\text{V}^{4+}$  in any intermediate members on the  $\text{MgAl}_2\text{O}_4$ - $\text{Mg}_2\text{VO}_4$  join even at high oxygen fugacities. This behavior indicates that the accommodation of specific V-valences can be strongly influenced by crystal-structural constraints, and any evaluation of oxygen fugacities during mineral formation based exclusively on V cation valence distributions in spinel should be treated with caution. The present study underlines that the V valency distribution in spinels is not exclusively reflecting oxygen fugacities, but also depends on activities and solubilities of all chemical components in the crystallization environment.

**Keywords:** Vanadate spinel, magnesiocoulsonite, electron microprobe, crystal synthesis, X-ray diffraction, optical absorption spectroscopy