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

Crystal chemistry of spinels in the system MgAl₂O₄-MgV₂O₄-Mg₂VO₄

FERDINANDO BOSI¹²*, HENRIK SKOGBY³, ROSA ANNA FREGOLA⁴, and ULF HÅLENIUS³

¹Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Roma, Italy
²CNR-Istituto di Geoscienze e Georisorse, UOS Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy
³Department of Geosciences, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden
⁴Dipartimento di Scienze della Terra e Geoambientali, Università di Bari Aldo Moro, via E. Orabona 4, I-70125 Bari, Italy

ABSTRACT

Eight spinel single-crystal samples belonging to the spinel sensu stricto-magnesiocoulsonite series (MgAl₂O₄-MgV₂O₄) 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, V⁵⁺, minor Mg, and very minor amounts of V⁴⁺. The latter occurs in appreciable amounts in the Al-free magnesium vanadate spinel, \( \text{Mg}_2\text{V}_4\text{O}_{12} \), showing the presence of the inverse spinel VMg₂O₄. The studied samples are characterized by substitution of Al³⁺ for V⁵⁺ and (Mg³⁺+V⁴⁺) for 2V⁴⁺ described in the system MgAl₂O₄-MgV₂O₄-VMg₂O₄.

The present data in conjunction with data from the literature provide a basis for quantitative analyses of two solid-solution series MgAl₂O₄-MgV₂O₄ and MgV₂O₄-VMg₂O₄. Unit-cell parameter increases with increasing V⁵⁺ along the series MgAl₂O₄-MgV₂O₄ (8.085–8.432 Å), but only slightly increases with increasing V⁴⁺ along the series VMg₂O₄-MgV₂O₄ (8.386–8.432 Å). Although a solid solution could be expected between the MgAl₂O₄ and VMg₂O₄ end-members, no evidence was found. Amounts of V⁴⁺ 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 MgAl₂O₄-MgV₂O₄ and MgV₂O₄-VMg₂O₄ series, the spinel structure seems to be unable to stabilize V⁴⁺ in any intermediate members on the MgAl₂O₄-Mg₂VO₄ 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

INTRODUCTION

Several substances crystallize in the spinel type structure, most of which are multiple oxides. These latter may be defined by the general formula AB₂O₄, where A and B are usually divalent, trivalent, and tetravalent cations in the so-called 2-3 spinels (A²⁺B³⁺O₄) and 4-2 spinels (A⁴⁺B²⁺O₄). The spinel structure is usually described in the space group Fd̅₃m as a slightly distorted cubic close packed array of oxygen anions, in which the A and B cations are distributed in one-eighth of all tetrahedrally coordinated sites (T) and half of all octahedrally coordinated sites (M). The unit-cell parameters (a, a, a) and oxygen fractional coordinates (u, u, u) define the resulting tetrahedral (T-O) and octahedral (M-O) bond lengths. The distribution of A and B cations over T and M leads to two different ordered site populations in the 2-3 spinels: (1) normal spinel, where the A³⁺ cation occupies T and the two B²⁺ cations occupy M (e.g., MgAl₂O₄, spinel sensu stricto); (2) inverse spinel, where one of the B³⁺ cations occupies T and the remaining A²⁺ and B²⁺ cations occupy M (e.g., Fe₂O₄, magnetite). Similarly, two different types of site populations occur in the 4-2 spinels: (1) normal spinels, in which an A⁴⁺ cation occupies the T site and two B²⁺ cations occupy the M site (e.g., γ-SiMgO₃, ringwoodite); (2) inverse spinels, in which a B²⁺ cation occupies T, and the remaining A⁴⁺ and B²⁺ cations occupy M (e.g., TiFe₂O₄, ulvöspinel). Vanadium-bearing spinels are very important in materials science for their electric and magnetic properties (e.g., Miyoshi et al. 2000; Liu et al. 2001) as well as in geosciences for their occurrence in a wide range of geological environments on Earth, Moon, Mars, and in meteorites (e.g., Papke et al. 2005; Righter et al. 2006a). Furthermore, their crystal chemistry has been shown to be sensitive to variations in temperature and oxygen fugacity (fO₂) conditions (e.g., Canil 1999; Connolly and Burnett 2003; Sutton et al.