Intersite distribution of Fe$^{2+}$ and Mg in the spinel (sensu stricto)–hercynite series by single-crystal X-ray diffraction

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ABSTRACT

The influence of composition on Fe$^{2+}$-Mg intracrystalline distribution was studied in eleven synthetic crystals belonging to the spinel (sensu stricto)–hercynite series (Mg$_{1-y}$Fe$_{2y}^{2+}$Al$_2$O$_4$, with 0 ≤ y ≤ 1, produced by flux-growth at 800 °C. Samples were analyzed by single-crystal X-ray diffraction and electron microprobe methods, and found to be chemically homogeneous with only minor Fe$^{3+}$, which substitutes for Al and increases up to 0.09 atoms per formula unit with total Fe. Structural parameters a, u, T-O, and M-O increase with hercynite content and, among bond distances, T-O shows the maximum change, from 1.920 to 1.968 Å. The a variation from 8.0855 to 8.1646 Å is essentially caused by the T-O increase that, in turn, is due to the cooperative effects of (1) Fe$^{2+}$ → Mg substitution and (2) decrease of inversion from 0.23 to 0.15 along the series.

Intracrystalline cation distribution was obtained by a minimization procedure that takes into account structural and chemical data. The T site is mainly populated by Mg and Fe$^{2+}$ but, at a given temperature, Fe$^{2+}$ shows a marked preference for tetrahedral coordination with respect to Mg. The influence of composition and temperature on Fe-Mg intracrystalline distribution was modeled within the framework of the general thermodynamic model of O’Neill and Navrotsky for spinel binary solid solutions. The inversion values observed in our samples agree very well with those calculated by the model. Both measured and calculated amounts of octahedral Fe$^{2+}$ (VIFe$^{2+}$) show a non-linear increase from spinel s.s. to hercynite. Consequently, the $^{60}$Fe$^{2+}$/Fe$^{2+}$ tot ratio is not constant along the join, but increases from zero to 15% toward the hercynite end-member. This behavior explains the very limited Fe$^{2+}$ inversion observed in natural spinels, which usually belong to the hercynite-poor part of the join.

INTRODUCTION

Spinelss have a very compact oxygen array, with cations in tetrahedral (T) and octahedral (M) coordination. They may be described by the $^{iv}(A_{1–i}B_i)^{vi}(B_{2–i}A_i)O_4$ structural formula, in which IV and VI represent tetrahedrally and octahedrally coordinated sites, A and B cations with variable valence distributed in T and M sites, and i the inversion parameter. Normal spinels show $i \equiv 0$ (e.g., MgAl$_2$O$_4$, FeAl$_2$O$_4$); inverse ones have $i \equiv 1$ (e.g., MgFe$_2$O$_4$, FeFe$_2$O$_4$). Symmetry is cubic (Fd$ar{3}$m), with the single oxygen atom at $u$, u, u fractional coordinates; T and M sites have fixed positions. Modifications of T-O and M-O bond distances to accommodate various chemical compositions and/or cation ordering determine variations in the oxygen positional parameter u and the cell edge a (Hafner 1960; Hill et al. 1979).

Within the spinel group, minerals of the (Mg,Fe$^{2+}$)(Al,Fe$^{3+}$)$_2$O$_4$ system are widespread in most geological environments. A complete solid solution exists between spinel sensu stricto (s.s.), MgAl$_2$O$_4$, and hercynite, FeAl$_2$O$_4$, whereas a large immiscibility gap is observed between hercynite and Mg-Fe$^{3+}$-ferrites (Turnock and Eugster 1962; Lehmann and Roux 1986). As a consequence, most natural crystals belong to the spinel s.s.-hercynite series with a minor ferrite component. This is the case, for example, for spinels from volcanic xenoliths (Lucchesi and Della Giusta 1997; Lucchesi et al. 1998a), websteritic dykes in a peridotite (Basso et al. 1984), and metamorphosed limestones (Carbonin et al. 1996).

In spinels, intracrystalline cation distribution depends on temperature and has been proposed as a potential geothermometer (Della Giusta et al. 1996; Harrison et al. 1998; Princivalle et al. 1999; Andreozzi et al. 2000). However, the influence of bulk composition on intracrystalline cation distribution has been pointed out as a crucial factor (O’Neill and Navrotsky 1983, 1984; Waerenborgh et al. 1994a, 1994b; Andreozzi et al. 2001). Both spinel s.s. and hercynite end-members are characterized by a nearly normal configuration, with progressive increase of inversion with increasing equilibration temperature (e.g., Roth 1964; Hill 1984; Bohlen et al. 1986; Harrison et al. 1998; Redfern et al. 1999; Andreozzi et al. 2000). The crystal chemistry of the hercynite end-member is complicated because of frequent deviations from stoichiometry due to Fe$^{3+}$ and cation vacancies (Slack 1964; Cremer 1969; Mason and Bowen 1981). The substitution of Fe$^{3+}$ for Fe$^{2+}$ and the presence of cation vacancies were claimed by Waerenborgh et al. (1994a) to be determinant in producing the discrepancy between their experimental data and those calculated using the O’Neill and Navrotsky (1984) model. Moreover, they suggested that the value of site preference enthalpy $\alpha_{Fe^{2+}-Al}$ estimated by O’Neill

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