Structural properties and heat-induced oxidation-dehydrogenation of manganoan ilvaite from Perda Niedda mine, Sardinia, Italy

PAOLA BONAZZI* AND LUCA BINDI

Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121, Florence, Italy

ABSTRACT

An unusually Mn-rich ilvaite sample from the Perda Niedda mine in Sardinia, Italy, was studied in order to clarify the Mn2+ distribution among the different structural sites, and to observe the structural response of the mineral upon thermally induced oxidation-dehydrogenation. The crystal structure and the chemical composition of one crystal were investigated. X-ray crystal-structure refinement, performed in the Pnam space group, and electron microprobe analyses yielded the formula (Ca0.98Mn0.72(Fe3+Fe2+)(Mn0.28Fe2.28)O2–(Si2O7)O(OH)). Crystal chemical details, compared to structural data from literature, led to the assumption that Mn2+ replaces Fe2+, mainly at the M2 site. Annealing experiments and structure refinements were performed in the temperature range 400–690 °C. No phase transition was observed over the entire temperature range. Oxidation of Fe2+ at the M1 site, with concomitant dehydrogenation, was deduced from examination of the structural adjustments occurring as the temperature was increased. A useful model to evaluate a possible OH– ↔ O2– substitution in ilvaite was obtained.

INTRODUCTION

Ilvaite, CaFe2[Fe3+(Si2O7)]O(OH), a mixed-valence iron sorosilicate, was considered to be orthorhombic (Belov and Mokeeva 1954; Beran and Bittner 1974; Haga and Takéuchi 1976) until Bartholomé et al. (1968) demonstrated the existence of a monoclinic phase (space group P21/a). Ilvaite undergoes a crystallographic phase transition between 60–117 °C (Ghose et al. 1984a; Ghose et al. 1985; Robie et al. 1988; Ghose et al. 1989; Ghazi-Bayat et al. 1992). In the high temperature orthorhombic phase, iron occupies two distinct octahedral positions: (1) the 8d position (labeled M1) and (2) the 4c position (labeled M2). The M1 site is randomly occupied by Fe2+ and Fe3+, whereas M2 is completely filled by Fe2+. Below the transition temperature, electron ordering between Fe2+ and Fe3+ cations occurs, causing a small deviation from the orthorhombic Pnam symmetry; as the mirror plane normal to the c axis is lost, the eightfold M1 site splits into two independent crystallographic sites, M11 (4e) and M12 (4e), which mainly accommodate Fe2+ and Fe3+, respectively.

Several monoclinic structure refinements have been performed using both single crystal X-ray intensities (Finger et al. 1982; Takéuchi et al. 1983; Ghose et al. 1985; Finger and Hazen 1987; Ghose et al. 1989; Takéuchi et al. 1993; Carrozzini 1994). Structural, thermophysical, magnetic, and electrical properties have been determined over a wide range of T–P conditions (Yamanaka and Takéuchi 1979; Nolet and Burns 1979; Evans and Amthauer 1980; Litterst and Amthauer 1984; Finger and Hazen 1987; Ghazi-Bayat et al. 1987; Robie et al. 1988; Ghose 1988; Xuemin et al. 1988; Ghazi-Bayat et al. 1989; Ghazi-Bayat et al. 1992; Ghazi-Bayat et al. 1993; Schmidbauer and Amthauer 1998; Amthauer et al. 1998).

Although not usually considered a rock-forming mineral, ilvaite is often an abundant constituent of Fe and Zn skarns (Burt 1971; Einaudi et al. 1981). It can replace hedenbergite (Logan 2000) and, as a result of an unusual set of conditions, it was found to occur as an alteration product replacing fayalitic olivine in the Skaergaard intrusion (Naslund et al. 1983). Ilvaite probably formed during serpentinization of peridotite (Agata and Adachi 1995), and ilvaite occurring in rodingites associated with serpentinite (Lucchetti 1989) has also been reported. The chemical composition of ilvaite is often close to that of the ideal end-member, with only minor amounts of other cations such as Ti4+, Mg2+, Al3+, and Mn2+. The most common and quantitatively relevant substituent is Mn2+, which mainly replaces Fe2+ at the octahedral sites but can also substitute for Ca at the seven-coordinated site (Carrozzini 1994). According to Ghazi-Bayat et al. (1992), Mn content affects the degree of monoclinicity (β angle close to 90.0° when Mn2+ = 0.19) and, therefore, the transition temperature, which decreases with increasing Mn2+ content (Amthauer et al. 1998). However, as Takéuchi et al. (1983) pointed out, the value of the monoclinic angle is not only related to the degree of disordering. An apparent orthorhombic symmetry, in fact, can be easily simulated by the co-existence of fine components polysynthetically twinned on both (001) and (100); such a twinning would be easily generated if positional mistakes in the cation array take place during the Fe2+-Fe3+ ordering process, which occurs when the crystal is cooled through the phase transition temperature (Takéuchi et al. 1994). Takéuchi et al. (1993, 1994) investigated crystals from Kamioka mine, with Mn ranging from 0.19–