Structure of NaFeSiO₄, NaFeSi₂O₆, and NaFeSi₃O₈ glasses and glass-ceramics

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ABSTRACT

The crystallization of iron-containing sodium silicate phases holds particular importance, both in the management of high-level nuclear wastes and in geosciences. Here, we study three as-quenched glasses and their heat-treated chemical analogs, NaFeSiO₄, NaFeSi₂O₆, and NaFeSi₃O₈ (with nominal stoichiometries from feldspathoid, pyroxene, and feldspar mineral groups, i.e., Si/Fe = 1, 2, and 3, respectively) using various techniques. Phase analyses revealed that as-quenched NaFeSiO₄ could not accommodate all Fe in the glass phase (some Fe crystallizes as Fe₃O₄), whereas as-quenched NaFeSi₂O₆ and NaFeSi₃O₈ form amorphous glasses. NaFeSi₃O₈ glass is the only composition that crystallizes into its respective isochemical crystalline polymorph, i.e., aegirine, upon isothermal heat-treatment. As revealed by Mössbauer spectroscopy, iron is predominantly present as fourfold-coordinated Fe³⁺ in all glasses, though it is present as sixfold-coordinated Fe³⁺ in the aegirine crystals (NaFeSi₃O₈), as expected from crystallography. Thus, Na-Fe silicate can form a crystalline phase in which it is octahedrally coordinated, even though it is mostly tetrahedrally coordinated in the parent glasses. Thermal behavior, magnetic properties, iron redox state (including Fe K-edge X-ray absorption), and vibrational properties (Raman spectra) of the above compositions are discussed.

Keywords: Mössbauer, Fe redox, Raman, glass transition, X-ray absorption

INTRODUCTION

Crystallization of iron-containing sodium silicate phases is important, both in the management of high-level nuclear wastes and in geosciences (Ahmadzadeh et al. 2017; Bailey and Schairer 1963, 1966; Cochain et al. 2012; Jantzen 2011; Jantzen and Edwards 2015; Jeoung et al. 2001). The complex high-level nuclear wastes (HLW) stored in steel tanks at the Hanford site can contain more than 20 elements, among which iron (Fe) concentrations vary from about 5 to more than 30 wt% iron (Fe₂O₃), for high-Al and high-Fe HLW, respectively (Kim et al. 2011). Vitrification is the process used to immobilize radioactive HLW by converting it into a solid stable glass. SiO₂ is added in considerable amounts (with lower levels of other additives) to vitrify the radioactive HLW into a glass for immobilization. Consequently, HLW glasses have high concentrations of Si, Fe, and Na, and are thus potentially prone to crystallization of iron sodium silicate phases.

In particular, aegirine (NaFeSi₂O₆, also known as acmite), which is a clinopyroxene silicate phase, has been known to crystallize within some HLW glasses (Hrma et al. 1999; Jantzen and Edwards 2015; Jantzen and Bickford 1984; Jantzen et al. 1984; Vienna et al. 1996). Studying the crystallization of more than 100 simulant HLW glass compositions, Kim et al. (1994) reported that aegirine forms upon isothermal heat-treatment of glasses with high Na₂O (>10 wt%) and Fe₂O₃ (>7 wt%) contents, while aegirine is not observed in samples that have been canister-centerline-cooled (slow cooling profile recorded at the centerline of the Hanford HLW canisters). Surface crystallization of aegirine from simplified HLW glasses was confirmed by Plaisted et al. (2000), who showed that the aegirine contains other elements such as Cr and Ni and that its composition varies by temperature of the heat treatment. The formation of aegirine causes a small to moderate decrease in the chemical durability of final HLW glass waste form (Jantzen and Bickford 1984; Jantzen et al. 1984, 2010). The spinel formation (i.e., magnetite Fe₃O₄ and related phases), however, has little or no effect on glass durability, whereas nepheline (NaAlSiO₄) and related aluminosilicate phases have the most detrimental impacts on aqueous chemical durability of crystallized HLW glass.

Iron and sodium are among the most common constituents of natural silicate melts, and both can have remarkable effects on their physical properties. Bailey and Schairer (1966) have extensively described how equilibrium crystalline and liquid phases in the system Na₂O-Al₂O₃-Fe₂O₃-SiO₂ are petrologically important for a wide range of alkali igneous rocks. These crystalline phases include aegirine (NaFeSi₂O₆), 5.1.8 (5Na₂O·Fe₂O₃·8SiO₂ or Na₃Fe₃Si₈O₂₀), nepheline (NaAlSiO₄, hexagonal), carnegieite (NaAlSiO₄, orthorhombic), albite (NaAlSi₃O₈), sodium metasilicate (Na₂SiO₃), hematite (Fe₂O₃), and different polymorphs of...