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 Fe₂O₃), whereas as-quenched NaFeSi₂O₆ and NaFeSi₃O₈ form amorphous glasses. NaFeSiO₄ 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 Fe⁵⁺ in the aegirine crystals (NaFeSiO₄), 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. Crystalline 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 alkaline igneous rocks. These crystalline phases include aegirine (NaFeSiO₄), 5.18 (5Na₂O·Fe₂O₃·8SiO₂ or Na₉Fe₃Si₈O₂₂), nepheline (NaAlSiO₄, hexagonal), carnegieite (NaAlSiO₄, orthorhombic), albite (NaAlSi₃O₈), sodium meta-silicate (Na₂SiO₃), hematite (Fe₂O₃), and different polymorphs of NaFeSiO₄, NaFeSi₂O₆, and NaFeSi₃O₈.

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