American Mineralogist, Volume 105, pages 1375–1384, 2020

Structure of $NaFeSiO_4$, $NaFeSi_2O_6$, and $NaFeSi_3O_8$ 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, $NaFeSiO_4$, $NaFeSi_2O_6$, and $NaFeSi_3O_8$ (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 $NaFeSiO_4$ could not accommodate all Fe in the glass phase (some Fe crystallizes as Fe_3O_4), whereas as-quenched $NaFeSi_2O_6$ and $NaFeSi_3O_8$ form amorphous glasses. $NaFeSi_2O_6$ 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 Fe^{3+} in all glasses, though it is present as sixfold-coordinated Fe^{3+} in the aegirine crystals ($NaFeSi_2O_6$), 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