"Cs-tetra-ferri-annite:" High-pressure and high-temperature behavior of a potential nuclear waste disposal phase

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ABSTRACT

Structure deformations induced by pressure and temperature in synthetic "Cs-tetra-ferri-annite" 1M [Cs_{1.78}(Fe^{2+}^{1.90}Fe^{3+}^{0.07})(Si_{6.15}Fe^{3+}^{1.80}Al^{0.05})O_{20}(OH)_{4}], space group C2/m, were analyzed to investigate the capability of the mica structure to store the radiogenic isotopes ^{135}Cs and ^{137}Cs. "Cs-tetra-ferri-annite" is not a mineral name, but for the sake of brevity is used here to designate a synthetic analog of the mineral tetra-ferri-annite. The bulk modulus and its pressure derivative determined by fitting the unit-cell volumes between 0 and 47 kbar to a third-order Birch-Murnaghan equation of state are K_0 = 257(8) kbar and K_0' = 21(1), respectively. Between 23 °C and 582 °C, the a and b lattice parameters remain essentially unchanged, but the thermal expansion coefficient of the c axis is α_c = 3.12(9) × 10^{-5} °C^{-1}. High pressure (P) and high temperature (T) produce limited internal strain in the structure. The tetrahedral rotation angle, α_t, is very small and does not change significantly throughout the P and T range investigated. Above 450 °C in air, "Cs-tetra-ferri-annite" underwent an oxidation of octahedral iron in the M2cis sites, balanced by the loss of H and shown by a decrease of the unit-cell volume.

Independent isobaric data on thermal expansion and isothermal compressibility data define the "geometric" equation of state for "Cs-tetra-ferri-annite": V/V_0 = 1 + 3.0(1) × 10^{-5} T - 2.68(9) × 10^{-7} P + 2.0(2) × 10^{-9} P^2 where T is in degrees Celsius, P is in kilobars. The α/β ratio of about 12 bar/°C indicate that the cell volume of "Cs-tetra-ferri-annite" remains unchanged under geothermal gradients of ~23 °C/km. On the whole, the data confirm that the structure of "Cs-tetra-ferri-annite" may be a suitable candidate for the storage of large ions, such as Cs in the interlayer and should be considered as a potential Synroc component.

INTRODUCTION

The storage of high-level radioactive waste is a liability of nuclear technologies (Lewis 1985). Potential containers for fission products are mineral-like phases capable of including several radionuclides in their structure, mostly as dilute solid solutions. They must have long-term stability and resistance to radiation damage and to chemical, physical, and mechanical agents. One such ceramic material with a simple manufacturing technology is "Synroc," a multi-phase immobilizing barrier based on geochemical principles (Ringwood 1985), which consists mainly of rutile, zirconolite, perovskite, and hollandite. Of these, hollandite can trap ^{135}Cs and ^{137}Cs, which are among the most problematic radiogenic isotopes because of their large ionic radius, strong activity, and medium half-life.

The recently synthesized one-layer mica "Cs-tetra-ferri-annite" was proposed as another promising candidate for the storage of radiogenic Cs isotopes (Mellini et al. 1996). "Cs-tetra-ferri-annite" was easily synthesized under hydrothermal conditions and the data available indicate it is a mica structure with limited internal strain, likely to have strong thermal stability. In this context, the structural response of Cs-mica to elevated pressure and elevated temperature should be known.

This study determines the compressibility of "Cs-tetra-ferri-annite" and its thermal expansion. Its structure was refined at a set of temperatures and pressures. The results are compared with those for phlogopite (Hazen and Finger 1978) and dioctahedral K and Na micas (Comodi and Zanazzi 1995; 1997) to elucidate the role of the interlayer cation in the mica under elevated T and P.