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Topotactic and reconstructive changes at high pressures and temperatures from Cs-natrolite to Cs-hexacelsian

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Abstract

Synchrotron X-ray powder diffraction experiments have been performed on dehydrated Cs-exchanged natrolite to systematically investigate successive transitions under high pressures and temperatures. At pressures above 0.5(1) GPa using H_2O as a pressure-transmitting medium and after heating to 100 °C, dehydrated $Cs_{16}Al_{16}Si_{24}O_{80}$ (deh-Cs-NAT) transforms to a hydrated phase $Cs_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$ (Cs-NAT-II), which has a ca. 13.9% larger unit-cell volume. Further compression and heating to 1.5 GPa and 145 °C results in the transformation of Cs-NAT-II to $Cs_{16}Al_{16}Si_{32}O_{96}$ (anh-Cs-POL), a H_2O-free pollucite-like triclinic phase with a 15.6% smaller unit-cell volume per 80 framework oxygen atoms ($80O_f$). At pressures and temperatures of 3.7 GPa and 180 °C, a new phase $Cs_{1.547}Al_{1.548}Si_{6.452}O_{16}$ (Cs-HEX) with a hexacelsian framework forms, which has a ca. 1.8% smaller unit-cell volume per $80O_f$. This phase can be recovered after pressure release. The structure of the recovered Cs-HEX has been refined in space group $P6_3/mcm$ with $a = 5.3731(2)$ Å and $c = 16.6834(8)$ Å, and also been confirmed by HAADF-STEM real space imaging. Similar to the hexacelsian feldspar (i.e., $BaAl_2Si_2O_8$), Cs-HEX contains Cs^+ cations that act as bridges between the upper and lower layers composed of tetrahedra and are hexa-coordinated to the upper and lower 6-membered ring windows. These pressure- and temperature-induced reactions from a zeolite to a feldspar-like material are important constraints for the design of materials for Cs^+ immobilization in nuclear waste disposal.

Keywords: Natrolite, hexacelsian, high pressure, phase transition, X-ray powder diffraction, radioactive wastes