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

## HUIJEONG HWANG<sup>1</sup>, DONGHOON SEOUNG<sup>1</sup>, G. DIEGO GATTA<sup>2</sup>, DOUGLAS A. BLOM<sup>3</sup>, THOMAS VOGT<sup>3</sup> AND YONGJAE LEE<sup>1,\*</sup>

<sup>1</sup>Department of Earth System Sciences, Yonsei University, Seoul 120-749, Korea <sup>2</sup>Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli, 23, I-20133 Milano, Italy <sup>3</sup>NanoCenter & Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, U.S.A.

## ABSTRACT

Synchrotron X-ray powder diffraction experiments have been performed on dehydrated Csexchanged natrolite to systematically investigate successive transitions under high pressures and temperatures. At pressures above 0.5(1) GPa using H<sub>2</sub>O 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<sub>16</sub>Al<sub>16</sub>Si<sub>24</sub>O<sub>80</sub>·16H<sub>2</sub>O (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<sub>16</sub>Al<sub>16</sub>Si<sub>32</sub>O<sub>96</sub> (anh-Cs-POL), a H<sub>2</sub>O-free pollucite-like triclinic phase with a 15.6% smaller unit-cell volume per 80 framework oxygen atoms (800<sub>f</sub>). At pressures and temperatures of 3.7 GPa and 180 °C, a new phase Cs<sub>1.547</sub>Al<sub>1.548</sub>Si<sub>6.452</sub>O<sub>16</sub> (Cs-HEX) with a hexacelsian framework forms, which has a ca. 1.8% smaller unit-cell volume per 800<sub>f</sub>. 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<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), Cs-HEX contains Cs<sup>+</sup> 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<sup>+</sup> immobilization in nuclear waste disposal.

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