

$P_{\text{H}_2\text{O}}$ -dependent structural phase transitions in the zeolite mesolite: Real- and reciprocal-space crystal structure refinements

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ABSTRACT

The response of the mesolite crystal structure ($\text{Na}_{16}\text{Ca}_{16}\text{Al}_{48}\text{Si}_{72}\text{O}_{240} \cdot 64\text{H}_2\text{O}$) to dehydration was evaluated as a function of temperature and partial pressure of water (i.e., $P_{\text{H}_2\text{O}}$ or relative humidity, RH) using laboratory X-ray powder diffraction (XRD; $\text{CuK}\alpha$ radiation) and synchrotron X-ray pair distribution function (PDF) methods. At 425 °C under low- $P_{\text{H}_2\text{O}}$ conditions ($P_{\text{H}_2\text{O}} \leq \sim 1.3$ mbar), dehydrated mesolite preserved the long-range ordered aluminosilicate framework structure, which has not been previously observed. This new dehydrated phase, x-metamesolite, has unit-cell parameters [$a = 16.731(3)$ Å, $b = 17.822(2)$ Å, $c = 6.312(1)$ Å, $V = 1882.5(5)$ Å³, and possible space group $Fdd2$] similar to those of other dehydrated natrolite phases (either $\alpha 1$ - or $\alpha 2$ -metanatrolite). Conversely, under high- $P_{\text{H}_2\text{O}}$ conditions ($P_{\text{H}_2\text{O}} > \sim 1.3$ mbar), dehydrated mesolite became amorphous (amorphous T_5O_{10}) at 425 °C. The local structure of amorphous T_5O_{10} was characterized by PDF analyses, which showed the formation of twisted T_5O_{10} nano-fibers [with dimensions (LWH) of $\sim 6.9 \times 6.9 \times 6.3$ Å] resulting from breakage of the mesolite aluminosilicate framework. The two distinct high-temperature $P_{\text{H}_2\text{O}}$ -dependent phase transition paths illustrate the importance of considering the combined effects of temperature and $P_{\text{H}_2\text{O}}$ in mesolite. In addition, the low-temperature phase transition in mesolite, involving order-disorder of the extraframework cations, also showed a $P_{\text{H}_2\text{O}}$ -dependent transition temperature. Although, there is no path dependence on $P_{\text{H}_2\text{O}}$ for this transition, the local arrangement of Na, Ca, and vacancies in disordered metamesolite (formed through the extraframework cation order-disorder phase transition) likely influences the thermal stability of the aluminosilicate framework during further heating.

Keywords: Phase transition, mesolite, XRD data, crystal structure