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Dehydration dynamics of levyne: a combined synchrotron XRPD and single crystal diffraction study

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Knowledge of the structural modifications induced by temperature in zeolites and of their stability fields is of prime importance to assess zeolite persistence and effectiveness in their technological applications. Some porous materials, when completely dehydrated, undergo irreversible changes in the framework topology. In general, these changes are due to the strain induced by migration of cations - initially located in the channels and surrounded by water molecules - to achieve a better coordination with framework anions after the water release.
Notwithstanding the spread interest for porous materials with levyne topology (LEV), their thermal behavior and stability have not been studied in detail up to now. In this work, the thermal induced structural modifications of a natural levyne from Fagridalur (Iceland) ($Ca_{7.8}$ $Na_{2.2}K_{1.1}Al_{19.8}Si_{31.2}O_{108}\cdot 51H_2O$, a= 13.3619(4) Å, c= 22.8820(1) Å, V = 3538.0(3) $Å^3$, s.g. R-3m) were studied by both temperature-resolved synchrotron X-ray powder diffraction experiments (SR-XRPD), and by conventional-source high-temperature single crystal X-ray diffraction (SC-XRD). LEV framework consists of stacking 6-rings perpendicular to [0001] (6mR) in the sequence AABCCABBC (Merlino et al. 1975). Levyne cage is confined by two pairs of 6mR (D6R building units), and contains the non-framework cations and water molecules. A three-dimensional channel system, confined by 8-membered rings, lies perpendicular to [0001]. The SR-XRPD patterns were collected in continuum from room-T to 800°C, while SC-XRD experiments were performed at room-T, 30, 100 and 250°C. Below 100°C a lattice parameter increases, while c decreases, accounting for a very low volume reduction and few water molecule loss. Between 100 and 200 °C, the release of more than 23 water molecules induces the cations migration toward the framework oxygen atoms, so to achieve a better coordination. Above 230°C, a further water loss induces the breaking of the oxygen bridges in the D6R, the edge-sharing tetrahedral phenomenon and the rising of a new topology. The two phases coexist in a percentage about 50% up to the highest investigated temperature. The new framework consists of a sequence of a new zeolitic cage and two cancrinite cages along [0001]. The structure – reported in the database of the hypothetical zeolite structure as 166_2_293 [2] –belongs to the ABC-6 family [3] and can be described with the following sequence: ABACACBCBA. The new cage can be described as a 20-hedron formed by fourteen 6mR and by six 4mR. The cations are distributed over 3 new sites: one at the center of the six membered ring shared by the two cancrinite cages, one near the center of the base of the new cage and one in a 6mR window of the new cage.

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