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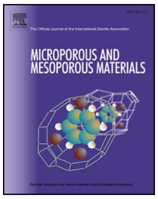

New topology of levyne B under quasi-equilibrium conditions: A temperature-dependent *in situ* single crystal X-ray diffraction study

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ABSTRACT

The dehydration behavior of natural levyne-Ca was investigated from 25 to 400 °C by *in-situ* single-crystal X-ray diffraction under dry conditions. The dehydration started at 50 °C. From 125 to 250 °C the structure changed to levyne B topology, characterized by statistical breaking of T1-O-T1 bonds in the original D6R units. At 275 °C, additional rupture of T2-O-T2 bonds in 6mR units started. This second rupture associated with the release of remaining water was not reported before. At 300 °C the structure is assumed to be anhydrous. The new levyne B topology, referred to levyne B′, is characterized by 37% T1B and 15% T2B that are new tetrahedral sites arising as a consequence of the T-O-T breaking process. In contrast to the T1B site, T2B is at general position, originating a system of T2B face sharing tetrahedra, mutually exclusive. Complete migration of T sites to the new positions would lead to different **LEV** topologies with different kind of cages and, as a consequence, of stacking sequences depending on the position occupied by the T2B tetrahedra.

The different results obtained in this study compared to previous ones, confirmed that the applied experimental set-up is fundamental in tracking the transformations upon dehydration in zeolitic materials. Understanding these differences is crucial for subsequent applications of these microporous compounds.

1. Introduction

Microporous materials of **LEV** framework-type are characterized by a sequence of single six-membered rings (6mR) and double six-membered rings (D6R) stacked along the **c** axis following the AABCCABB-CAA sequence [1,2]. This sequence forms columns along [001] composed of levyne cages ([$4^9 6^5 8^3$] polyhedra) alternating with double six-rings ([$4^6 6^2$] polyhedra). Two-dimensionally interconnected channels (free diameters 3.6 × 4.8 Å) confined by eight-membered rings run perpendicular to [001].

The natural porous material with **LEV** topology is represented by the mineral series levyne comprising levyne-Ca and levyne-Na [3]. Originally levyne, corresponding nowadays to levyne-Ca, had species status with the ideal chemical formula $NaCa_{2.5}(Al_6Si_{12}O_{36})\cdot 18H_2O$, space group *R*-3*m*, $a_{hex} = 13.35$ $c_{hex} = 22.90$ Å, $V = 3534$ Å^3, Z = 3 [4]. Levyne-Ca is usually found in vugs of massive volcanic rocks. Its chemical composition shows a rather constant Si/(Si + Al) ratio (0.62–0.70) with Ca and Na as dominant extraframework cations [5]. The crystal structure of levyne at room temperature was firstly solved and refined by Merlino et al. [2] and described in the space group *R*-3*m*. Subsequently, it was demonstrated that natural crystals of levyne are twinned by 180° rotation along the **c** axis simulating *P6/mmm* symmetry [6]. The distribution of the extraframework (EF) occupants is variable from sample to sample [6–9]. Several synthetic phases, mainly phosphates, with **LEV** topology have also been produced [10–13].

The thermal behavior of a natural sample of levyne-Ca was investigated by temperature resolved synchrotron X-ray powder diffraction (SR-XRPD). The authors reported above 230 °C a transformation from levyne to a new topology, called levyne B. The anhydrous levyne B structure is characterized by a system of edge sharing tetrahedra, mutually exclusive, formed as a consequence of broken T-O-T bonds in the D6R [8]. Due to poor data quality reliable structural refinements could not be performed between 283 and 433 °C. Thus, only structures from RT to 266 °C and at 458 °C (levyne B) were reported. Water release and EF cation diffusion during the heating process could not continuously be monitored [8].

In this study the dehydration of a natural sample of levyne-Ca was tracked by means of *in situ* single-crystal X-ray diffraction with the aim to: i) get a complete picture of the dehydration process associated with T-O-T rupture; ii) describe the eventual differences arising as a consequence of the used experimental procedure.

2. Experimental methods

A single crystal (0.08 × 0.20 × 0.25 mm) of levyne-Ca from Beech Creek, Oregon, U.S.A. (sample number A7827 of Natural History

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Museum of Bern) with chemical composition $Ca_{2.53}Na_{0.72}K_{0.23}(Al_{6.26}Si_{11.8}O_{36})\cdot 17.58H_2O$ [5] was glued on the tip of a glass fiber and mounted on a goniometer head. Diffraction data were collected on a BRUKER APEX II diffractometer equipped with a Mo*K*α radiation (λ = 0.71073 Å) and a CCD area detector. The dehydration process was studied in the temperature range 25–400 °C using a self-constructed temperature controlled N_2 blower (dry conditions, RH ~ 0). The temperature was increased in steps of 25 °C from RT to 300 °C and in steps of 50 °C from 300 to 400 °C. Before starting the data collection, the sample was equilibrated for ca. 40 min at each temperature step. Each data collection lasted ca. 7 h. From 275 to 400 °C, the exposure time of runs at low theta-angles was increased from 10 to 40 s in order to obtain stronger intensities. Thus, the data collection time was prolonged to ca. 15 h. At 400 °C the reflections were significantly smeared and only the cell parameters were extracted.

The data were integrated and corrected for absorption by using the Apex 2v. 2011.4–1 software package. Structures were solved by using Shelxtl-2008 [14] and structural refinements were carried out by SHELXL-2014 [15] using neutral atomic scattering factors.

The structures were solved in space group *R*-3*m* [2] in the whole temperature range. As in previous studies [6,8] the structures were reverse-obverse twinned, twin matrix [-100 0-10 001]. According to Sheldrick [15] two methods can be applied to handle the twinning: i) using a reflection file with HKLF 4 format and a TWIN instruction to generate the indices of the remaining twin components; ii) generating a *.hkl* file of HKLF 5 format (i.e. with the number of the twin component as additional column) and performing the refinement without inserting the TWIN command. Usually HKLF 5 is required if the reciprocal lattices of the components are not exactly superimposed [15]. Both models were tested (*.hkl* file with HKLF 5 format was generated by using Platon/TwinRotMat software [16]). Up to 200 °C no significant differences were found. However, from 200 to 350 °C the first model (HKLF 4 plus TWIN command) significantly increased the quality of the refinements, therefore it was adopted for all data sets.

Systematic absence violations, with intensities of ca. 1% compared to the strongest one, were found for each data collection from RT to 350 °C. These violations were attributed to stacking faults or intergrowth with other framework topology, i.e. erionite, as frequently reported for levyne-Ca crystals from this locality [17,18].

Starting coordinates and atomic labels of framework atoms were those reported by Sacerdoti [6]. Extraframework cations and H_2O molecules were located by difference Fourier maps. Above 200 °C the new sites arising as a consequence of the rupture of T-O-T connections were named following the nomenclature adopted for levyne B in Arletti et al. [8]. The N suffix added to the EF labels indicates those sites, which were here reported for the first time.

Crystal data and refinement details of levyne-Ca structures at RT, 75, 125, 200, 225, 275, and 350 °C are reported in Table 1a,b. All structure drawings have been produced by VESTA software [19]. Cif files of the refined crystal structures were submitted as supplementary material.

3. Results

3.1. Structure at RT

The crystal structure of levyne-Ca at RT was in agreement with that reported by previous studies [2,6–8]. In the investigated sample, five EF cationic sites were located C1, C2, C3, C4, and C5 plus five sites occupied by H_2O molecules, W1, W2, W3, W4, and W5 (Table 2).

3.2. Dehydration

The dehydration started at 50 °C when the structure lost ca. 2 H_2O pfu (of 15.5 H_2O refined at RT), mainly released from the W3 and W4 sites. The low occupied site C4 disappeared, and the corresponding EF cations rearranged over the remaining sites. At this temperature a new peak (named O3A) at ca. 0.60 Å from O3 appeared. It was refined with O scattering factors and the sum of O3 plus O3A occupancy was constrained to be equal to 1. At 75 °C the release of water proceeded. In addition, EF cations dispersed from the C2 site to other existing EF sites (Table 3). At 100 °C, all H_2O at W3 was released.

At 125 °C, the structure lost H_2O at W4 (Table 4). At this point, a new residual peak (C1A) appeared in the difference Fourier maps close to the C1 site indicating the beginning of a disordered distribution of EF cations along the 3-fold axis. This disorder, accompanied by the water release, increased up to 200 °C. At this temperature the rupture of the T1-O2-T1 and T1-O3-T1 links started with migration of the T1 site toward the new position T1B (occ. = 0.066(4)) (Table 5). At 225 °C the percentage of broken connections increased (T1B occ. = 0.142(3)) and the new oxygen apices OB1 and OB2 were detected (Table 6). The structural topology is that reported by Arletti et al. [8] for levyne B with the connections T1B-OB1-T1B and T1B-OB2-T1B forming a new 6mR stacked along [001]. Subsequent increase of temperature is accompanied by further increase of broken bonds and by additional disorder of EF cations.

At 275 °C, the rupture of the T2-O5-T2 link set in. Such rupture was not observed before and led to the occurrence of a new T site (T2B occ. = 0.066(3)) at 1.922(15) Å from the original T2 site (Table 7). T2B is at a general position, with the short distance (T2B-T2B = 2.05(3) Å) between T2B at x, y, z and the equivalent one at y-1/3, x + 1/3, -z + 1/3, mutually exclusive. The new oxygen apex (OB3) of site symmetry 2/*m* has a distance of 1.895(16) Å to two T2B sites. Thus, similarly to the $T1BO_4$ tetrahedron, the new T2B site shares two oxygen apices (O1) with the original T2 site. Nevertheless, at this temperature the O5 site remained fully occupied. This is not surprising considering the low percentage (ca. 10%) of broken T2-O5-T2 connections. At 350 °C, the O5 occupancy decreased to 0.852(6) and the new apex OB4 of the distorted $T2BO_4$ tetrahedron was detected (Table 8). This led to the formation of the T2B-OB4-T2B connection and of a new single 6mR unit of T2B tetrahedra. The OB3 site was displaced from the two-fold axis and refined at special position (at *.m*) similarly to OB4. The percentage of broken bonds at this temperature was 37% and 15% for T1-O2-T1/T1-O3-T1 and T2-O5-T2, respectively.

The change of the unit-cell volume as a function of temperature is displayed in Fig. 1. The volume contracted in the investigated temperature range by −5%, accompanied by decrease of the *a* parameter (−5%) and increase of *c* (+5%).

From 200 °C to 350 °C the quality of the refinement (R_1) decreased significantly (Table 1a,b). This was due to the streaking of the reflections along **c*** in the 0*kl* plane (Fig. 2) as a consequence of the T-O-T breaking process. At 400 °C, it was impossible to solve the structure, and only the unit-cell parameters were extracted.

4. Discussion

4.1. Dehydration mechanism: at what temperature does the structure become anhydrous?

The main transformations occurring in the levyne structure upon dehydration take place in two steps: the breaking of T1-O2-T1 and T1-O3-T1 bonds in the D6Rs at 200 °C and that of T2-O5-T2 in the 6mR units at 275 °C. The first process is related to the loss of water and subsequent migration of the extraframework cations toward new positions. In particular, the diffusion of EF cations within the voids can be described by the disorder of Ca atoms at C5, splitting in C5A and C5B positions, and the emptying of the C1 site mainly in favor of the C6 site (and to minor extent of C8 and C8A). This is a gradual process, which continues up to 275 °C with the migration of EF cations to new partially occupied sites (C9, CN1, CN2, CN3, CN4) distributed along the 3-fold axis. The second breaking (rupture of T2-O5-T2) is linked to additional release of water. According to the structural refinements, all water is