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In situ dehydration behavior of zeolite-like cavansite: A single-crystal X-ray study

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Abstract

To track dehydration behavior of cavansite, $Ca(VO)(Si_4O_{10})\cdot 4H_2O$ [space group *Pnma*, a = 9.6329(2), b = 13.6606(2), c = 9.7949(2) Å, V = 1288.92(4) Å^3] single-crystal X-ray diffraction data on a crystal from Wagholi quarry, Poona district (India) were collected up to 400 °C in steps of 25 °C up to 250 °C and in steps of 50 °C between 250 and 400 °C. The structure of cavansite is characterized by layers of silicate tetrahedra connected by $V^{4+}O_5$ square pyramids. This way a porous framework structure is formed with Ca and H_2O as extraframework occupants. At room temperature, the hydrogen bond system was analyzed. Ca is eightfold coordinated by four bonds to O of the framework structure and four bonds to H_2O molecules. H_2O linked to Ca is hydrogen bonded to the framework and also to adjacent H_2O molecules. The dehydration in cavansite proceeds in four steps.

At 75 °C, H_2O at O9 was completely expelled leading to 3 H_2O pfu with only minor impact on framework distortion and contraction [V = 1282.73(3) Å^3]. The Ca coordination declined from originally eightfold to sevenfold and H_2O at O7 displayed positional disorder.

At 175 °C, the split O7 sites approached the former O9 position. In addition, the sum of the three split positions O7, O7a, and O7b decreased to 50% occupancy yielding 2 H_2O pfu accompanied by a strong decrease in volume [V = 1206.89(8) Å^3]. The Ca coordination was further reduced from sevenfold to sixfold.

At 350 °C, H_2O at O8 was released leading to a formula with 1 H_2O pfu causing additional structural contraction (V = 1156(11) Å^3). At this temperature, Ca adopted fivefold coordination and O7 rearranged to disordered positions closer to the original O9 H_2O site.

At 400 °C, cavansite lost crystallinity but the VO^{2+} characteristic blue color was preserved. Stepwise removal of water is discussed on the basis of literature data reporting differential thermal analyses, differential thermo-gravimetry experiments and temperature dependent IR spectra in the range of OH stretching vibrations.

Keywords: Cavansite, dehydration, crystal structure, hydrogen bonding