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

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To track dehydration behavior of cavansite, $Ca(VO)(Si_4O_{10})4H_2O$ (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_2Oas extraframework occupants. At room temperature, the hydrogen bond system was analyzed. Ca is eight-fold 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 eight-fold to seven-fold 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 strong decrease in volume (V = 1206.89(8) Å^3). The Ca coordination was further reduced from seven-fold to six-fold.

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 five-fold 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 thermogravimetry experiments and temperature dependent IR spectra in the range of OH stretching vibrations.