

Thermal behavior and structural transformation in the chabazite-type zeolite willhendersonite, $\text{KCaAl}_3\text{Si}_3\text{O}_{12}\cdot 5\text{H}_2\text{O}$

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ABSTRACT

Single crystals of the chabazite-type zeolite mineral willhendersonite, $\text{KCaAl}_3\text{Si}_3\text{O}_{12}\cdot 5\text{H}_2\text{O}$ (from Bellerberg, eastern Eifel district, Germany), were studied by X-ray diffraction methods between 100 and 500 K. The zeolite shows a phase transition from triclinic to rhombohedral symmetry between 350 and 375 K under dry nitrogen and between 450 and 475 K under humid air. Under these conditions, the unit-cell parameters change from $P\bar{1}$ at 350 K [a, b, c (Å); α, β, γ (°); V (Å³) = 9.210, 9.210, 9.405; 92.75, 92.80, 90.80; 795.8] to $R\bar{3}$ at 375 K ($a = 9.380$ Å, $\alpha = 91.40^\circ$, $V = 824.5$ Å³), and from $P\bar{1}$ at 450 K [a, b, c (Å); α, β, γ (°); V (Å³) = 9.215, 9.215, 9.415; 92.65, 92.85, 90.75; 797.5] to $R\bar{3}$ at 475 K ($a = 9.375$ Å, $\alpha = 91.35^\circ$, $V = 823.8$ Å³), respectively. The crystal structures were refined based on X-ray diffraction data collected at room temperature [$P\bar{1}$; a, b, c (Å); α, β, γ (°); V (Å³) = 9.248(5), 9.259(5), 9.533(5); 92.313(5), 92.761(5), 89.981(5); 814.7(8)], at 373 K [$P\bar{1}$; a, b, c (Å); α, β, γ (°); V (Å³) = 9.205(5), 9.231(5), 9.442(5); 92.550(5), 93.086(5), 90.519(5); 800.3(8)], and at 423 K [$R\bar{3}$, $a = 9.411(4)$ Å, $\alpha = 91.48(1)^\circ$, $V = 832.7(6)$ Å³]. Upon heating, the elliptical 8-rings of willhendersonite expand to a triangular shape in the rhombohedral structure with upper and lower rings in the double 6-ring (D6R) twisted by 60° to each other corresponding to the center of symmetry in the center of the D6R. The changes in the framework are accompanied by migration of cations, partly assuming unfavorably low coordinations in the high temperature structure due to the loss of H₂O molecules. Rehydration at room temperature yields the triclinic structure of willhendersonite, although the single crystals become polysynthetically twinned.

Keywords: Willhendersonite, chabazite, zeolite, dehydration, crystal structure, nonambient conditions