

Topotactic transformation and dehydration of the zeolite gismondine to a novel Ca feldspar structure

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ABSTRACT

Temperature-dependent single-crystal X-ray data were collected on gismondine (GIS) $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot 18\text{H}_2\text{O}$ from Rio Pian del Foco, Genova province, Italy, in steps of 25 °C up to 600 °C. At room temperature, gismondine has space group $P2_1/c$ with $a = 10.0214(1)$, $b = 10.5997(1)$, $c = 9.8327(1)$ Å, $\beta = 92.363(1)^\circ$, $V = 1043.58(2)$ Å³. This structure remained stable up to 50 °C. The dehydration behavior then divided into two different pathways depending on the sample. In the more frequent path I, the LT $P2_12_12_1$ structure (phase B) $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32})\cdot 12\text{H}_2\text{O}$ [$a = 13.6801(8)$, $b = 10.4670(6)$, $c = 13.8667(9)$ Å, $V = 1985.6(2)$ Å³] formed at 75 °C. The orthorhombic structure has a doubled volume relative to the monoclinic room-temperature structure. At 150 °C the HT $P2_12_12_1$ structure (phase C) with 8 H₂O pfu [$a = 13.9014(12)$, $b = 8.9469(8)$, $c = 13.9697(14)$ Å, $V = 1737.5(3)$ Å³] occurred. This phase C has strongly compressed elliptical channels with Ca ions bonding to adjacent walls. At high temperature (300 °C), the quality of the diffraction pattern in path I further degraded and became inclusive.

In path II the diffraction patterns were of considerably higher quality and at 75 °C the phase LT $I2/a$ with 16 H₂O pfu [$a = 9.790(2)$, $b = 10.437(2)$, $c = 9.790(2)$ Å, $\beta = 90.97(3)^\circ$, $V = 1000.1(4)$ Å³] formed, changing at 150 °C to HT $I2/a$ [at 225 °C: $a = 9.434(4)$, $b = 9.044(2)$, $c = 9.695(2)$, $\beta = 89.04(1)^\circ$, $V = 827.0(4)$ Å³] with 4 H₂O. Above 250 °C the HT $I2/a$ structure topotactically transformed by a reconstructive mechanism to a triclinic $C\bar{1}$ Ca feldspar structure [$a = 8.152(5)$, $b = 12.917(5)$, $c = 7.126(4)$ Å, $\alpha = 93.26(3)$, $\beta = 116.37(6)$, $\gamma = 88.72(5)^\circ$, $V = 671.2(7)$ Å³], which does not follow Loewenstein's (1954) rule, as the framework has ordered corner-linked AlO_4 tetrahedra. As a consequence of the GIS to Ca feldspar transformation T-O bonds within four-membered rings break and reconnect to a new framework type. The HT $I2/a$ structure with strongly twisted double crankshaft chains acts as precursor for the feldspar formation without an intermediate X-ray amorphous phase usually found after complete dehydration of most natural zeolites.

This study reports for the first time a low-temperature topotactic transformation from gismondine to Ca feldspar and explains the highly unusual occurrence of ordered Al-O-Al clusters in this feldspar structure.

Keywords: Zeolite, gismondine, dehydration, crystal structure, Ca feldspar, Loewenstein's rule