American Mineralogist, Volume 102, pages 1727–1735, 2017

Reconstructive phase transitions induced by temperature in gmelinite-Na zeolite

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Abstract

Gmelinite is a natural zeolite whose framework can be described as a parallel stacking of double six rings of tetrahedra in the ABAB sequence. Its space group is $P6_3/mmc$ with a = 13.76 and c = 10.08 Å. This study describes the topological transformations of its Na-form $|Na_{6.98}K_{0.27}Ca_{0.15}(H_2O_{22.43})|[Al_{7.41}Si_{16.55}O_{48}]$-GME, which occur when heating in air above 300 °C. Ex situ X-ray single-crystal analysis showed that gmelinite-Na transforms into a new structure with an AFI-type topology at about 300 °C. Its space group is $P6/mcc$ with a = 13.80 and c = 8.50 Å. In situ X-ray powder diffraction patterns highlighted that, in the approximate 330–390 °C temperature range, GME → AFI transformation goes through a new intermediate phase whose topology differs from both GME and AFI. This phase transforms over the space of a few minutes into the AFI-type phase. This new "transient" phase is characterized by the presence of framework tetrahedra, which are only three-connected. Based on real time synchrotron powder diffraction data, the "transient" phase was modeled in space group $P31c$ with a = 13.97 and c = 9.19 Å. Its crystal structure can be seen as an intermediate step between the GME and AFI crystal structures. The existence of this intermediate metastable phase could be due to the ~2 Å difference in the c parameter between the GME and AFI phases. The c parameter value in the "transient" metastable phase, which is roughly intermediate between the c value in GME and AFI, suggests that the "transient" phase exists as a way of avoiding the abrupt collapse of the GME structure along z direction during the GME-AFI topological transformation. The transformation of a natural gmelinite-Na in a material with AFI topology shows that it is possible to obtain Al-rich AFI materials whose properties are of particular importance in evaluating their potential as catalysts and adsorbents.

Keywords: Zeolite, gmelinite-Na, thermal behavior, phase transitions, AFI-type topology