

## 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  $[\text{Na}_{6.98}\text{K}_{0.27}\text{Ca}_{0.15}(\text{H}_2\text{O}_{22.43})][\text{Al}_{7.41}\text{Si}_{16.55}\text{O}_{48}]$ -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  $\rightarrow$  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  $\sim 2$  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