A reply to Comment on “An experimental study of symmetry lowering of analcime”

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Abstract

The symmetry lowering of analcime reported by Sugano and Kyono (2018) was re-investigated by using field-emission scanning electron microscopy. The results of scanning electron microscopic observation show the fractures can be characterized by smoothly curved surfaces, called sub-conchoidal fracture, and neither the lamellar twin nor the domain walls of twin was found on the surfaces of the analcimes. In addition, the lamellar twin is generally formed by transformation from the high-temperature phase or from pseudomorphic replacement under strong alkaline conditions. Actually, the symmetry lowering of analcime reported by Sugano and Kyono (2018) occurs at 200 ^{o}C. The temperature is a much lower than the transformation from the high-temperature phase. In the hydrothermal experiment (Sugano and Kyono 2018), moreover, the analcimes were synthesized under acidic condition and reheated in pure water. No twin domain is likely to be formed under the hydrothermal condition. These facts strongly deny the possibility that the twin domains cause the pseudo-symmetry of tetragonal analcime. Consequently, it can be concluded that the observed forbidden reflections for the cubic *Ia*3*d* symmetry is not due to the presence of twin domains, but due to the symmetry lowering of analcime from cubic *Ia*3*d* to orthorhombic *Ibca*.

Keywords: analcime, hydrothermal treatment, SEM, fracture surface

The crystal structure of analcime, ideal chemical formula $NaAlSi_2O_6 \cdot H_2O$, is composed of a three dimensional framework of SiO_4 and AlO_4 tetrahedra with the ANA-type topology (Baerlocher et al. 2007). The maximum symmetry of the ANA framework is cubic with space group *Ia*3*d*, but naturally occurring analcimes possess at least four different symmetries: cubic space group *Ia*3*d*, tetragonal space group $I4_1/acd$, orthorhombic space group *Ibca*, and monoclinic space group *I*2/*a* (Ferraris et al. 1972; Mazzi and Galli 1978; Hazen and Finger 1979; Pechar 1988). It has long been recognized that the symmetry lowering of analcime from cubic *Ia*3*d* to orthorhombic *Ibca* is caused by the ordering of Si and Al cations in the framework *T* sites (Mazzi and Galli 1978). Recently, we reported that the hydrothermal heating of analcime influences the degree of ordering of Si and Al over the framework *T* sites, which lowers its symmetry from cubic *Ia*3*d* to orthorhombic *Ibca* (Sugano and Kyono 2018). In the comment on “An experimental study of symmetry lowering of analcime” (Nespolo 2018), however, the author points out that the reheated analcimes are not orthorhombic *Ibca* but tetragonal $I4_1/acd$. The author mentions that the presence of twin domains is extremely probable because of the pronounced cubic pseudo-symmetry of tetragonal analcime. As it is well known, fine lamellar on {110} is present as a pseudo-merohedral twining in the non-cubic analcimes (Deer et al. 2004). The lamellar twin texture observed in the analcimes ranges from several tens of micrometers down to approximately 100 nm (Xia et al. 2009). Therefore, if the “pseudo-single crystal” of analcimes is composed of the twin domains with different orientations, it is observable by electron microscopy. In the paper we report on the observation of fracture surfaces by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-IT300HR).

Figure S1A shows the lamellar domains of analcime covered on the surface (Xia et al. 2009). Figures S1B to D display the representative fracture surfaces of hydrothermally treated analcime grains (Sugano and Kyono 2018). The fractures of analcime single crystals used in Sugano and Kyono (2018) can be characterized by smoothly curved surfaces, called sub-conchoidal fracture. It is usually found in naturally occurring analcime (Anthony et al. 2004). Neither the lamellar twin nor the domain walls of twin has been, however ,found on the surfaces of these analcimes. This result denies the possibility that the presence of twin domains leads to the pseudo-symmetry of tetragonal analcime.

In addition, the fine lamellar is considered due to transformation from the high-temperature phase (Coombs 1955; Liou 1970; Takéuchi et al. 1979). These authors described that the transformation takes place above at least temperatures exceeding 300 ^{o}C. The symmetry lowering of analcime (Sugano and Kyono 2018), however, occurs at 200 ^{o}C. The temperature is a much lower than the transformation from the high-temperature phase. Although the fine lamellar texture of analcime occurs at 210 ^{o}C by hydrothermal treatment (Xia et al. 2009), it exhibits a strong pH-dependent. The formation of twin domains favor the strong alkaline conditions, whereas in the hydrothermal experiment (Sugano and Kyono 2018), the analcimes were synthesized under acidic condition and reheated in pure water. These facts also deny the possibility that the twin domains causes the pseudo-symmetry of tetragonal analcime. Therefore, no twin domain is present in the analcimes used in Sugano and Kyono (2018). That is, the observed forbidden reflections for the cubic *Ia*3*d* symmetry is not ascribed to the presence of twin domains, but to the symmetry lowering of analcime. Based on the all results of single-crystal XRD measurements and SEM observation, it can be concluded that the hydrothermal heating of analcime influences the degree of ordering of Si and Al over the framework *T* sites, leading to the phase transformation from cubic *Ia*3*d* to orthorhombic *Ibca*.

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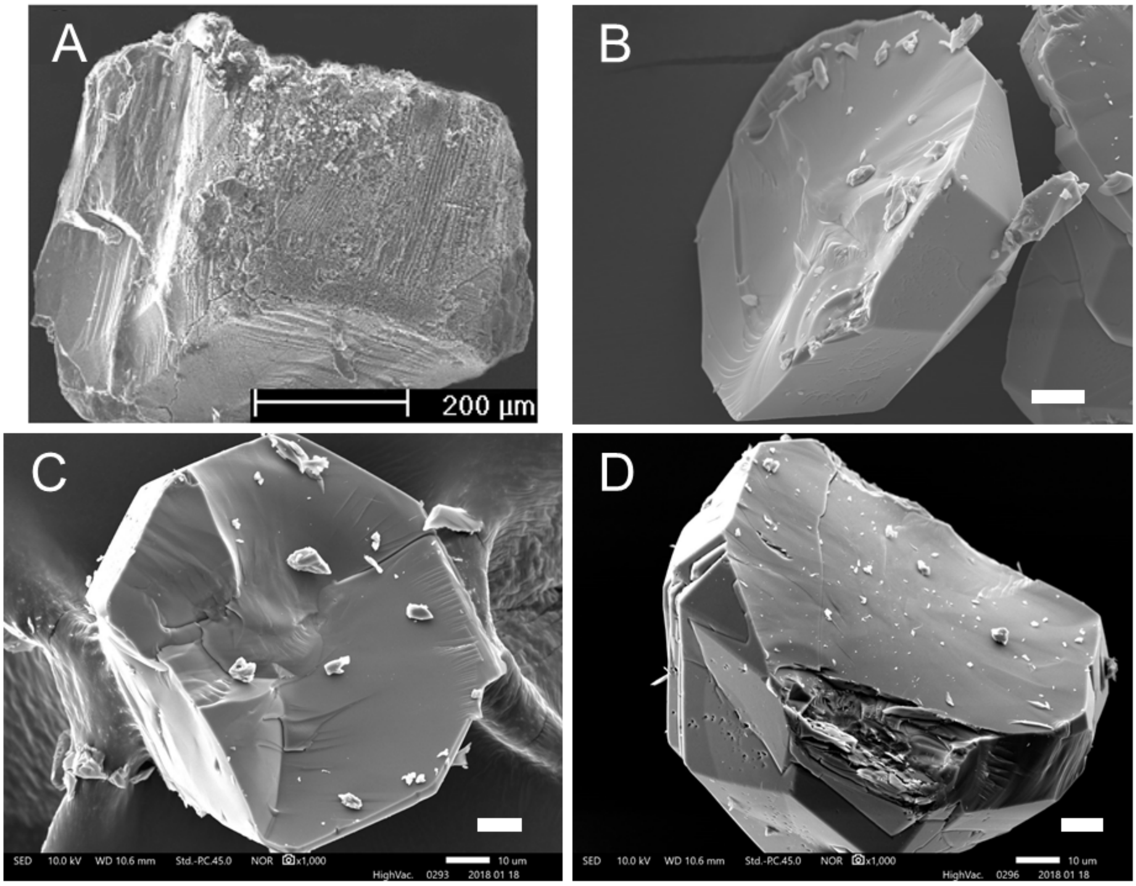
Captions for Figures and Tables

Figure S1 (A) The lamellar twin texture of analcime covered on the surface reported by Xia et al. (2009). Fracture surfaces of analcime single crystal (B) used as a starting material by Sugano and Kyono (2018), (C) reheated hydrothermally for 24 h, and (D) for 48 h. Scale bar = 10 μm.



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