Symmetry reduction of analcime with Al/Si ordering

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Analcime is a sodium aluminosilicate hydrate ($NaAlSi_2O_6 \cdot H_2O$) with the ANA type of zeolite framework. It occurs widely in hydrothermal and diagenetic environments. Symmetry of analcime is well known to be changed with distribution of framework cations and extra-framework cations. Naturally occurring analcime generally exhibits cubic symmetry space group *Ia*-3*d*, which is the maximum topological symmetry, but it can crystallize in at least three different symmetries; tetragonal space group $I4_1/acd$, orthorhombic space group *Ibca*, and monoclinic space group $I2/a$. However, crystallization conditions affecting the symmetry change have not been fully understood yet. In the study, we hydrothermal synthesized single crystals of analcime and hydrothermally re-heated under various heating time. Single crystals obtained from the different processes were refined by using single-crystal X-ray diffraction method.
Single crystals ranging in size from 50 to 120 μm were grown from gels of $Al_2(SO_4)_3$ and Na_2SiO_3. They show deltoidal icositetrahedron habit with well-developed 24 equivalent {2 1 1} crystal faces. Single crystals grown from gels possess cubic *Ia*-3*d* symmetry, in which Si and Al are totally disordered over the framework *T* sites. Single crystals of analcime hydrothermally reheated for 24h, however, exhibit tetragonal $I4_1/acd$ symmetry. The tetragonal analcime shows a weak site preference of Si for *T*1 site and Al for *T*2 site. Single crystals of analcime hydrothermally reheated for 48h display orthorhombic *Ibca* symmetry. In the orthorhombic analcime, Si and Al are strongly ordered over the *T* sites. Si is preferentially distributed into *T*11 and *T*12 sites whereas Al is into *T*2 site. The crystal structural analysis revealed continuous symmetry reduction from cubic *Ia*-3*d* to orthorhombic *Ibca* through tetragonal $I4_1/acd$ depending on heating time. On the other hand, Na atoms are equally distributed over the extra-framework sites during the symmetry reduction. The result of the study clearly shows the heating time significantly influences the Al/Si ordering over the framework *T* sites rather than the ordering of extra-framework cations. The symmetry reduction in analcime would be useful for understanding of petrological and geochemical history of rocks.

Keywords: analcime, single-crystal X-ray diffraction, Al/Si ordered distribution

