

Influence of framework and extra-framework cations substitutions on the zeolite structure:
Single crystal X-ray diffraction analysis of analcime and wairakite solid solutions[(Ca_{0.5x}
Na_{1-x})AlSi₂O₆·H₂O]

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Zeolite is generally composed of Si/AlO₄ three-dimensional framework structure with interconnected cages and open channels. Cations and water molecules occupy the extra-framework space in the structure. Because the extra-framework cations can be substituted with different charged cations, consequently the Si/Al distribution in the framework is reordered to maintain its charge balance. The diversity of chemical composition caused by the coupled substitution gives the evidence of an effect of temperature, pressure and chemical potential on the mineral formation. Therefore, investigating the relationship between structural change and chemical composition may provide the clues to understanding the condition of rock forming processes at the near surface environment. The study aimed to clarify the structural change associated with chemical composition in a solid solution between analcime (NaAlSi₂O₆·H₂O) and wairakite (Ca_{0.5}AlSi₂O₆·H₂O). Single crystals with compositions between analcime and wairakite were synthesized by hydrothermal method. Aluminium sulfate, sodium metasilicate nonahydrate, and some calcium reagents gelled with distilled water were heated for 24 - 48 hours at 150 - 250 °C. The hydrothermally synthesized crystalline materials were analyzed by scanning electron microscope (SEM), electron probe micro-analyser (EPMA), and powder and single-crystal X-ray diffraction analyses. SEM images showed that the grown single crystals exhibited an euhedral trapezohedron shape ranging 100 - 200µm in size. From the EPMA analysis, we succeeded to synthesize the continuous solid solution exhibiting the chemical composition up to Ca/(Na+Ca) = 10 mol%. However, starting material with high Ca/Na ratio led to yield fine products such as calcite and calcium sulfate. These by-products inhibited the crystallization in the solid solution on the high Ca/Na side. Structure refinements based on the single-crystal X-ray diffraction data exhibited that crystal structures with the cubic Iad kept approximately unchanged with increase of Ca content in spite of the variation of Si/Al distribution in the framework. Lattice parameter *a* was monotonously increased from 13.713 (1) Å to 13.741 (1) Å as a function of Ca concentration. The contraction of the 6-membered oxygen rings was closely associated with exchanged Ca cations and reordered framework Si/Al cations. This study indicates that a geometry of micro-porous zeolite structure known as a molecular sieve is significantly influenced by the substitution of extra-framework cations followed by reordering of framework cations.

Keywords: zeolite, single crystal X-ray diffraction analysis