島根県浜田市産ネフェリンの4配位席におけるイオン置換と変調構造の関係
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Distribution of cations on tetrahedral sites in nepheline from Hamada, Shimane Prefecture, and its relation to incommensurate structure
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Crystal structure and crystal chemistry of nepheline (X8T14T24T34T44O32 (Z = 1)) from Hamada, Shimane Prefecture, Japan, were investigated using single-crystal X-ray diffraction method and high-resolution transmission electron microscope (HRTEM) in order to reveal a relation between ionic substitution among four independent tetrahedral sites and incommensurate (IC) structure.

Four Hamada nepheline crystals, Nep1, Nep2, Nep3 and Nep4, were picked up from Hamada melilite-olivine nephelinite. Average Si contents of Hamada nepheline are 1.024-1.042 atoms per formula unite (apfu), thus, Hamada nephelines contain slightly excess Si. Na and K contents are 0.675-0.715 and 0.280-0.283 apfu, respectively.

Hamada nepheline crystals are mounted on fiber glass and analyzed at -173 °C and room temperature. The Mo X-ray tube generator was operated at 50 kV and 30 mA. The crystal structure was determined by direct method and refined by SHELXL-97 program. Space group was determined as P63. R1 factors and Goodness-of-fit (S) are converged to 2.3 - 4.2 % and 1.05 - 1.22, respectively, by taking twinning by merohedry into refinement. The degree of twinning by merohedry is 23 – 40 %. The average T2-O and T3-O distances with 1.602 - 1.623 Å and average T1-O and T4-O distances with 1.707 - 1.738 Å were resulted. They indicate that T1 and T4 sites are essentially filled with Al, whereas T2 and T3 with Si. Therefore, in tetrahedral sites of nephelines in this study, Si and Al are in the ordered arrangement. This result is consistent with space group P63.

In this study, derivation of O1 atom from triad axis was observed in sample Nep2, Nep3 and Nep4, suggesting existence of incommensurate structure. In nepheline structure, the deviation of O1 atom from triad axis and the decrease of T1-O1-T2 angle from 180º cause displaceic incommensurate structure. In Nep1, deviation of O1 atom from triad axis was not observed at both room temperature and -173 °C. However, Nep1 nepheline may contain IC structure as a local modulation.

To examine the existence of IC structure in nepheline Nep3 in which the O1 oxygen atoms deviate from triad axis, electron diffraction patterns were observed, using a HRTEM which was operated at accelerating voltage of 200kV. However, nepheline was damaged by electron beam, and the crystal structure was broken down. Thus, the satellite reflection could not be observed.

Synthetic and natural nephelines with space group of P63 have been reported repeatedly. However, P63 nephelines in which twinning by merohedry exists have been reported only for synthetic NaAlSiO4-nepheline but not for natural nepheline, and this study is the first report of existence of twinning by merohedry in natural P63 nepheline. The result in this study suggests that, in the crystal structure refinement of natural nepheline, possible twinning by merohedry should be taken into account.

Keywords: nepheline, incommensurate structure, X-ray single-crystal diffraction, twinning by merohedry
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