Kinetic effect on the cation-ordering of mineral in crystal growth process

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1 Introduction

Symmetry of crystal structure is related to cations ordering in the sites. Under thermodynamic behaviour, the order-disorder of cations at a site is controlled by temperature and pressure conditions. Usually, ordering degree of cations is higher with decreasing temperature. However, in two decades, it has been clarified that the growth process on the crystal surface affects the ordering degree of cation sites. The kinetic effects of crystal growth are also important factor for symmetry of crystal.

The texture caused by the order-disorder transition is similar to that produced by growth process. Therefore, the cation ordering is complex and controversial issue. We propose here a study based on X-ray diffraction analyses to elucidate the cation ordering controlled by the growth process. For that purpose, the cation ordering of each growth domain of a crystal were measured by single X-ray diffraction method.

2 Experiment

Samples of andradite-grossular garnet obtained from Kose Mine, Tenkawa village, Nara prefecture, Japan and from Kayas, Mali were studied. The crystal is approximately 1 cm in diameter. The crystal form is consisted of well-developed {110} faces and small {211} faces. Garnet crystals were cut into thin sections perpendicular to the [001] direction and (110) face across the center of the crystal for the optical observation, chemical analysis and preparing the sample for the X-ray experiment. The garnet crystals show birefringence under the crossed polarizer and monoclinic or triclinic symmetry is suggested.

The single-crystal X-ray diffraction experiment was conducted using synchrotron radiation (λ = 0.71215 Å) at the beam line BL-10A, Photon Factory, KEK, Japan. The wavelength of synchrotron radiation was calibrated by the unit cell volume of the NIST ruby standard. Unit-cell parameters of the specimen were determined by least squares fitting of 24 centered reflections in the 2θ range from 20˚ to 30˚. Reflection intensity data were collected by ω–scan method for the half reciprocal space ($\pm h$, $+k$, $\pm l$) with maximum $2\theta = 60°$. The extinction rule for the body-centered lattice (hkl: $h + k + l = 2n$) was applied for the reflection data collection. The space groups of both samples were determined as $I\overline{1}$ based on the observations of reflections violating the extinction rule. Especially, for the {211} specimen, the ψ-scan method was applied to distinguish a multiple scattering phenomenon.

3 Results and Discussion

[Kose sample]

The unit-cell parameters were obtained as follows; a = 12.0540(17) Å, b = 12.0580(13) Å, c = 12.0612(13) Å, α = 89.986(9)º, β = 90.994(10)º and γ = 89.994(10)º. Violate reflections indicate that all glide plane is absent and triclinic symmetry with the space group $I\overline{1}$ should be suitable for the structure refinement. The refinement with a $I\overline{1}$ model was convergent with R = 3.19 %. The Fe^{3+} occupancies of the $Y11$, $Y12$, $Y13$, $Y14$, $Y21$, $Y22$, $Y23$ and $Y24$ were determined as 86.9(6), 96.1(6), 90.9(6), 98.0(6), 95.1(6), 91.3(6), 93.7(6) and 99.6(6) %, respectively. The Fe^{3+} occupancy of the $Y11$ site is relatively lower, and that of the $Y24$ site is higher.

[Mali sample]

Reflections (e.g. 013, 103, 130) violated the extinction rule for the space group $Ia3d$, and crystal structure models for both the $\{110\}_c$ and $\{211\}_c$ sectors should have triclinic symmetry with the space group $I\overline{1}$. The unit-cell parameters of both growth sectors were respectively obtained as follows: a = 11.974(1) Å, b = 11.974(1) Å, c = 11.974(1) Å, α = 89.999(9)˚, β = 90.098(9)˚ and γ = 89.99(1)˚ for the $\{110\}_c$ sector; a = 11.952(6) Å, b = 11.952(6) Å, c = 11.957(6) Å, α = 90.01(4)˚, β = 90.01(4)˚ and γ = 89.94(4)˚ for the $\{211\}_c$ sector. Structure refinements for $I\overline{1}$ models of both sectors were converged with R = 3.02 % and R = 3.36 %, respectively. Fe^{3+} occupancies of Y11, Y12, Y13, Y14, Y21, Y22, Y23 and Y24 sites in the $\{110\}_c$ sector were determined as follows: 66.9(8), 66.0(8), 63.4(8), 60.2(8), 49.9(8), 49.5(8), 47.8(8) and 46.9(8) %. The eight octahedral Y sites of $\{110\}_c$ can be divided into two groups. In view of symmetry, Fe^{3+} distribution in Y site of {110} sector seems to be orthorhombic. In contrast, Fe^{3+} distributions in Y sites of the $\{211\}_c$ sector were refined as follows: 60.0(10), 41.0(10), 62.7(10), 69.1(10), 55.5(10), 53.2(10), 55.7(10) and 43.5(10) %. The Fe^{3+} occupancies in Y sites of the {211} sector are at random. There are significant differences of Fe^{3+} distribution trend in octahedral Y sites between the $\{110\}_c$ and $\{211\}_c$ sectors.

These observations implied that the differences of Fe^{3+} distribution trend between both sectors would be strongly affected by the growth process in each sector.

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