LETTER

Thermal behavior of modulated haüyne from Eifel, Germany: In situ high-temperature single-crystal X-ray diffraction study

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In-situ high-temperature single-crystal X-ray diffraction experiments on modulated haüyne obtained from Eifel, Germany, were conducted to re-evaluate its thermal behavior. The linearity of its thermal expansion is lost between 600 and 700 °C. Satellite peaks, indicating the modulated structure, were clearly observed up to 600 °C, but disappeared at 700 °C. These results indicate that the modulated haüyne structure changed in this temperature region. In addition, according to the observation of X-ray oscillation images taken at ambient conditions, the modulated structure of the sample heat-treated below 1000 °C remained unchanged, whereas modulation of the parent crystal structure changed when the sample was heat-treated above 1000 °C. This structural change to the unique modulated structure can be attributed to be the possible rearrangement of Al/Si distribution in the tetrahedral sites forming the framework.

Keywords: High-temperature, Modulated structure, Haüyne, Single-crystal X-ray diffraction

INTRODUCTION

Haüyne is a type of alumino-framework silicate mineral belonging to the sodalite group. This group includes sodalite (Na₈Al₆Si₆O₂₄Cl₂), nosean (Na₈Al₆Si₆O₂₄SO₄·H₂O), haüyne [Na₆Ca₂Al₆Si₆O₂₄(SO₄)₂], and lazurite (Na₆Ca₂Al₆Si₆O₂₄S₂). A complete solid solution appears to exist between the nosean and haüyne compositions, whereas a limited solid solution occurs in the sodalite–nosean and sodalite–haüyne compositions (Van Peteghem and Burley, 1963).

The framework of the sodalite group minerals ideally comprises a completely ordered tetrahedral combination of SiO₄ and AlO₄, according to the Al avoidance rule (the Löwenstein rule). Only three crystallographic sites are present for the framework atoms in the P43n space group: 6d site for Al, 6e site for Si, and 24i site for O. One of the structural properties of the sodalite group of minerals is that their framework is a large cage composed of four-membered rings parallel to {100}, and six-membered rings parallel to {111}. The cage in the crystal structure can include cations, anions, and H₂O molecules.

The framework structures of the minerals in this group are topologically similar but differ in the distribution of cations and anions in the cage.

Saalfeld (1961) found the existence of a modulated structure in haüyne obtained from Eifel, Germany, and discussed the modulated structures of the sodalite group minerals based on the average structure of the reference lattice with the cubic symmetry (P43n, a = 9.05 Å). The use of a reference lattice is a convenient method to compare a haüyne sample with a modulated structure whose symmetry is lower than the cubic symmetry. Since this discovery, many modulated structures of haüyne, nosean and lazurite have been reported, and the possible mechanism underlying the modulated structures has been discussed (e.g., Ito et al., 1966; Taylor, 1967; Schulz, 1970; Tsuchiya and Takéuchi, 1985; Hassan and Buseck, 1989a; Xu and Veblen, 1995).

Saalfeld (1961) also investigated the thermal behavior of haüyne obtained from Eifel, Germany, at temperatures up to 1100 °C by taking precession images at room temperature (RT) after heating. He reported that the minimum interval between the satellite reflections was retained up to 1000 °C but changed between 1000 and 1100 °C. Taylor (1968, 1972) investigated the thermal behavior of sodalite, nosean, haüyne, and other alumino-framework silicate minerals using the X-ray diffraction method, and reported that the trends of thermal ex-
pansion in haüyne with various chemical compositions changed between 550 and 700 °C. These unique trends were discussed based on the tetrahedral rotation in the framework structure, i.e., the degree of framework collapse. Hassan et al. (2004) reported that satellite peaks in haüyne disappeared between 390 and 407 °C during in situ high-temperature (high-T) synchrotron powder X-ray diffraction experiments. They characterized this phenomenon as a phase transition, although their synchrotron Rietveld analysis showed no significant difference between the structures of modulated haüyne before and after the phase transition at 390 and 407 °C, respectively. They also reported a discontinuity in the temperature dependence of the a-axis length at ~ 585 °C. The temperature was apparently higher than the phase transition temperature, indicating the disappearance of the corresponding modulated structure.

The purpose of this study, therefore, is to re-evaluate the thermal behavior of haüyne with the modulated structure using an in situ high-T single-crystal X-ray diffraction method (SC-XRD).

**EXPERIMENTAL PROCEDURE**

**Samples**

The samples were obtained from two localities: 1) Eifel, Germany (EG), and 2) Sacrofano, Italy (SI). The chemical characterizations of these samples were analyzed by a field-emission-type scanning electron microscope (FE-SEM; JEOL, JSM-7001F) with an energy-dispersive X-ray spectrometer (EDS) type detector (Oxford, INCA system). The chemical compositions of both samples were homogeneous with no chemical zoning. In the quantitative chemical analyses, the following standard materials were used: wollastonite for Ca and Si, corundum for Al, albite for Na, orthoclase for K, pyrite for S, and KCl for Cl. The chemical formulae were determined using the calculation method proposed by Taylor (1967): (Na₃.66Ca₁.96K₀.40)Si₆.12Al₅.94O₃₄(SO₄)₀.96Cl₀.08 for the EG sample and (Na₄.54Ca₂.2₈K₁.1₂)Si₅.9₈Al₆₀₂O₂₄(SO₄)₂.₀₀ for the SI sample. The chemical formula of the EG sample is similar to that of the sample 4 in Taylor (1967), for the SI sample. The chemical formula of the EG sample with the modulated structure.

In-situ high-T SC-XRD experiments were performed with an imaging plate type X-ray diffractometer (Rigaku, R-AXIS IV++) using a high-T apparatus (Huber, High-T attachment). Monochromatic Mo Kα radiation (λ = 0.71073 Å) was used at 50 kV and 80 mA. The film-sample distance (L = 100.33 mm) was calibrated based on the lattice parameters [a = 4.754(3) Å, b = 10.197(3) Å, c = 5.981(2) Å] of the synthesized single-crystal forsterite at RT conditions. Oscillation images of the EG samples were taken to investigate their thermal behaviors. Despite larger fluctuations in high-T conditions, the temperature was controlled within at most ±10 °C in our experiments. In all measurements, the exposure time was 2 min for every oscillation width (0.5°). CrystalClear software (Rigaku/MSC and Rigaku, 2001) was used to process the data obtained. Thermal expansion was measured at eight temperature points: 20, 100, 200, 300, 400, 500, 600, and 700 °C. Additional experiments were conducted to confirm the phenomena observed by Saalfeld (1961). In the additional experiments, the EG samples were heated between 1000 and 1100 °C using the same apparatus. After heating, the samples were cooled to RT but not quenched, and oscillation images were taken at RT.

Although our EG sample shows a modulated structure up to around 700 °C, the thermal expansion was evaluated by using the size of the reference lattice (a). The periodicity of modulation was estimated using the minimum interval of satellite reflections between the main reflections.

**RESULTS AND DISCUSSION**

**Variations of the reference cell with increasing temperature**

The lattice parameters (a) of the reference lattice measured at each temperature are summarized in Table 1. The coefficient of linear thermal expansion, α = (1/α₀)(∂α/∂T), was calculated as α = 4.14(6) × 10⁻⁵ K⁻¹ using the data for temperatures under 600 °C, where α₀ is the lattice parameter at 20 °C. As shown in Figure 1, the trend of our EG sample is in especially good agreement with that result for our SI samples agrees well with that reported by Hassan and Grundy (1991). Samples for in situ high-T SC-XRD experiments were hand-picked using a microscope and enclosed into a silica-glass capillary with a fine silica rod to hold the crystal. It should be noted that the present high-T SC-XRD study was conducted for the EG sample with the modulated structure.
of sample 4 in Taylor (1968). The temperature of the discontinuity point of haüyne does not seem to depend on its chemical composition, although the thermal expansion behavior of the haüyne samples shown in Figure 1 indicates the influence of the chemical compositions of the samples. Hassan et al. (2004) explained that the thermal expansion of haüyne is controlled by the rotation of the AlO$_4$ and SiO$_4$ tetrahedra in the framework structure (Fig. 2). According to the structural analyses by Hassan et al. (2004), the angles of rotation ($\phi_{\text{Al}}$ and $\phi_{\text{Si}}$) for AlO$_4$ and SiO$_4$ tetrahedra decrease with increase in temperature up to 600 °C. The crystal structure of modulated haüyne around 600 °C is not in a fully expanded state, but the angles are nearly constant beyond this temperature. The high-temperature variation of $\phi_{\text{Al}}$ and $\phi_{\text{Si}}$ corresponds well with the overall trend of the thermal expansion behavior.

**Table 1.** Lattice parameter ($a$) of the EG sample at each temperature point and $\Delta a$

| $T$ (°C) | $a$ (Å)  | $\Delta a$ |
|---------|---------|------------|
| 20      | 9.0866  | 0.0068     |
| 100     | 9.0934  | 0.0111     |
| 200     | 9.1045  | 0.0126     |
| 300     | 9.1171  | 0.0122     |
| 400     | 9.1293  | 0.0138     |
| 500     | 9.1431  | 0.0183     |
| 600     | 9.1614  |            |
| 700     | 9.1687  | 0.0073     |

**Figure 1.** Lattice parameter ($a$) of modulated haüyne with increasing temperature. Data of Taylor (1968) and Hassan et al. (2004) are shown as reference. Discontinuities in the $a$-axis length were observed between 600 and 700 °C in each data set.

**Figure 2.** (a) Ideally fully expanded framework structure of the sodalite group of minerals. (b) Collapsed framework structure of the sodalite group of minerals (modified after Hassan and Grundy, 1984). The large sphere is for oxygen atom, the dark colored tetrahedron is for Si tetrahedron, and the light colored one is for Al tetrahedron. Crystal structures were drawn by VESTA software (Momma and Izumi, 2011).

**Thermal behavior of the modulated structure in haüyne**

Oscillation images of the EG sample at the selected temperatures are shown in Figure 3. Satellite peaks, indicating the modulated structure, are observed up to 600 °C, but disappear at 700 °C. Therefore, the modulated structure of haüyne is lost between 600 and 700 °C. Furthermore, at temperatures up to 600 °C, the EG sample ex-
hibited periodicity that was approximately eight times that of its reference lattice. The temperature at which the satellite peaks in our sample disappear is significantly different than that reported by Hassan et al. (2004). The discrepancy may be attributed to the difference in the chemical compositions of the samples. In our experiments, the change in thermal expansion behavior occurs at almost the same temperature as the disappearance of satellite reflections and seems to be closely related to the phase transition.

It is important to note that the periodicity of the modulated structure of the EG sample at RT changed from approximately eight times that of the reference lattice to six times (Fig. 4) after heat treatment at 1100 °C. However, periodicity did not change at temperatures lower than 1000 °C (Figure 3). A similar phenomenon has been reported by Saalfeld (1961). These findings are important for clarifying the origin of the modulated structure in the sodalite group minerals.

**Origin of the modulated structure of haüyne**

Several explanations have been put forth by previous researchers about the factors that impact the modulated structures in the sodalite group of minerals: 1) an inter-

growth of two kinds of slabs such as haüyne-like and no-

Figure 3. Oscillation photos of modulated haüyne at selected temperatures. Oscillation angle is 3° for all photos. (a) At RT, (b) at 500, (c) at 600, (d) at 700 °C, and (e) at RT after heating experiment (maximum temperature of 700 °C). The additional peaks derived from a modulated structure disappeared at 700 °C.

Figure 4. Oscillation photos of modulated haüyne before and after heating experiments, taken at RT. (a) Before heating experiments, in <110>* direction; approximately eight times larger periodicity compared to its reference lattice was observed. In contrast, (b) After heating experiment at temperatures beyond 1000 °C, the periodicity fell to six times greater periodicity compared to reference lattice in the same <110>* direction. The arrows show typical points of the interval length change.
temperatures higher than 1440 °C in the case of cordierite, Mg2Al4Si5O18 (Schreyer and Schairer, 1961). In view of these facts, the irreversible structural change of haüyne, as a result of heat-treatment at temperatures higher than 1000 °C, is attributed to the rearrangement of the Al/Si distribution in tetrahedral sites. This rearrangement promotes positional change with respect to the interstitial cations and anions, and this structural change also leads to a change in modulation periodicity.

It may be noted that the SI samples used in the present study do not show any modulated structure. The Al/Si ratio of the SI sample in this study is close to unity (1.007), which fulfills the Al/Si ordered structure requirement of the Löwenstein rule. In contrast, the Al/Si ratio (0.954) of the EG sample with a modulated structure deviates from unity and is suggested as a possible cause of the Al/Si disorder in its framework structure. Our present study view is that the Al/Si ratio can be used as an index to check whether a structure is modulated or not.

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REFERENCES

Carpenter, M.A., Putnis, A., Navrotsky, A. and McConnell, D.C. (1983) Enthalpy effects associated with Al/Si ordering in anhydrous Mg-cordierite. Geochimica et Cosmochimica Acta, 47, 899-906.

CrystalClear (2001) Rigaku/MSC and Rigaku Corporation, Tokyo, Japan.

Hassan, I. and Buseck, P.R. (1989a) Cluster ordering and antiphase domain boundaries in haüyne. Canadian Mineralogist, 27, 173-180.

Hassan, I. and Buseck, P.R. (1989b) Incommensurate-modulated structure of nosean, a sodalite group mineral. American Mineralogist, 74, 393-410.

Hassan, I. and Grundy, H.D. (1984) The crystal structure of soda-lite-group minerals. Acta Crystallographica, B40, 6-13.

Hassan, I. and Grundy, H.D. (1989) The structure of nosean, ideally Na[Al12Si4O24]SO4·H2O. Canadian Mineralogist, 27, 165-172.

Hassan, I. and Grundy, H.D. (1991) The crystal structure of haüyne at 293 and 153 K. Canadian Mineralogist, 29, 123-130.

Hassan, I., Antao, S.M. and Parise, J.B. (2004) Haüyne: phase transition and high-temperature structures obtained from synchrotron radiation and Rietveld refinements. Mineralogical Magazine, 68, 499-513.

Ito, T., Nakajima, Y., Morimoto, N. and Sadanaga, R. (1966) On the polysynthetic structure of haüyne. Acta Crystallographica, 21, A55.

Momma, K. and Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44, 1272-1276.

Putnis, A. (1980) Order-modulated structures and the thermodynamics of cordierite reactions. Nature, 287, 128-131.

Schreyer, W. and Schairer, J.F. (1961) Compositions and structural states of anhydrous Mg-cordierite: a reinvestigation of the central part of the system MgO-Al2O3-SiO2. Journal of Petrology, 2, 324-406.

Schulz, H. (1970) Struktur- und Überstrukturrentersuchungen an Nosean-Einkristallen. Zeit für Kristallographie, 131, 114-138 (in German Language).

Saalfeld, H. (1961) Strukturbesonderheiten des Haüngitters. Zeitschrift für Kristallographie, 115, 132-140 (in German Language).

Taylor, D. (1967) The sodalite group of minerals. Contributions to Mineralogy and Petrology, 16, 172-188.

Taylor, D. (1968) The thermal expansion of the sodalite group of minerals. Mineralogical Magazine, 36, 761-769.

Taylor, D. (1972) The thermal expansion of the framework silicates. Mineralogical Magazine, 38, 593-604.

Tsuchiya, N. and Takéuchi, Y. (1985) Fine texture of hauyne having modulated structure. Zeitschrift für Kristallographie, 173, 273-281.

Van Peteghem, J.K. and Burley, B.J. (1963) Studies on solid solution between sodalite, nosean and haüyne. Canadian Mineralogist, 7, 808-813.

Xu, H. and Veblen, D.R. (1995) Transmission electron microscopy study of optically anisotropic and isotropic haüyne. American Mineralogist, 80, 87-93.

Xu, H., Jin, S. and Noil, B.C. (2016) Incommensurate density modulation in a Na-rich plagioclase feldspar: Z-contrast imaging and single-crystal X-ray diffraction study. Acta Crystallographica, B72, 904-915.

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