Crystal structure, large distortion of the Zn tetrahedron, and statistical displacement of water molecules in skorpionite

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The crystal structures of skorpionite from the Skorpion zinc deposit in Namibia [Ca$_3$Zn$_2$(PO$_4$)$_2$CO$_3$(OH)$_2$·H$_2$O; monoclinic; $a = 19.0715(8)$, $b = 9.3321(3)$, $c = 6.5338(3)$ Å, $\beta = 92.6773(12)$$^\circ$; space group $C2/c$] and [$a = 19.0570(14)$, $b = 9.3346(5)$, $c = 6.5322(4)$ Å, $\beta = 92.752(2)$$^\circ$; space group $Cc$] are analyzed using single-crystal X-ray diffraction and refined to yield $R$ values of 0.0253 and 0.0272 for 1576 and 2446 unique reflections with $F_o > 4\sigma(F_o)$, respectively. Hydrogen atoms in the structure determined by the difference Fourier method. Although two space groups, $C2/c$ and $Cc$, are possible, the $Cc$ space group without center of symmetry is more likely the structure of skorpionite, which shows that skorpionite is a ferroelectric mineral. The disordered structure is induced in skorpionite by twinning and/or domain structures because of the relaxation of the natural polarization caused by the arrangement of polarized water molecules. The space group $Cc$ model without the center of symmetry eliminates the need for statistical distribution. Bond valence sum calculations and hydrogen bond networks can be explained in detail by the model. In the complicated structure caused by the chemical composition, the local structure with a non-ideal coordination environment is observed near the Zn sites. Hydrogen atoms are continuously arranged with regular arrangements of water molecules in the tunnel structure.

Keywords: Skorpionite, Hydrogen bonding, Crystal structure, Structure refinement

INTRODUCTION

Skorpionite [Ca$_3$Zn$_2$(PO$_4$)$_2$CO$_3$(OH)$_2$·H$_2$O] was discovered as a secondary mineral from the Skorpion zinc deposit in Namibia. This deposit comprises a non-sulfide ore body formed by supergene oxidation of Neoproterozoic sediment- and volcanic-hosted disseminated sulfides in the Pan-African Gariep Belt (Borg et al., 2003). The zinc deposit was described in detail by Kärner (2006), and the crystal structure of skorpionite with hydrogen atoms was determined by Krause et al. (2008). They proposed a disordered structure with the split atom model only for around the H$_2$O molecules. This mineral is composed of carbonate, phosphate, hydroxide, and water molecules and has anion complexes, molecule, complex structure with statistical distribution of the oxide ion and a complicated chemical composition; and a split atom model of the water molecule is proposed. However, the amount of Ca and Zn is proportional to the stoichiometry, and the symmetry of the structure is a monoclinic c-lattice. Skorpionite is a unique mineral because of its complex structure and composition.

Water molecules in the mineral have various roles in its structure such as water in the framework structure, zeolite water, and interlayer water. It is important to clarify the role of the water molecules and the interactions of hydrogen bonding in the crystal structure of the mineral. The arrangement of the water molecules in skorpionite is unusual (Krause et al., 2008). It is necessary to clarify why this unique statistical arrangement only occurs around water molecules in the structure. Water molecules cause the crystal to become dielectric because of their polarizability. We show that the statistical arrangement in skorpionite can be explained by the polarization and that arrangement of water molecules in skorpionite is similar to that in ice crystals.

In this study, we re-examined the irregular structure in skorpionite from the same locality. We reported the space group, charge balance, unique coordination poly-
hedron of Zn with a large distortion, and disturbance of the three-dimensional periodicity in this mineral with its complex composition.

EXPERIMENTS

Material and data collection

In this study, crystals of skorpionite are from the type locality, Skorpion Zinc–mine, Namibia. The skorpionite crystals are clear and colorless. The chemical compositions were determined using a JEOL scanning electron microscope (SEM, JSM-7001F operated at 15 kV, 0.5 nA) equipped with Oxford energy dispersive X-ray spectroscopy (EDS, INCA SYSTEM), as per the methods reported by Yoshiasa et al. (2016a) and Hongu et al. (2018). The mean of results of 16 analyses provided the following wt%: CaO 31.1(3), ZnO 28.9(3), and P2O5 25.3(5), thereby providing a total of 85.3 wt%. The empirical formula is Ca3Zn2(PO4)2CO3(OH)2·H2O. The following standard materials were employed: wollastonite for Ca, pure Zn for Zn, and KTiPO5 for P. Although small amounts of sulfur and copper were detected as trace or contaminating elements, essentially no transition metals other than zinc were detected in these crystals. No significant minor elements, which would affect structural analyses, were observed.

We selected single crystals suitable for crystal structure analyses. The crystalline qualities of the single crystal specimens were checked with a four-circle diffractometer at the BL-10A beam line of the Photon Factory, KEK, Japan. High resolution monochromatized synchrotron X-ray radiation was used to confirm the peak separation, diffuse scattering, and the super-lattice. The diffraction peaks of most crystals were asymmetric and broad profiles with orientation, even though they were relatively good as specimen 2. Structure refinement was performed using reflection intensity data obtained by a Rigaku RAPID diffractometer with an imaging plate (graphite–monochromatized MoKα radiation, λ = 0.71069 Å) as per the methods reported by Jinnouchi et al. (2016) and Yoshiasa et al. (2016b). Focused MoKα radiation was used, and the conventional oscillation technique was applied. We have previously explored the hydrogen atom position and judgement chirality using the equipment (Jinnouchi et al., 2016; Yoshiasa et al., 2016b). After Lorentz and polarization corrections, an absorption correction was performed using the integration method based on the shape of the specimen (Higashi, 1995). Systematic absences indicated the space groups C2/c (centrosymmetric) or Cc (non-centrosymmetric). The experimental details and crystallographic data are summarized in Table 1.

| Crystal structure refinement and determination of hydrogen atom positions |
|---|
| Crystal structure refinement was carried out using the SHELXL97 program (Sheldrick, 2008). Scattering factors were taken from International Tables for Crystallography, Volume C (Wilson, 1992). A total of 4279 and 4396 reflections were collected from specimen 1 and specimen 2, respectively. After the initial structures were solved by the direct method, 1674 and 2673 unique reflections were used for refinement with Fo > 4σ(Fo) by the full matrix–least-square method. We analyzed several crystals using the C2/c and Cc models and introduced two results of specimen 1 using the C2/c model and specimen 2 using the Cc model. Because of the correlation among the parameters, the model analyzed by space group Cc did not converge by the least squares refinement in specimen 1. We analyzed the Cc model by struc-

Table 1. Experimental details and crystallographic data of skorpionite

| Specimen | C2/c | Cc |
|---|---|---|
| Skorpionite | 31.1(3) | 28.9(3) | 25.3(5) |
| a (Å) | 19.0715(8) | 19.0570(14) |
| b (Å) | 9.3221(3) | 9.3346(5) |
| c (Å) | 6.5338(3) | 6.5322(4) |
| β (°) | 92.6773(13) | 92.752(2) |
| V (Å³) | 1161.60(8) | 1161.67(13) |
| Space group | C2/c | Cc |

Crystal size (μm) | 69 × 84 × 149 | 68 × 76 × 106 |
Diffractionometer | RAPID |
Radiation | MoKα (λ = 0.71069 Å) |
2θ range [°] | 7.76 < 2θ < 61.04 |
θmax [°] | 29.99 | 30.52 |
Range of h, k, l | -17 ≤ h ≤ 27 | -17 ≤ h ≤ 27 |
| -12 ≤ k ≤ 13 | -12 ≤ k ≤ 13 |
| -9 ≤ l ≤ 9 | -9 ≤ l ≤ 9 |
Total reflections | 4269 | 4396 |
Unique reflections | 1674 | 2673 |
Reflections [Fo > 4σ(Fo)] | 1576 | 2446 |
Refined parameters | 108 | 200 |
R1 [Fo > 4σ(Fo)] | 0.0173 | 0.0177 |
R1 (all) | 0.0253 | 0.0272 |
wR2 (all) | 0.0286 | 0.0304 |
GooF (all) | 0.0972 | 0.0934 |
Min./max. residuals [eÅ³] | -0.886/0.944 | -0.897/0.918 |
tural analysis (floating origin restraints, Flack and Schwarzenbach, 1988) in the case where there was no center of symmetry, as adopted in the SHELX program (Sheldrick, 2008). In this case, it is not necessary for any atoms to be fixed. The position of hydrogen in the Cc model was determined by the Fourier method, and the coordinates were then processed in the riding model. After the least-square refinements without hydrogen atoms, each R index (\(\Sigma|F_o|-|F_c|/\Sigma|F_o|\)) converged less than 0.04 using the anisotropic atomic displacement factors. Difference Fourier calculations were performed to obtain the position of all hydrogen atom in the specimens (Fig. 1). The positional parameters and anisotropic atomic displacement parameters for specimens 1 and 2 are shown in Tables 2 and 3, respectively. Each crystal structure was illustrated using VESTA (Momma and Izumi, 2011). Careful examination of the difference Fourier maps indicated the positions of all hydrogen atoms: H71 near O7 and H81 and H82 near O8 in C2/c model specimen 1 and H11 near O1, H51 near O5, and H141 and H142 near O14 in Cc model specimen 2. Atomic coordinates for hydrogen were taken from the difference Fourier maps, and the coordinates in the Cc model were then processed in the riding model. In specimen 1 analyzed by the space group C2/c model, the Ca1, C, O5 and H81 sites were the 4e special positions of Wyckoff notation on a two-fold rotational axis. In specimen 2 analyzed by the space group Cc model, all atomic sites were the 4a general positions. In the model using the space group C2/c, we used a statistical displacement model in which half of the O8 and H82 sites were occupied by oxygen and hydrogen atoms.

RESULT AND DISCUSSION

Structures, hydrogen bonding, and ferroelectricity of skorpionite

Figure 2 shows the crystal structures of skorpionite for specimen 1 using a C2/c model and for specimen 2 using a Cc model. The atomic arrangements of both the specimens show good agreement with the structural model by Krause et al. (2008) except around the water molecules. In specimen 1 using the space group C2/c with center of symmetry, there are one type each of Zn\(^{2+}\), P\(^{5+}\), and C\(^{4+}\) sites and two types of Ca\(^{2+}\) sites. The two types of Ca\(^{2+}\) sites form a CaO\(_6\)(OH\(_2\)) pentagonal bipyramid and a CaO\(_7\)(OH) dodecahedron. The Zn\(^{2+}\), P\(^{5+}\), and C\(^{4+}\) sites form a ZnO\(_3\)(OH) tetrahedron, PO\(_4\) tetrahedron (phosphate group), and CO\(_3\) triangular plane (carbonate group), respectively.

Local distortions are not observed in most parts of this structure, although large fluctuation is observed around the water molecule coordinated to the Ca1 site. In specimen 1 analyzed by the C2/c model, the Ca1–O8 distance of 2.366(4) Å in the Ca1O\(_6\)(OH\(_2\)) pentagonal bipyramid is significantly shorter than the average Ca1–O distance of 2.411 Å, and the oxygen O8 of the water molecule strongly bonds with the Ca1 ion. In specimen 2 analyzed by the Cc model, the bonding distance between O14 of the water molecule and the Ca1 ion (Ca1–O14 = 3.387 Å)
2.344(4) Å) is also significantly shorter than the average Ca1–O distance of 2.408 Å. These short bonding distances were also observed in köttigite, where water molecules strongly bond to cations with shorter distances and become members of the framework (Yoshiasa et al., 2016a).

In the model using the space group $C2/c$, we adapt a statistical arrangement model in which half of the O8 sites are occupied by oxide ions. The other half of the O8 sites are coordinated to Ca1 in Ca1O$_6$(OH$_2$). Figure 3b shows a local arrangement of water molecules around the O8 sites of the $C2/c$ model. In Figure 3b, the H81 site is on the two-fold rotation axis, and oxygen and hydrogen atoms occupy half of the O8 and H82 sites, respectively.

Krause et al. (2008) proposed a statistically arranged model of the O$_{\text{water}}$ site divided into two kinds of Ow (Ow1 and Ow2) that occupied one quarter of the water molecules coordinated to Ca (Fig. 3a). The Hw1 site is on the two-fold rotation axis, oxide ions occupy one quarter of each of the Ow1 and Ow2 sites, and hydrogen atoms occupy half of the Hw2 site. In the model proposed by Krause et al. (2008), each quarter of the Ow1 and Ow2 sites is coordinated to Ca1 in the Ca1O$_6$(OH$_2$) pentagonal bipyramid. In the model proposed by Krause et al. (2008), the position of hydrogen shows a normal statistical distribution, whereas the oxide atom of the water molecule shows an unusual statistical arrangement. In comparison with the model by Krause et al. (2008), our model using the space group $C2/c$ is simple, but the atomic displacement factor $U_{eq}$ for O8 (Table 2) shows a large value of 0.0353(14) Å$^2$.

It is strongly suggested that the structure of skorpionite is the space group $Cc$ without a center of symmetry, and the model analyzed by the space group $Cc$ may not converge because of the correlation among the parameters because of the low quality of the crystal in specimen 1. A comparison of the results of the atomic coordinates (Tables 2 and 3) and interatomic distances (Tables 4 and 5) show that the difference in structure between both models using the space group of $C2/c$ and $Cc$ is small except for the arrangement around the water

### Table 2. Positional parameters and isotropic/anisotropic thermal displacement parameters for skorpionite, specimen 1 ($C2/c$)

| Site          | $x$  | $y$  | $z$  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ |
|---------------|------|------|------|----------|----------|----------|----------|
| Zn            | 0.17072(2) | 0.04400(3) | 0.41146(4) | 0.0117(2) | 0.0160(2) | 0.0114(2) | -0.00222(9) |
| Ca1           | 0    | 0.59770(7) | 0.25 | 0.0083(3) | 0.0115(3) | 0.0096(3) | 0        |
| Ca2           | 0.16426(2) | 0.33523(5) | 0.12164(7) | 0.0099(2) | 0.0095(2) | 0.0094(2) | -0.00005(14) |
| P             | 0.17799(3) | 0.66658(6) | 0.15076(8) | 0.0081(3) | 0.0093(3) | 0.0066(3) | -0.00076(18) |
| C             | 0    | 0.2812(4) | 0.25 | 0.0121(14) | 0.0123(14) | 0.0105(13) | 0        |
| O1            | 0.21625(9) | 0.7666(2) | 0.3027(3) | 0.0126(8) | 0.0172(8) | 0.0092(7) | -0.0046(6) |
| O2            | 0.22783(10) | 0.55005(17) | 0.0686(3) | 0.0114(8) | 0.0106(8) | 0.0179(9) | 0.0060(6) |
| O3            | 0.12143(9) | 0.5837(2) | 0.2628(3) | 0.0100(8) | 0.0159(8) | 0.0118(8) | -0.0014(6) |
| O4            | 0.14508(10) | 0.74810(18) | -0.0348(3) | 0.0164(8) | 0.0122(7) | 0.0084(7) | -0.0001(6) |
| O5            | 0    | 0.1459(3) | 0.25 | 0.0174(13) | 0.0115(11) | 0.0358(16) | 0        |
| O6            | 0.02960(9) | 0.3549(2) | 0.1068(3) | 0.0143(8) | 0.0163(8) | 0.0111(7) | -0.0031(6) |
| O7            | 0.13477(9) | 0.07368(18) | 0.1252(3) | 0.0087(7) | 0.0129(7) | 0.0085(7) | 0.0018(6) |
| O8            | 0.0057(5) | 0.8493(4) | 0.2098(8) | 0.064(4) | 0.0156(16) | 0.027(4) | -0.002(2) |
| H71           | 0.0895 | 0.8888 | 0.1411 |
| H81           | 0    | 0.9429 | 0.25 |
| H82           | 0.0106 | 0.8419 | 0.0583 |

Site occupancy of the O8 and H82 sites were fixed to 0.5.

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Table 3. Positional parameters and isotropic/anisotropic thermal displacement parameters for skorpionite, specimen 2 (Cc)

|     | x       | y       | z       | U_{11} | U_{22} | U_{33} | U_{12}  | U_{13}  | U_{23}  | U_{eq}/U_{iso} |
|-----|---------|---------|---------|--------|--------|--------|---------|---------|---------|----------------|
| Zn1 | 0.65281(4) | 0.04378(13) | 0.90165(10) | 0.0114(6) | 0.0165(6) | 0.0116(6) | -0.0024(5) | 0.0001(4) | 0.0055(4) | 0.0132(3) |
| Zn2 | 0.81139(4) | 0.45576(13) | 0.07878(10) | 0.0116(6) | 0.0152(6) | 0.0109(5) | -0.0020(5) | 0.0003(4) | 0.0040(4) | 0.0126(3) |
| Ca1 | 0.48223(16) | 0.59768(7) | 0.7398(4) | 0.0081(3) | 0.0112(3) | 0.0097(3) | -0.0004(9) | -0.0008(3) | -0.0011(9) | 0.00972(17) |
| Ca2 | 0.64640(10) | 0.3352(2) | 0.6117(3) | 0.0111(8) | 0.0081(7) | -0.0005(6) | -0.0013(7) | 0.0020(7) | 0.0086(3) |
| Ca3 | 0.81788(10) | 0.8353(2) | 0.8683(3) | 0.0128(9) | 0.0075(7) | 0.0106(7) | -0.0004(6) | 0.0013(7) | -0.0015(7) | 0.0103(4) |
| P1  | 0.66004(14) | 0.6667(3) | 0.6405(3) | 0.0059(10) | 0.0090(10) | 0.0086(10) | -0.0006(8) | -0.0010(9) | -0.0007(8) | 0.0079(5) |
| P2  | 0.80408(14) | 0.1664(3) | 0.8390(3) | 0.0099(11) | 0.0090(10) | 0.0047(9) | 0.0009(8) | 0.0006(8) | -0.0008(8) | 0.0079(5) |
| Cl  | 0.4796(8)  | 0.7185(4) | 0.2433(18) | 0.008(2) | 0.0135(14) | 0.0097(15) | 0.000(3) | 0.0021(15) | -0.010(3) | 0.0105(9) |
| O1  | 0.6175(4)  | 0.9259(7) | 0.1139(9) | 0.005(3) | 0.015(3) | 0.004(3) | -0.004(2) | -0.001(2) | 0.004(2) | 0.0079(12) |
| O2  | 0.7536(4)  | 0.0497(8) | 0.9233(13) | 0.011(3) | 0.008(3) | 0.020(3) | -0.003(2) | 0.004(3) | 0.004(2) | 0.0128(14) |
| O3  | 0.6290(4)  | 0.2518(8) | 0.9529(9) | 0.017(4) | 0.011(2) | 0.006(2) | 0.000(3) | -0.006(3) | 0.002(2) | 0.0114(13) |
| O4  | 0.7094(4)  | 0.5503(8) | 0.5610(12) | 0.010(3) | 0.014(3) | 0.015(3) | -0.003(2) | 0.002(3) | 0.002(2) | 0.0130(14) |
| O5  | 0.8479(4)  | 0.4268(7) | 0.3634(11) | 0.013(4) | 0.010(3) | 0.014(3) | -0.001(2) | 0.004(3) | 0.002(2) | 0.0124(14) |
| O6  | 0.8384(4)  | 0.2477(8) | 0.0219(10) | 0.013(3) | 0.013(2) | 0.011(3) | 0.001(2) | 0.001(3) | 0.004(2) | 0.0126(13) |
| O7  | 0.6992(4)  | 0.7679(8) | 0.7931(11) | 0.013(4) | 0.015(3) | 0.011(3) | -0.005(2) | -0.006(3) | -0.003(2) | 0.0132(14) |
| O8  | 0.6047(3)  | 0.5836(7) | 0.7506(11) | 0.004(3) | 0.016(3) | 0.008(3) | 0.000(2) | 0.002(2) | 0.002(2) | 0.0098(13) |
| O9  | 0.7669(5)  | 0.2654(8) | 0.6878(10) | 0.011(4) | 0.019(3) | 0.008(3) | 0.004(3) | 0.006(3) | 0.002(2) | 0.0125(14) |
| O10 | 0.8619(4)  | 0.0839(8) | 0.7247(12) | 0.015(4) | 0.014(3) | 0.014(3) | 0.003(3) | 0.001(3) | -0.003(2) | 0.0148(15) |
| O11 | 0.4516(4)  | 0.6454(8) | 0.3846(10) | 0.021(4) | 0.016(3) | 0.011(3) | -0.005(3) | 0.005(3) | 0.002(3) | 0.0159(15) |
| O12 | 0.5109(4)  | 0.6448(8) | 0.0986(10) | 0.008(3) | 0.017(3) | 0.010(3) | 0.001(2) | 0.000(2) | -0.002(2) | 0.0117(13) |
| O13 | 0.4834(7)  | 0.8540(3) | 0.242(2)  | 0.0168(16) | 0.0110(11) | 0.0369(17) | 0.001(4) | 0.0118(14) | 0.001(4) | 0.0212(7) |
| O14 | 0.4820(12) | 0.8488(4) | 0.743(4)  | 0.075(4) | 0.0138(17) | 0.127(6) | -0.001(7) | -0.033(4) | 0.008(8) | 0.073(2) |
| H11 | 0.5672     | 0.9133   | 0.1293   |         |         |        |         |         |         | 0.012     |
| H51 | 0.8988     | 0.4117   | 0.3619   |         |         |        |         |         |         | 0.019     |
| H141| 0.4836     | 0.9479   | 0.7361   |         |         |        |         |         |         | 0.110     |
| H142| 0.4739     | 0.8467   | 0.9272   |         |         |        |         |         |         | 0.110     |
molecules. The model analyzed by space group \( Cc \) has no center of symmetry, and there is no statistical arrangement in the structure. There are three types of \( \text{Ca}^{2+} \) sites, two types of \( \text{Zn}^{2+} \) sites, and two types of \( \text{P}^{5+} \) and \( \text{C}^{4+} \) sites in the \( Cc \) model. The \( \text{H}_{2}\text{O} \) molecule is formed by \( \text{O}^{14}, \text{H}^{141}, \text{H}^{142} \), and each site is fully occupied by atoms (Fig. 3c). Half occupancy of the water molecule because of the existence of the two-fold rotation axis in the \( C2/c \) model was changed to full occupancy as the rotation axis disappeared. The structure model using the \( Cc \) space group could be more realistic, considering the local structural arrangement around water molecules and the hydrogen bonding network; the \( Cc \) model does not require breaking of the hydrogen bond network. It is also notable, however, that the bond distance between \( \text{O}^{14} \) and \( \text{H}^{142} \) [1.22(3) Å] is unusually long. This unusually long distance is estimated to be caused by the local static distribution by twinning, which is not eliminated in the vicinity of water molecules. This distance corresponds to \( U_{33}^{1} \) [0.127(6) Å\(^2\)] for \( \text{O}^{14} \), which is large toward the

| \( \text{P} - \text{O} \) | \( \text{Zn} - \text{O} \) | \( \text{C} - \text{O} \) | \( \text{Ca}^{1} - \text{O} \) | \( \text{Ca}^{2} - \text{O} \) |
|----------------|----------------|----------------|----------------|----------------|
| \( 1.540(2) \) | \( 1.970 \) | \( 1.294 \) | \( 2.411 \) | \( 2.501 \) |
| \( \Delta \) | \( 0.0323 \) | \( 0.108 \) | \( 0.047 \) | \( 0.208 \) | \( 0.263 \) |



| \( \text{P} - \text{O} \) | \( \text{Zn} - \text{O} \) | \( \text{C} - \text{O} \) | \( \text{Ca}^{1} - \text{O} \) | \( \text{Ca}^{2} - \text{O} \) |
|----------------|----------------|----------------|----------------|----------------|
| \( 1.540(2) \) | \( 1.970 \) | \( 1.294 \) | \( 2.411 \) | \( 2.501 \) |
| \( \Delta \) | \( 0.0323 \) | \( 0.108 \) | \( 0.047 \) | \( 0.208 \) | \( 0.263 \) |



Table 4. Selected interatomic distances (Å) and angles (°) for skorpionite, specimen 1 (\( C2/c \) model)

| \( \text{P} - \text{O} \) | \( \text{Zn} - \text{O} \) | \( \text{C} - \text{O} \) | \( \text{Ca}^{1} - \text{O} \) | \( \text{Ca}^{2} - \text{O} \) |
|----------------|----------------|----------------|----------------|----------------|
| \( 1.540(2) \) | \( 1.970 \) | \( 1.294 \) | \( 2.411 \) | \( 2.501 \) |
| \( \Delta \) | \( 0.0323 \) | \( 0.108 \) | \( 0.047 \) | \( 0.208 \) | \( 0.263 \) |



Table 5. Selected interatomic distances (Å) and angles (°) for skorpionite, specimen 2 (\( Cc \) model)

| \( \text{P} - \text{O} \) | \( \text{Zn} - \text{O} \) | \( \text{C} - \text{O} \) | \( \text{Ca}^{1} - \text{O} \) | \( \text{Ca}^{2} - \text{O} \) |
|----------------|----------------|----------------|----------------|----------------|
| \( 1.540(2) \) | \( 1.970 \) | \( 1.294 \) | \( 2.411 \) | \( 2.501 \) |
| \( \Delta \) | \( 0.0323 \) | \( 0.108 \) | \( 0.047 \) | \( 0.208 \) | \( 0.263 \) |



T. Tobase, A. Yoshiasa, S. Jinnouchi, G. Kitahara, H. Hongu, M. Tokuda, M. Okube and K. Sugiyama
H142 hydrogen. The $U_{iso}$ values of the H141 and H142 hydrogen atoms in the Cc model are larger than those of H81 and H82 in the C2/c model. In the skorpionite structure, the effect of positional disorder in the oxide ions of the water molecules is caused by positional disorder. Unfortunately, we were unable to obtain any more specimens to enable more precise structural analyses of the natural mineral skorpionite. The observation that the structural parts except for the water molecules were almost the same between the C2/c and Cc models and the ordering part was oxygen with low X-ray scattering intensity makes the space group uncertain. The measurement of the ferroelectric property will help in determining the space group. In Figure 4, spontaneous polarization occurs because of the arrangement of the water molecules parallel to the c-axis direction in the Cc model, and structural relaxation such as a twin or domain structure can be inferred. It is common for statistical displacement to occur because of charge relaxation of spontaneous polarization. We propose that statistical displacement occurs around the water molecules because of a ferroelectric relaxation process in the crystal. It is considered that the displacement direction of O14 extends in the c-axis direction, which is related to the relaxation mechanism. We proposed two structural models for this mineral in this study. It is likely that the structure of skorpionite is essentially the non-centrosymmetric space group Cc and that the apparent symmetry is raised to C2/c by the same size twin and/or domain structures to relax ferroelectricity.
Tunnel structure and proton conduction in skorpionite

The structure of skorpionite has voids in the framework formed by sharing of corners and edges of cation polyhedra. The voids are continuously parallel to the c-axis and form tunnels (Fig. 5). The structure of skorpionite can be regarded as a one-dimensional tunnel structure continuing parallel to the c-axis. The oxygen O8 of the water molecule, O5 of the carbonate group, and all hydrogen atoms are located in the tunnel of the C2/c model. The oxygen O14 of the water molecule and O13 of the carbonate group are located in the tunnel of the Cc model. The oxide ions of O8 and O5 or O14 and O13 only bond to Ca1 and C, respectively, except for hydrogen. The O5 and O13 oxide ions protrude into the tunnel; therefore, they have large values of atomic displacement factors of 0.0213(6) Å² and 0.0212(7) Å², respectively. The O8 or O14 oxide ions of the water molecules strongly bond to Ca1. On the basis of the location of these oxides, the positional displacement is estimated to become large.

Figure 5 shows the local structures around hydrogen atoms H71, H81, and H82 in the C2/c model and H11, H51, H141, and H142 in the Cc model. Details of the hydrogen bonding distances estimated in the model structure of C2/c and Cc are shown in Tables 4 and 5, respectively. All hydrogen bonds belong to a normal linear bond. It is unusual that only the O5 or O13 atoms, which constitute the carbonate group, are the acceptor atoms for all hydrogen bonds in both the C2/c and Cc models. This is similar to one of the four oxygen atoms of the sulfate group being the acceptors of the three hydrogen bonds in alunite (Schukow et al., 1999).

The protons occupy fixed sites in the structure, and most protons are in fixed local positions. H2O molecules in the hydrogen bonds form a series of hydrogen–donor oxygen–hydrogen … acceptor oxygen … hydrogen–donor oxygen–hydrogen … in the tunnel-like ferroelectric ice (Fig. 4). Proton conductivity depends on the activation energies of proton hopping and reorientation (Ogawa et al., 2014). Hopping and reorientation strongly depend on the Roo (O…O distance), i.e., hopping occurs smoothly if Roo is smaller than 2.6 Å and reorientation is dominant if Roo is larger than 2.6 Å. Both short and long Roo distances are necessary for proton conduction. The rotation of water molecules proposed by Ogawa et al. (2014) cannot be assumed within this structure. In addition, the
The O...O distance at O-H...O in this structure is significantly longer than 2.6 Å. Therefore, proton migration does not occur, and hopping in the low temperature range cannot be expected. Instead, ferroelectric properties develop around room temperature. Even if the Roo distance extends from 2.6 to 2.9 Å by about 10%, the activation energy does not decrease on the log scale. Moreover, when Roo is 2.9 Å, proton hopping still depends on temperature. For proton hopping to take place, O-H bonds need to be cut off by O-H stretching vibration. In the high temperature range, proton hopping occurs after an increase in amplitude of stretching vibration. The tunnel structure, where hydrogen bonds are continuously connected, is considered to be a conduction path for protons. The continuity of the proton hopping path is necessary for superionic conductors. It is also necessary that there be an appropriate site in the jump destination. In the case of this structure, defects need to be present. The proton conduction in skorpionite is associated with defects, and proton conductivity should be high.

### Structural misfits in a complicated structure and bond valence sum calculation

Tables 6 and 7 show the results of the bond valence sum calculation of the $C2/c$ model and $C$ model, respectively. The bond valence values of hydrogen bonding are determined based on the distance between the hydrogen...
atoms and the acceptor O atoms (Brown, 1976; Brown and Altermatt, 1985). Each bond valence sum for a cation of the C2/c model andCc model shows a reasonable value corresponding to each oxidation state. However, the bond valence sums of the oxide ions for O1 (1.815 valence unit, v.u.) in the C2/c model and for O7 (1.772 v.u.) and O9 (1.872 v.u.) in the Cc model deviate from the ideal value of 2.0. A local anomaly is observed at the bond valence sum calculation for the O1 atoms in the C2/c model and at those for the O7 and O9 atoms in the Cc model. Figure 6 shows the partial structure around the O7 atoms of the Cc model. The Zn1 atom leaves the center of the tetrahedron and moves towards the O7 site. Zn-O distances in the largely distorted Zn1-tetrahedron have values dispersed from 1.917(7) to 2.025(8) Å. The distance of 2.824(8) Å for Zn1-O7 is longer than the ideal distance of $^{4}\text{Zn}^{2+}$-O (2.08 Å), which is derived from Shannon ionic radii (Shannon, 1976), but the distance is close to the longest Ca$^{2+}$-O distance. An electrostatic contribution is considered, and van der Waals bonding can be assumed between the Zn and O7 sites. As with this situation, there will also be van der Waals bonding between Zn and O1 [2.832(2) Å] in the C2/c model and between Zn2 and O9 [2.839(8) Å] in the Cc model.

Coordination environments of largely distorted Zn and Cu polyhedra are found in some minerals, for example, legrandite (Jinnouchi et al., 2016) and clinoclase (Eby and Hawthorne, 1990). The Zn five-coordinated trigonal-bipyramidal site is common in the structure of zinc arsenate and zinc phosphate minerals. The Zn3-O1 bonds in legrandite [Zn$_3$AsO$_4$(OH)$_2$H$_2$O] have similar structural inconsistencies (Jinnouchi et al., 2016). It is presumed to be a structural misfit that occurs to satisfy the three-dimensional periodicity of the structure of skorpionite with a complex composition. The crystal structure of skorpionite has a partial disordered structure related to the polarization of its water molecules. The structure also has a complicated chemical composition with various complex anions and a unique local structure that differs from the partial structure around the water molecules in the tunnel observed in skorpionite. O1 in the C2/c model and O7 and O9 in the Cc model are hardly influenced by hydrogen bonding and the atomic displacements around the tunnel. We thus propose that the O1 atom in the C2/c model and the O7 and O9 atoms in the Cc model cannot be located at their ideal positions because of the complexity of the chemical composition. Zn is located away from the center of the distorted tetrahedral site.

CONCLUSION

It can be inferred that skorpionite is a ferroelectric mineral with symmetry of the space group Cc. In this structure, the arrangement of polarized water molecules induces spontaneous polarization. The relaxation of the spontaneous polarization generated the disordered structure of skorpionite by twinning and/or domain structures, and the apparent symmetry is increased to C2/c with statistical distribution. Skorpionite is a phosphate carbonate hydroxide hydrous mineral and is composed of various complex anions and acid radicals. Based on the complicated structure formed by the composition, the local structure cannot be the ideal structure. Distortion is concentrated near the Zn site. The oxygen atom of the carbonate group is the acceptor of three hydrogen bonds. Skorpionite with a one-dimensional tunnel structure, in which hydrogen atoms are continuously arranged, should have high proton conductivity.

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SUPPLEMENTARY MATERIALS

Color versions of Figures 2–6 are available online from https://doi.org/10.2465/jmps.180801.

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