A Refinement of the Crystal Structure of Synthetic Tengerite-(Y)

Ritsuro Miyawaki and Satoshi Matsubara

Department of Geology and Paleontology, National Science Museum,
3–23–1, Hyakunin-cho, Shinjuku, Tokyo 169–0073, Japan

Abstract　The crystal structure of synthetic equivalent of tengerite-(Y) has been refined in the anisotropic mode to $R1=0.0253$ for 469 independent reflections [$I>2\sigma(I)$] in an XRD data set for a single crystal of $Y_2(CO_3)_3 \cdot 2H_2O$ measured with Cu$K\alpha$ radiation. The refined parameters for orthorhombic lattice with space group of $Bb2_1m$ are $a=6.0815(5)$, $b=9.1596(9)$, $c=15.0956(10)$ Å, $V=840.89(12)$ Å^3, $Z=4$. The refinement confirms the previous analysis of crystal structure. The anisotropic displacement features of all non-hydrogen atoms have been clarified, and probable positions of hydrogen atoms of water molecule have been proposed.

Key words :　tengerite, crystal structure, refinement.

Introduction

Tengerite-(Y) is a hydrous carbonate mineral of yttrium with small amounts of lanthanides. It occurs as a secondary mineral on the original rare earth mineral such as gadolinite-(Y). The redefinition of tengerite-(Y), as orthorhombic $Y_2(CO_3)_3 \cdot 2–3H_2O$, was made with mineralogical comparison of more than ten specimens from worldwide localities and synthetic substances (Miyawaki *et al.*, 1993), and wiped out the confused history in its definition. In the work for redefinition, an analysis on the crystal structure of tengerite-(Y) was carried out with a single crystal of synthetic equivalent of tengerite-(Y). However, anisotropic displacement parameters were used only for a part of crystallographic sites, Y, C2 and O5 in the refinement. The imperfection in the analysis seems to be due to the choice of X-ray source. The significant anomalous dispersion of MoKα radiation on an yttrium compound can be considered as the major cause of the interference on the analysis. Consequently, we have initiated a refinement of the crystal structure on the same single crystal with Cu$K\alpha$ radiation as the X-ray source.

Data Collection and Refinement

The intensity data were collected with a RIGAKU AFC7R diffractometer with graphite monochromatized Cu$K\alpha$ radiation (50 kV, 200 mA). The sample is the same single crystal used in the previous analysis (Miyawaki *et al.*, 1993). The approximate dimension of the crystal is $0.050\times0.075\times0.125$ mm. The crystal was removed from the glass rod (ca. 0.1 mmϕ), which used in the previous measurement, onto a glass fiber ($10\,\mu$mϕ) to reduce the absorption effect from the glass. The data were collected with 2θ–ω scan and the scanning rate of 2°/min (in ω) for 2θ range up to 150°. A total of 844 reflections were collected, and merging of equivalent reflections gave 474 unique reflections ($R_{int}=0.0259$), of which 469 were classified as observed [$I>2\sigma(I)$]. The cell parameters refined from 25 reflections with 2θ range between 50 and 60° are; $a=6.0815(5)$, $b=9.1596(9)$, $c=15.0956(10)$ Å, $V=840.89(12)$ Å^3, for which $Z=4$.

The diffraction data were converted into the F^2 data by a computer program written by Sugiyama (personal communication). The ψ-scan technique was applied to the empirical absorption correction (North *et al.*, 1968). SHELXL-97 (Sheldrick, 1997) was employed as the refine-

ment program. Scattering factors for neutral atoms and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography, Volume C (1992). Initial parameters were adopted from the results of the previous crystal structure analyses of tengerite-(Y) (Miyawaki *et al.*, 1993). A full-matrix least-squares refinement was performed by refining a scale factor, positional parameters, and anisotropic displacement parameters. The refinement was converged to $R1$ [$I > 2\sigma(I)$]$=0.0253$, $R1$ (all reflections)$=0.0255$, w$R2$ (all reflections)$=0.1127$, Goodness of Fit$=1.156$, Final $\Delta\rho_{min}=-1.487$ and Final $\Delta\rho_{max}=0.552$ e/Å^3.

The final positional parameters and equivalent isotropic displacement parameters are given in Table 1. Table 2 shows anisotropic displacement parameters. The selected interatomic distances and bond angles are summarized in Table 3.

Description of Structure

The present refinement confirms the atomic positional parameters in the previous structure analysis (Miyawaki *et al.*, 1993). Significant improvements could be made for accuracy in lattice and atomic parameters in this refinement. It is noteworthy that the two modifications in experimental procedures, the employment of Cu$K\alpha$ radiation instead of Mo$K\alpha$ radiation and replacement of glass fiber as a sample supporter, are effective for precision in refinement. In the present study, the anisotropic displacement parameters could be refined for all of the sites. Figures 1 and 2 are the ORTEP (Burnett and Johnson, 1996; Farrugia, 1997) drawings showing anisotropic displacement of individual atoms. The displacement parameters of carbon and oxygen atoms in the carbonate group of C1 are apparently smaller than those in the other carbonate group of C2 (Tables 1and 2, Fig. 1b). The directions of displacements of oxygen atoms within the individual carbonate groups are mutually parallel (Fig. 1b). The anisotropies of oxygen atoms in the C2-carbonate group are almost perpendicular to the CO$_3$ triangle plane.

The maximum residual electron density in this refinement, 0.552 e/Å^3, is smaller than that in the previous analysis, 0.9 e/Å^3 (Miyawaki *et al.*, 1993). Among the residual peaks in the final result, two could be refined as the hydrogen positions with full occupancy of the H atoms. The extra refinement with the two H sites converged to $R1$ [$I > 2\sigma(I)$]$=0.0246$ with final $\Delta\rho_{max}=0.530$ e/Å^3. The positional and isotropic displace parameters, x, y, z and U_{iso}, are as follows: H1; 0.23(3), 0.460(18), 0.455(9), 0.09(4); H2; 0.09(2), 0.498(11), 0.401(6), 0.05(3). The intro-

Table 1. Final atomic coordinates, equivalent isotropic displacement parameters.

	x	y	z	$U_{eq.}$
Y	0.49886(6)	0.0049(6)	0.34217(2)	0.0078(4)
C1	0.2567(6)	0.2592(6)	0.1966(3)	0.0081(8)
C2	0.2771(10)	0.0671(8)	0.5000	0.0128(13)
O1	0.3174(5)	0.1322(4)	0.2270(2)	0.0126(9)
O2	0.1057(5)	0.2554(4)	0.13533(19)	0.0105(6)
O3	0.3249(8)	0.3786(4)	0.2229(2)	0.0139(10)
O4	0.4727(11)	0.014(2)	0.5000	0.0214(14)
O5	0.1879(6)	0.0906(5)	0.4245(3)	0.0267(11)
O6	0.1808(7)	0.4064(5)	0.4075(3)	0.0262(10)

Table 2.   Final anisotropic displacement parameters.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Y	0.0067(5)	0.0099(6)	0.0068(5)	0.0013(2)	−0.00028(11)	−0.00010(11)
C1	0.0089(15)	0.0087(19)	0.0068(18)	−0.0047(19)	−0.0028(13)	−0.0012(19)
C2	0.008(3)	0.016(3)	0.014(3)	0.000	0.000	0.003(2)
O1	0.0094(19)	0.013(2)	0.0158(17)	0.0079(13)	−0.0007(12)	−0.0027(17)
O2	0.0110(12)	0.0147(15)	0.0056(12)	0.0070(14)	−0.0031(10)	−0.0046(16)
O3	0.013(2)	0.016(3)	0.0120(18)	0.0056(15)	−0.0042(13)	−0.0049(13)
O4	0.029(3)	0.031(4)	0.004(3)	0.000	0.000	0.008(4)
O5	0.0116(19)	0.051(3)	0.0177(19)	0.010(2)	0.0009(12)	0.0062(17)
O6	0.0099(19)	0.041(3)	0.0275(19)	0.0113(19)	0.0016(15)	−0.0007(16)

Table 3. Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses.

Y –O6	2.363(5)	C1 –O3	1.236(7)
–O1	2.366(5)	–O2	1.304(5)
–O3	2.394(5)	–O1	1.304(7)
–O2	2.397(7)	mean	1.281
–O4	2.3894(7)		
–O5	2.395(4)	C2 –O5	1.281(5)
–O2	2.409(7)	–O5	1.281(5)
–O3	2.486(5)	–O4	1.284(10)
–O1	2.491(5)	mean	1.282
mean	2.410		
O1–C1–O2	115.2(4)	O4–C2–O5	117.1(3)×2
O2–C1–O3	119.2(4)	O5–C2–O5	125.8(6)
O3–C1–O1	125.6(4)		

duction of the two H atoms in this extra refinement showed no any significant differences in the atomic parameters for the non-H atoms from those in the final refinement without the H atoms. Although this extra refinement with two H atoms resulted in the "non positive definite" for principal mean square atomic displacements, U, of C1 and O2 atoms, the interatomic distances and bond angle between these two H atoms and neighboring O atom are reasonable as values for water molecule; O6–H1 0.93(15) Å, O6–H2 1.00(12) Å and H1–O6–H2 79(10)°. The distances from these two H positions towards the next neighboring O atoms, H1···O4 1.98(16) Å and H2···O5 1.94(13) Å, indicate hydrogen
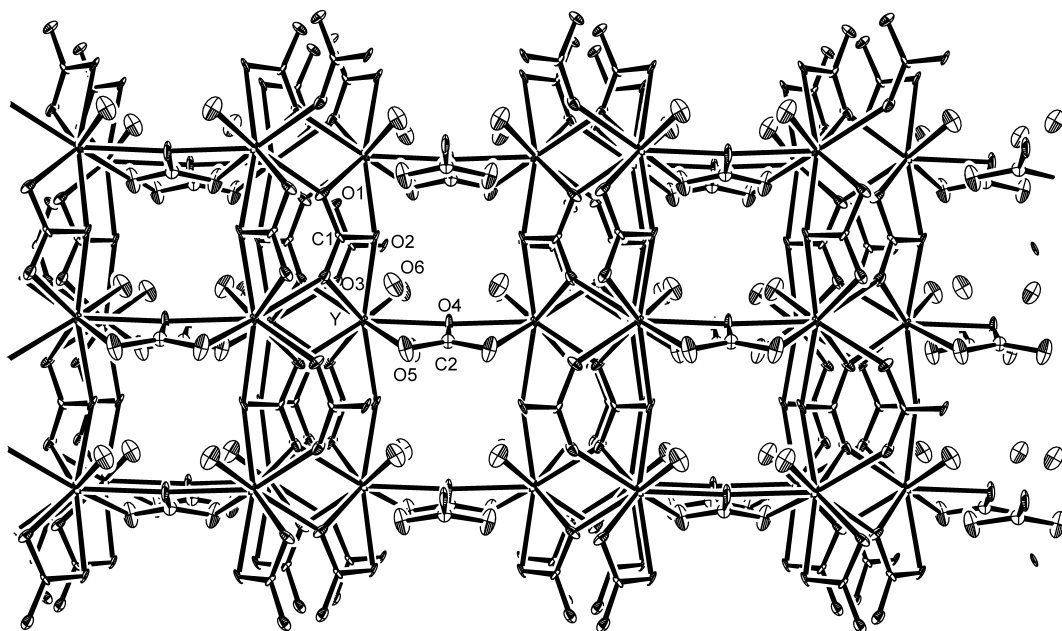

Fig. 1. A view along *a* showing the connection between corrugated sheets.

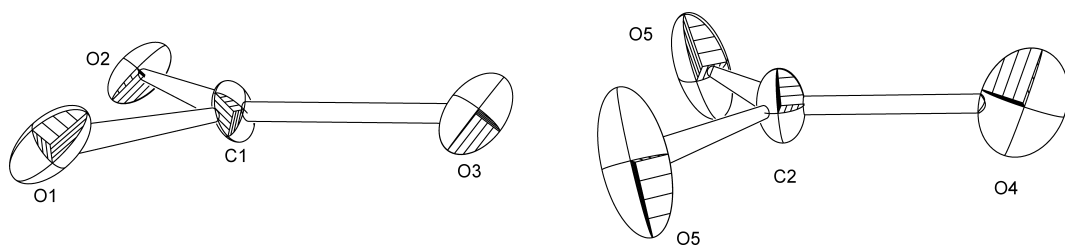Fig. 2. Enlarged view of the triangles of carbonate groups.

bonds between them, respectively. While two hydrogen bonds were proposed for one $O5\cdots H–O6$ and another $O5\cdots H–O6$ in the previous analysis (Miyawaki *et al.*, 1993), the present refinement indicates the other hydrogen bond of $O4\cdots H–O6$.

References

Burnett, M. N. and Johnson, C. K., 1996. ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge National Laboratory Report ORNL-6895.

Farrugia, L. J., 1997. ORTEP-3 for Windows. *J. Appl. Crystallogr.*, **30**: 565.

Miyawaki, R., Kuriyama, J. & Nakai, I., 1993. The redefinition of tengerite-(Y), $Y_2(CO_3)_3\cdot 2–3H_2O$, and its crystal structure. *American Mineralogist*, **78**: 425–432.

Wilson, A. J. C. (ed.), 1992. International Tables for Crystallography, Volume C, Kluwer Academic Publishers, Dordrecht.

North, A. C. T., Phillips, D. C. and Mathews, F. S., 1968. A semi-empirical method of absorption correction. *Acta Crystallographica*, **A25**: 351–359.

Sheldrick, G. M., 1997. SHELXL-97. Program for crystal-structure refinement. University of Göttingen, Germany.