

The Rietveld analysis of crystal structure of an additive telluromolybdate CoTeMoO_6

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Abstract

Additive telluromolybdates $\text{M}^{\text{II}}\text{TeMoO}_6$ ($= \text{M}^{\text{II}}\text{O} \cdot \text{TeO}_2 \cdot \text{MoO}_3$; $\text{M}^{\text{II}} = \text{Co, Mn, Zn}$), which were prepared by the solid phase reaction of molybdates $\text{M}^{\text{II}}\text{MoO}_4$ with TeO_2 , showed high activity comparable with the crystalline active species $\alpha\text{-Te}_2\text{MoO}_7$ in the vapor-phase selective oxidation of ethyl lactate to the pyruvate. The crystal structure of CoTeMoO_6 was analyzed by the Rietveld method. The atomic coordinates of three metallic components were (x, y, z) : $\text{Co}(0, 0.5, 0.2725)$, $\text{Mo}(0, 0, 0.5498)$, $\text{Te}(0, 0, 0.0127)$ with weighted-pattern R -value (criteria of fit) $R_{\text{wp}} = 26.27$ without accounting for oxygen, and $R_{\text{wp}} = 17.5$ considering 12 oxygen atoms, for orthorhombic space group $P 2_1 2_1 2$ with $Z = 2$, $a = 5.2432(8)$, $b = 5.0520(8)$, $c = 8.8432(4)$ Å. The layer structure was quite different from the structure of the reference binary oxide $\alpha\text{-Te}_2\text{MoO}_7$, but tellurium is again located adjacent to molybdenum linked through lattice oxygen for composing active site. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Binary oxides, $\text{TeO}_2\text{-MoO}_3$, converted ethyl lactate selectively to the pyruvate in a fixed-bed flow system at 250–300°C [1–4]. A synergy in activity was observed for the $\text{TeO}_2\text{-MoO}_3$ catalysts calcined at 500°C, showing a sharp maximum at a composition of $\text{MoO}_3 \cdot 2\text{TeO}_2$, and $\alpha\text{-Te}_2\text{MoO}_7$ was suggested as the active species [2]. Additive telluromolybdates $\text{M}^{\text{II}}\text{TeMoO}_6$ ($= \text{M}^{\text{II}}\text{O} \cdot \text{TeO}_2 \cdot \text{MoO}_3$) of ternary oxide system

with a divalent cation $\text{M}^{\text{II}} = \text{Co, Mn, Zn}$ were also active catalysts even for $\text{M}^{\text{II}} = \text{Zn}$, while both the component molybdate ZnMoO_4 and TeO_2 were inactive [3].

The powder patterns of ternary additive telluromolybdates ($\text{M}^{\text{II}} = \text{Co, Mn, Zn}$) are already indexed [5,6], and the structures of these compounds are isotypic with orthorhombic space group $P 2_1 2_1 2$ and $Z = 2$, but the atomic coordinates for three metal atoms are not yet given. By analogy of the structure of $\alpha\text{-Te}_2\text{MoO}_7$ obtained by the single crystal analysis [7] (Fig. 1a), an estimated structure of ZnTeMoO_6 was proposed as given in Fig. 1b based on the

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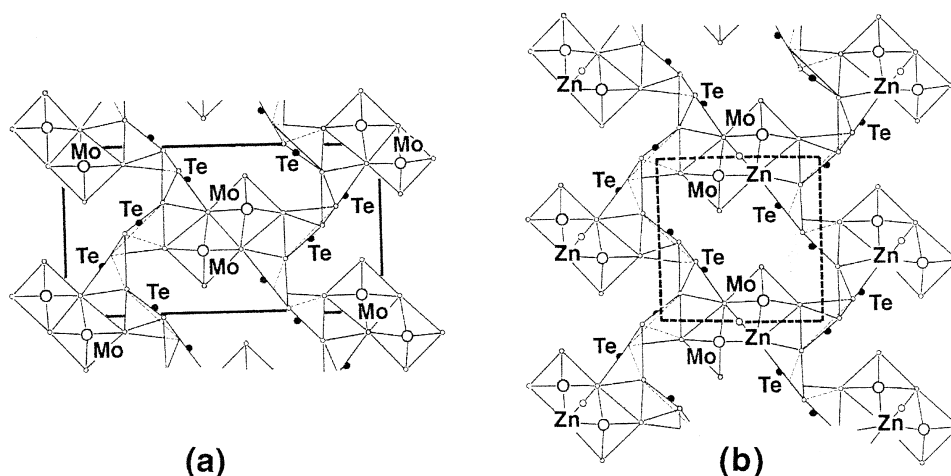


Fig. 1. Crystal structure of $\alpha\text{-Te}_2\text{MoO}_7$ (a) [7] and proposed structure of ZnTeMoO_6 based on the vibrational spectra (b) [8].

vibrational spectra (IR and Raman) [8]. However, the dashed block in Fig. 1b is evidently inadequate as the unit cell, and the proposed structure does not satisfy the required symmetry of given space group $P 2_1 2_1 2$ and $Z = 2$.

In the present work, atomic coordinates of three metals of an additive telluromolybdate CoTeMoO_6 was analyzed by the Rietveld method. The concluded layer structure appears quite different from the reference binary oxide $\alpha\text{-Te}_2\text{MoO}_7$, but tellurium is again located adjacent to molybdenum linked through lattice oxygen for composing active site.

2. Experimental and analysis

Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer RINT 2000 of Rigaku, Tokyo, over $2\theta = 8\text{--}65^\circ$ by the step-scan mode with a step-width of 0.02° using $\text{CuK}\alpha$ radiation at 40 kV and 30 mA to obtain 2850 reflection intensities, where the sampling time was set up to assure 10 000 counts for the strongest (112) reflection. Fine powders of

CoTeMoO_6 calcined at 620°C in air were used for the Rietveld analysis [9] employing a crystal structure program RIETAN, installed in the XRD system. Infrared spectra were measured for catalyst powder tabletted with KBr by a spectrometer, Model FTIR-3 of Japan Spectroscopic, Tokyo. Differential thermal analysis-thermogravimetric analysis (DTA-TGA) was measured by a thermal analyzer, Model TAS-100 of Rigaku, Tokyo, for samples kneaded and dried at 80°C .

3. Results and discussion

3.1. Crystal structure of $\alpha\text{-Te}_2\text{MoO}_7$

The crystalline $\alpha\text{-Te}_2\text{MoO}_7$ is monoclinic with $a = 4.286$, $b = 8.618$, $c = 15.945$ Å, $\beta = 95.67^\circ$, $Z = 4$ and space group $P 2_1/c$ [7], where a pair of MoO_6 octahedra are linked by edge sharing to $[\text{Mo}_2\text{O}_{10}]$ unit and the double chains of distorted molybdenum octahedra connected at corners along the a -direction are linked by tetrahedral oxotellurium, Te^{IV} , chains to build

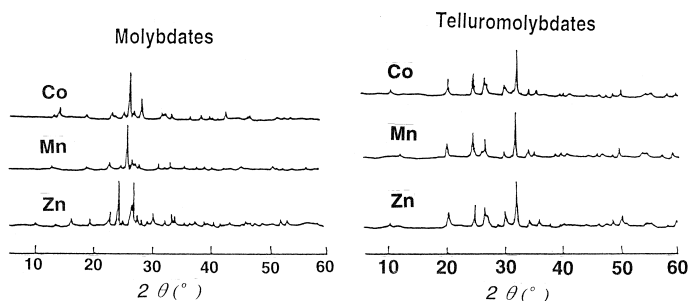


Fig. 2. Powder XRD patterns of molybdates $M^{II}MoO_4$ (a) and telluromolybdates $M^{II}TeMoO_6$ (b). $M^{II} = Co, Mn, Zn$.

up the three-dimensional arrangement [7]. Each MoO_6 octahedron has a non-bridging $Mo=O$ (1.745 Å; IR 906 cm^{-1}) [10]. Three $Mo-O$ distances of crystalline $\alpha\text{-Te}_2MoO_7$ obtained by EXAFS analysis [4] were similar to those of MoO_3 . The basic unit of the structure of TeO_2 is built up from four oxygen atoms coordinated to one tellurium atom to form a trigonal bipyramid with one of the equatorial position unoccupied [10]. A pair of the TeO_4 units are connected by edge sharing to $[Te_2O_6]$ followed by the linkage at corners to chains of oxotellurium polyhedra [11]. The $Te-O$ distances [10] of 1.90 Å (equatorial) and 2.08 Å (axial) are rather close together, and a single $Te-O$ as average was obtained in EXAFS [3].

3.2. Preparation and characterization of telluromolybdates

Additive telluromolybdates are usually prepared by calcination of kneaded paste of an

equimolar mixture of the corresponding molybdate and TeO_2 at 500°C in air [5]. Powder XRD patterns and IR spectra of the component molybdates are clearly different each other (Figs. 2 and 3), while those of telluromolybdates are similar together, signifying their structures to be isotopic [5,6]. However, differential thermal analysis showed sharp indications of solid-phase reaction at 551° and 592°C as given in Fig. 4 followed by melting at 662° and 676°C for $ZnMoO_4\text{-}TeO_2$ and $CoMoO_4\text{-}TeO_2$, respectively, suggesting the calcination temperature of 500°C taken in the literature [5] was not enough for solid-phase reaction, and the sample was calcined at 620°C in the present work.

Melts of the binary $TeO_2\text{-}MoO_3$ system are easily fixed in a glassy state at normal cooling rates [4,12]. The short-range atomic order in glass was suggested by EXAFS analysis to be similar to the arrangement in the crystalline state [4]. Thus, $\alpha\text{-Te}_2MoO_7$ was quickly recryst-

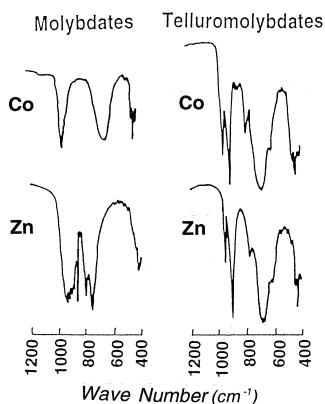


Fig. 3. Infrared spectra of molybdates and telluromolybdates.

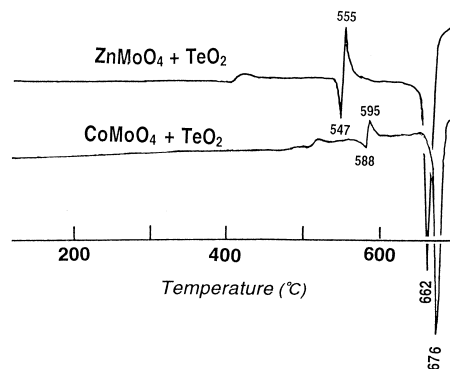


Fig. 4. Differential thermal analysis of $M^{II}MoO_4\text{-}TeO_2$ systems. $M^{II} = Co, Zn$.

tallized again with high purity on heating the orange glass at 450–500°C. Amorphous material [3] was obtained, similarly as in Te_2MoO_7 , by quenching at room temperature after melting CoTeMoO_6 and ZnTeMoO_6 at 700°C, but the ternary telluromolybdates attempted to recrystallize on heating at 620°C did not reproduce the initial crystals as shown in Fig. 5. The strong intensity of (002) reflection in the recrystallized material suggests an oriented crystal growth along c -axis.

3.3. Crystal data and structure of $M^{\text{II}}\text{TeMoO}_6$ proposed in literature

The indexed powder data for CoTeMoO_6 are summarized in Table 1 [6,13] and the structure proposed in the literature [8] for an isotopic crystal ZnTeMoO_6 is given in Fig. 1b.

3.4. Rietveld analysis of ternary CoTeMoO_6

3.4.1. Crystal structure factor

The observed intensity of a given reflection (hkl) is proportional to the squared crystal structure factor:

$$I \propto |F_{hkl}|^2, \quad (1)$$

where

$$F_{hkl} = f_j \exp 2\pi i(hx_j + ky_j + lz_j) \quad (2)$$

and f_j is atomic structure factor.

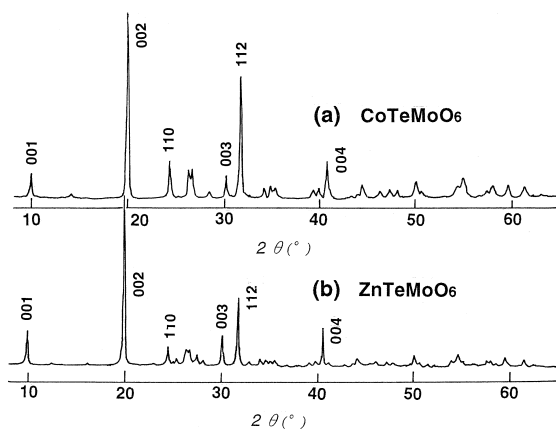


Fig. 5. Oriented crystal growth of telluromolybdate along c -axis in the recrystallization. Quenching at room temperature in an amorphous state after melting at 700°C, and then recrystallized at 620°C. (a) CoTeMoO_6 , (b) ZnTeMoO_6 .

Table 1

X-ray powder data for CoTeMoO_6 [6,13] orthorhombic space group $P 21212$, $Z = 2$, $a = 5.262$, $b = 5.062$, $c = 8.857$ Å

2θ	d (Å)	I/I_0	hkl
9.99	8.85	10	001
20.09	4.42	30	002
24.40	3.64	50	110
26.37	3.38	30	111
30.25	2.955	5	003
31.79	2.817	100	112
34.09	2.63	17	200
44.67	2.0029	5	014
50.07	1.822	21	220

The general positions for the present space group $P 2_12_12$ (Int. Table No. 18) [14] are: (1) x, y, z ; (2) $-x + 1/2, y + 1/2, -z$; (3) $-x, -y, z$; (4) $x + 1/2, -y + 1/2, -z$, but the presence of two formula weights in the unit cell ($Z = 2$) requires special positions for Co, Te and Mo atoms [5]. Thus, the atomic coordinates available for these three metals would be (0, 0, z); (1/2, 1/2, $-z$) for $2a$ -site and/or (0, 1/2, z); (1/2, 0, $-z$) for $2b$ -site.

Substituting $(x, y, z) = (0, 0, z)$ for $2a$ -site and $(x, y, z) = (0, 1/2, 0)$ for $2b$ -site, we obtain the crystal structure factors for $f_j = f$:

$$F = 2f[\exp 2\pi i(lz) + \exp 2\pi i\{(h+k)/2 + l(-z)\}] \quad (3)$$

for $2a$ -site, and

$$F = 2f[\exp 2\pi i\{k/2 + l(-z)\} + \exp 2\pi i\{h/2 + l(-z)\}] \quad (4)$$

for $2b$ -site, respectively.

Let us examine F -values of arbitrarily selected four reflections of the strongest (112), the second strongest (110), and two weak reflections (003) and (014).

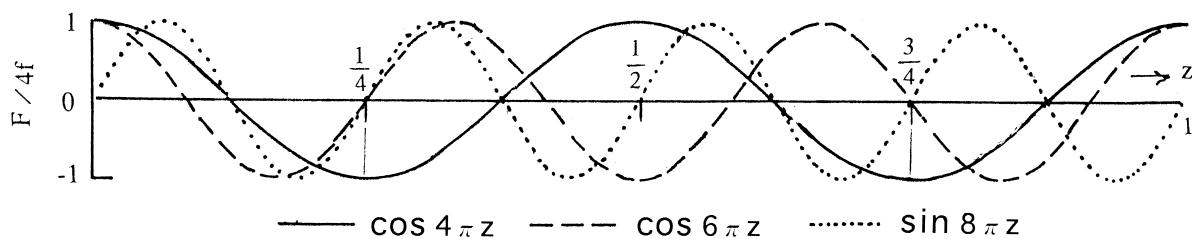
(i) The strongest (112); $I/I_0 = 100$; As (hkl) = (112) in Eqs. (3) and (4),

$$F = 2f[\exp 2\pi i(2z) + \exp 2\pi i(-2z)] = 4f \cos 4\pi z$$

for $2a$ -site, and

$$F = 2f[\exp 2\pi i(1/2 + 2z) + \exp 2\pi i(1/2 - z)] = -4f \cos 4\pi z$$

for $2b$ -site, respectively.



z	0	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{3}{16}$	$\frac{1}{4}$	$\frac{5}{16}$	$\frac{3}{8}$	$\frac{7}{16}$	$\frac{1}{2}$	$\frac{9}{16}$	$\frac{5}{8}$	$\frac{11}{16}$	$\frac{3}{4}$	$\frac{13}{16}$	$\frac{7}{8}$	$\frac{15}{16}$	1
Strong (112) $\cos 4\pi z$	1		0		-1		0		1		0		-1		0		1
Weak (014) $\sin 8\pi z$	0	1	0	-1	0	1	0		0		0	-1	0	1	0	-1	0
Weak (003) $\cos 4\pi z$	1				0				-1				0				1

Fig. 6. Illustrative procedure for selection of z -values for strong (112) with weak (003) and (014) reflections.

(ii) The second strongest (110); $I/I_0 = 50$

$F = 0$ for $2a$ -site and $F = -4f$ for $2b$ -site

(iii) Weak (003); $I/I_0 = 5$

$F = 4f \cos 6\pi z$ both for $2a$ - and $2b$ -site

(iv) Weak (014); $I/I_0 = 5$

$F = 4fi \sin 8\pi z$ for $2a$ -site and

$F = -4fi \sin 8\pi z$ for $2b$ -site

Among four reflections (112), (110), (003) and (014) arbitrarily selected above, the intensity of the second strongest (110) is independent of z -values and related only with the atomic structure factor. For the remaining three reflections, the procedure to find z -values which give a large F for strong (112) and small F -values both for weak (003) and (014) reflections is illustrated in Fig. 6. Thus, we get $z = 1/4$ or $3/4$ for special positions $(0, 0, z)$ and/or $(0, 1/2, z)$, leading to a set of coordinates $(0, 0, 1/4)$, $(0, 0, 3/4)$ and $(0, 1/2, 3/4)$ for three metals.

3.4.2. Initial structure model

The location of the three metal atoms is not yet specified at present, and at first Co and Mo were tentatively located at $2a$ -site and Te at $2b$ -site, respectively, as an initial structure model. The crystal structure factor F thus obtained are as follows.

$$F_{112} = 4[f_{\text{Co}} \cos 4\pi z + f_{\text{Mo}} \cos 4\pi z - f_{\text{Te}} \cos 4\pi z] \quad (5)$$

$$F_{110} = 4[f_{\text{Co}} + f_{\text{Mo}} - f_{\text{Te}}] \quad (6)$$

$$F_{003} = 4[f_{\text{Co}} \cos 6\pi z + f_{\text{Mo}} \cos 6\pi z - f_{\text{Te}} \cos 6\pi z] \quad (7)$$

$$F_{014} = 4[f_{\text{Co}} \sin 8\pi z + f_{\text{Mo}} \sin 8\pi z - f_{\text{Te}} \sin 8\pi z] \quad (8)$$

The intensity I of each reflections is proportional to the squared crystal structure factor $|F|^2$

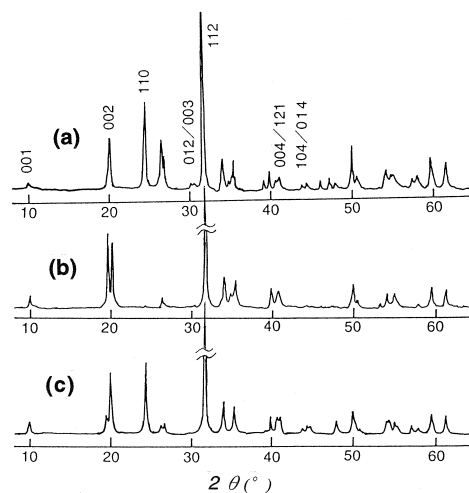


Fig. 7. Powder XRD patterns of CoTeMo_6 . (a) Observed; (b) Calcd., presumed: Co 0.52, Mo 0.01 for $2a$ -site and Te 0.26 for $2b$ -site; (c) Calcd., presumed: Te 0.52, Mo 0.024 for $2a$ -site and Co 0.26 for $2b$ -site.

Table 2
Atomic coordinates for CoTeMoO₆ Orthorhombic space group *P* 2₁2₁2, *Z* = 2

Lattice constant (Å)	<i>a</i>	<i>b</i>	<i>c</i>
This work	5.2432(8)	5.0520(8)	8.8432(4)
Ref.[6]	5.262(2)	5.062(2)	8.857(3)
Atomic coordinate	<i>x</i>	<i>y</i>	<i>z</i>
Co ²⁺	0	0.5	0.2725(7)
Mo ⁶⁺	0	0	0.5498(3)
Te ⁶⁺	0	0	0.0127(9)
<i>R</i> -factor	<i>R</i> _{wp}	<i>R</i> _e	χ ²
Three metals	26.27	5.03	27.3336
With 8 oxygen atoms	20.58	–	–
With 12 oxygen atoms	17.5	–	–

as given in Eq. (1). Presuming the atomic coordinates for three metal atoms as: Co (0, 0, 0.51); Mo (0, 0, 0.001); Te (0, 0.5, 0.26), the calculated pattern is compared with the observed XRD pattern in Fig. 7, where the second strongest reflection (110) in the observed pattern (a) disappeared in the calculated pattern (b), and the third strongest (002) reflection was split in two.

Crystal structure factor of (110) reflection disappeared in the calculated pattern (b) depends only on the atomic structure factor as in Eq. (6). The atomic structure factor *f* generally increases with increasing atomic number, and $f_{\text{Co}} < f_{\text{Mo}} < f_{\text{Te}}$. Thus, it is of benefit to replace

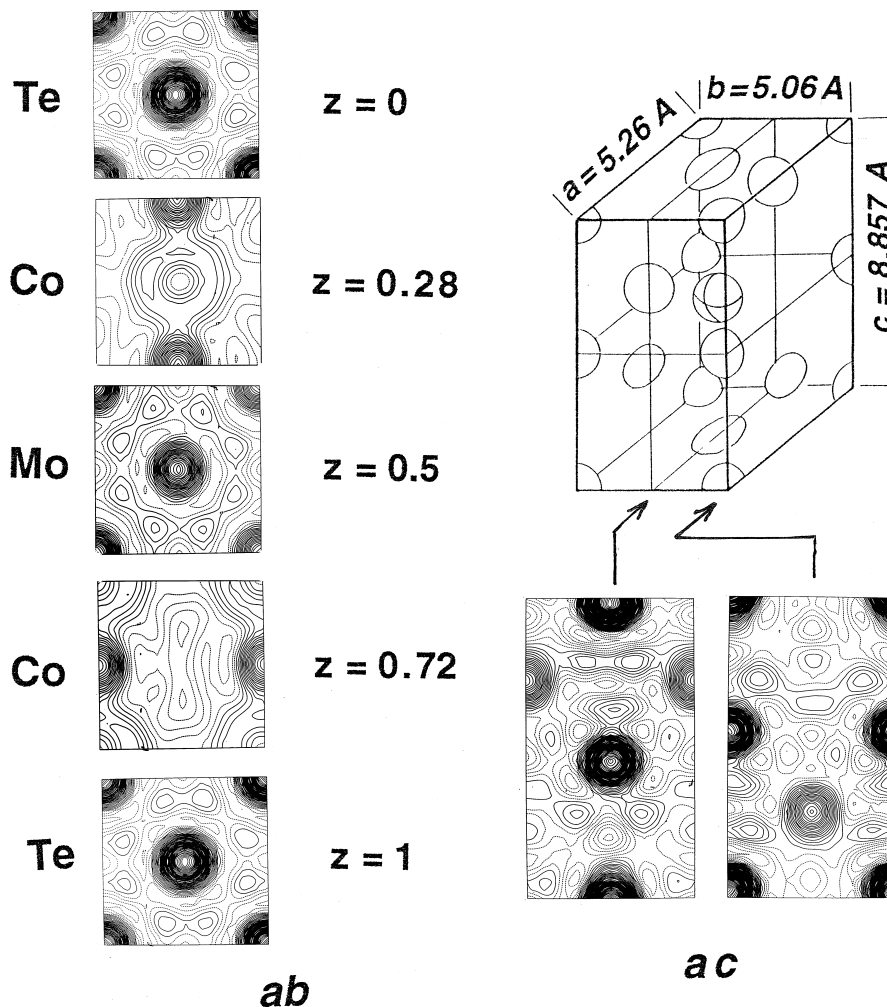


Fig. 8. 3D-location of three metallic components of CoTeMoO₆ with Fourier maps of *ab*/*ac*-planes.

f_{Te} with f_{Co} in Eq. (6) to get a large F -value for the strong reflection (110):

$$F_{110} = 4[f_{\text{Te}} + f_{\text{Mo}} - f_{\text{Co}}] \quad (9)$$

The results are rather in good agreement with the observed pattern as given in Fig. 7c.

3.4.3. Rietveld refinement and atomic coordinate

Attempted refinement in the Rietveld analysis still diverted, but replacing the location of Mo with Te and continued asymptotic trials with z -variable resulted in a rather good convergence capable of specifying the atomic coordinates of three metals as

$$(x, y, z): \text{Co} (0, 0.5, 0.2725), \text{Mo} (0, 0, 0.5498), \text{Te} (0, 0, 0.0127)$$

with weighted-pattern R -value (criteria of fit) [9] of $R_{\text{wp}} = 26.27$ without accounting for oxygen atoms, and $R_{\text{wp}} = 17.5$ considering 12 oxygen atoms as summarized in Table 2. The 3D-location of metallic components of CoTeMoO_6 with Fourier maps is illustrated in Fig. 8. The layer structure revealed in the present analysis is consistent with an oriented crystal growth along c -axis in recrystallization evidenced in Fig. 5, showing the estimated structure (Fig. 1b) [8] proposed for ZnTeMoO_6 should be corrected. The layer structure appears quite different from the reference binary oxide $\alpha\text{-Te}_2\text{MoO}_7$ (Fig. 1a) [7], but tellurium in the ternary telluromolybdate CoTeMoO_6 is again located adjacent to molybdenum linked through lattice oxygen. The active site for oxidation would be $\text{Mo}=\text{O}$ in the telluromolybdate catalysts. Entrapping the substrate lactate as alkoxide on the basic $\text{O}-\text{Te}-\text{O}$ site followed by the oxidative attack at $\text{C}-\text{H}$ bond by $\text{Mo}=\text{O}$ would proceed cooperatively, leading to the synergy in activity.

4. Conclusions

The Rietveld analysis of an additive telluromolybdate CoTeMoO_6 revealed the layer structure, specifying the atomic coordinates of three metals as (x, y, z) : Co (0, 0.5, 0.2725), Mo (0, 0, 0.5498), Te (0, 0, 0.0127) for orthorhombic space group $P 2_1 2_1 2$ with $a = 5.2432(8)$, $b = 5.0520(8)$, $c = 8.8432(4)$ Å and $Z = 2$. The structure was quite different from that of the reference binary telluromolybdate $\alpha\text{-Te}_2\text{MoO}_7$, but tellurium is again located adjacent to molybdenum linked through lattice oxygen for composing active site.

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