Electron Crystallography of CaMoO₄ Using High Voltage Electron Microscopy

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The three-dimensional structure of an inorganic crystal, CaMoO₄ (space group $I4_1/a$, a = 5.198(69) Å and c = 11.458(41) Å), was determined by electron crystallography utilizing a high voltage electron microscope. An initial structure of CaMoO₄ was determined with 3-D electron diffraction patterns. This structure was refined by crystallographic image processing of high resolution TEM images. X-ray crystallography of the same material was performed to evaluate the accuracy of the TEM structure determination. The cell parameters of CaMoO₄ determined by electron crystallography coincide with the X-ray crystallography result to within 0.033-0.040 Å, while the atomic coordinates were determined to within 0.072 Å.

Key Words : CaMoO₄, High voltage electron microscope, Electron crystallography, X-ray crystallography

Introduction

The determination of crystal structures at the atomic scale is a fundamental step to understand the properties of materials. Such determination is commonly performed *via* one of a few methods of X-ray crystallography. However, such methods are insufficient to investigate individual crystals in nanometer scale because X-rays interact weakly with matter. On the other hand, interaction of fast electrons with matter is several orders of magnitude stronger than that of X-rays. Recently, the structural determination of nano-sized crystalline materials by electron crystallography has been intensively studied and widely used as an alternative technique for ascertaining crystal structures.[1-3] Especially, Hovmöller group determined the atomic coordinates of heavy atoms in metal oxides with 0.1 Å accuracy using high resolution transmission electron microscopy (HRTEM) images and crystallographic image processing (CIP).[4] Weirich *et al.* have determined and refined the unknown structure, Ti₁₁Se₄, using both HRTEM images and electron diffraction (ED) data.[5] One of fundamental problems causing slow development of electron crystallography is the dynamical nature of electron scattering except for very thin samples.[2,6,7] Therefore it is important to take great care to set up experimental conditions for quantitative structure analysis by TEM properly.

Generally, there are two methods for structural determination by electron crystallography: HRTEM image analysis and quantitative electron diffraction (QED) analysis.[8] For HRTEM image analysis, the CIP method, exit wave reconstruction method, and phase extension method have been developed.[9-11] In contrast, for QED, Patterson analysis, direct method, maximum entropy method, and multi-slice least square (MSLS) method have been developed.[12-15] Combined techniques of HRTEM image and QED analysis were also tried in studying Al-Mg-Si.[16] Its rough structure model was obtained by the exit wave reconstruction of HRTEM images

and then refined by the MSLS method (overall R value of 3.1%) in which dynamical scattering effects on ED data were fully taken into account.

In this paper, we present a structural analysis utilizing the high voltage electron microscope (HVEM) at the Korea Basic Science Institute (KBSI). The utilized HVEM has the capabilities of high energy (1,250 keV), atomic resolution (1.17 Å, point-to-point) and high tilting (± 60°, ± 45°) as well as energy-filtering. It was expected that these capabilities would enhance the reliability of a 3-D structural analysis of nano-sized crystalline materials by electron crystallography. We previously determined SmZn₀.₆₇Sb₂ by the CIP method and evaluated several microscopic parameters on the structural refinement processes.[17,18] The refinement results agreed well with the X-ray results because the structure of SmZn₀.₆₇Sb₂ is comparatively simple. Here, we report the 3-D structural determination of a more complicated structure, CaMoO₄, by the CIP method and the direct method.

Experimental Section

Specimen preparation. The sample was prepared as a fine powder from a single crystal of powellite, CaMoO₄, grown by the Czochralski method. The as-prepared powder was intimately dispersed in ethanol and then was loaded as a droplet of the prepared suspension on a carbon-supported Cu grid and dried on air.

TEM measurements. Examination of the specimen was carried out using a JEM-ARM 1300S (JEOL Ltd.). HRTEM images and selected-area electron diffraction patterns from 15 different zone axes were obtained utilizing a high tilting goniometer and specimen holder (± 60°, ± 45°). All HRTEM images were zero-loss filtered with an energy-filtering system (HV-GIF, Gatan Inc.). Instrumental conditions, such as specimen thickness, focus conditions, and tilting, were strictly controlled.[2,17]

Data analysis. Calibrations of magnifications and camera constants were performed with a standard sample using the program Digital Micrograph (Gatan Inc.) and ELD.[19] respectively. Intensities of all reflections for each ED pattern were extracted by ELD. TRICE was used for reconstructing the 3-D reciprocal lattice from each ED tilt series.[20] 2-D intensities of ED patterns were scaled and merged into 3-D intensities by the program TRIPLE referring the common reflections of the ED patterns.[21] SIR2002 was used to determine an initial structure of CaMoO₄ through direct method.[13] The CIP procedure of HRTEM images for structural determination was carried out using the program CRISP.[5,9] ATOMS (Shape Software Inc.) was employed for drawing the CaMoO₄ structure.

X-ray crystallography. Analysis of the CaMoO₄ crystal was carried out with a Bruker SMART diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation. Accurate cell parameters and orientation matrices were determined through the least-squares fit of 885 reflections. Intensities of an asymmetric unit were collected in the ω scan mode. The structure was determined by the direct method, and the least-squares refinement of the structure was performed by the program SHELXL97.[22]

Experimental Results and Analysis

Electron diffraction analysis. The first step for structural analysis using ED patterns is to determine the lattice parameters. To get the lattice parameters from 2-D ED patterns, it is necessary to reconstruct a 3-D reciprocal space through tilt series acquisition of ED patterns along the one common reciprocal axis. Three tilt series of ED patterns shown in Figure 1 were obtained along the [010], [110] and [001] axes. To calculate the intensity difference between the strongest and the weakest reflections, these ED patterns of 15 zone axes were recorded with different exposure times (0.5, 1, 2, and 4 seconds). The 3-D reciprocal space of the crystal structure was constructed by TRICE referring angular relations between three or more ED patterns. As summarized in Table 1, the CaMoO₄ structure is considered to be an orthorhombic or a tetragonal system. After the determination of lattice parameters, the program ELD carried out indexing and intensity extraction for all reflections by a shape fitting method. The ED intensities obtained from each zone axis were scaled and merged by TRIPLE referring the common reflections. The merging procedure plays an important role in the final result, since intensities of the common reflections from different zone axes are usually different due to dynamical scattering effects. Quality of the data can be judged from R_{merge} value which is the average difference between the data in the two ED patterns. R_{merge} values below 10% were used in this study. Determination of the space group was achieved with 1,384 reflections by comparison of extinction conditions for all 68 tetragonal space groups. The crystal structure
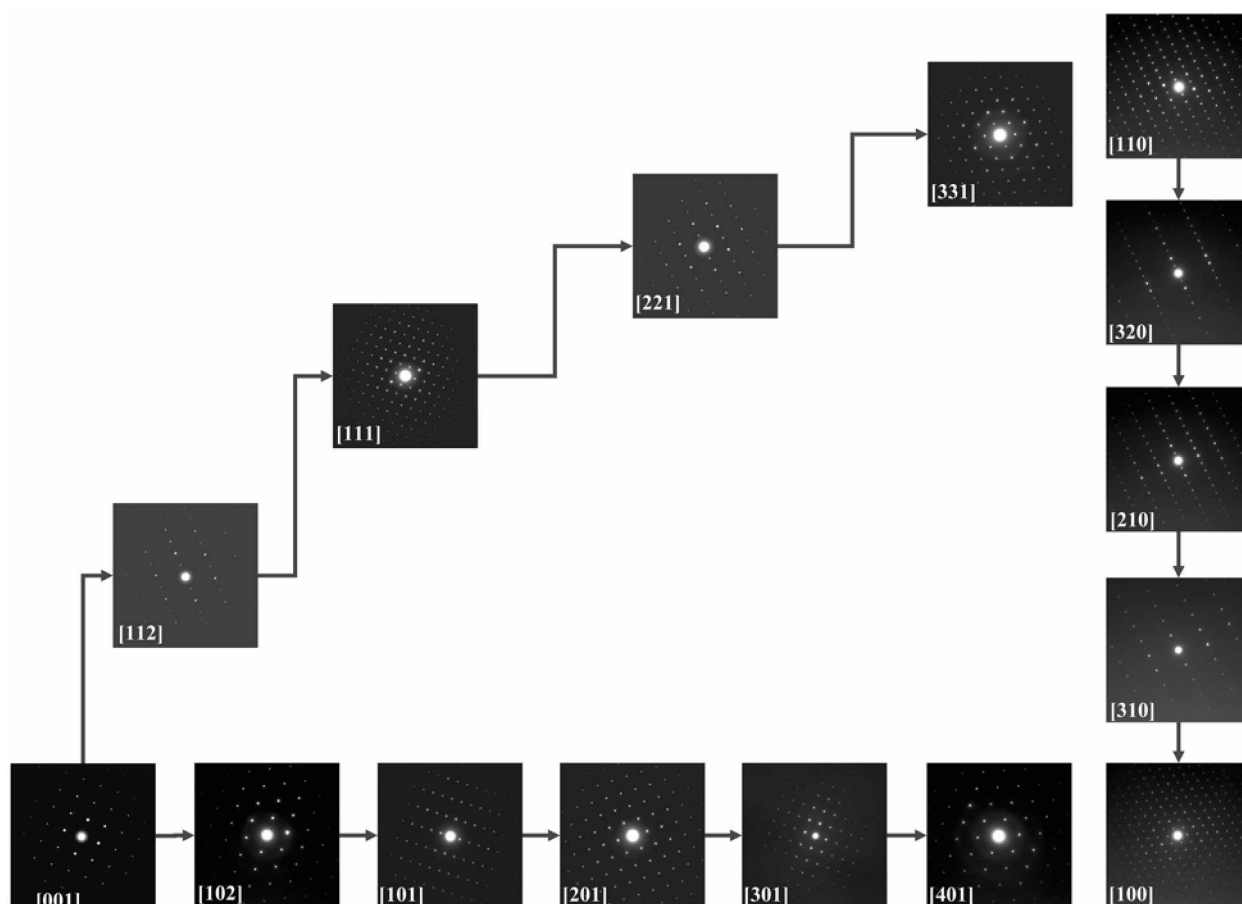
**Figure 1.** Tilt series of the three zone axes used for 3-D reciprocal space construction of the CaMoO₄ structure.

Table 1. Cell parameters of CaMoO₄ determined by three series of electron diffraction patterns

No	Zone axes	Experimental tilting angle (°)	Calculated tilting angle (°)	Estimated cell parameters
#1	[110] → [310] → [100]	26.4, 43.1	26.6, 45.0	a = 5.42 Å, α = 90.4° b = 5.26 Å, β = 89.9° c = 11.46 Å, γ = 92.3°
#2	[001] → [112] → [221]	18.2, 53.1	17.9, 52.3	a = 5.23 Å, α = 90.3° b = 5.21 Å, β = 90.0° c = 11.26 Å, γ = 90.3°
#3	[001] → [101] → [201]	24.6, 42.2	24.6, 42.4	a = 5.18 Å, α = 89.3° b = 5.16 Å, β = 90.0° c = 11.52 Å, γ = 90.1°
Average cell parameters		a = 5.27(10) Å, b = 5.21(4) Å, c = 11.41(11) Å α = 90.0(5)°, β = 89.9(4)°, γ = 90.9(9)°		

Table 2. Atomic coordinates, selected bond lengths, and bond angles by ED patterns analysis

Atomic coordinates				Selected bond lengths (Å) & bond angles (°)
Atoms	x	y	z	
Mo	0.0000	0.2500	0.1250	Mo-O 1.93(3)
Ca	0.0000	0.2500	0.6250	Ca-O 2.16(3)
O	0.099(6)	0.453(6)	0.284(3)	O-Mo-O 117.7(4), 105.5(4)

of CaMoO₄ was determined with 377 independent reflections by the direct-method program SIR2002. As a result, the space group, $I4_1/a$, and the cell parameters, a = 5.182(4) Å and c = 11.392(2) Å, were determined. The R_{sym} value, which is the symmetry difference of symmetry-related reflections according to the space group, was 14.7%. The final R(F) factor, which reflects the reliability of the structure
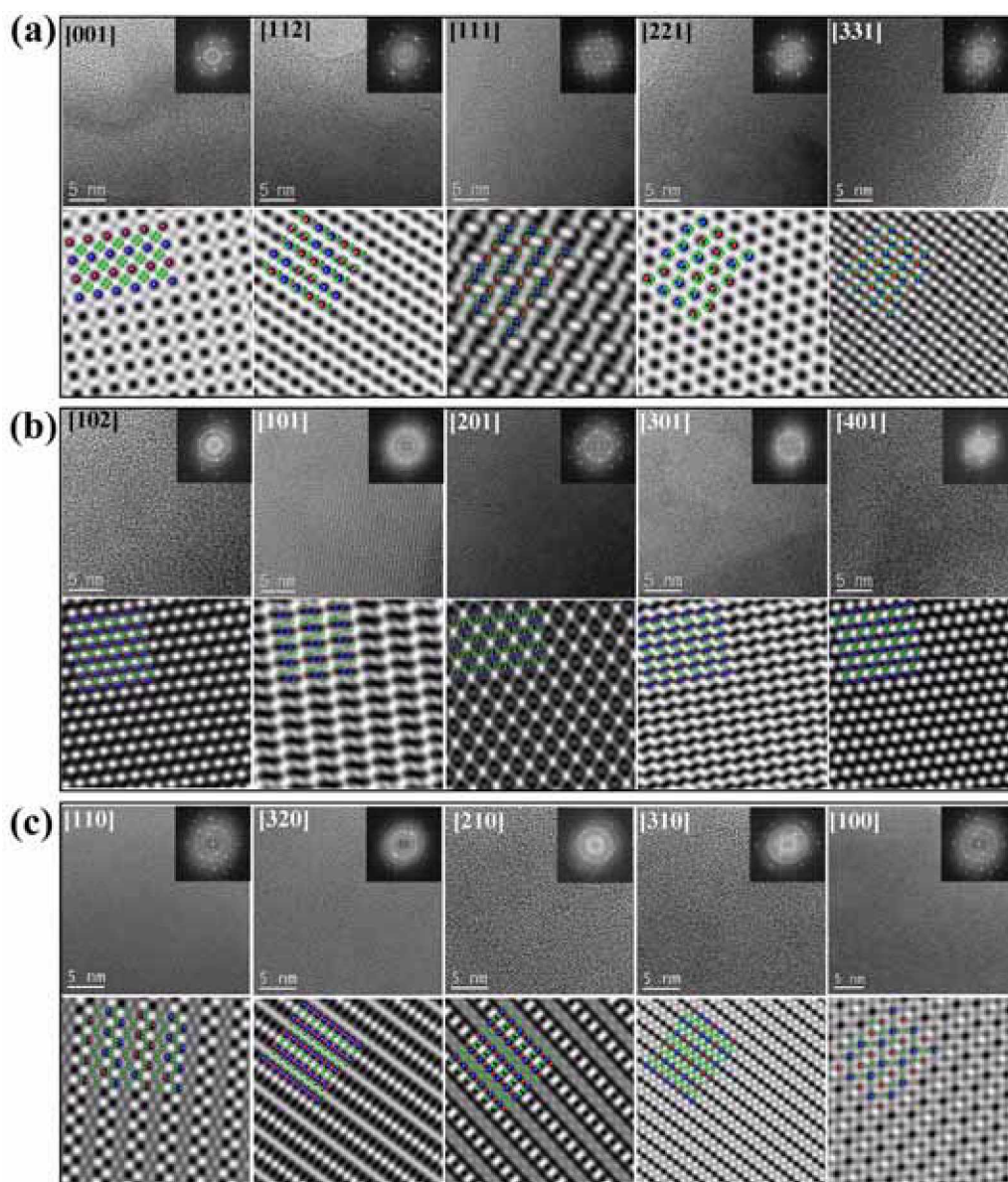
Figure 2. Three tilt series of HRTEM images along three zone axes: (a) [001] → [110] tilt series, (b) [001] → [100] tilt series, (c) [110] → [100] tilt series. The upper and lower HRTEM images are the original images and the CIP images of each zone axes, respectively. The red, blue and green shapes on the CIP images indicate the Ca, Mo and O atoms, respectively.

Table 3. Summary of CIP results of 15 HRTEM images

Zone axes	Cell parameters	2-D symmetry	$\varphi_{res}(°)^*$
[001]	a = 5.26 Å, b = 5.26 Å, γ = 90.0°	*p4m*	16.7
[112]	a = 3.71 Å, b = 3.51 Å, γ = 90.0°	pmg	5.5
[111]	a = 4.77 Å, b = 4.74 Å, γ = 79.3°	*p2*	11.9
[221]	a = 3.71 Å, b = 2.24 Å, γ = 90.0°	pm	0.5
[331]	a = 3.68 Å, b = 5.05 Å, γ = 91.4°	*p2*	18.0
[102]	a = 5.12 Å, b = 5.76 Å, γ = 117.1°	*p2*	6.5
[101]	a = 5.23 Å, b = 4.77 Å, γ = 89.4°	*p2*	7.5
[201]	a = 6.45 Å, b = 6.55 Å, γ = 106.6°	*p2*	5.9
[301]	a = 5.24 Å, b = 4.68 Å, γ = 90.6°	*p2*	5.6
[401]	a = 5.73 Å, b = 5.04 Å, γ = 115.5°	*p2*	8.1
[110]	a = 11.44 Å, b = 3.65 Å, γ = 90.0°	pg	3.5
[320]	a = 11.50 Å, b = 4.33 Å, γ = 90.0°	pg	2.5
[210]	a = 11.51 Å, b = 4.64 Å, γ = 90.0°	pmg	8.5
[310]	a = 11.44 Å, b = 4.91 Å, γ = 90.0°	pgg	12.0
[100]	A = 11.40 Å, b = 5.11 Å, γ = 90.0°	pmg	18.6

$^*\varphi_{res}(°) = \Sigma[w(h\ k)\ \varphi_{obs}(h\ k) - \varphi_{sym}(h\ k)]/\Sigma w(h\ k)$

analysis, was 37.88%. Table 2 displays atomic coordinates, selected bond lengths, and bond angles. It shows that the Ca and Mo atoms are located at special positions and the O atoms are located at general positions. In the MoO_4 anion group, angles of the O-Mo-O are 117.7(4)° and 105.5(4)°. The O sites are arranged in approximately tetrahedral coordination around each Mo sites.

HRTEM image analysis. HRTEM images of $CaMoO_4$ were obtained from the 15 different zone axes corresponding to the ED patterns. To minimize the multiple scattering and non-linear effects, HRTEM images were taken at the thinnest area. The amorphous part was included to determine the contrast transfer function (CTF).[1,2] Figure 2 shows three tilt series of HRTEM images: [001] → [110], [001] → [100], and [110] → [100]. The upper and lower HRTEM images are the original images and the CIP images of each zone axes, respectively. The structure modeling was performed using prior knowledge of the scheelite structure, ABO_4

type.[23] The red, blue, and green shapes on the CIP images indicate the Ca, Mo, and O atoms, respectively. As shown in Figure 2, it is clear that the CIP images coincide well with the structure model. The 2-D crystallographic information from each HRTEM images was extracted by the CIP method and is listed in Table 3. The 2-D symmetry for each HRTEM images can be determined by analyzing the phase value because each 2-D symmetry has different phase relations and restrictions.[2,24] Once the phase errors for individual symmetries are calculated by CRISP, the correct symmetry of the HRTEM image can be deduced by comparing these phase errors. Usually, the symmetry with the lowest number of phase errors is considered as the correct symmetry. If two or more symmetries have similar phase errors, the highest symmetry should be chosen. The 2-D symmetries of three principle axes, [001], [100], and [110] were *p4m*, *pmg*, and *pg* and the average phase errors were 16.7°, 18.6°, 3.5°, respectively. The cell parameters of $CaMoO_4$ determined by HRTEM analysis were a = 5.198(69) Å and c = 11.458(41) Å, which are consistent with the ED analysis to within 0.016 Å-0.066 Å. Atomic positions of the heavy elements, Ca and Mo, could be determined directly from HRTEM images due to their high contrast and interatomic distances longer than the instrumental resolution. However, the atomic positions of the light element, O, could not be determined directly from HRTEM images due to its low contrast and interatomic distances shorter than the instrumental resolution.

The 3-D reconstruction method using amplitudes and phases extracted from HRTEM images were used to determine the full atomic positions.[25] The potential difference between the heavy and light atoms is very large as shown in Figure 3. Considering this factor, 24 atomic positions in the unit cell were determined by applying the suitable threshold value as indicated in Table 4. All atomic coordinates were reassigned into equivalent positions by symmetry relationship, which resulted in the average atomic positions of the Mo, Ca and O atoms to be, respectively, 0.0016(12), 0.2500(29), 0.1248(8); 0.0024(25), 0.2500(20), 0.6247(5); and
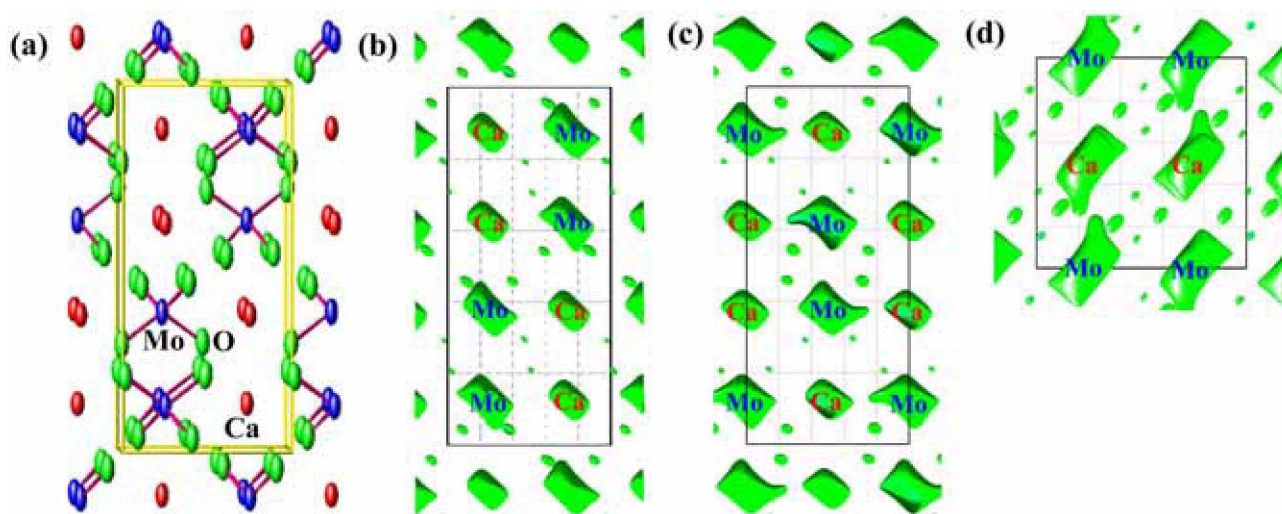
Figure 3. (a) An ATOMS drawing of $CaMoO_4$ with the atomic labeling scheme based on X-ray analysis. 2-D potential maps of the [100] direction (b), [010] direction (c) and [001] direction (d).

Table 4. Atomic coordinates determined by 3-D reconstruction

Atoms	x	y	z	Atoms	x	y	z
Mo1	0.5013	0.7467	0.6240	O5	0.7520	0.9008	0.9582
Mo2	0.4987	0.2480	0.3760	O6	0.2480	0.0940	0.0418
Mo3	0.0000	0.2454	0.1253	O7	0.2507	0.4021	0.4569
Mo4	0.0000	0.7467	0.3760	O8	0.7493	0.5927	0.5431
Ca1	0.0000	0.7493	0.8747	O9	0.6527	0.4726	0.2950
Ca2	0.5013	0.2480	0.8747	O10	0.3473	0.5222	0.7050
Ca3	0.4987	0.7467	0.1253	O11	0.8460	0.0209	0.2063
Ca4	0.0000	0.2480	0.6240	O12	0.1540	0.9739	0.7937
O1	0.7102	0.1201	0.4569	O13	0.8642	0.4804	0.7911
O2	0.2898	0.8747	0.5431	O14	0.1358	0.5144	0.2089
O3	0.2115	0.6214	0.9556	O15	0.6371	0.0131	0.7102
O4	0.7885	0.3734	0.0444	O16	0.3629	0.9817	0.2898
Average atomic coordinates*	Mo : 0.0016(12), 0.2500(29), 0.1248(8)						
	Ca : 0.0010(7), 0.2500(20), 0.6247(5)						
	O : 0.1426(119), 0.4814(170), 0.2072(16)						

*Average atomic coordinates were reassigned into equivalent positions by symmetry relationship.

0.1426(119), 0.4814(170), 0.2072(16). As expected, the standard deviation of the O sites was relatively large. Additionally, the fast Fourier Transform (FFT) data contained in the 8-bit information did not have enough pixels to quantify intensities of reflections. To solve this problem, it is recommended that HRTEM images should be recorded by a 4 K CCD camera or an imaging plate (IP). Alternatively, the phase information obtained from the CIP images should be combined with intensity data obtained from the QED analysis.

X-ray crystallography. X-ray crystallography of CaMoO₄ was used in an attempt to evaluate the accuracy of the structural determination by electron crystallography. The cell parameters of CaMoO₄ by X-ray crystallography were a = 5.2384(17) Å and c = 11.425(7) Å and the R-factor was 1.3%. Table 5 shows atomic coordinates, selected bond lengths, and bond angles. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CSD-417513). That data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Compared to X-ray crystallography, cell parameters determined by electron crystallography were consistent to within 0.033 Å-0.040 Å, while the atomic coordinates were determined to within 0.072 Å.

Discussion

As a whole, the accuracy of structural determination by electron crystallography could not be better than that of X-ray crystallography. ED data are usually obtained from the thicker and broader area of the specimen due to instrumental limitations, and these data are easily affected by severe dynamical scattering, which gives rise to incorrect intensity data. In this study, the atomic coordinates of the Mo and Ca atoms determined by ED analysis were identical to the X-ray results; however, the errors for the O sites, 0.91 Å, were unacceptably large. A newly developed ED method, precession ED[26,27] method, is expected to reduce dynamical scattering considerably by employing conical beam illumination and rapid precession.

In the refinement results by HRTEM image analysis, the atomic coordinates of the Mo and Ca atoms were nearly identical to the X-ray results. On the other hand, the difference in the O sites was about 0.072 Å, a significant improvement compared to the results of ED analysis. One of the major reasons for this improvement is probably in the inherent nature of HRTEM images. In order to obtain an HRTEM image, the specimen should be thin, usually less than 10 nm, which reduces dynamical scattering. Another reason is probably related to the longer mean free path of high-energy electrons in HVEM, which also reduces dynamical scattering. However, the effect of the phase information, present in HRTEM images but absent in ED data, on the O site refinement is uncertain and should be evaluated in detail.

HVEM has the distinct advantages of both high tilting capability and atomic resolution, which play an important role in electron crystallography. On the other hand, electron crystallography by HVEM needs to be examined for several effects.[18] Since specimens are irradiated by intense electrons in the HVEM experiment, beam damage is often induced and the crystalline materials are transformed to amorphous structures. The CaMoO₄ structure also undergoes beam-induced transformation during through-focus imaging and specimen tilting. For the structural determination only, however, the beam damage effect on structure refinement could be avoided by obtaining the data from the undamaged area. It is even possible to use an amorphous structure in the damaged area to evaluate the optimum defocus value. For three-dimensional structural analysis, thickness increase due to specimen tilting degrades the image quality and increases the phase errors. To reduce the tilting effect, the tilting direction of the goniometer should be toward the zero-tilt

Table 5. Atomic coordinates, selected bond lengths, and bond angles of CaMoO₄ by X-ray crystallography

Atoms	Atomic coordinates			Selected bond lengths (Å) & bond angles (°)
	x	y	z	
Mo	0.0000	0.2500	0.1250	Mo-O 1.7770(13)
Ca	0.0000	0.2500	0.6250	Ca-O 2.4464(16), 2.4774(13)
O	0.1480(2)	0.4934(2)	0.2094(1)	O-Mo-O 114.24(9), 107.14(4)

position. This tilting effect could be reduced by energy-filtering, especially by plasmon-loss HRTEM imaging.

Overall electron crystallography by HVEM has great potential to overcome the present limitations of X-ray crystallography for studying the atomic structures of nano-sized crystalline materials that often exist in extremely small quantities. HRTEM images, which can be easily obtained from the nm^2 area of the specimen, turn out to be especially useful to determine the atomic positions of light elements.

Conclusion

The crystal structure of an inorganic crystal, $CaMoO_4$, was detrmined by electron crystallography utilizing HVEM. The results of this analysis have established the following conclusions:

1) The 2-D symmetry of the three principle axes, [001], [100] and [110], are *p4m, pmg,* and *pg* and the average phase errors (φ_{res}) are 16.7°, 18.6°, and 3.5°, respectively.

2) The cell parameters determined by HRTEM image analysis were a = 5.198(69) Å and c = 11.458(41) Å. These values coincide with the X-ray crystallography results to within 0.033-0.040 Å.

3) The atomic coordinates determined by HRTEM image analysis were consistent to within 0.072 Å, compared to the X-ray crystallography data for the same sample.

References

1. Spence, J. C. H. *High-Resolution Electron Microscopy.* 3rd ed.; Oxford: New York. U. S. A., 2003; p 401.
2. Zou, X. D. *Electron Crystallography of Inorganic Structures;* Stockholm Univ.: Stockholm. Sweden. 1995; p 107.
3. Jun, Y. W.; Jang, J. T.; Cheon, J. W. *Bull. Korean Chem. Soc.* **2006**, *27*, 961.
4. Hovmöller, S.; Sjögren, A.; Farrants, G.; Sundberg, M.; Marinder,

B. *Nature* **1984**, *311*, 238.
5. Weirich, T. E.; Ramlau, R.; Simon, A.; Hovmöller, S.; Zou, X. D. *Nature* **1996**, *382*, 144.
6. Dorset, D. L. *Structural Electron Crystallography.* Plenum Press: New York and London. 1995; pp 135-166.
7. Weirich T. E.; Labor, J. L.; Zou, X. D. *Electron Crystallography.* NATO Science Series: Springer: 2006; p 536.
8. Gilmore, C. J. *Crystallography Reviews* **2003**, *9*, 17.
9. Hovmöller, S. *Ultramicroscopy* **1992**, *41*, 121.
10. Zandbergen, H. W.; Bokel, R.; Connolly, E.; Jansen, J. *Micron* **1999**, *30*, 395.
11. Fan, H. F. *Microscopy Research and Technique* **1999**, *46*, 104.
12. Bougerol-Chaillout, C. *Micron* **2001**, *32*, 473.
13. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115.
14. Gilmore, C. J. *Microscopy Research and Technique* **1999**, *46*, 117.
15. Jansen, J.; Tang, D.; Zandbergen, H. W.; Schenk, H. *Acta Cryst.* **1998**, *A54*, 91.
16. Znadbergen, H. W.; Andersen, S. J.; Jansen, J. *Science* **1997**, *277*, 29.
17. Kim, J. G.; Kang, S. K.; Kim, W. C.; Kim, Y. J. *Korean J. Electron Microscopy* **2004**, *34*, 255. (in Korean)
18. Kim, J. G.; Kim, Y. M.; Kim, J. S.; Kim, Y. J. *Korean J. Electron Microscopy* **2006**, *36. Special Issue 1*, 1.
19. Zou, X. D.; Sukharev, Y.; Hovmöller, S. *Ultramicroscopy* **1993**, *49*, 147.
20. Zou, X. D.; Hovmöller, A.; Hovmöller, S. *Ultramicroscopy* **2004**, *98*, 187.
21. *Calidirs,* Manhemsvägen 4. SE-106 91. Sollentuna, Sweden.
22. Sheldrick, G. M. *SHELXL97-Program for Refinement of the Crystal Structures.* University of Goettingen: Germany. 1997.
23. Zhang, Y.; Holzwarth, N. A.; Williams, R. T. *Phys. Rev. B* **1998**, *57*, 12738.
24. *International Tables for Crystallography.* Vol. A: Hahn, T., Ed.; Kluwer Academic Publishers: Dordrecht/Boston, 1983; p 854.
25. Zou, X. D.; Mo, Z. M.; Hovmöller, S.; Li, X. Z.; Kuo, K. H. *Acta Cryst.* **2003**, *A59*, 526.
26. Vincent, R.; Midgley, P. A. *Ultramicroscopy* **1994**, *53*, 271.
27. Weirich, T. E.; Portillo, J.; Cox, G.; Hibst, H.; Nicolopoulos, S. *Ultramicroscopy* **2006**, *106*, 164.