Short Communication

Neutron Powder Diffraction Profile Refinement Studies on $CaMoO_4$. A Comparison with Single-Crystal Data

G. Wandahl and A. Nørlund Christensen*

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

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The last decade has shown a strong development in structure analysis based on neutron powder diffraction data, and reviews on this subject by Cheetham and Taylor,[1] and by Taylor[2] have appeared in recent years. The combination of a high neutron flux at a fixed wavelength, and a diffractometer with an array of detectors like the instrument D1A at ILL[3,§] or the diffractometer at LLB* used in this investigation makes it possible to record a complete powder diffraction pattern in less than a day. An essential breakthrough in the application of neutron powder diffraction data in investigations of the structure of solids came with the profile refinement method developed by Rietveld.[4]

Taylor[2] has recently reviewed how well powder diffraction analysis using the Rietveld profile refinement method[4] has performed in comparison with single crystal investigations. The aim was to examine how well the positions of oxygen atoms in metal-oxygen containing inorganic compounds can be determined.

A neutron diffraction profile refinement can also supplement a neutron single-crystal investigation if the powder pattern can be measured to considerably greater values of $\sin\theta/\lambda$ than those used in the single-crystal measurement. The profile refinement of the structure of $CaMoO_4$ described below illustrates this.

$CaMoO_4$ has the scheelite ($CaWO_4$) structure, and one of the recent investigations of the structure was a neutron single-crystal measurement employing a total of 35 independent reflections by Gürmen *et al.*[5] (see Table 1).

The sample of $CaMoO_4$ used in this investigation was prepared from a stoichiometric mixture of CaO, made from $CaCO_3$ by ignition in a crucible furnace at 900° for 24 h, and MoO_3 (Merck *p.a.*). The mixture was pressed isostatically to a cylindrical rod that was kept in a MgO crucible in a crucible furnace at 1000 °C for 24 h. The rod of $CaMoO_4$ was crushed in a boron carbide mortar, and a Guinier photograph showed that the sample was pure $CaMoO_4$.

The neutron powder diffraction pattern was recorded on the diffractometer at channel 3T2 at the ORPHEE reaction at the *Laboratoire Léon Brillouin,* Saclay. The neutron wavelength was 1.226 Å, and the 2θ range was 8–110°. The scattering lengths used in the profile refinements were: Ca 0.3449, Mo 0.661 and O 0.577, all in 10^{-12} cm units.[6] The profile refinement program[7] yielded the coordinates listed in Table 1, with the parameters from Ref. 5 as starting values. From Table 1 it is observed that the precision obtained in this investigation is higher than that arrived at in Ref. 5. In the single-crystal investigation reflections were measured only to what in the present work corresponds to $\sin\theta/\lambda = 0.58$, and some reflections were systematically omitted. When reflections with $\sin\theta/\lambda > 0.58$ were omitted in the profile refinement, the precision was still better

*To whom correspondence should be addressed.
§*Institut Laue-Langevin* (Grenoble).
**Laboratoire Léon Brillouin* (Saclay).

Table 1. Crystallographic data for $CaMoO_4$. Space group $I4_1/a$ (No. 88), $Z = 4$.

This work						Ref. 5			
a = 5.2235(1) Å c = 11.4298(4) Å 194 reflections, R = 7.14 %						a = 5.226 Å c = 11.43 Å 35 reflections, R = 7.3 %			
Atom	Site	x	y	z	B(Å^2)	x	y	z	B(Å^2)
Ca	4(b)	0	0	1/2	0.819(67)	0	0	1/2	0.606(280)
Mo	4(a)	0	0	0	0.496(47)	0	0	0	0.364(205)
O	16(f)	0.2436(4)	0.1490(3)	0.0842(2)	0.778(27)	0.2428(10)	0.1465(10)	0.0826(3)	0.747(178)
Mo–O distance			1.775(2) Å			1.757(5) Å			
Mo–O distance			1.776(3) Å[a]						

[a]Reflections with $\sin\theta/\lambda > 0.58$ omitted.

than that obtained in Ref. 5. It has been reported[8] that the standard deviations estimated for Rietveld refinements are too low. However, even if the value for the standard deviation arrived at for the Mo–O distance [1.775(2) Å] is doubled, the estimated standard deviation is still not greater than that reported in Ref. 5.

Fig. 1 shows the observed and calculated profiles for the diffraction pattern of $CaMoO_4$. The pattern has weak contributions from aluminium from the sample container, and the 2θ regions with stronger aluminium reflections, viz. 30.15–30.65, 34.80–35.50, 60.25–61.00, 74.35–74.65 and 82.40–83.00, have been omitted. It is possible that the profile shape function is not a pure Gaussian function, as assumed in the program used. The reflection at the 2θ position 22.80° shows misfit on the two sides of the peak close to the background level. For this reason the profile refinement was repeated using the program EDINP,[9] in which a Voigt profile function is applied. This is a convolution of a Gaussian and a

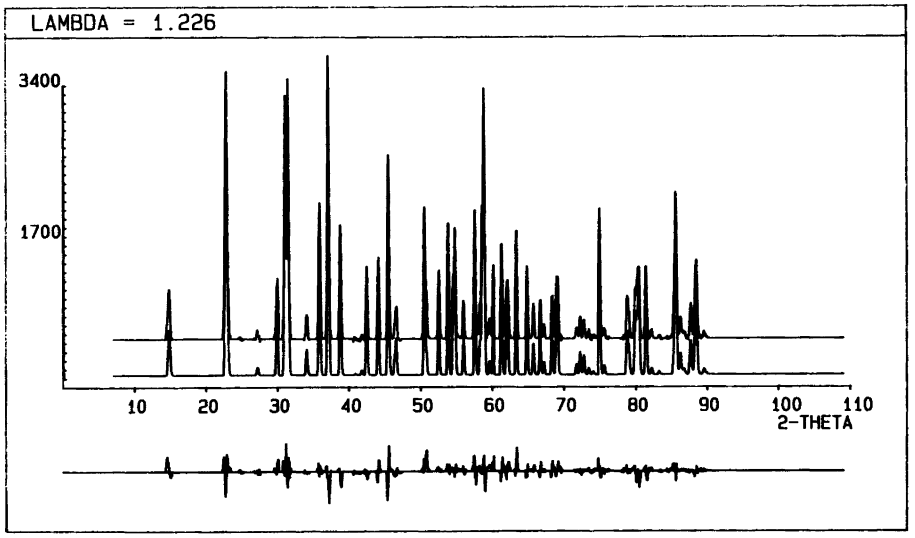

Fig. 1. Neutron powder diffraction diagram for $CaMoO_4$ obtained with 1.226 Å neutrons. Upper curve: observed intensity; lower: calculated intensity; below the abscissa: difference between observed and calculated intensities.

Lorenzian function. This refinement gave no improvement in the precision of the structure.

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