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Ab initio determination of the framework structure of the heavy-metal oxide $Cs_xNb_{2.54}W_{2.46}O_{14}$ from 100 kV precession electron diffraction data

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Abstract

The present work deals with the ab initio determination of the heavy metal framework in $Cs_x(Nb, W)_5O_{14}$ from precession electron diffraction intensities. The target structure was first discovered by Lundberg and Sundberg [Ultramicroscopy 52 (1993) 429–435], who succeeded in deriving a tentative structural model from high-resolution electron microsopy (HREM) images. The metal framework of the compound was solved in this investigation via direct methods from *h k 0* precession electron diffraction intensities recorded with a Philips EM400 at 100 kV. A subsequent (kinematical) least-squares refinement with electron intensities yielded slightly improved co-ordinates for the 11 heavy atoms in the structure. Chemical analysis of several crystallites by EDX is in agreement with the formula $Cs_{0.44}Nb_{2.54}W_{2.46}O_{14}$. Moreover, the structure was independently determined by Rietveld refinement from X-ray powder data obtained from a multi-phasic sample. The compound crystallises in the orthorhombic space group Pbam with refined lattice parameters $a = 27.145(2)$, $b = 21.603(2)$, and $c = 3.9463(3)$ Å. Comparison of the framework structure from electron diffraction with the result from Rietveld refinement shows an average agreement for the heavy atoms within 0.09 Å.

Keywords: Precession electron diffraction; Electron diffraction structure analysis; Heavy-metal oxide; Electron crystallography

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1. Introduction

Our understanding of the properties of materials is almost always based on structural information on the atomic scale. Such information is commonly obtained by the wide spread method of X-ray crystallography. However, due to the relatively weak interaction of matter with X-rays, this method is insufficient to investigate extremely small volumes or individual crystals at the sub-μm scale. Materials with pronounced twinning or new compounds that only exist as part of a complex multi-phase powder sample are thus extremely difficult to treat with this standard method for structure determination. It should be noted that these problem cases also include many technologically relevant products such as small precipitates in a metallic matrix, catalysts, pharmaceuticals, pigments and thin films, which a priori exist only in small quantities or rarely grow as large crystals. Hence, ample motivation exists to develop alternative approaches capable for structural analysis of extremely small volumes and crystallites. However, the only real alternative to X-rays are fast electrons, since their interaction with matter is several orders of magnitude stronger than that of X-rays. Electron diffraction structure analysis (EDSA) makes it, thus, possible to obtain structural information at the atomic level even for the steadily growing number of nanocrystalline materials. On the other hand, structure analysis with electron data is rarely straightforward and fully automated, as it is the case with X-ray data. In particular, the non-kinematical nature of the diffracted intensities is a great concern for structure analysis with electron diffraction data and has hindered EDSA from becoming very popular since its foundation in Russia more than 65 years ago. While a large number of light-atom structures have been investigated by electron diffraction in the past [1–4], it has only succeeded in a few cases to solve structures with heavier atoms directly from electron diffraction spot patterns (see Table 1). In order to avoid these problems, an alternative approach was developed for such non-light-atom structures. This approach exploits the low-order structure factor phases extracted from high-resolution electron microscopy (HREM) images, to assign phases to the higher-order electron diffraction amplitudes [5–9]. In the most favourite case when the scattering power of the elements in the structure is not too different, the complete structure can be solved from HREM images and subsequently refined with electron diffraction data [10,11]. Despite such hybrid methods proved very efficient, it is still highly desirable to also develop methods which allow solving heavy-atom structures directly from the measured electron diffraction amplitudes. As mentioned earlier, the non-kinematical (dynamical) nature of the electron intensities is the main concern in this endeavour because its influence on the diffracted intensities is very difficult to control in the diffraction experiment. However, today it is generally believed that the precession electron diffraction method, developed in the early 1990s by Vincent and Midgley [12], is the most promising way out from this quandary. In the precession method, a small focussed or parallel electron beam is scanned at a constant angle around the optic axis to produce a hollow-cone illumination of the sample. Those electron beams leaving the specimen exit-plane are then descanned in such a way that a stationary spot diffraction pattern is

Table 1
Selected heavy-atom structures that have been solved by electron diffraction spot patterns only

	Z_{heavy}/Z_{light}	Lighter atoms are visible in the potential map	
Zr_2Se	1.2	Yes	[29]
Ti_2S	1.4	Yes	[26]
Ti_2P	1.5	Yes	[18]
β-Ti_2Se	1.6	Yes	[26]
MCM-22	1.8	No	[39]
Al_mFe	2.0	Yes	[17]
Ta_2P	4.9	No	[41]
$(Ga, In)_2SnO_4$	6.3	No	[19]
$Cs_{0.44}Nb_{2.54}W_{2.46}O_{14}$	≈7.2	No	Present study
Nd_2CuO_4	7.5	No	[37]
$\phi-Bi_8Pb_5O_{17}$	10.4	No	[38]

From the table it is seen that detecting the lighter atoms in the presence of heavier ones becomes more difficult with increasing ratio Z_{heavy}/Z_{light} of the atomic numbers.