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On the Lattice of Ba_3UO_6

R. DE BLIECK,* E. VAN CAPPELLEN,* G. VAN TENDELOO,* S. AMELINCKX,*,† R. GENS,‡,[1] AND J. FUGER‡

University of Antwerp (RUCA), Groenenborgerlaan 171, 2020 Antwerpen, †SCK/CEN, 2400-MOL, and ‡Laboratory of Analytical Chemistry and Radiochemistry, University of Liège, B-4000 Liège, Belgium

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Electron diffraction has allowed the determination of the superlattice of Ba_3UO_6. The structure is a commensurate one-dimensional long-period superstructure of the perovskite structure, the long period being oriented along the $[351]_c$ direction.

Introduction

In chronological order the structure of Ba_3UO_6 has been described in the literature successively as cubic (*1*), tetragonal (*2*), orthorhombic (*3*), and triclinic (*4, 5*). The lattice parameters of the different proposed crystallographic descriptions are summarized in Table I.

It is the purpose of this short note to show that the electron diffraction patterns of this compound clearly demonstrate that the room-temperature structure must be a one-dimensional commensurate long-period superstructure of a cubic or pseudocubic perovskite structure. The most striking feature is the direction of the long-period modulation, which is $[531]_c$, when referred to the basic cubic unit cell (as indicated by the subscript c).

[1] Recipient of a fellowship of IRSIA (Brussels). Presently at Institut des Radioéléments, B 6220 Fleurus, Belgium.

Experimental

As described in detail for several complex oxides (*6, 7*), Ba_3UO_6 was prepared by repeated grinding (in a dry box) and heating (in flowing O_2) at increasing temperatures (up to 1420 K) of stoichiometric amounts of U_3O_8 (nuclear grade) and $BaCO_3$ (reagent grade). Results of the analysis and the analytical techniques used are given in Refs. (*6, 7*). Samples identified as A in (*7*) were used in the present study.

The electron microscopy specimens were prepared by grinding the material and dispersing fragments on a holey grid.

Results and Discussion

Figures 1 and 2 show the diffraction patterns along different zones. Figure 1a shows the $[001]_c^*$ zone and Fig. 1b the $[\bar{1}11]_c^*$ zone, but the most informative pattern is that produced along the $[\bar{1}12]_c^*$ zone (Fig. 1c).

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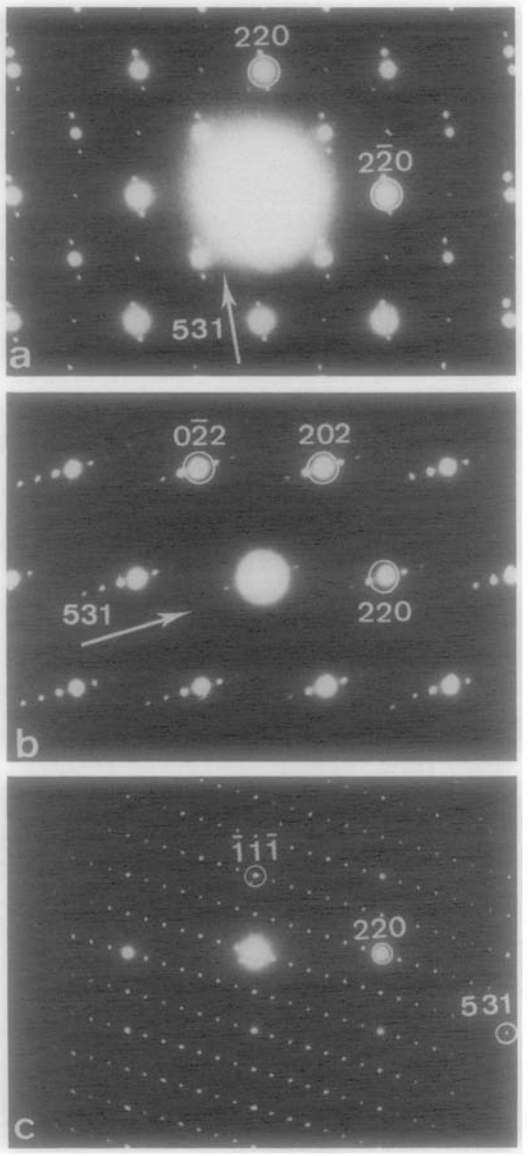

FIG. 1. Electron diffraction patterns of Ba_3UO_6. (a) $[001]^*_c$ zone; (b) $[\bar{1}11]^*_c$ zone; (c) $[\bar{1}12]^*_c$ zone.

In the $[001]^*_c$ zone only two superstructure satellites are visible whereas in the $[\bar{1}11]^*_c$ zone four or five satellites can be observed. In both cases these diffraction spots are due to spikes from higher-level reciprocal lattice nodes along inclined rows of nodes, which are sufficiently close to Ewald's sphere. In the $[\bar{1}12]$ zone a satellite row is tangent to Ewald's sphere and is therefore fully excited; the 531 spot is separated from the origin by 13 equally spaced superstructure spots, proving that the superstructure interplanar spacing is $14 \times d_{531c}$, i.e., about 2.1 nm.

TABLE I

CRYSTALLOGRAPHIC CHARACTERISTICS OF Ba_3UO_6

Symmetry	Lattice parameters	Reference
Cubic	a = 0.89 *nm*	(*1*)
Tetragonal	$a = b$ = 0.6285 nm	(*2*)
	c = 0.8943 nm	ASTM
Orthorhombic	a = 4.46 nm	
	b = 4.43 nm	(*3*)
	c = 0.897 nm	
Triclinic	a = 2 × 0.626 nm	
	b = 2 × 0.630 nm	
	c = 2 × 0.898 nm	(*4*)
	α = 90°1′	(*5*)
	β = 90°2′	
	γ = 90°	

The long period can be visualized directly by means of high-resolution electron microscopy. The diffraction pattern along the $[1\bar{3}4]^*_c$ zone and the corresponding high-resolution image are shown in Fig. 2, where the 2.1-nm period has been indicated.

The strongly contrasted fringes with a spacing of ~0.4 nm inclined with respect to the long-period fringes are mainly due to the most intense superlattice reflections along the second noncentral rows of spots (Figs. 1 and 2, circled).

In Fig. 3 we have summarized our observations by means of a schematic representation of the reciprocal lattice. The basic reflections of the cubic sublattice are represented by large dots and the superstructure reflections by small dots. The structure is based on the space group $P\bar{1}$.

Many more sections of reciprocal space were observed; they could all be indexed consistently on the basis of this reciprocal lattice.

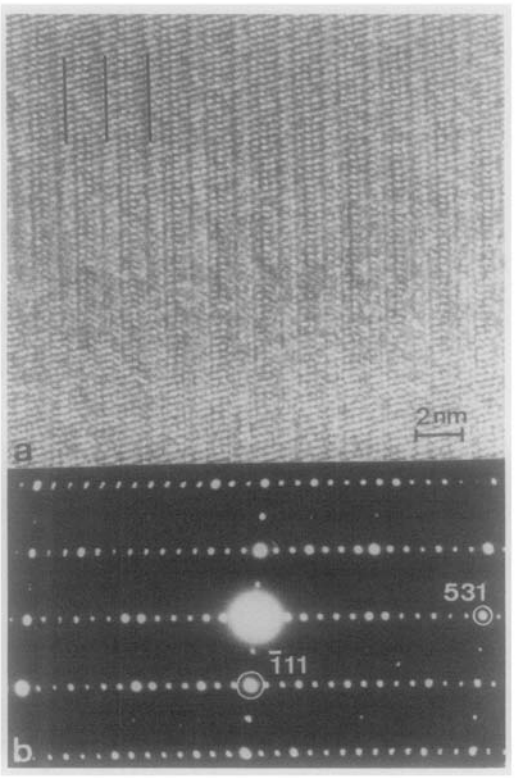

FIG. 2. Electron diffraction pattern and corresponding high-resolution image along the $[1\bar{3}4]^*_c$ zone. The superperiod of 2.1 nm is indicated in (a).

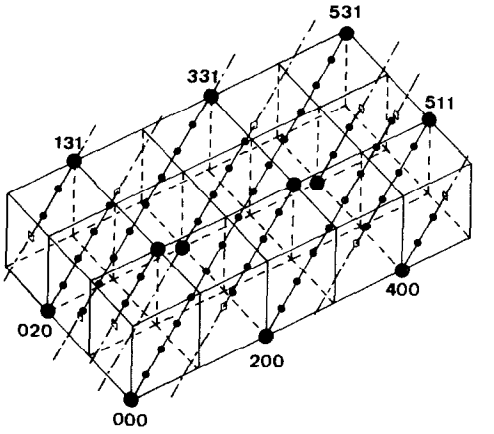

FIG. 3. Reciprocal lattice of Ba_3UO_6. The basic reflections are indicated as large dots whereas the small dots indicate superlattice reflections.

A priori the direction of the long period can of course occur along any one of the {531} zones of the basic cubic structure. This means that within the same single crystal of the perovskite basic structure no less than 24 orientation variants can be formed. Figure 4 shows, for instance, the diffraction pattern taken across the contact plane between two orientation variants with their long-period directions along $[531]_c$ and $(53\bar{1}]_c$. It is the presence of such a large number of orientation variants which has restricted the use of X-ray diffraction to powder methods, thus leaving room for ambiguities in the indexing and hence in the determination of the symmetry and the lattice parameters.

Within the limits of the analytical methods used (1–2%) the compound was found to be stoichiometric. However, it cannot be excluded that the presence of the long period is related to small deviations from the ideal stoichiometry.

The present observations clearly demonstrate the power of electron diffraction and electron microscopy in elucidating the geo-

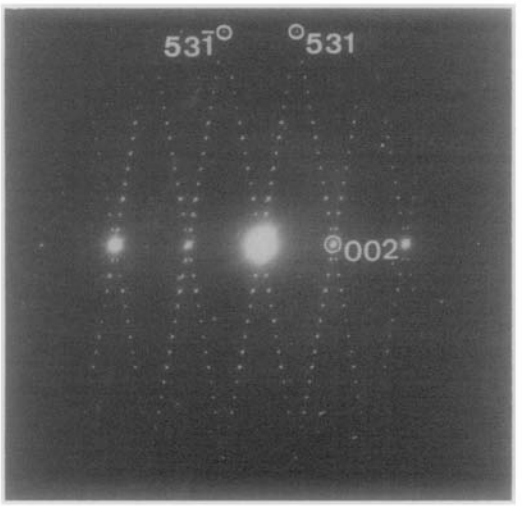

FIG. 4. Diffraction patterns along the $[3\bar{5}0]^*_c$ zone axis taken across the boundary between two orientation variants.

metrical features of complicated structures, especially of domain fragmented crystals.

Using these techniques single domain diffraction patterns can be obtained even though the crystals are only a fraction of a micron in size.

On the other hand, an accurate structure determination cannot be based on intensities derived from electron diffraction patterns since the scattering is not kinematical. Nevertheless, the knowledge of the lattice may be a first step in allowing a structure determination by means of X-ray diffraction.

Conclusions

The crystal lattice of the compound Ba_3UO_6 has been determined unambiguously; it is a long-period superlattice of the perovskite structure with its long-period direction along the [351] cubic direction.

Acknowledgments

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