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Modulated phase of $K_2Mo_xW_{1-x}O_4$ mixed compounds using orthorhombic symmetry: A powder diffraction study

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High-resolution x-ray powder diffraction data have been used to study the modulated phase of the K_2WO_4, $K_2Mo_{0.5}W_{0.5}O_4$, and K_2MoO_4 compounds. Literature considers K_2WO_4 and K_2MoO_4 as exceptions among the members of $A'A''BX_4$ family because their thermotropic phase transitions do not follow the commonly observed sequence and because their modulation wave vector, unusually, lies on the pseudohexagonal plane. Until now, the modulated phases of these compounds have been interpreted using hexagonal symmetry. The present work indicates, however, that a model consisting of threefold twinned orthorhombic modulated domains better describes the satellites observed in the temperature range of 620–740 K. The *Ccmm* space group is proposed for the average structure of the whole family $K_2Mo_xW_{1-x}O_4$, whereas the $Ccmm(\alpha 00)000$ with the wave vector $\boldsymbol{q}=(0.5+\delta)\boldsymbol{a}^*$ is the appropriate superspace group for the description of the modulated structures. The coexistence of three orthorhombic domains, each of which is rotated by 120° from each other, indeed reproduces a pseudohexagonal basis, which is a common feature in the $A'A''BX_4$ family. The usage of the twinning model allows a much simpler interpretation of the diffraction pattern and provides a more consistent way to describe the phase-transition sequence shown by the mixed $K_2Mo_xW_{1-x}O_4$ crystals.

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I. INTRODUCTION

The lack of translational symmetry on the three-dimensional space and the implications this fact has on the structural properties of modulated phases, as well as the physical mechanisms driving phase transitions (from regular to the modulated ones) catches the attention of many solid-state physicists.

Many different theories have been proposed to explain the origins of incommensurability, as well as to describe their crystallographic structures.[1–3] An accepted explanation for the existence of incommensurate modulation on the majority of the systems is the frustrating competition between interatomic or interspin forces that are responsible for either structural or magnetic ordering. Among the accepted models describing incommensurate phases, one can highlight the axial next-nearest-neighbor Ising model (ANNNI), which is capable of describing a large variety of such systems.[4] The first *ab initio* investigation of a prototype of a large class of dielectric incommensurate materials, namely, K_2SeO_4, has been recently reported characterizing the electronic, structural, dielectric, and dynamical properties of the structure of the above mentioned complex in two different nonmodulated phases,[5] which is an improvement toward the better understanding of the complex behavior of such material and a necessary step before more fundamental studies on the modulated phases.

The compounds with a general formula $A'A''BX_4$ probably comprise the widest class of inorganic crystals showing modulated phases[1]—the A_2BX_4 subclass encloses the largest part—and many of them exhibit a vast number of structurally different phases. Phase transitions occur due to temperature and pressure modifications; the structural phase can also be dependent on the crystal composition. Some of the A_2BX_4 crystals present a high-temperature phase with hexagonal α-K_2SO_4 type structure—$P6_3/mmc$ space group—while others present a high-temperature phase with orthorhombic pseudohexagonal β-K_2SO_4 type structure—*Pnma* space group. Cooling the crystals down from the high-temperature phase, the occurrence of thermotropic phase transitions leading to a modulated phase with orthorhombic symmetry is observed in many compounds of the family.[1,6] Generally, the modulation wave vector $\boldsymbol{q}$ of this phase is perpendicular to the pseudohexagonal basal plane and frequently its modulus q varies continuously with temperature, indicating an incommensurate character. At even lower temperatures the crystals may experience another thermotropic phase transition leading to a lock-in phase: the modulation wave vector "locks" on a commensurate value giving rise to a superstructure commensurate phase; common values for q in these cases are 1/2, 1/3, and 1/4 (twofold, threefold, and fourfold superstructures, respectively). A few exceptions are found where the lock-in transition leads to a normal phase with $q=0$ (Refs. 7 and 8); these cases can be considered as a onefold superstructure in the context of group-subgroup relationship. A survey of the available structural information on the A_2BX_4 compounds that are isostructural to β-K_2SO_4 indicates special correlations among some structural parameters (degree of packing, ratio of the lattice parameters a/b, ratio of the atomic radii of the constituent elements, etc.) and the presence of low-temperature instabilities, which in many cases leads to phase transitions to modulated phases.[6] Additionally to incommensurate phases, ferroelectric and ferroelastic transitions are also observed in some members of the $A'A''BX_4$ family.[1]

A typical diagram representing the main aspects of the sequence of phase transitions of A_2BX_4 is shown below where the temperature increases from left to right, regarding that the hexagonal phase is not observed in some cases:

$$\underset{\text{lock-in}}{\text{Commensurate}} \leftrightarrow \underset{q\geq 0.29}{\text{Incommensurate}} \leftrightarrow \underset{\beta\text{-}K_2SO_4}{\text{Orthorhombic}} \leftrightarrow \underset{\alpha\text{-}K_2SO_4}{\text{Hexagonal}}.$$

According to the literature[1] it is possible to distinguish the potassium and rubidium tungstates (K_2WO_4,Rb_2WO_4) and potassium molybdate (K_2MoO_4) from the $A'A''BX_4$ family due to the fact that their modulated phase occurs immediately below the α-K_2SO_4 phase. A schematic diagram of the phase transitions sequence found for the potassium molybdate and tungstate in a heating process is shown below:

$$\text{Monoclinic} \rightarrow \underset{q\geq 0.29}{\text{Modulated}} \rightarrow \underset{\alpha\text{-}K_2SO_4}{\text{Hexagonal}}$$

In the cooling process both K_2MoO_4 and K_2WO_4 seems to present an additional metastable orthorhombic phase that is still under investigation.[9,10]

Despite the fact of having been studied for more than thirty years, no conclusive results about the intermediate modulated phase of these compounds are found in literature. In most of the works so far, hexagonal symmetry was used to describe the modulated phase of both potassium molybdate and potassium tungstate.[5,11–13] Based on precession photos, van den Berg *et al.*[11] interpreted the modulated phase using hexagonal symmetry and the satellite reflections were indexed by the wave vectors $\boldsymbol{q}=q(m\boldsymbol{a}^*+n\boldsymbol{b}^*)$, with $(m,n) = \pm(1,0)$, $\pm(0,1)$, or $\pm(1,\bar{1})$, where $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ are the unit vectors of the reciprocal hexagonal lattice. Based on x-ray powder diffraction results, Warczewski[13] proposed a commensurate modulated phase for K_2WO_4, and an incommensurate modulated and a lock-in phase for K_2MoO_4 using an equivalent indexation. He found $0.29<q<0.30$ for K_2MoO_4, between 593 and 733 K, and $q=0.25$ for the K_2WO_4, between 643 and 773 K. A few years later van den Berg *et al.*[14] proposed a model for the average structure of the K_2MoO_4 in the incommensurate phase using orthorhombic symmetry.

More recently, Bzowski *et al.*[7] reported some results obtained with x-ray powder diffraction for the modulated phase of $K_2Mo_xW_{1-x}O_4$ mixed compounds. Using a hexagonal unit cell they describe this phase as incommensurately modulated with the modulation wave vector q varying almost linearly with the composition from $q=0.306$ for the potassium molybdate ($x=1$) to $q=0.247$ for the potassium tungstate ($x=0$). These results correspond to data obtained at 693 K.

The present work proposes a different interpretation of the experimental results obtained for the modulated phase of the $K_2Mo_xW_{1-x}O_4$ mixed compounds. Detailed experiments using high-resolution x-ray powder diffraction have been performed in the temperature range from room temperature up to nearly 900 K, covering three different phases. Results obtained with K_2WO_4, $K_2Mo_{0.5}W_{0.5}O_4$, and K_2MoO_4 compounds are discussed.

II. EXPERIMENTAL

Polycrystalline $K_2Mo_xW_{1-x}O_4$ mixed compounds were synthesized in seven different compositions ($x=0$, 0.2, 0.4, 0.5, 0.6, 0.8, and 1) by means of solid-state reaction of stoichiometric masses of potassium carbonate, and of molybdenum and/or tungsten oxides, according to the equation

$$K_2CO_3 + xMoO_3 + (1-x)WO_3 \rightarrow K_2Mo_xW_{1-x}O_4 + CO_2. \tag{1}$$

Procedure details of the synthesis can be found in the work of Guarnieri and co-workers.[9,15]

Several attempts to grow untwinned crystals suitable for single-crystal experiments failed so powder samples have to be used for the x-ray diffraction analysis. Due to the high hygroscopic character of the compounds the samples were handled on a nitrogen-atmosphere glove box where they were crushed into fine powders, and then placed into glass capillaries of 0.4 and 0.5 mm in diameter.

X-ray powder diffraction experiments were performed using synchrotron radiation from the BM1B line of the *Swiss Norwegian Beam Line* (SNBL) at the *European Synchrotron Radiation Facility* (ESRF) in Grenoble, France. The BM1B line was equipped with a two-circle diffractometer and six counting chains with an offset in 2θ, each of which is associated to a Si-111 analyzer crystal and a Na-I scintillation counter. Monochromatic radiation ($\lambda=0.499\,049$ Å) in transmission geometry, with 2θ ranging from 3° up to 16°, was used during the whole data collection process. A noncalibrated home-built furnace was used to heat up the samples from room temperature up to nearly 900 K. Diffraction data have been collected in both heating and cooling processes. The absolute temperatures of the corresponding phase transitions were taken from differential scanning calorimetry experiments.[9,15,16] Accordingly, the temperature ranges for the modulated phase are 640(5)–734(5) K, 601(5)–727(5) K, and 593(5)–730(5) K for K_2WO_4, $K_2Mo_{0.5}W_{0.5}O_4$, and K_2MoO_4, respectively.

The diffraction patterns have been analyzed using the Jana2000 suite.[17] The Rietveld method[18,19] was employed to refine the data obtained in the temperature ranges corresponding to monoclinic phase and to the high-temperature hexagonal phase. The study and analyses of the data obtained in the temperature range corresponding to the intermediate phase were based on the Le Bail method.[20] Pseudo-Voigt functions were used to fit the powder diffraction peaks which full width at half maximum followed the Caglioti formula.[21] No asymmetry correction was employed and the background was adjusted using Legendre polynomials.

III. RESULTS AND DISCUSSION

Crystallographic results obtained for the nonmodulated hexagonal and monoclinic phases are equivalent to those found in literature,[9,22–25] and will not be further discussed in this paper. Concerning results found in literature, the modulated phase of K_2WO_4 and K_2MoO_4 has generally been interpreted using hexagonal symmetry;[10–13] however neither a superspace group nor a crystallographic model has ever been proposed to describe the referred structures. The indexation of the satellite reflections using this symmetry choice requires two modulation vectors with the same modulation

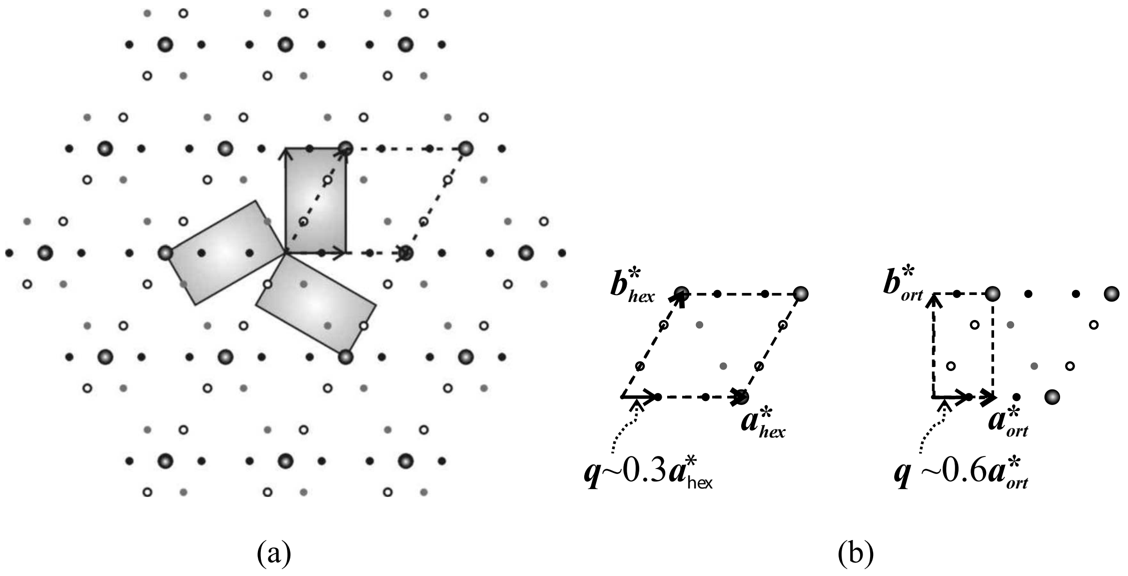

FIG. 1. Depiction of the ($hk0$) reciprocal plane of $K_2Mo_xW_{1-x}O_4$ mixed compounds in the modulated phase. Large circles represent main reflections, common to the three domains, and the small ones represent the satellite reflections: black, gray, and hollow circles stand for each of the three domains. Dashed lines represent the hexagonal reciprocal vectors; the shadow boxes represent the three orthorhombic reciprocal cells. (a) Superimposition of three orthorhombic reciprocal cells (shadow boxes), rotated by 120° one to the other, give rise to the illusory hexagonal reciprocal lattice (dashed lines); (b) the modulation wave vector has different values when expressed in hexagonal (left) or in orthorhombic (right) symmetry.

wavelength and, consequently, five Miller indices are needed to index each satellite. Hexagonal symmetry had also been used to interpret the modulated phase of other compounds in the $A'A''BX_4$ family, as in the interesting case of $LiKSO_4$.[26–30] As a matter of fact, studies on the modulated phase of $LiKSO_4$ gave rise to controversial results for years and only recently the ambiguity on the real symmetry of the modulate phase was solved by Ventura *et al.*[31] Their results evidenced that these crystals in the modulated phase are, in fact, composed of three superimposed orthorhombic domains rotated by 120° with respect to one another, with each domain having an incommensurate structure with average orthorhombic symmetry.

In order to find a more suitable description for the modulated phase of K_2WO_4, $K_2Mo_{0.5}W_{0.5}O_4$, and K_2MoO_4, different symmetry possibilities were tested employing Le Bail fittings of high-resolution x-ray powder diffraction data. Several attempts of fitting the obtained patterns provided unsatisfactory results when performed using hexagonal symmetry, as emphasized in the next paragraphs. Keeping in mind that attempts of growing crystals of potassium molybdate and potassium tungstate generally end up in twinned samples, the possibility of using orthorhombic symmetry was then considered.

The twinned orthorhombic domains description of the modulated phase of $K_2Mo_xW_{1-x}O_4$ crystals is depicted in Fig. 1, following the model of three superimposed orthorhombic domains proposed by Ventura *et al.*[26] This figure shows the basal reciprocal plane ($hk0$), i.e., the plane perpendicular to the pseudohexagonal axis $\boldsymbol{c}^*$. In real space the corresponding orthorhombic unit cell is C centered and is twice as big as the hexagonal one, and is usually referred to as orthohexagonal cell. The relationships between orthorhombic and hexagonal reciprocal vectors are

$$\boldsymbol{a}^*_{\rm ort} = \frac{1}{2}\boldsymbol{a}^*_{\rm hex} \quad \text{and} \quad \boldsymbol{b}^*_{\rm ort} = \boldsymbol{b}^*_{\rm hex} - \frac{1}{2}\boldsymbol{a}^*_{\rm ort}, \tag{2}$$

where the subscript "ort" and "hex" refer to the orthorhombic and hexagonal lattices, respectively.

Defining the modulation vector using the main reflections and the corresponding nearest satellite ones, and considering the lattice relationship given in Eq. (2), the relation $\boldsymbol{q} \cong 0.3\boldsymbol{a}^*_{\rm hex} \cong 0.6\boldsymbol{a}^*_{\rm ort}$ can be established as illustrated in Fig. 1(b). On the orthorhombic lattice setting all the satellite reflections can be indexed with a single modulation vector in each domain. By keeping the cell orientation during the phase-transition process, one finds the modulation wave vector q to be nearly $0.6\boldsymbol{a}^*_{\rm ort}$ for K_2MoO_4 and equal to $0.5\boldsymbol{a}^*_{\rm ort}$ for K_2WO_4 pure compounds.

Diffraction data obtained for K_2MoO_4 at 663 and at 683 K have been systematically analyzed using Le Bail fit in order to test the possible models. The strategy consisted on comparing fitting results obtained with different orthorhombic and hexagonal space groups. On the initial trials the lower symmetry orthorhombic *Pmmm* and hexagonal *P*6 space groups were used. Once they present no systematic absence rules, all the reflections consistent with each symmetry—and the corresponding cell parameters—should be indexed.

Comparative results obtained for data collected at 663 K using orthorhombic and hexagonal symmetries are shown in Fig. 2, for two intervals where the difference between orthorhombic and hexagonal fits is remarkable. Results obtained at this temperature are representative in the modulated phase of the studied mixed $K_2Mo_xW_{1-x}O_4$.

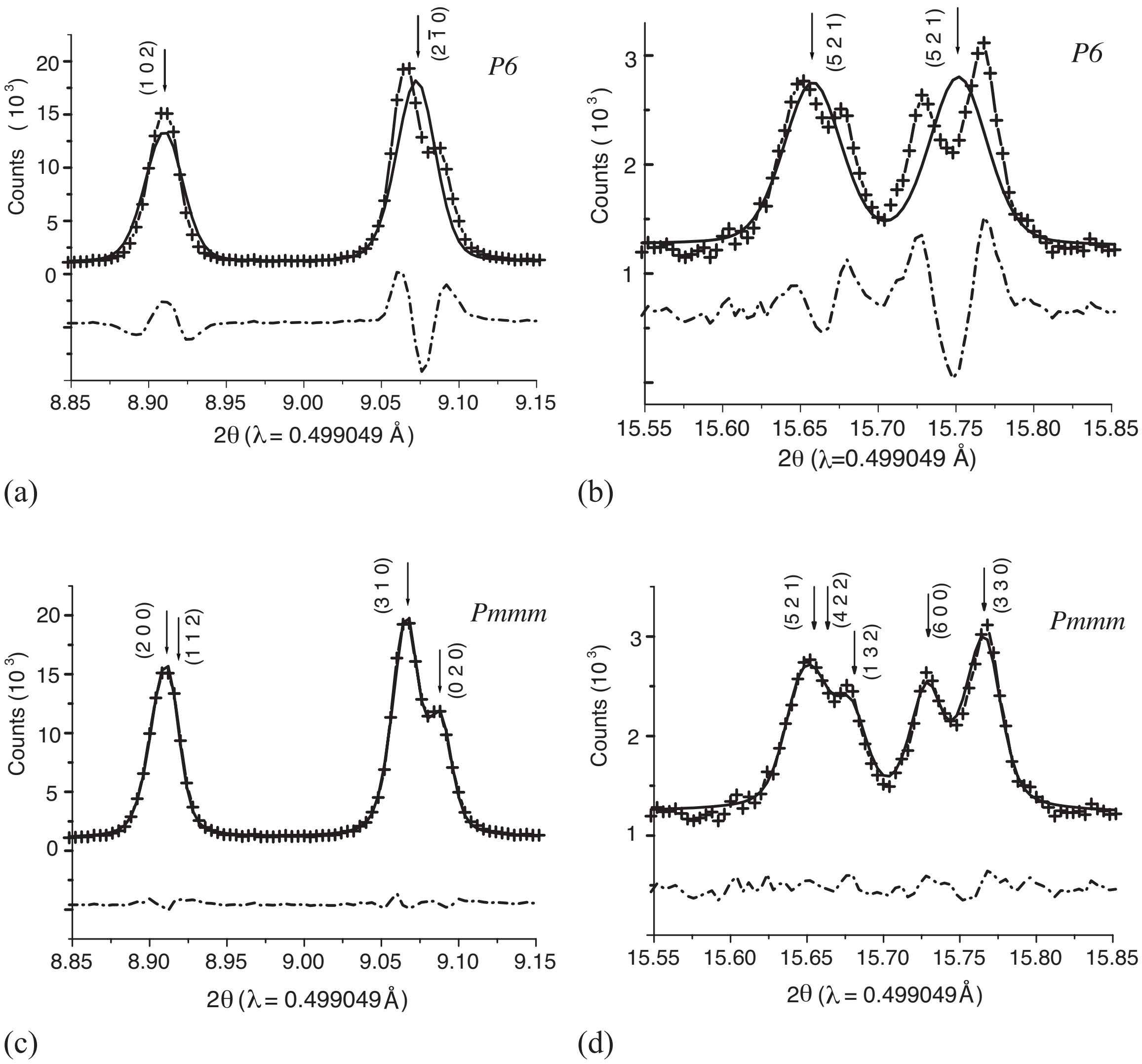

FIG. 2. Most relevant angular intervals showing the Le Bail fits of K_2MoO_4 data collected at 663 K using hexagonal *P*6 space group on (a) and (b), and orthorhombic *Pmmm* space group on (c) and (d). Lines with crosses stand for the measured data, continuous lines stand for the calculated profile, and vertical small bars indicate the calculated positions of Bragg peaks. The difference between collected and calculated data is shown in the lower doted line.

The Le Bail fits were performed in the whole patterns, i.e., for $3.52\ \text{Å} < \lambda/\sin\theta < 10.77\ \text{Å}$ but the analysis of the two most intense peaks at $2\theta \cong 8.9°$ and $2\theta \cong 9.1°$ were the key to decide about the more appropriate description. The superiority of the fit using orthorhombic symmetry is noticeable in Fig. 2. In the hexagonal setting only one Bragg peak is assigned to each line, i.e., $(1\ 0\ 2)_{\text{hex}}$ and $(2\bar{1}0)_{\text{hex}}$, respectively, which are clearly insufficient to fit the pattern. When the orthorhombic symmetry is used, two Bragg reflections are assigned to each peak, i.e., $(2\ 0\ 2)_{\text{ort}}$ and $(1\ 1\ 2)_{\text{ort}}$ for the first, and $(3\ 1\ 0)_{\text{ort}}$ and $(0\ 2\ 0)_{\text{ort}}$ for the second one. Finally, the overall fit using orthorhombic symmetry also produces better *R* values: at 663 K, $R_p=2.75$ and $R_{wp}=5.01$ using *Pmmm* space group while $R_p=3.33$ and $R_{wp}=5.83$ when *P*6 space group is used. Taking these facts into consideration it is correct to conclude that the use of orthorhombic symmetry is more suitable than hexagonal one for the description of the modulated phase of K_2MoO_4. Equivalent results are obtained for K_2WO_4 and $K_2Mo_{0.5}W_{0.5}O_4$.

The search for the best orthorhombic space group to fit the data was carried out by analyzing the list of reflections produced in Le Bail fits and identifying those which are systematically absent, keeping in mind that the model of three orthorhombic domains gives rise to a *C* centered lattice. Although preliminary inspections might detect the presence of peaks at the positions of reflections (2 3 0), (4 1 0), and (4 1 2), a further detailed examination reveal that these peaks correspond to the most intense satellite reflections identified by van den Berg *et al.*[11] using a hexagonal lattice. These peaks would correspond to the satellites $(4\ 2\ 2\ \bar{1})$, (4 1 0 0), and $(2\ 0\ 3\ \bar{1})$, and (2 2 2 1), respectively, indexed in the orthorhombic setting. Taking this fact into account, the reflection condition $hkl: h+k=2n$ is actually observed and it is possible to assign the space-group *Ccmm* to the symmetry of the average crystal structure.

The Le Bail fits were carried out using the *Ccmm* space group on corresponding data of compounds $K_2Mo_xW_{1-x}O_4$ with $x=0$, $x=0.5$, and $x=1$, at several different temperatures.

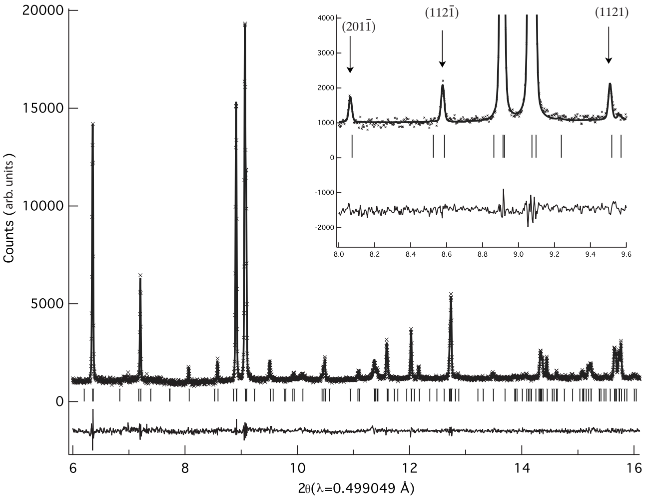

FIG. 3. Le Bail fit of K_2MoO_4 data (663 K) using the superspace group $Ccmm(\alpha00)000$. The inset shows a zoom in the region of the most intense satellites, pointed out by the arrows which are $(201\bar{1})$, $(112\bar{1})$, and (1121), respectively. The refinement converged to $q=0.6138(1)$.

With no exception, all peaks not indexed with *Ccmm* space group could be successfully identified as satellite reflections. The indexation of these satellite reflections revealed the four-dimensional reflection conditions $0klm{:}l=2n$ which allowed the assignment of the superspace group $Ccmm(\alpha00)000$ for the crystal structure in the modulated phase. Considering this superspace group, Le Bail fits were carried out including the satellites and refining the modulation wave vector q, which led to remarkably improved fits. The modulation wave vector q converged to values consistent to the expected ones—results of detailed study of the modulation wave vectors are given in the following subsection. The fitting results obtained for K_2MoO_4 at 663 K are illustrated in Fig. 3, which are similar for the other two compositions studied, and other temperature values corresponding to the modulated phase.

A. Modulation wave vectors as a function of temperature

In the temperature range corresponding to the modulated phase, K_2MoO_4 and $K_2Mo_{0.5}W_{0.5}O_4$ were studied during the heating and cooling processes while K_2WO_4 was studied only when cooling. The modulation wave vector and the lattice parameters could be determined with very high accuracy by means of the Le Bail fittings of the x-ray powder diffraction data. The modulation wave vector q as a function of temperature is shown in Fig. 4.

For the potassium molybdate $(x=1)$ q decreases linearly as the temperature increases, presenting a relatively large variation which evidences the incommensurate character of K_2MoO_4 modulated phase; its values change from 0.6281(2) at $T=623$ K down to 0.5905(2) at $T=723$ K when sample was heated. For the potassium tungstate $(x=0)$, q was found to be constant with an average value 0.5004(5), which indicates that this phase is commensurate with $\boldsymbol{q}=0.5\boldsymbol{a}^*_{\text{ort}}$. For $K_2Mo_{0.5}W_{0.5}O_4$ the modulation wave vector q varies almost linearly between 0.5392(1) at $T=653$ K and 0.5378(1) at 703 K, also characterizing this phase as incommensurate.

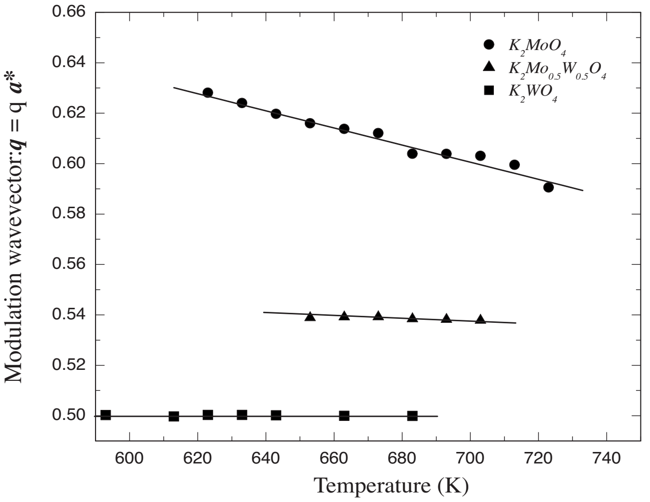

FIG. 4. The modulation wave vector as a function of temperature.

It has to be noted that the values obtained for q in each compound are approximately twice as big as those given in the literature,[11–13] as expected by the use of the orthorhombic domains model.

The results shown in this section evidences the commensurate/incommensurate character of the modulation of the pure compounds K_2MoO_4 and K_2WO_4. For the mixed $K_2Mo_{0.5}W_{0.5}O_4$ the modulation wave vector has intermediate values between the pure compounds and presents small variation with temperature. One might say that the competition between commensurate character of K_2WO_4 and the incommensurate character of K_2MoO_4 gives rise to an incommensurate structure with a small variation in the modulation wave vector.

IV. CONCLUSIONS

In this work a detailed x-ray powder diffraction analysis of the modulated phase of the compounds K_2WO_4, $K_2Mo_{0.5}W_{0.5}O_4$, and K_2MoO_4 is presented. High-resolution x-ray powder diffraction data were collected at the BM1B beamline of the SNBL-ESRF, on the temperature range comprising the modulated phases of the above cited compounds.

Hexagonal and orthorhombic symmetries have been considered on the Le Bail method, and the use of hexagonal symmetry made impossible to accurately describe the experimental data: careful inspections on some Bragg peaks revealed splits that could not be properly modeled using the hexagonal symmetry. A consistent model to describe the symmetry of modulated phase of these compounds, based on the use of three superimposed orthorhombic domains rotated by 120° from each other, allowed both the indexation of all the satellite reflections and the assignment a four-dimensional superspace group for the modulated phase, namely, $Ccmm(\alpha00)000$, with the wave vector $\boldsymbol{q}=(0.5+\delta)\boldsymbol{a}^*$ ($\delta=0$ for K_2WO_4 and varies with temperature for $K_2Mo_{0.5}W_{0.5}O_4$ and K_2MoO_4). Such a model allows a better interpretation of the phase-transition sequence of the $K_2Mo_xW_{1-x}O_4$ mixed compounds once the group-subgroup relationships turn out to be a bit simpler. Moreover, the threefold twinned orthorhombic model allowed a much simpler interpretation of the diffraction pattern since a single modulation vector is sufficient for the symmetry description.

The reduced number of observed satellite reflections make impossible the proposing of a structural model for the modulated structure, mainly because of the intrinsic difficulty in structure determination with powder diffraction data. Further attempts to obtain real single crystals of these compounds have to be considered.

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