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Crystal structures and phase transitions of the double-perovskite oxides Sr_2CaWO_6 and Sr_2MgWO_6

M Gateshki and J M Igartua¹

Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, PO Box 644, Bilbao 48080, Spain

E-mail: wmpigalj@lg.ehu.es

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Abstract

In the present work we report x-ray powder diffraction measurements of Sr_2CaWO_6 and Sr_2MgWO_6 , at different temperatures. The crystal structures at room temperature of both compounds are determined; and results showing the existence of phase transitions in them are presented. For the structure at room temperature of the Ca containing compound, the space group $P2_1/n$ is obtained, which is different from that previously suggested. The evolution with temperature of the structure of this compound shows the presence of two phase transitions, a discontinuous one at 1130 K and a continuous one at 1250 K, with the following phase transition sequence: $P2_1/n \rightarrow I4/m \rightarrow Fm\bar{3}m$. The crystal structure of the Mg containing compound at room temperature has the $I4/m$ space group. The temperature evolution of the structure has revealed a continuous phase transition at 570 K, changing the symmetry from tetragonal ($I4/m$) to cubic ($Fm\bar{3}m$).

1. Introduction

In recent years compounds with general formula $\text{A}_2\text{BB}'\text{O}_6$ and double-perovskite structure have been extensively studied. This attention is due to the fact that many compounds of this family present interesting electrical and magnetic properties that could be used in technological applications [1, 2]. However, the structural properties of these materials have been relatively less studied. The double-perovskite structure can be represented as a three-dimensional network of alternating BO_6 and $\text{B}'\text{O}_6$ octahedra, with A atoms occupying the interstitial spaces. This structure is rather simple, but the real crystal structure is sometimes difficult to determine, due to the pseudo-cubic symmetry, and due to the relative B-cation disorder that is present in many double-perovskite compounds. Another difficulty has to do with the

¹ Author to whom any correspondence should be addressed.

fact that single crystals of these materials have rarely been grown [3, 4], and thus most of the structural information has been obtained from powder diffraction data: conventional x-ray and neutrons. The study of the structural phase transitions, for understanding the properties of double-perovskite oxides, is very important; and can be exemplified by the fact that, recently, a coincidence between the tetragonal to cubic phase transition temperature, the Curie temperature and the metal–insulator transition temperature has been found in $\text{Sr}_2\text{FeMoO}_6$ [5, 6]. Although the role of the structural change is not very clear, the coincidence of the mentioned transition temperatures suggests that such a relation probably exists.

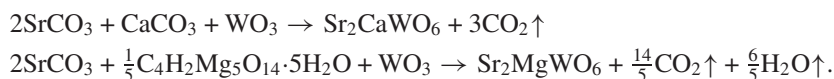
In a recent publication [7], we presented experimental results for the crystal structures and phase transitions of the double-perovskite oxides Sr_2MWO_6 ($M = \text{Ni}, \text{Zn}, \text{Co}, \text{Cu}$) studied with the x-ray powder diffraction method. The Zn and Co containing compounds were found to present the $P2_1/n$ (monoclinic, No 14, non-standard setting) $\rightarrow I4/m$ (tetragonal, No 87) $\rightarrow Fm\bar{3}m$ (cubic, No 225) [8] phase transition sequence; for Sr_2NiWO_6 , the $I4/m \rightarrow Fm\bar{3}m$ phase transition was observed; and for Sr_2CuWO_6 , experimental evidence was found that suggested the $I4/m \rightarrow I4/mmm \rightarrow Fm\bar{3}m$ phase transition sequence (later confirmed in [9] by means of neutron and synchrotron radiation diffraction measurements). In order to extend the studies of the phase transitions of the Sr_2MWO_6 compounds, we have synthesized and studied with x-ray diffraction methods the crystal structures of the title compounds. Diffraction measurements at high temperatures have been used to explore the possibility of the occurrence of structural phase transitions in these compounds.

The aim of the present work is to report the structural re-determination of Sr_2CaWO_6 , and the structural determination of Sr_2MgWO_6 , which, to the best of our knowledge, is the first one of this compound. We also present the phase transitions observed in Sr_2CaWO_6 and Sr_2MgWO_6 .

2. Experimental details

2.1. Sample preparation

For the preparation of the samples, the standard method of solid state chemical reaction has been used. Stoichiometric amounts of the reacting compounds were mixed according to the following chemical reactions:



The reacting compounds (all supplied by Sigma-Aldrich) had the following purities: SrCO_3 , 99.995%; WO_3 , 99.995%; CaCO_3 , 99.995%; and $\text{C}_4\text{H}_2\text{Mg}_5\text{O}_{14}\cdot 5\text{H}_2\text{O}$, 99%. All compounds were used as received, with the exception of CaCO_3 , which was heated at 420 K for 12 h, before starting the synthesis procedure. The starting materials were mixed and ground in an agate mortar, and heated in air in alumina crucibles. The following heat treatment was used: 24 h at 1170 K; 24 h at 1270 K; and 48 h at 1370 K.

After each heating, the samples were cooled down slowly (3 K min^{-1}), and re-ground (re-mixed) to improve homogeneity. In order to control the quality of the obtained materials, x-ray diffraction measurements were performed after each heating.

In the case of Sr_2CaWO_6 , a gradual increment with time of the amount of SrWO_4 was observed in the sample. For this reason, immediately before the diffraction measurements, the sample was heated up to 1370 K. This treatment was found to be enough for the reincorporation of SrWO_4 into the crystal lattice of Sr_2CaWO_6 . This reincorporation was observed in the high-temperature x-ray measurements, and also in the differential scanning calorimetry (DSC)

Table 1. Weight fractions of the phases contained in the studied samples. The quantitative analysis was done using the results of the Rietveld refinement.

Studied sample	Sr ₂ MWO ₆	SrWO ₄	Sr ₂ WO ₅
Sr ₂ CaWO ₆	99.73(10)%	0.14(5)%	0.13(5)%
Sr ₂ MgWO ₆	99.75(10)%	—	0.25(10)%

measurements, where a non-reversible endothermic effect was observed at about 720 K. A similar effect (amount of the impurity SrMoO₄ gradually increasing with time) was recently observed in a sample of Sr₂FeMoO₆ [10]. The explanation that this was due to atmospheric moisture was given.

Small amounts of the impurities SrWO₄ and Sr₂WO₅ were found in our samples (table 1). These impurities were included as known additional phases in the Rietveld refinements of the structures of the studied compounds. SrWO₄ has symmetry *I4₁/a* [11], and Sr₂WO₅ has symmetry *Pnma* [12]. Known structural parameters from the literature [11], and from our own results [12], were used; and these were not refined. The scale factors obtained in the Rietveld refinement were used for quantitative analysis, the results of which are shown in table 1.

2.2. Differential scanning calorimetry (DSC) measurements

DSC measurements from room temperature to 770 K have been performed with a Perkin-Elmer DSC7, with heating and cooling rates of 10° min⁻¹. Low temperature DSC measurements (100–420 K) have been made with a Perkin-Elmer Pyris 1 differential scanning calorimeter, with the same heating and cooling rates.

2.3. X-ray powder diffraction measurements

Conventional x-ray powder diffraction data were obtained using a Philips X'Pert MPD system with Cu K α (Ni filter) radiation, equipped with a proportional detector. Intensity data were collected by continuous scanning with 2θ steps of 0.01°; and counting times of 12 s at each step. The 2θ range covered was 15°–120°. The Bragg–Brentano parafocusing geometry was used. X-ray diffractograms at high temperatures were obtained using an Anton Paar HTK16 temperature chamber, with a temperature stability of 0.5 K, mounted on the same diffractometer. The specimens for high temperature measurements were prepared by mixing the material under study with high temperature resin (Zapon lacquer). Then the mixture was 'painted' over the Pt alloy heater of the chamber. The high temperature x-ray data were collected in narrow 2θ regions, with small temperature steps. From these high temperature diffractograms only the unit cell constants were refined. Special attention was paid to the additional peaks belonging to the Pt sample heater that are present in the high temperature diffractograms, and that overlap with the peaks originating from the samples studied. These peaks were excluded from the refinement. The presence of these additional diffraction peaks made the high temperature diffractograms not suitable for accurate structural determination; however, they are good enough for lattice determination. For this reason, we do not report results for atomic positions at high temperatures.

One single diffraction measurement of Sr₂MgWO₆ at 26 K was performed in the X7A beam-line at the National Synchrotron Light Source (Brookhaven National Laboratory, US) [13]. The wavelength used was 0.8005 Å. It was obtained using a Si(111) monochromator, and was calibrated with a CeO₂ standard sample. A Ge(220) analyser was used. Scattered radiation was collected by a linear position sensitive detector (PSD) mounted on the 2θ arm of

the diffractometer at a distance of 1 m from the sample. The cooling of the sample was done by means of a closed circuit cryostat: Displex, with a temperature stability of 0.5 K. In this case, also, the Bragg–Brentano parafocusing arrangement was used.

The Rietveld refinement of the structures was performed with the FULLPROF program [14].

3. Results and discussion

3.1. Sr_2CaWO_6

The first preparation of Sr_2CaWO_6 was reported in [15]. It was observed that the structure of this compound is pseudocubic, and the distortion of its unit cell was described as ‘considerable’; however, the crystal structure was not determined. The room temperature structure of Sr_2CaWO_6 was studied in [16]. It was reported to be of the ordered perovskite type, with the orthorhombic $Pmm2$ (No 25) space group. This space group was chosen because of the piezoelectric properties observed in Sr_2CaWO_6 by the authors of [16]; however, no experimental results evidencing such properties were presented. The $Pmm2$ space group can accommodate the B-cation ordering and the presence of a polar moment in the structure. The structure of Sr_2CaWO_6 , presented in [16], was refined using conventional x-ray powder diffraction data. In this structure, the CaO_6 and WO_6 octahedra are deformed, but without any tilt or rotation. Also, the cations $Ca^{2+}yW^{6+}$ were found to be displaced from the centres of their respective octahedra. Due to this structural determination, Sr_2CaWO_6 was included in the list of non-centrosymmetric oxides of Shiv Halasiamani *et al* [17].

In another work [18], the room temperature crystal structure of Sr_2CaWO_6 was referenced as orthorhombic; however, no structural details were reported.

Experimental results for the behaviour of the lattice constants of Sr_2CaWO_6 in the range from room temperature up to 1273 K were reported in [16]. These data revealed the presence of a continuous phase transition at about 1133 K; although the authors classified it as first order. This phase transition changes the symmetry from orthorhombic to cubic ($Fm\bar{3}m$). In the temperature behaviour of the unit cell volume, the authors of [16] observed a turning point at the temperature of the phase transition. In the cubic phase the unit cell volume increases considerably faster than in the orthorhombic phase. This transition was also observed at about 1133 K in the differential thermal analysis (DTA) measurements.

The room temperature powder diffraction data that we obtained from the sample of Sr_2CaWO_6 are shown in figure 1.

The attempt to refine the structure of Sr_2CaWO_6 using a structural model with the $Pmm2$ space group was not successful, because important differences between the observed and calculated profiles were found. The $Pmm2$ model could not account for the splitting of some diffraction lines. One such splitting is shown in figure 2.

In order to explain this line splitting, it was necessary to find a structural model with a lower symmetry than the orthorhombic. Also, we observed that the diffraction reflections with $h0l$; $h+l=2n+1$ were absent, indicating the presence of a n glide plane, perpendicular to the b axis. Analysing the different structural models expected in the case of double-perovskite structures [7, 19], we found that the model with the $P2_1/n$ space group could explain all features of the diffraction profile. The results from the refinement of the structure of Sr_2CaWO_6 at room temperature with the space group $P2_1/n$ are shown in table 2.

With respect to the piezoelectric properties observed in Sr_2CaWO_6 by the authors of [16], it should be pointed out that a structure with the $P2_1/n$ space group, which is centrosymmetric, cannot present such properties. If the crystal structure had a symmetry described by some of the non-centrosymmetric subgroups of $P2_1/n$ ($P2_1$, Pn , or $P1$), additional diffraction

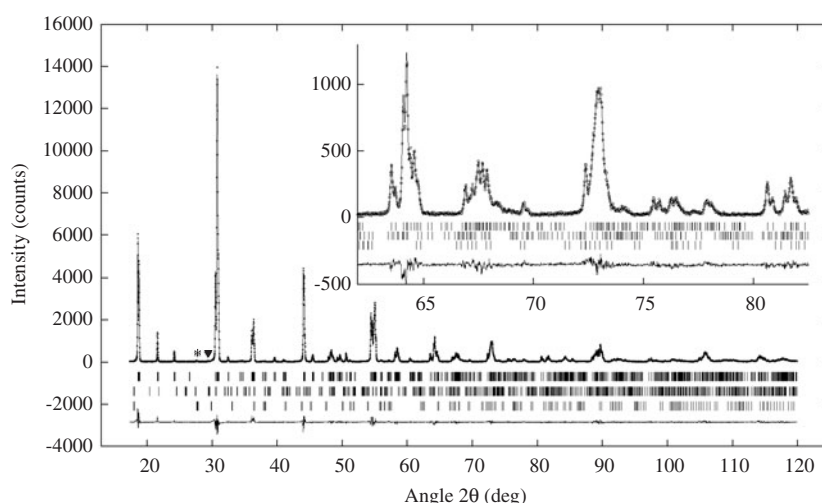


Figure 1. Observed (·), calculated (—) and difference diffraction profiles for the Rietveld refinement of Sr_2CaWO_6 at room temperature using a structural model with the $P2_1/n$ space group. The impurities Sr_2WO_5 and SrWO_4 are included in the refinement as known additional phases; see the text. The two markers, ▼ and *, indicate peaks corresponding to the impurities Sr_2WO_5 and SrWO_4 , respectively. The top barred pattern corresponds to Sr_2CaWO_6 , the middle barred pattern to Sr_2WO_5 , and the bottom barred pattern to SrWO_4 .

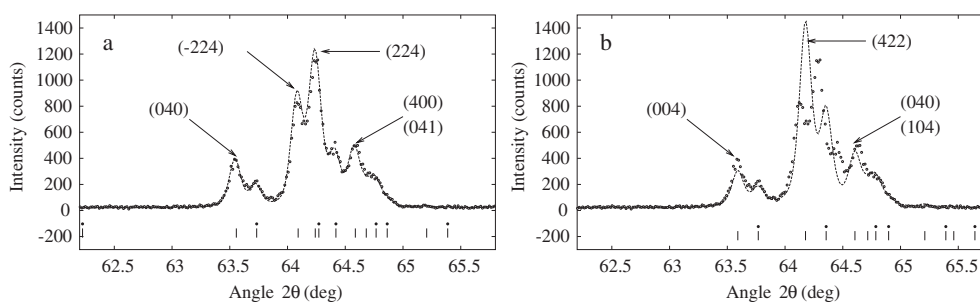


Figure 2. Refinement of the structure of Sr_2CaWO_6 in the $P2_1/n$ space group (a) can explain the shapes of the diffraction peaks. In (b), we show, for comparison with (a), the refinement of the structure using the $Pmm2$ space group. The Bragg positions for both $\text{Cu K}\alpha_1$ and $\text{Cu K}\alpha_2$ (marked with dots) are given.

peaks should be observed, since these space groups have different extinction conditions. Such additional peaks could not be observed in our diffraction data. It was not possible, on the basis of conventional x-ray powder diffraction data, to confirm that Sr_2CaWO_6 is non-centrosymmetric.

The temperature evolution of the structure of Sr_2CaWO_6 was studied by means of conventional x-ray diffraction measurements at different temperatures. As seen in figure 3(a), the distortion of the unit cell gets smaller at higher temperatures: the diffraction lines get closer to each other. At about 1100 K, the splitting of the diffraction lines almost disappears. At the same temperature, the reflections of the type hkl ; $h+k+l = 2n+1$ also disappear (figure 3(b)). These reflections are characteristic for a primitive unit cell. The disappearance of these peaks can also be observed in figure 4.

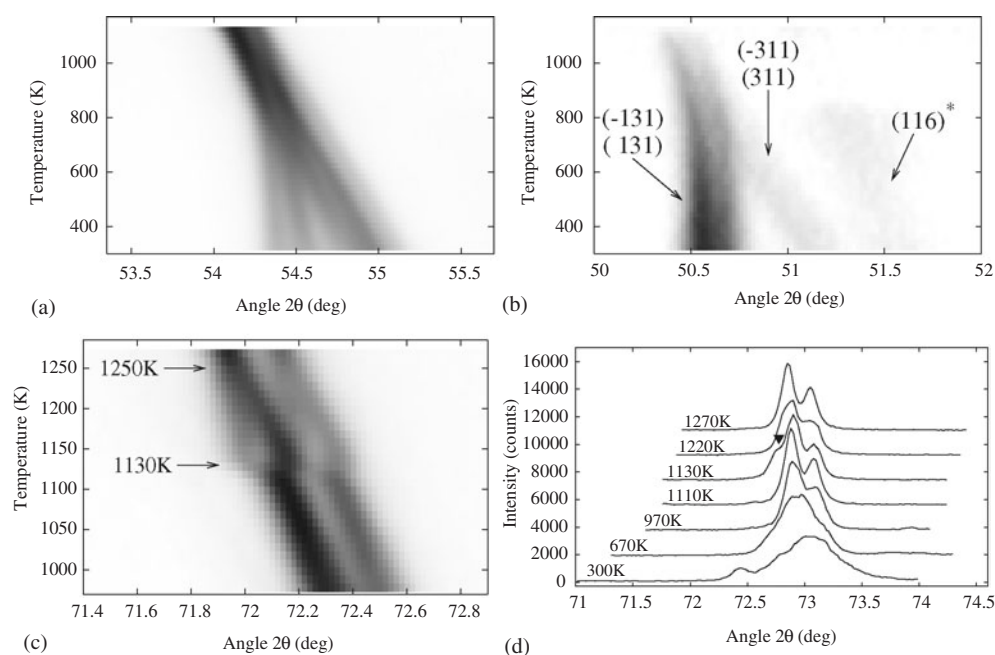


Figure 3. Temperature evolution of three groups of diffraction lines of Sr_2CaWO_6 . In (a), cubic reflection (422), the continuous approximation of the diffraction lines at high temperatures can be observed. In (b), a group of diffraction lines with hkl ; $h+k+l = 2n+1$ is shown. It can be seen that these lines gradually disappear at high temperatures. The diffraction line marked with * belongs to SrWO_4 and disappears at about 800 K. In (c) and (d) the temperature evolution of the (620) cubic reflection is shown. The tetragonal splitting existing in the temperature range from 1130 and 1250 K can be observed. The shoulder appearing at 1130 K is marked with \blacktriangledown in (d). For better representation, the high temperature diffraction patterns are shifted towards higher angles.

Table 2. Crystal structure data and refinement results for Sr_2CaWO_6 at room temperature. The atomic positions (in fractional coordinates) and temperature factors were refined in the space group $P2_1/n$. (Note: $a = 5.7672(1) \text{ \AA}$; $b = 5.8506(1) \text{ \AA}$; $c = 8.1931(1) \text{ \AA}$; $\beta = 90.165(1)^\circ$; $R_p = 9.94\%$; $R_{wp} = 14.5\%$; $R_{exp} = 8.81\%$; $\chi^2 = 2.70$.)

Atom	Site	x	y	z	$B (\text{\AA}^2)$
W	2a	0	0	0	0.01(2)
Ca	2b	0	0	1/2	0.12(6)
Sr	4e	0.0094(3)	0.5370(2)	0.2509(2)	0.46(3)
O1	4e	0.071(2)	0.025(1)	-0.222(1)	0.3(1)
O2	4e	0.262(2)	-0.177(2)	0.046(2)	0.3(1)
O3	4e	0.185(2)	0.263(1)	0.050(1)	0.3(1)

These observations could indicate that, at about 1100 K, the structure transforms from monoclinic (at low temperatures) to cubic $Fm\bar{3}m$ (at high temperatures). This behaviour coincides with that observed by the authors of [16]. The temperature of the transition also coincides. However, as seen in figure 3(c), at about 1130 K the splitting of the diffraction lines appears again, in a discontinuous manner.

This shows that the phase that exists above 1130 K is not cubic. The analysis of the diffraction data in the temperature range from 1130 to 1250 K has shown that this phase is tetragonal, with body centred unit cell. In the framework of rigid octahedra, this phase could

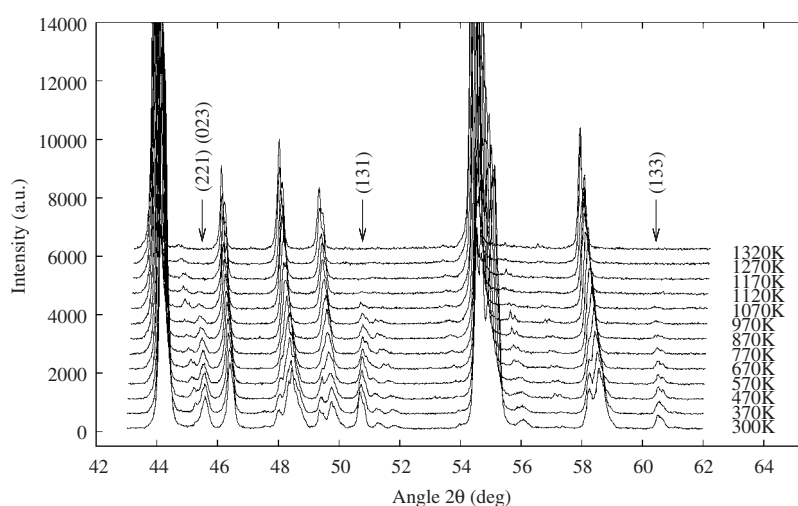


Figure 4. Diffraction measurements of Sr_2CaWO_6 at different temperatures. The diffraction peaks with $h + k + l = 2n + 1$ are absent in the measurements at 1120 K, and above.

have the $I4/m$ space group. The structural refinement at 1173 K with this space group has given good results. At about 1250 K, the splitting of the diffraction lines disappears, in a continuous way. This indicates the presence of another phase transition that changes the structure from tetragonal ($I4/m$) to cubic ($Fm\bar{3}m$). The refinement of the structure at 1323 K has confirmed that, at this temperature, the structure can be described with the $Fm\bar{3}m$ space group.

The variation with the temperature of the lattice constants of Sr_2CaWO_6 is shown in figures 5(a), (b). It can be observed that, in the monoclinic phase, the metric parameters ($a\sqrt{2}$, $b\sqrt{2}$, c) change continuously; and, at 1130 K, become almost equal. At the same time, the monoclinic angle β reduces abruptly to 90° with increasing temperature. This behaviour of the monoclinic angle is consistent with a first-order phase transition. Figure 5(d) shows the variation with the temperature of the unit cell volume of Sr_2CaWO_6 (multiplied by two for the monoclinic and tetragonal phases). As seen in the figure, our results do not show the important increment of the unit cell volume above 1130 K that was observed in [16]. Probably, that result was due to the misinterpretation of the tetragonal phase as a cubic one. Our data have shown a small change of the unit cell volume at the monoclinic to tetragonal phase transition, and apparently no influence of the tetragonal to cubic phase transition.

In the DSC measurements, covering the range from 100 to 770 K, the only effect that could be observed was a non-reversible endothermic anomaly at around 720 K. This temperature is close to the temperature at which the peaks related to the SrWO_4 impurity disappear from the diffraction pattern (800 K). No anomalies indicative for phase transitions in the material were observed. It should be mentioned that the temperatures of the phase transitions observed in the x-ray diffraction measurements are well above the range covered in the DSC measurements.

3.2. Sr_2MgWO_6

The synthesis of Sr_2MgWO_6 has been reported on several occasions [15, 18, 20–22]. However, the only information with respect to the structure that we have found in the literature is that the unit cell of this compound was classified as ‘moderately’ distorted (with respect to a cubic cell with lattice constant $a = 7.9 \text{ \AA}$) [15]; and that, in [18], the structure was referenced as

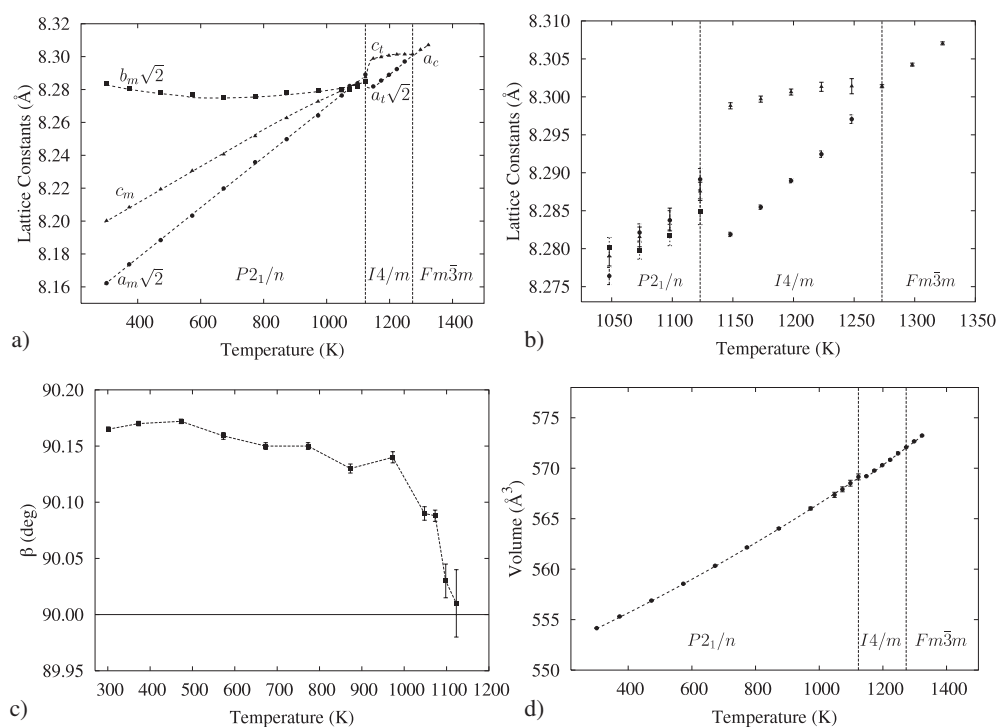


Figure 5. Variation with the temperature of the lattice constants ((a), (b)), the monoclinic angle (c) and the unit cell volume (d) of Sr_2CaWO_6 . Dashed lines are a guide for the eye.

Table 3. Crystal structure of Sr_2MgWO_6 at room temperature. The atomic positions (in fractional coordinates) and temperature factors were refined in the $I4/m$ space group, using conventional x-ray diffraction data obtained with radiation $\text{Cu K}\alpha$. (Note: $a = 5.5817(1)$ Å; $c = 7.9390(1)$ Å; $R_p = 8.66\%$; $R_{wp} = 12.5\%$; $R_{exp} = 5.27\%$; $\chi^2 = 5.64$.)

Atom	Site	x	y	z	B_{iso} (Å^2)
W	2a	0	0	0	0.10(1)
Mg	2b	0	0	1/2	0.25(7)
Sr	4d	0	1/2	1/4	0.54(2)
O1	8h	0.209(1)	0.270(1)	0	1.3(2)
O2	4e	0	0	0.235(1)	0.5(2)

tetragonal; but no values for the lattice constants were reported. The rest of the works [20–22] were dedicated to the study of the electronic and vibrational spectra, of samples doped with U. We have not found any data about structural studies of Sr_2MgWO_6 at temperatures different from the ambient.

The diffraction profile of Sr_2MgWO_6 that we have obtained at room temperature is shown in figure 6.

The diffraction peaks could be indexed with a tetragonal body-centred unit cell. If rigid octahedra are assumed, the only possible space group compatible with such a unit cell is $I4/m$ [7]. The structural parameters obtained in the Rietveld refinement with this space group are shown in table 3. Attempts to refine the structure with structural models having symmetries $I4/mmm$ or $I4mm$ gave results with worse reliability parameters.

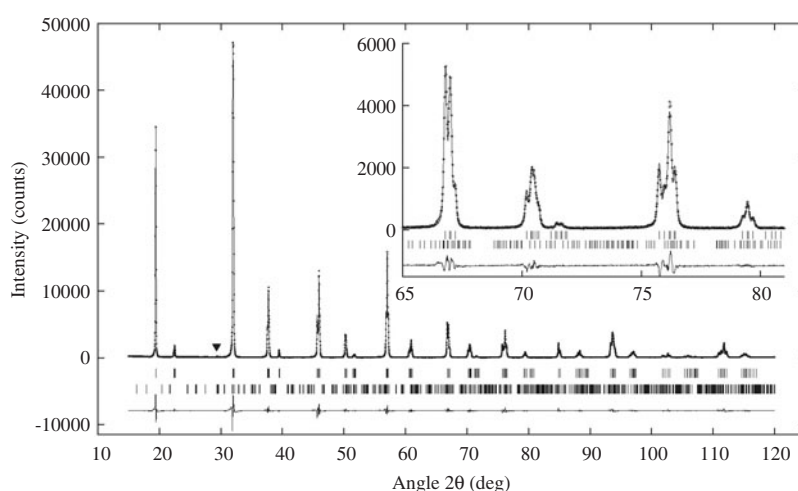


Figure 6. Observed (·), calculated (—) and difference diffraction profiles for the Rietveld refinement of Sr_2MgWO_6 at room temperature using a structural model with the $I4/m$ space group. The impurity Sr_2WO_5 is included in the refinement as a known additional phase; see the text. The marker, ▼, indicates a peak corresponding to the impurity. The top barred pattern corresponds to Sr_2CaWO_6 and the bottom barred pattern to Sr_2WO_5 .

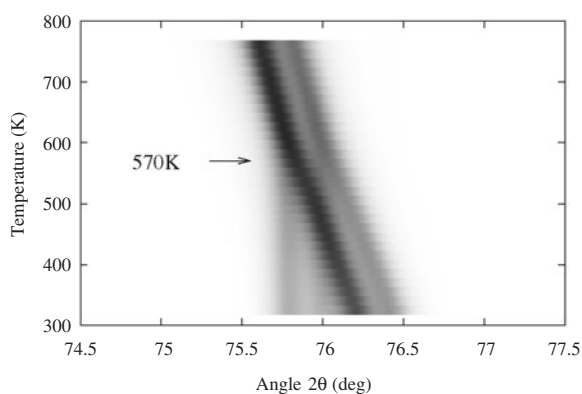


Figure 7. Temperature evolution of the (620) cubic reflection of Sr_2MgWO_6 . The cubic to tetragonal continuous phase transition at about 570 K is evidenced by the splitting of the diffraction line.

At about 570 K the unit cell transforms, in a continuous way, from tetragonal to cubic, see figure 7. The variation of the lattice constants with the temperature is essentially the same as that observed in other double-perovskite materials presenting the $I4/m \rightarrow Fm\bar{3}m$ phase transition [7]. The tetragonal distortion of the unit cell is a result of the homogeneous strain coupled to the order parameter. The order parameter of the phase transition $I4/m \rightarrow Fm\bar{3}m$ in double-perovskite structures is related to the angle of rotation of the BO_6 and $\text{B}'\text{O}_6$ octahedra around the fourfold axis. This angle is zero in the high symmetry cubic phase and different from zero in the tetragonal phase. Figures 8(a) and (b) show the variation with the temperature of the lattice constants and the unit cell volume of Sr_2MgWO_6 . The diffraction data obtained at 26 K have shown that the tetragonal structure is preserved, at least down to this temperature.

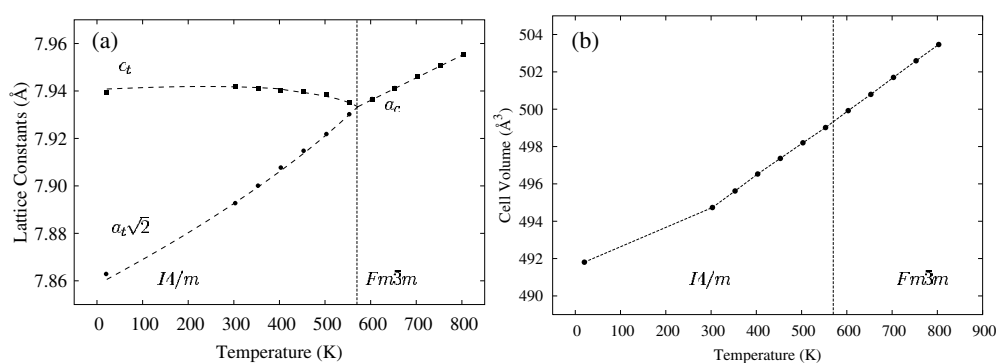


Figure 8. Variation with the temperature of the lattice constants (a) and unit cell volume (b) of Sr_2MgWO_6 . Dashed lines are a guide for the eye.

In the DSC measurements of Sr_2MgWO_6 , no thermal anomaly that could be related to a phase transition was observed. Therefore, the DSC measurements could not confirm the presence of the phase transition observed with powder x-ray diffraction. The same result was obtained for the materials reported in [7], where the continuous phase transitions observed with XRD did not give any observable anomaly in the DSC measurements. The discontinuous phase transitions in the materials from [1] were clearly observed. It is known that the DSC technique is not sensitive to continuous phase transitions. For this reason, we believe that the absence of a thermal anomaly at the temperature of the phase transition in Sr_2MgWO_6 is a confirmation of its continuous character.

4. Conclusions

For the crystal structure at room temperature of Sr_2CaWO_6 the space group $P2_1/n$ is suggested, which is different from that previously reported ($Pmm2$). The evidence of monoclinic distortions of the unit cell observed in the diffraction patterns is presented. The crystal structure at room temperature of Sr_2MgWO_6 is determined for the first time; and the $I4/m$ space group is suggested for it. Two phase transitions are observed in Sr_2CaWO_6 : $P2_1/n \rightarrow I4/m$, at 1130 K; and $I4/m \rightarrow Fm\bar{3}m$, at 1250 K. In Sr_2MgWO_6 , one phase transition $I4/m \rightarrow Fm\bar{3}m$ is observed at 570 K. The mechanism of these phase transitions is related to the mismatch of the size of the A cation and the cuboctahedral space between the WO_6 and $\text{Ca}(\text{Mg})\text{O}_6$ octahedra. The bigger size of the Ca^{2+} cation, with respect to that of the Mg^{2+} cation, leads to a structure with lower symmetry at room temperature. The symmetries suggested for the different phases of the two compounds are in accordance with those obtained previously for similar materials, as well as with the theoretical predictions. Further work is necessary to confirm the presence of a centre of symmetry in the structure of Sr_2CaWO_6 at room temperature.

Acknowledgments

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