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Abstract

As a result of a pseudosymmetry search, the double perovskite compounds Sr_2MWO_6 (M = Ni, Zn, Co, Cu) were identified as good candidates for presenting Landau-type phase transitions at high temperatures. In the present work, the phases observed at different temperatures are reported and the phase transitions are discussed. The Sr_2MWO_6 (M = Ni, Zn, Co) compounds present $I4/m$–$Fm\bar{3}m$ phase transitions, while Sr_2CuWO_6 shows an $I4/m$–$I4/mmm$ phase transition. All these transitions are second order and are consistent with the pseudosymmetry concept. Sr_2ZnWO_6 and Sr_2CoWO_6 also show $P2_1/n$–$I4/m$ phase transitions and Sr_2CuWO_6 presents a phase transition of the type $I4/mmm$–$Fm\bar{3}m$. These transitions are first order. Alongside the experimental results a discussion of some aspects of the study of phase transitions in double perovskite materials is presented.

1. Introduction

During the last few years transition metal oxide materials with rock-salt ordered perovskite structure ($A_2BB'O_6$) have been extensively studied, mainly due to their magnetic and electric properties. Materials with this structure have been found to present colossal magnetoresistance (Sr_2FeMoO_6) [1], superconducting properties ($Sr_2YRu_{0.95}Cu_{0.05}O_6$) [2] etc. However, the structural properties of these materials have been relatively less studied. One of the reasons for that is the very strong cubic pseudosymmetry of these materials. Thus, in order to obtain reliable structural data, one needs both high quality samples (good crystallization grade, low amount of impurities) and very high resolution diffraction measurements. An additional difficulty for the accurate structural determination lies in the fact that single crystals of these materials have rarely been grown [3, 4]. Hence, most of the structural information has been obtained from

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powder diffraction data (conventional x-ray or neutron). In many cases the structure resolution is complicated by the presence of relative B cation disorder and/or oxygen deficiency. For instance, in [5] it is shown how an oxygen deficiency of about 8% in the structure of Sr_2CoSbO_6 causes it to change from rhombohedral to cubic symmetry. Another difficulty is that the low sensitivity of the x-ray diffraction to the positions of the oxygen atoms often prevents accurate determination of the structure; and, in some cases, the symmetry of the proposed structures is overestimated or misassigned. In this sense, the case of Sr_2FeMoO_6 is very noticeable; for this compound four different space groups have been proposed by different authors in just the last few years: $I4/mmm$ [4], $I4/m$ [6], cubic [7] (the authors point out that the synthesis technique modifies the final structure) and $P4_2/m$ [8]. These difficulties, concerning the structure determination of double perovskites, can explain the relatively small amount of attention that has been paid to the structural transformations occurring in such materials.

The importance of the study of the structural phase transitions for understanding the properties of double perovskite oxides can be exemplified by the fact that recently a coincidence between the tetragonal–cubic phase transition temperature, the Curie temperature and the metal–insulator transition temperature has been found in Sr_2FeMoO_6 [6, 9]. Although the role of the structural change in the magnetic properties of this compound is not very clear, the coincidence of the transition temperatures suggests that such a relation probably exists.

The majority of the oxide materials with ordered perovskite structures are reported to be monoclinic $P2_1/n$ [10] (rarely $I2/m$ [11] and $P2_1/m$ [12]) or cubic $Fm\bar{3}m$ [10]. A smaller number of materials have been found to have tetragonal symmetry, mainly $I4/m$ [13], but also $I4/mmm$ [4, 14], $I4mm$ [15], $P4_2/n$ [16], $P4_2/m$ [8]; rhombohedral ($R\bar{3}m$ [5], $R\bar{3}$ [11]); orthorhombic $Pmm2$ [17, 18]; or even triclinic $I\bar{1}$ [19]. We only know of a few reports concerning phase transitions between some of these phases [20, 21]; and, to the best of our knowledge, the only oxide materials with double perovskite structure for which two phase transitions have been reported are Sr_2ZnWO_6 and Sr_2ZnTeO_6 [20]. Here we are not concerned with the case of materials with A = Pb, where several phase transitions may occur [22, 23] and in some cases even incommensurate phases are present.

The aim of this paper is to present x-ray powder diffraction and DSC results concerning the crystal structures and structural phase transitions found in four double perovskites: Sr_2NiWO_6, Sr_2ZnWO_6, Sr_2CoWO_6 and Sr_2CuWO_6. Sr_2NiWO_6 and Sr_2CuWO_6 were identified as possible candidates for showing Landau-type phase transition after a systematic pseudosymmetry search [24] among the compounds with space group $I4/m$ (No 87) in the Inorganic Crystal Structure Database (ICSD) [25]. Sr_2NiWO_6 showed pseudosymmetry with the supergroup $Fm\bar{3}m$ and Sr_2CuWO_6 with $I4/mmm$. Sr_2CoWO_6 and Sr_2ZnWO_6 were included in the study because there is a reference in the literature [26] suggesting that these compounds have tetragonal structures, although no space groups or atomic positions have been reported. As we show further in this work, they also have phases with the $I4/m$ space group. All four compounds are known to become cubic at high temperatures.

2. Structural modifications of the double perovskite structures

The question of the possible modifications of the perovskite structure was first studied by Glazer [27]. He assumed that the simple perovskite structure (ABX_3) is comprised of equal rigid octahedra: the B atoms are in the centres of the octahedra, the X atoms are on the vertices and the A atoms occupy the interstitial spaces between the octahedra. He found 23 possible tilts of these octahedra. Then, by inspection, he assigned a space group to each of these possible tilts. Later, Woodward [28] generalized this classification scheme for the case of 1:1 ordered double perovskite materials ($A_2BB'X_6$). This was done by the determination
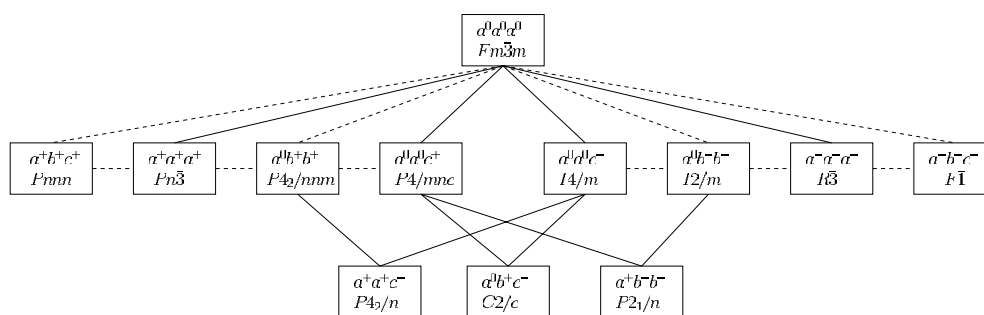
Figure 1. Possible modifications of the double perovskite structure due to octahedral tilts. For each modification, the corresponding space group symbol and tilt system [27] are given. Dashed lines connect the space groups among which the phase transitions must be first order. Continuous lines represent the relations for which second order transitions are allowed.

of a subgroup that allows ordering between the B cations and that preserves the octahedra undeformed, for each of the Glazer groups. On the basis of group theory considerations, the number of possible space groups was reduced to 15 by Howard and Stokes [29], for the case of simple perovskite structures. Following the same formalism as in [29] we identified 12 possible space groups for the case of 1:1 ordering (figure 1). These are isotropy subgroups of $Fm\bar{3}m$ corresponding to the $\Gamma_4^+ \bigoplus X_3^+$ reducible representation. The three tilt systems that are not included in figure 1, in comparison with [29], are $a^0b^-c^-$, $a^-b^-b^-$ and $a^+b^-c^-$. These tilt systems do not appear in the representation analysis, which means that they cannot be obtained through the action of two order parameters with symmetries Γ_4^+ and X_3^+. Figure 1 also shows the possible phase transitions due to tilts of the octahedra in double perovskites. Dashed lines represent transitions that must be first order according to the Landau theory of phase transitions. The fulfilment of the conditions for a second order phase transition was tested using the program *ISOTROPY* [30].

In addition to the octahedral tilting, two other types of modification are also possible in the double perovskite structure: distortion of the octahedral units and cation displacements. These modifications lead, in general, to space groups not presented in figure 1. This is the case for Ba_2CuWO_6 [14] and Sr_2MnSbO_6 [15] double perovskites, for which the space groups $I4/mmm$ and $I4mm$, respectively, have been found. In these two compounds, the presence of the Jahn–Teller active ions Cu^{2+} and Mn^{3+} causes strong distortions of their respective octahedra. Structures where B cations are displaced from their ideal positions would lose their centre of symmetry; and, in general, they could be described by one of the polar subgroups of the corresponding Glazer group. For instance, due to the observed ferroelectric properties, the space group $P2_1cn$ ($Pna2_1$) was assigned to the structure of Pb_2CoWO_6 below 235 K [31], instead of the centrosymmetric $Pmcn$ ($Pnma$). Although many types of polar distortion are possible in the perovskite structure, it is worth mentioning that Shiv Halasyamani and Poeppelmeier in their classification of non-centrosymmetric oxides [32], based on a search in the ICSD, found only three examples of double perovskite materials with non-centrosymmetric structure. They are: Sr_2MnSbO_6 with symmetry $I4mm$, Sr_2TmNbO_6 with $P2nn$ ($Pnn2$) and Sr_2CaWO_6, for which the orthorhombic $Pmm2^{Note\ 2}$ symmetry was proposed in [17].

Finally, structures with hexagonal symmetry, such as Ba_2CrTaO_6 [33] and Ba_2CrNbO_6 [34], show different arrangement of the octahedra and they cannot be described as

2 Our study on Sr_2CaWO_6, which will be reported elsewhere, has shown clear evidence that the structure of this material is monoclinic. So, in our opinion, the previously assigned symmetry is not correct.

distorted perovskite phases. In the case of Ba_2CrNbO_6 a phase transition from the hexagonal to a cubic phase is observed at high temperature (930 °C) and high pressure (80 kbar).

3. Experimental procedures

3.1. Sample preparation

Stoichiometric amounts of $SrCO_3$ (99.995%), WO_3 (99.995%), CuO (99.99%), NiO (99.99%), CoO and ZnO (99.999%), all from Sigma-Aldrich, were mixed according to the equation

$$2SrCO_3 + MO + WO_3 \rightarrow Sr_2MWO_6 + 2CO_2\uparrow$$
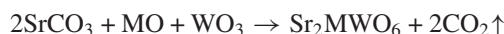
where M represents Ni, Zn, Co or Cu respectively. The mixtures were ground in an agate mortar and heated in air at 1000 °C in a Pt crucible for 24 h, then cooled slowly to room temperature, reground and heated again to 1100 °C for 2 days.

3.2. DSC measurements

DSC measurements from room temperature to 500 °C have been performed with a Perkin-Elmer DSC7, with heating and cooling rates of 10 °C min^{-1}. Low temperature DSC measurements (-170 to 150 °C), have been made with a Perkin-Elmer Pyris 1 differential scanning calorimeter, with the same heating and cooling rates.

3.3. X-ray powder diffraction

Powder diffraction data were obtained using a Philips X′Pert MPD System with Cu Kα (Ni-filter) radiation, equipped with a proportional detector. The specimen for diffraction at room temperature was prepared by depositing sample powder on a Si plate. 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°. X-ray diffractograms at high temperatures were obtained using an Anton Paar HTK16 temperature chamber 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 in order to observe the temperature behaviour of selected reflections (see below) which were found to show greater sensitivity to the tetragonal distortions of the unit cell and, in the case of Sr_2CuWO_6, to the rotations of WO_6 and MO_6 octahedra. 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 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. For this reason, we do not report results for atomic positions at high temperatures. The only exception is the structure of Sr_2ZnWO_6 at 100 °C that was refined from x-ray data collected over the whole 2θ range 15°–120°. In this case the influence of the heater was small and the diffraction data were good enough for the refinement to be made. Diffraction data were collected from the sample of Sr_2CoWO_6 at -73 °C in the X7A beamline of NSLS (Brookhaven National Laboratory) using synchrotron radiation with $\lambda = 0.8005$ Å.

The Rietveld refinement of the data was performed with the program FullProf [35].

Table 1. Weight fractions of the phases present in the samples studied. Quantitative analysis was done using the results from the Rietveld refinement.

Sample studied	Main compound (%)	$SrWO_4$ (%)	Sr_2WO_5 (%)
Sr_2NiWO_6	97.0	0.8	2.2
Sr_2ZnWO_6	98.7	0.3	1.0
Sr_2CoWO_6	97.9	—	2.1
Sr_2CuWO_6	91.2	5.0	3.8

Table 2. Crystal structure data and refinement results for Sr_2MWO_6 (M = Ni, Zn, Co, Cu). The atomic positions were refined in the space group $I4/m$. (The five atoms in the asymmetric unit occupy the following sites: W 2a (0, 0, 0); Ni, Zn, Co or Cu 2b (0, 0, 1/2); Sr 4c (0, 1/2, 1/4); O1 8h (x, y, 0) and O2 4e (0, 0, z).)

	Sr_2NiWO_6	$Sr_2ZnWO_6^a$	Sr_2CoWO_6	Sr_2CuWO_6
a (Å)	5.5608(1)	5.5973(2)	5.5820(1)	5.4291(1)
c (Å)	7.9191(1)	7.9889(3)	7.9774(1)	8.4154(1)
O1 (x)	0.209(2)	0.202(2)	0.201(1)	0.202(1)
O1 (y)	0.280(2)	0.292(2)	0.274(1)	0.298(1)
O2 (z)	0.244(1)	0.241(2)	0.238(1)	0.224(1)
R_p (%)	8.58	9.72	11.8	15.3
R_{wp} (%)	10.2	12.1	16.3	15.9
R_{exp} (%)	4.96	5.37	7.63	8.57
χ^2	4.23	5.08	4.26	3.45

[a] The data for the structure of Sr_2ZnWO_6 are at 100 °C. For the rest of the compounds, the data correspond to the room temperature structures.

Small quantities of $SrWO_4$ and Sr_2WO_5 impurities were found to be present in our samples—see table 1—and were treated as known additional phases in a multiphase refinement (no structural parameters of the impurities were refined).

The diffraction data obtained confirmed the complete ordering of the B site cations. The difference in oxidation state between the B and B′ cations is 4, which guaranties the complete ordering of the cations [10]. This affirmation is also supported by the great difference between the ionic radii [36] of the W^{6+} cation (0.74 Å) and the M cations (Ni^{2+} (0.83 Å), Zn^{2+} (0.88 Å), Co^{2+} (0.885 Å) or Cu^{2+} (0.87 Å)). No indications of oxygen deficiency were observed.

4. Results and discussion

The results obtained for the crystal structures of the compounds discussed in this work and the reliability parameters of the refinements are given in tables 2–4.

In table 5 we have summarized available structural data from previous works together with the results that we have obtained for the room temperature (100 °C for Sr_2ZnWO_6) phase of each of the title compounds. The a and c unit cell parameters for the tetragonal phase are shown in the first two columns of the table. In the third column we have placed the $c/a\sqrt{2}$ parameter, a measure of the cubicity of the metrics of the lattice. It is worth noting the significant difference between the values of this parameter for the Cu-containing compound ($c/a\sqrt{2} \approx 1.10$) and the rest of the compounds ($c/a\sqrt{2} \approx 1.01$). This fact is related to the presence of the Jahn–Teller Cu^{2+} ion, responsible for the deformation of the octahedra in which it is located. This, in turn, deforms the unit cell. The deformation of the octahedra is also seen in the following three columns where we have reported the values for the basal oxygen–cation distance and sagittal oxygen–cation distance and the ratio between them in the

Table 3. Crystal structure data for Sr_2ZnWO_6 at room temperature. The atomic positions were refined in the space group $P2_1/n$. ($a = 5.6312(1)$ Å; $b = 5.6063(1)$ Å; $c = 7.9222(1)$ Å; $\beta = 89.958(1)°$; $R_p = 5.60\%$; $R_{wp} = 7.58\%$; $R_{exp} = 4.54\%$; $\chi^2 = 2.79$.)

Atom	Site	x	y	z	B (Å^2)
W	2a	0	0	0	0.12(1)
Zn	2b	0	0	1/2	0.37(1)
Sr	4e	−0.0020(4)	0.5084(1)	0.2503(1)	0.54(1)
O1	4e	0.045(1)	−0.008(1)	0.236(1)	0.45(6)
O2	4e	−0.220(1)	0.261(1)	0.028(2)	0.45(6)
O3	4e	0.251(1)	0.220(1)	−0.021(2)	0.45(6)

Table 4. Crystal structure data for Sr_2CoWO_6 at $-73\,°C$. The atomic positions were refined in the space group $P2_1/n$. ($a = 5.61448(4)$ Å; $b = 5.58862(4)$ Å; $c = 7.89992(5)$ Å; $\beta = 89.964(1)°$; $R_p = 12.5\%$; $R_{wp} = 16.4\%$; $R_{exp} = 9.6\%$; $\chi^2 = 2.88$.)

Atom	Site	x	y	z	B (Å^2)
W	2a	0	0	0	0.17(1)
Co	2b	0	0	1/2	0.50(3)
Sr	4e	−0.0032(7)	0.5091(3)	0.2490(2)	0.43(2)
O1	4e	0.048(2)	−0.006(2)	0.248(1)	0.3(1)
O2	4e	−0.215(2)	0.272(2)	0.033(2)	0.3(1)
O3	4e	0.252(2)	0.232(2)	−0.023(3)	0.3(1)

MO_6 octahedra. Note that in the copper compound the above mentioned ratio is ≈ 1.2 and in the rest of the compounds it is ≈ 1.0. The next column gives the angle of rotation of the WO_6 octahedra around the c axis. This angle has been calculated from the atomic positions given in the literature references or obtained in the present work. In the case of Sr_2NiWO_6 it is worth noting the big difference between the two values calculated from the literature data. The column heading T_c stands for the temperature of the transition from the tetragonal phase to the cubic phase. Important differences can be observed among the values of the temperatures reported by the different authors. The cause of the scatter in these values is not clear and could be related to both synthesis and measurement conditions. This effect could be why some authors have observed, for instance in the Sr_2ZnWO_6 compound, a tetragonal phase at room temperature instead of a monoclinic one, as in the present work. We performed two independent syntheses of Sr_2ZnWO_6; however, no significant differences between the corresponding transition temperatures were observed for the two samples. The last column gives the pseudosymmetry parameter Δ, obtained as the maximum atomic displacement in the pseudosymmetry search. The presence of pseudosymmetry indicates that there is a high probability of the compound undergoing a continuous phase transition at high temperature by means of which it could adopt a more symmetric structure. For one compound to be considered pseudosymmetric, there are two conditions that must be fulfilled [45]: the Δ parameter must be less than approximately 1 Å; and the unit cell must be suitable for this pseudosymmetry (in our case, pseudo-cubic). Sr_2NiWO_6, Sr_2CoWO_6 and Sr_2ZnWO_6 comply with these two conditions and we consider them pseudosymmetric with space group $Fm\bar{3}m$. Sr_2CuWO_6, however, has a unit cell that is not pseudo-cubic. For this reason the pseudosymmetry in this compound is limited to the minimal supergroup $I4/mmm$, which requires the same atomic displacements as $Fm\bar{3}m$ and is compatible with the unit cell of the room temperature phase.

Table 5. Structural details and phase transition temperatures of the title compounds. The data shown are as follows: literature reference ('Ref.'); lattice constants (a, c); M–O1 and M–O2 distances inside the MO$_6$ octahedra (d_1, d_2); angle of rotation of the WO$_6$ octahedra around the c axis (φ); temperature of the phase transition from the tetragonal to the cubic phase (T_c); pseudosymmetry parameter for the $Fm\bar{3}m$ space group (Δ). 'PW' stands for present work.

Compound	Ref.	a (Å)	c (Å)	$c/a\sqrt{2}$	d_1 (Å)	d_2 (Å)	d_2/d_1	φ (deg)	T_c (°C)	Δ (Å)
Sr$_2$NiWO$_6$										
	[37]	5.56	7.91	1.01	—	—	—	—	400	—
	[26]	5.575	7.918	1.004	—	—	—	—	300	—
	[38]	5.559	7.918	1.007	—	—	—	—	260	—
	[13]	5.559	7.918	1.007	2.029	2.051	1.011	1.4	307	0.09
	[39]	5.5571	7.9131	1.0069	2.042	2.018	0.988	7.3	—	0.49
	PW	5.5608	7.9191	1.0070	2.029	2.027	0.999	8.3	315	0.56
Sr$_2$ZnWO$_6$										
tetragonal	[37]	5.60	8.01	1.0114	—	—	—	—	570	—
	[26]	5.579	7.976	1.0109	—	—	—	—	430	—
	[20]	—	—	—	—	—	—	—	400[a]	—
	PW[b]	5.5973	7.9889	1.0092	2.034	2.068	1.016	10.3	500	0.71
Sr$_2$CoWO$_6$										
	[37]	5.58	7.98	1.0112	—	—	—	—	—	—
	[26]	5.596	7.978	1.0081	—	—	—	—	400	—
	PW	5.5820	7.9774	1.0106	2.092	2.090	0.999	8.7	430	0.58
Sr$_2$CuWO$_6$										
	[40]	5.42	8.40	1.10	—	—	—	—	—	—
	[41]	5.431	8.410	1.095	—	—	—	—	920	—
	[14, 20][c]	5.422	8.395	1.095	1.9384	2.2834	1.1780	8.9	897	0.60
	[42]	5.426 93	8.4087	1.0956	1.9604	2.3250	1.1860	10.5	—	0.70
	[43]	5.4315	8.4024	1.0939	—	—	—	—	—	—
	[44]	5.4290	8.4155	1.0961	1.9339	2.3227	1.2010	8.6	—	0.58
	PW	5.4291	8.4154	1.0961	1.955	2.322	1.188	10.9	920	0.74

[a] This value was taken from a figure.

[b] At 100 °C.

[c] Measurements obtained with neutron powder diffraction. All other results are obtained with x-ray powder diffraction.

4.1. Sr$_2$NiWO$_6$

This compound was extensively studied in the past and its structural, electric and magnetic properties are considered well known [3, 26, 37, 38]. The crystal structure at room temperature has been reported several times [13, 39] (table 5). It was found to have the $I4/m$ space group. There are some small differences in the structural details reported by different authors; anyway, our pseudosymmetry test gives the same result for all of them: the $Fm\bar{3}m$ space group, but with different values for the Δ parameter. There is one phase transition observed previously in Sr$_2$NiWO$_6$. It changes the symmetry from tetragonal $(I4/m)$ to cubic $(Fm\bar{3}m)$. In order to confirm the presence of this transition in our sample, we obtained 28 diffraction profiles at different temperatures with a step of 15 °C. For the representation of the diffraction intensities in figure 2 a greyscale is used (black for the highest intensities and white for the lowest). The measurements at different temperatures are grouped to form a Guinier camera-like image. As seen from the figure, at about 315 °C a splitting of some diffraction lines occurs. The phase above this temperature is indexed as $Fm\bar{3}m$ and the phase below as tetragonal and body centred, presumably $I4/m$, since no other change is observed between 315 °C and room temperature. The temperature dependence of the unit cell parameters is obtained from the positions of the
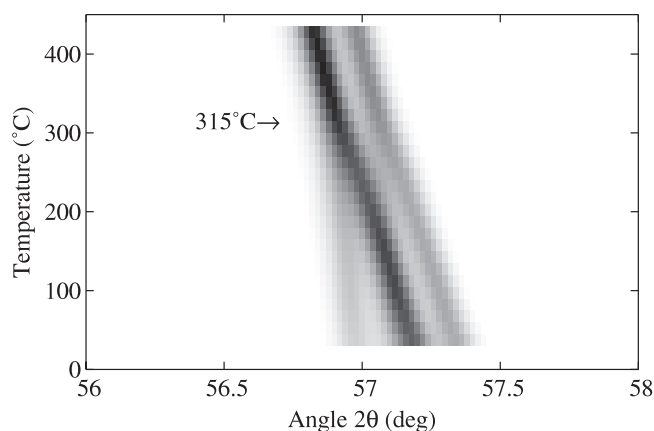
Figure 2. The temperature evolution of the (422) cubic reflection of Sr_2NiWO_6. The continuous phase transition from the cubic to the tetragonal phase at 315 °C is evidenced by the splitting of the diffraction line.
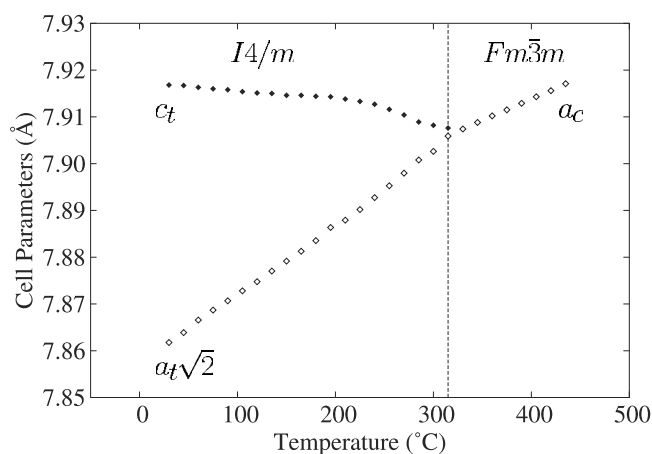

Figure 3. The temperature behaviour of the unit cell parameters of Sr_2NiWO_6. There is a continuous phase transition at about 315 °C changing the structure from cubic at high temperatures to tetragonal ($c > a\sqrt{2}$) at low temperatures. Subscripts t and c stand for tetragonal and cubic, respectively.

diffraction lines at each temperature; see figure 3. The unit cell transforms, in a continuous way, from tetragonal at low temperatures to cubic above 315 °C.

A phase transition with the $Fm\bar{3}m$–$I4/m$ symmetry change is observed also in some other ordered double perovskite materials [21], as well as in a number of fluoride and bromide elpasolites [46]. The order parameter of this transition is related to the angle of rotation of the BO_6 and $B'O_6$ octahedra. The tetragonal distortion of the unit cell is a result of the homogeneous strain coupled to the order parameter. This transition takes place due to the mismatch between the size of the A site cation (Sr^{2+}) and the cuboctahedral interstitial space between the BO_6 and $B'O_6$ octahedra and also due to the softening of the Γ_4^+ phonon [47].

When the pseudosymmetry search is restricted to the minimal supergroups, the result obtained for Sr_2NiWO_6 is that it has pseudosymmetry with the $I4/mmm$ space group. It should be pointed out that, for the case of double perovskite structures with $I4/m$ space
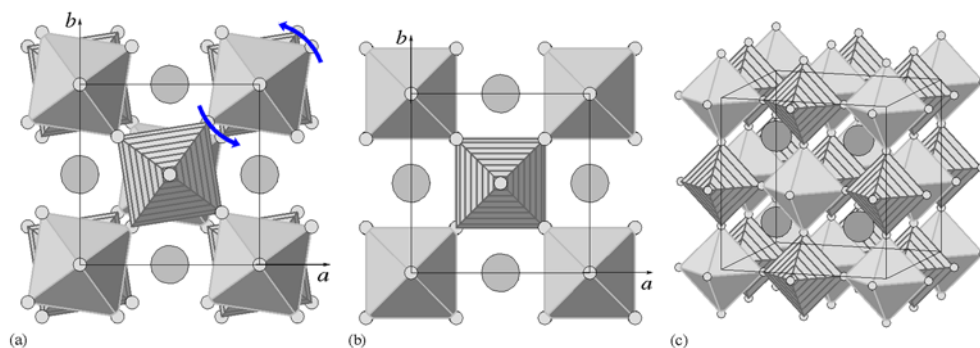
Figure 4. Ordered perovskite structure models with space groups $I4/m$ (a) and $I4/mmm$ (b). In the structure in (a) the octahedral units are rotated about the c axis. The order parameter of a possible transition between these two structures would be related to the angle of rotation φ of the octahedra. In $I4/m$, $\varphi \neq 0$; in $I4/mmm$, $\varphi = 0$. Part (c) represents the archetype structure (no cation displacements or octahedral rotations and distortions) of 1:1 ordered double perovskite with $Fm\bar{3}m$ symmetry. Note that the unit cell is different for the cubic structure with respect to the tetragonal; a and b lattice constants now coincide with the diagonals of the a–b faces of the tetragonal cell.

(This figure is in colour only in the electronic version)

group, $I4/mmm$ is the only minimal supergroup that can be accessed with displacements of the atoms.

As a result of this pseudosymmetry, new symmetry elements appear: for example, two mirror planes in the a–c and b–c planes. From a microscopic point of view this is represented by the rotation of the octahedral units in the a–b plane until the oxygen atoms O1 reach the diagonal planes (figures 4(a), (b)). If the rotation of the octahedra was the only effect in the material, the high temperature symmetry should be $I4/mmm$. However, the disappearance of the homogeneous strain (tetragonal distortion), coupled to the rotation, makes the high temperature symmetry $Fm\bar{3}m$ instead of $I4/mmm$. In the present analysis the fact that the tetragonal distortion of the unit cell is small is an important point. Actually, the unit cell of this compound is pseudo-cubic. Therefore, if we try to predict the high temperature structure, it is reasonable to expect that this (very small) distortion will disappear (the Sr$_2$CuWO$_6$ compound, presented further in this work, shows that this is not always the case). Although the group–subgroup chain connecting $Fm\bar{3}m$ and $I4/m$ includes $I4/mmm$ as an intermediate group, the phase transition discussed is performed in one step. We can state that the observed $I4/m$–$Fm\bar{3}m$ continuous phase transition is consistent with the pseudosymmetry found in Sr$_2$NiWO$_6$.

4.2. Sr$_2$ZnWO$_6$

Syntheses of this compound have been reported on several occasions (table 5); however, no structural determination was performed. According to [37] and [26] (PDF 15-572) the room temperature structure of Sr$_2$ZnWO$_6$ is tetragonal. This result was later confirmed in [48]. In another study [20], the room temperature structure is reported as monoclinic, $C2/m$, which transforms to tetragonal at about 60 °C. In spite of these differences, all authors agree that this compound shows a continuous tetragonal–cubic phase transition (table 5).

It was not possible to perform the pseudosymmetry test for this compound, because no data for the atomic positions were found in the literature. In order to fill this gap, a structural study was necessary. The assumption that the room temperature structure of Sr$_2$ZnWO$_6$ is tetragonal
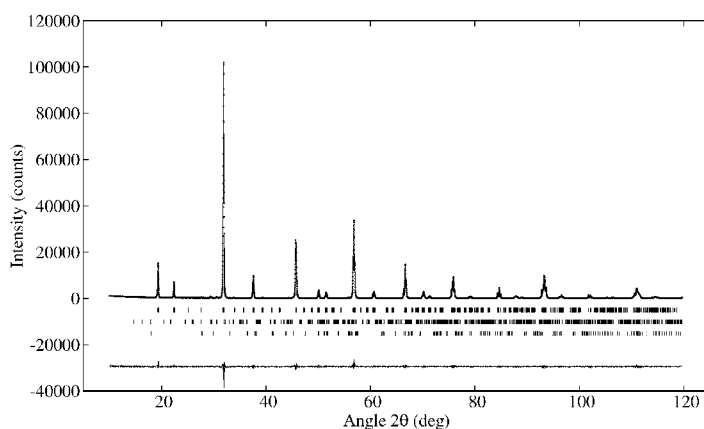
Figure 5. Observed (·), calculated (——) and difference profiles for the Rietveld refinement of Sr_2ZnWO_6 at room temperature using a structural model with the $P2_1/n$ space group. The impurities $SrWO_4$ and Sr_2WO_5 are included in the refinement as known additional phases.
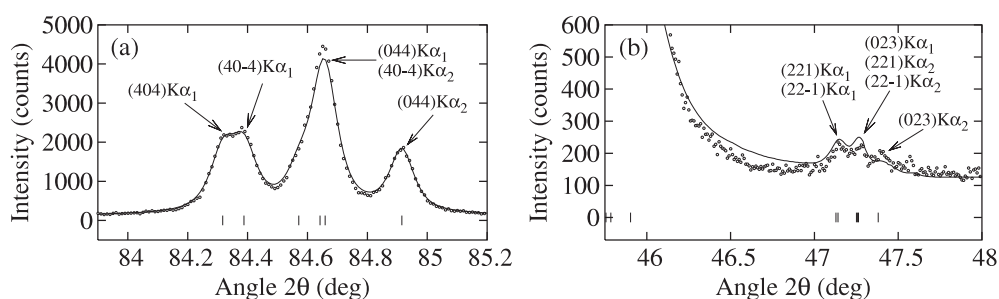

Figure 6. Refinement of the structure of Sr_2ZnWO_6 in the $P2_1/n$ space group accounts for the peak shapes (a) and the very low intensity peaks (b) presented in the diffraction pattern.

was ruled out on the basis of the x-ray diffraction data (figure 5), where a number of unindexed lines were found. The automatic indexing procedures pointed to a possible orthorhombic structure; however, the shapes of some peaks could not be explained. This problem was solved by adopting a monoclinic unit cell with angle β very close to 90°; see figure 6(a). After having included in the refinement the known impurities, just a few lines with relative intensities less than 0.1% remained unindexed. In order to assign the correct symmetry we tested all the space groups expected for an ordered perovskite structure (figure 1). Best results for the refinement parameters were obtained for the $P2_1/n$ space group ($a^+b^-b^-$ octahedral tilt system). The previously suggested $C2/m$ [20] space group ($a^0b^-b^-$ tilt system) did not account for some peaks with relative intensities of up to 0.2% (figure 6(b)). Although the $P2_1/n$ space group was taken into consideration in order to explain some very weak diffraction peaks, the improvement of the reliability parameters was significant. This allows us to affirm that the $P2_1/n$ space group describes the room temperature structure of Sr_2ZnWO_6 better than $C2/m$. It should be pointed out that $P2_1/n$ is the space group most frequently found for the symmetry of the monoclinic perovskites. The refined structural parameters are shown in table 3. The unit cell of Sr_2ZnWO_6 at room temperature is shown in figure 7.

The temperature evolution of some diffraction lines is shown in figure 8; and the temperature dependence of the lattice parameters of Sr_2ZnWO_6 is shown in figure 9. The
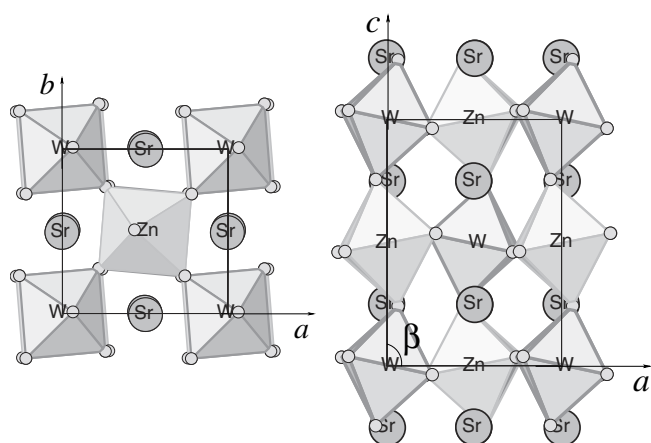
Figure 7. A schematic representation of the structure of Sr_2ZnWO_6 in the monoclinic phase. The tilt system that corresponds to the $P2_1/n$ space group is $a^+b^-b^-$.
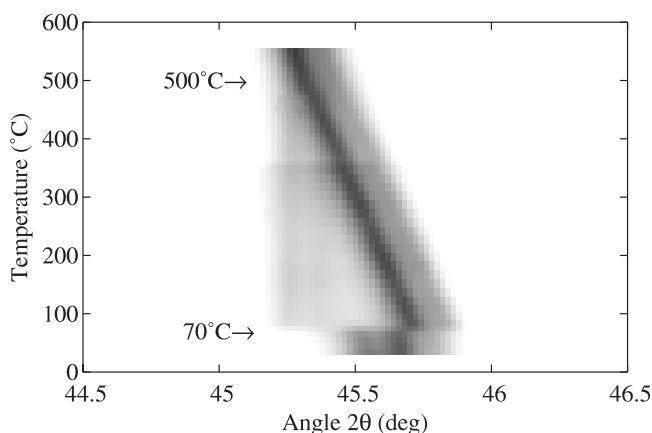

Figure 8. The temperature evolution of the (400) cubic reflection of Sr_2ZnWO_6. The continuous phase transition from the cubic to the tetragonal phase at $500\,°C$ is evidenced by the splitting of the diffraction line. The discontinuity of the diffraction line at $70\,°C$ reveals the presence of a second phase transition in this compound.

diffraction pattern at temperatures higher than $500\,°C$ was indexed with a cubic unit cell and the extinction conditions were compatible with the $Fm\bar{3}m$ space group. We observed a splitting in some lines at temperatures below $500\,°C$. This splitting can be explained by considering a tetragonal distortion of the unit cell. Analysing the extinction conditions, the unit cell of this tetragonal phase was identified as body centred. The space groups considered were $I4/mmm$, $I4/m$ and $I4mm$. No reliable structural determination could be performed at these temperatures, but there are indications that the correct space group for the tetragonal phase is $I4/m$, rather than $I4/mmm$ or $I4mm$. For instance, in figure 1, the only possible body centred tetragonal space group is $I4/m$ (corresponding to the $a^0a^0c^-$ tilt). Both groups, $I4/mmm$ and $I4mm$, involve some deformations of the octahedral units but not tilts and rotations, which are the modifications of the perovskite structure most frequently observed. The crystal structure at $100\,°C$ was refined in the $I4/m$ space group and details are given in table 2.
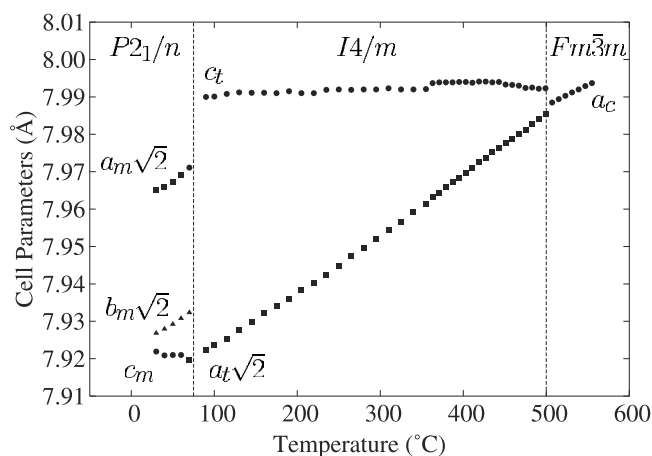
Figure 9. The temperature behaviour of the unit cell parameters of Sr_2ZnWO_6. The high temperature structure of this compound is cubic. Below $500\,^\circ C$ it transforms to tetragonal. There is also another phase transition at about $70\,^\circ C$, changing the symmetry from tetragonal to monoclinic. The data shown in this figure are obtained from two different x-ray diffraction measurements: one covering the temperature range from room temperature to $350\,^\circ C$ and the second that from 350 to $560\,^\circ C$.

The high temperature phase transition from $Fm\bar{3}m$ to $I4/m$ is continuous. In the DSC measurements we did not find any thermal effect at the temperature of this phase transition, which can be considered as a confirmation of its continuous character. It is important to point out that a symmetry change of the type $Fm\bar{3}m$–$I4/m$ is allowed by the Landau theory of phase transitions to be continuous, while the $Fm\bar{3}m$–$I4/mmm$ change is not [49].

We also observed another phase transition at about $70\,^\circ C$. This transition is discontinuous and changes the symmetry from tetragonal ($I4/m$) to monoclinic (presumably $P2_1/n$, since no other change is observed in the diffractogram between $70\,^\circ C$ and room temperature). The first order type of this transition is consistent with the fact that there is no group–subgroup relation between $I4/m$ and $P12_1/n1$. The DSC measurements (figure 10) revealed a thermal hysteresis of $11\,^\circ C$ for this transition when the sample was heated and cooled at a $10\,^\circ C\ min^{-1}$ rate.

The observed phase transition sequence, $Fm\bar{3}m$–$I4/m$–$P2_1/n$, connects the three space groups most frequently found for ordered perovskites. Such a sequence is also found for some fluoride elpasolites [46].

4.3. Sr_2CoWO_6

This compound was reported to have a tetragonal unit cell (table 5) at room temperature [26, 37]. However, as in the case of Sr_2ZnWO_6, no atomic positions have been reported prior to the present work[3]. Sr_2CoWO_6 is known to have one structural phase transition changing the symmetry from tetragonal to cubic [26]. We have refined the room temperature structure in the $I4/m$ space group (table 2). The pseudosymmetry test showed similar results to those for Sr_2NiWO_6 but with a slightly higher value of the Δ parameter.

The temperature evolution of the structure of Sr_2CoWO_6 is essentially the same as that of Sr_2NiWO_6, with the only difference being that the $Fm\bar{3}m$–$I4/m$ transition occurs at a higher temperature (figures 11 and 12). This phase transition is continuous.

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[3] During the publication process the authors became aware of the recent work [50] where results similar, but not identical, to those presented here are reported.
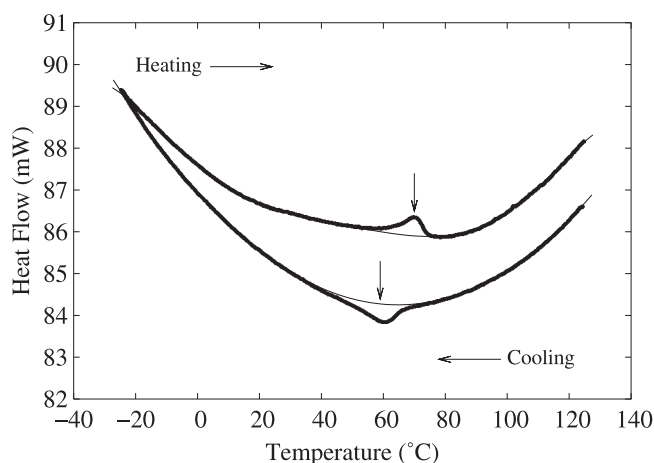
Figure 10. DSC measurement results for Sr$_2$ZnWO$_6$. The measured enthalpy of the phase transition is 0.28(1) J g^{-1}. Thick lines represent the experimental data. Thin lines are polynomial fits to the experimental data in the regions far from the phase transitions. Arrows point to the observed thermal anomalies.
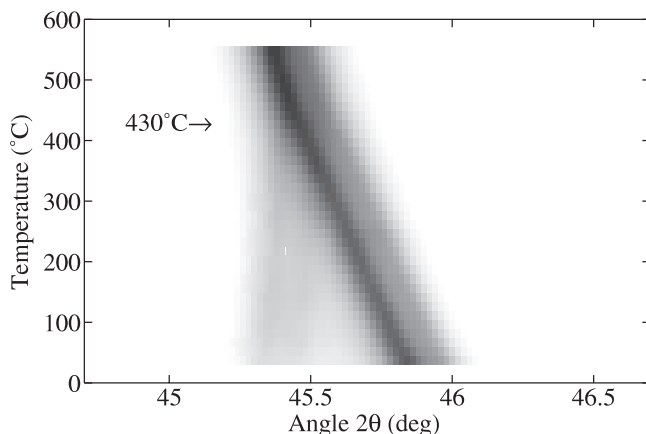

Figure 11. The temperature evolution of the (400) cubic reflection of Sr$_2$CoWO$_6$. At 430 °C a continuous splitting appears, evidencing the presence of a second order phase transition from a cubic to a tetragonal phase.

The unit cell parameters of Sr$_2$CoWO$_6$ at room temperature are very close to those of Sr$_2$ZnWO$_6$ at 70 °C. This fact and the assumption that the structural properties of the two compounds are similar, were the reasons for expecting another transition in Sr$_2$CoWO$_6$ equivalent to the first order transition at 70 °C observed in Sr$_2$ZnWO$_6$. Such a transition was found at about −15 °C (figure 13). The structure of Sr$_2$CoWO$_6$ at −73 °C was refined in the $P2_1/n$ space group using synchrotron-radiation diffraction data and the structural details are shown in table 4.

4.4. Sr$_2$CuWO$_6$

The first successful synthesis of Sr$_2$CuWO$_6$ was reported in [40]. The room temperature symmetry was found to be tetragonal with $c/a\sqrt{2} = 1.10$. The important tetragonal distortion was explained [40] by the cooperative Jahn–Teller effect. The room temperature crystal
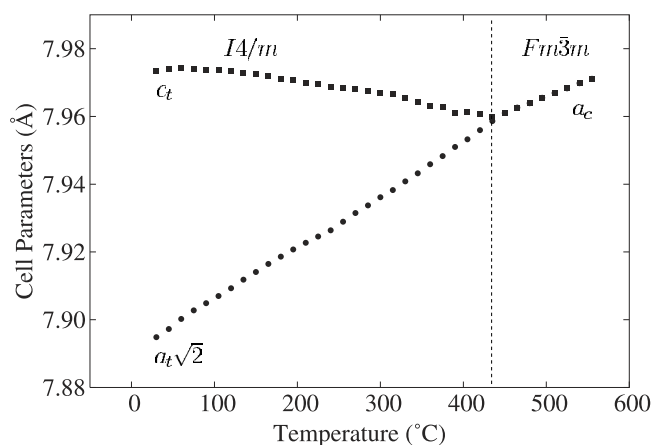
Figure 12. The temperature behaviour of the unit cell parameters of Sr_2CoWO_6. The high temperature structure of this compounds is cubic ($Fm\bar{3}m$). At about $430\,°C$ it transforms to tetragonal ($I4/m$ with $c > a\sqrt{2}$). This symmetry is preserved down to room temperature.
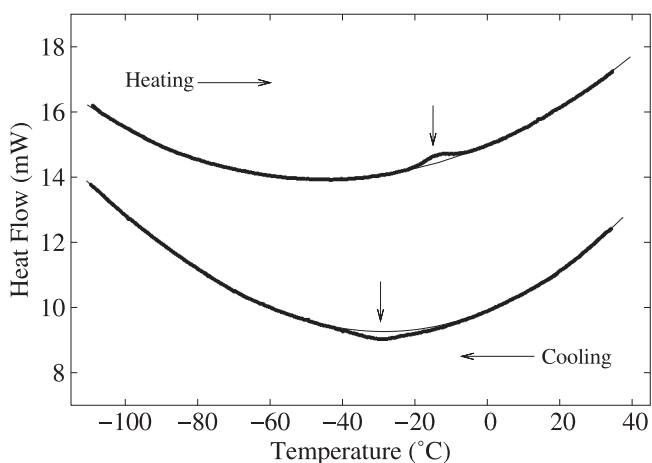

Figure 13. DSC measurement results for Sr_2CoWO_6. The measured enthalpy of the phase transition is $0.12(1)$ $J\,g^{-1}$. Thick curves represent the experimental data. Thin curves are polynomial fits to the experimental data in the regions far from the phase transitions. Arrows point to the observed thermal anomalies.

structure of this compound was determined in [14] on the basis of neutron powder diffraction measurements. According to the reported atomic positions, the octahedral units of the structure are slightly rotated about the tetragonal c axis. The CuO_6 octahedra were found to be strongly elongated along the same c axis, while the WO_6 octahedra were reported to be almost regular. The space group assigned was $I4/m$. These results were later confirmed by other authors [42, 44]. Pseudosymmetry with the $I4/mmm$ space group was found with very close values of the Δ parameter for the different refinements (see table 5). A phase transition in Sr_2CuWO_6 was reported at $920\,°C$ [41, 51]. This transition was classified as ferroelectric, although no experimental results or structural details were given. In [20] a first order phase transition was found at $897\,°C$, changing the symmetry from $Fm\bar{3}m$ at high temperature to $I4/m$ at low temperature. In that work no ferroelectric properties were reported (note that such

properties are not allowed in the centrosymmetric group $I4/m$). Both works attributed the origin of the observed phase transition as the Jahn–Teller effect. Although there is a difference of 23 °C between the reported temperature values, we assume that they refer to the same phase transition.

In the analysis of the temperature evolution of Sr$_2$CuWO$_6$ there is one important point that does not seem to have been stressed earlier. As mentioned, at room temperature the CuO$_6$ octahedra are not only stretched, which should lead to a structure with the $I4/mmm$ space group, but they are also rotated. This rotation does not change the environment of the Cu atoms and therefore the Jahn–Teller effect cannot be the only mechanism giving rise to the room temperature symmetry, as considered until now. Assuming two different mechanisms (octahedral rotations and Jahn–Teller distortions), there are two possible scenarios for the temperature evolution of the structure of Sr$_2$CuWO$_6$. In the first, the two mechanisms are coupled and there is only one phase transition lowering the symmetry from $Fm\bar{3}m$ at high temperature directly to $I4/m$ at low temperature. In the second scenario, the two mechanisms are independent and two phase transitions are present: one of the Jahn–Teller type, changing the symmetry from $Fm\bar{3}m$ to $I4/mmm$; and the other one, at lower temperature, rotating the octahedra and leading to $I4/m$.

In order to study the temperature behaviour of the structure of Sr$_2$CuWO$_6$ we performed conventional x-ray powder diffraction measurements. The results, obtained for the room temperature structure (table 2), are in good agreement with the previously reported ones. As in the previous cases, the search for phase transitions was carried out by performing diffraction measurements at different temperatures. The temperature dependence of the unit cell parameters, as calculated from the positions of the diffraction lines at each temperature, is shown in figure 14. At 920 °C a strong discontinuous phase transition was observed (figures 14, 15(b)). The high temperature phase was indexed as cubic $Fm\bar{3}m$ and the low temperature one as tetragonal, body centred. No changes in the set of observed reflections were found below this temperature, suggesting that the unit cell does not change in the temperature range from 920 °C to room temperature. However, at about 670 °C a change in the intensity of some peaks is observed (figure 16). This change was found to be reversible in temperature and was repeatedly confirmed in several independent diffraction measurements of samples from two syntheses. As seen in figure 16 the intensity of the (222) reflection is, more or less, constant above 670 °C and gradually decreases below this temperature. This behaviour is compatible with a continuous phase transition. In order to verify whether such a change of intensity could be produced by a $I4/m$–$I4/mmm$ phase transition, we performed simulations of the diffraction pattern for different values of the rotation angle (φ) of the octahedra, assuming these as rigid. In a double perovskite structure with the $I4/mmm$ space group the octahedra are not rotated, the φ angle is zero and therefore there is no change in the intensity of the (222) reflection with the temperature. In a double perovskite structure with the $I4/m$ space group, however, the octahedra are rotated. In this case, there is a change in the intensity of the (222) reflection with the rotation angle: the bigger the value of the rotation angle, the smaller the height of the peak. Thus, the assumption that there is a continuous phase transition at 670 °C, for which the order parameter is proportional to the rotation angle, could explain the behaviour observed in the (222) reflection.

Finally, further evidence of the presence of a phase transition at 670 °C is provided by the anomalous behaviour of the positions of almost all diffraction lines around this temperature. The normal situation is that the lines change their position monotonically with the temperature, due to the thermal expansion. However, as can be seen in figure 15, the behaviour in this case is more complex. On our assumption that at 670 °C there is a phase transition under way, this anomaly can be explained as produced by the homogeneous strain coupled to the order
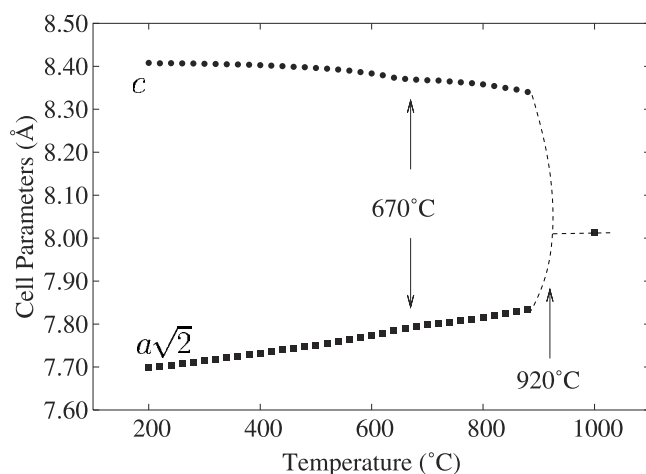
Figure 14. Temperature behaviours of the unit cell parameters of Sr_2CuWO_6. At about 920 °C a strong first order phase transition is observed that changes the unit cell from cubic to tetragonal. Between 900 and 1000 °C the two phases coexist and the cell parameters were not determined. At about 670 °C, a small effect is observed, which could be related to the second phase transition.
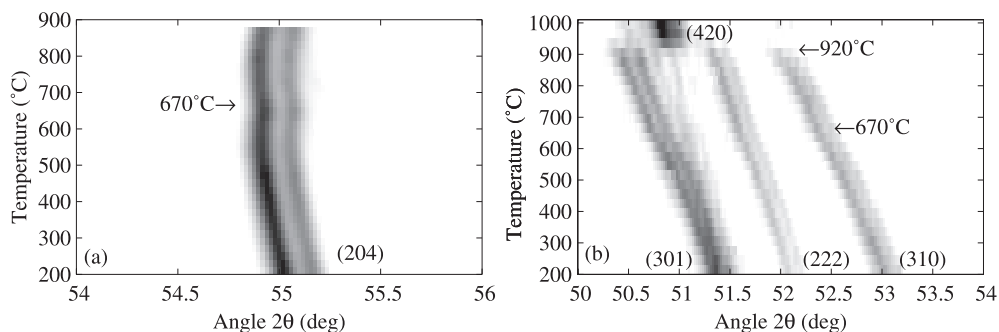

Figure 15. Sections of the x-ray powder pattern of Sr_2CuWO_6, showing the temperature evolutions of selected diffraction peaks. The data were collected with a temperature step of 20 °C. The intensity scales used on the two figures are different, in order to account for the different relative intensities. (a) (204) tetragonal reflection with a relative intensity of 25%. Anomalous behaviour of the position of this reflection around 670 °C is observed. This is interpreted as evidence for the presence of a tetragonal–tetragonal phase transition. (b) (420) cubic reflection and the group of tetragonal reflections originating from it after the first order transition at 920 °C. The anomalous behaviour of the positions around 670 °C can be observed in all the reflections represented in the figure. At high temperatures the (116) reflection of the impurity $SrWO_4$ is also observed close to the (301) tetragonal reflection of Sr_2CuWO_6. The relative intensity of the (310) tetragonal reflection is about 2.2%.

parameter. It is not easy to observe a transition of the type $I4/mmm$–$I4/m$, because the two space groups have the same extinction conditions (no peak splitting or appearance of new peaks is expected). It should also be pointed out that the refinement of the room temperature structure in the $I4/m$ space group gives better reliability parameters than the refinement in the $I4/mmm$ group, although the difference is small. This is due to the fact that x-ray diffraction is not very sensitive to the positions of the oxygen atoms. The fact that the transition is continuous and at relatively high temperature makes most of the thermal analysis methods unsuitable for its
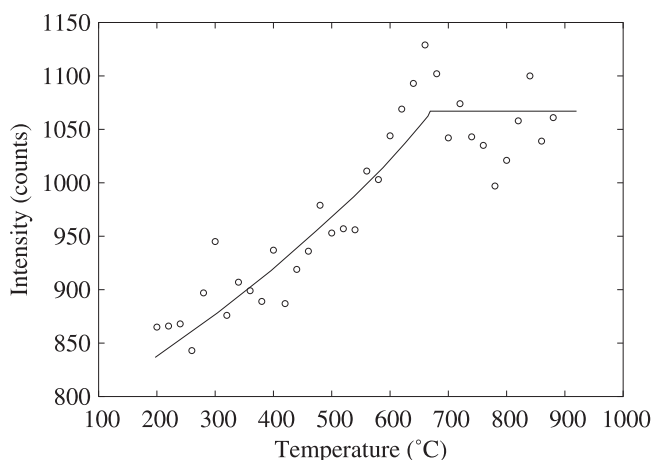
Figure 16. The change of the intensity of the (222) diffraction reflection with temperature; $\bigcirc$: experimental data; ——: a guide to the eye. This reflection, with a relative intensity of about 1.3%, is among the most sensitive to the octahedral rotations expected at a phase transition changing the symmetry from $I4/m$ to $I4/mmm$.

detection. However, in our opinion, the experimental evidence presented here is enough to affirm the existence of such a transition. The mechanism of this $I4/m$–$I4/mmm$ transition is of the same type as that of the $I4/m$–$Fm\bar{3}m$ transition found in the other compounds reported in the present work and in some other oxide materials with double perovskite structure.

In conclusion we suggest that the lowering of the symmetry from $Fm\bar{3}m$ to $I4/m$ in Sr₂CuWO₆ is performed in two steps, $Fm\bar{3}m$–$I4/mmm$–$I4/m$, and not just in one as previously reported [20]. We consider two independent phase transition mechanisms, which could explain the structural behaviour of Sr₂CuWO₆.

5. Conclusions

The temperature evolution of the structures of Sr₂MWO₆ (M = Ni, Zn, Co, Cu) has been studied using the x-ray powder diffraction method and DSC. Sr₂NiWO₆ shows one phase transition from a tetragonal structure with the $I4/m$ space group to a cubic structure with space group $Fm\bar{3}m$. Sr₂ZnWO₆ and Sr₂CoWO₆ show sequences of two phase transitions: $P2_1/n$–$I4/m$–$Fm\bar{3}m$. The sequence presented by Sr₂CuWO₆ is $I4/m$–$I4/mmm$–$Fm\bar{3}m$. The phases and phase transitions in Sr₂MWO₆ (M = Ni, Zn, Co) have been discussed in the framework of rigid octahedra rotations and it has been shown that the experimental results presented in this work are consistent with the theoretical predictions. In the case of Sr₂CuWO₆, the structure is strongly influenced by the Jahn–Teller effect. This leads to a new phase with symmetry $I4/mmm$ where the CuO₆ octahedra are elongated along the fourfold axis, but are not rotated. It has been shown that the $I4/m$–$Fm\bar{3}m$ transitions in Sr₂MWO₆ (M = Ni, Zn, Co) and the $I4/m$–$I4/mmm$ transition in Sr₂CuWO₆ are of second order and that they are in accordance with what was expected from the pseudosymmetry search.

Acknowledgments

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