

Crystal structures of the double perovskites $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$

W.T. Fu*, S. Akerboom, D.J.W. IJdo

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

Structures of the double perovskites $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ have been studied by the profile analysis of X-ray diffraction data. The end members, Ba_2SrWO_6 and Ba_2CaWO_6 , have the space group $I2/m$ (tilt system $a^0b^-b^-$) and $Fm\bar{3}m$ (tilt system $a^0a^0a^0$), respectively. By increasing the Ca concentration, the monoclinic structure transforms to the cubic one via the rhombohedral $R\bar{3}$ phase (tilt system $a^-a^-a^-$) instead of the tetragonal $I4/m$ phase (tilt system $a^0a^0c^-$). This observation supports the idea that the rhombohedral structure is favoured by increasing the covalency of the octahedral cations in $\text{Ba}_2MM'\text{O}_6$ -type double perovskites, and disagrees with a recent proposal that the formation of the π -bonding, e.g., d^0 -ion, determines the tetragonal symmetry in preference to the rhombohedral one. © 2007 Elsevier Inc. All rights reserved.

Keywords: Perovskites; X-ray powder diffraction; Crystal structure

1. Introduction

The double perovskites $A_2MM'\text{O}_6$ have attracted much interest as they exhibit rich structural and physical properties. For example, the monoclinic $\text{Ba}_2\text{Bi(III)Bi(V)O}_6$ is the parent compound of the superconducting $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ system [1] with a maximum transition temperature (T_c) of about 12 K. It is known that the Pb substitution rapidly destroys the ordered arrangement of Bi(III)–Bi(V) presented in $\text{Ba}_2\text{Bi(III)Bi(V)O}_6$, resulting in a series of the phase transitions [2]. The superconductivity occurs only in a tetragonal phase region with $0.05 < x < 0.35$. On the other hand, some ordered perovskites are interesting candidates for microwave dielectric resonators widely used in today's telecommunication systems. It has been shown that the dielectric properties of the materials depend strongly on the degree of ordering [3] as well as on the ionic size which determine the symmetry of the structure [4]. Therefore, the detailed crystallographic information is of importance in understanding the material properties and for searching new materials with controllable physical properties.

Recently we have systematically investigated the room temperature structures of several double perovskite families with the formula $\text{Ba}_2\text{Ln(III)M(V)O}_6$ (Ln = lanthanides and Y and M = Ru, Ir, Sb, and Nb) in relationship with their tolerance factors t [5–8]. We showed that the monoclinic space group $P2_1/n$ or triclinic space group $P\bar{1}/\bar{1}$ once reported for many of these compounds are incorrect. $\text{Ba}_2\text{LaIrO}_6$ ($t = 0.967$) [5], $\text{Ba}_2\text{LaRuO}_6$ ($t = 0.968$) [6] and $\text{Ba}_2\text{LnSbO}_6$, (Ln = La, Pr and Nd, with $t = 0.960, 0.970$ and 0.971 , respectively) [7] all have the rhombohedral structure with the space group $R\bar{3}$. The other members containing smaller lanthanide ions with the tolerance factor above about 0.98 adopt the cubic space group $Fm\bar{3}m$. In the series of $\text{Ba}_2\text{LnNbO}_6$ [8], however, the observed space groups are $I2/m$ for Ln = La, Pr, Nd and Sm (t between 0.956 and 0.968), $I4/m$ for Ln = Eu, Gd, Tb and Dy (t between 0.970 and 0.978) and $Fm\bar{3}m$ with further decreasing the size of lanthanide ions. The occurrence of the tetragonal symmetry in the later system is quite unusual as the rhombohedral space group was observed in others similar double perovskites with comparable tolerance factors. Considering that the rhombohedral structure is seen in the systems that contain the pentavalent or trivalent ions in the right hand side of the periodic table (e.g., Ru, Ir, Sb, Bi), we speculated that the increase of the electronegativity, i.e., the covalency, at the octahedral sites favors

*Corresponding author. Fax: +31 71 5274537.

E-mail address: w.fu@chem.leidenuniv.nl (W.T. Fu).

the rhombohedral symmetry [8]. This idea seems to be supported by the analysis of the stabilization force in ABO_3 -type perovskites [9]. The rhombohedral tilt system ($a^-a^-a^-$) results, as compared to others, in the highest coulomb attraction between ions, but it maximizes, at the same time, the repulsive energy as well. Therefore, when the charge of A -cation is high and the tilting angle is small to moderate, the rhombohedral structure is preferred because the attractive term overweighs the repulsive one. Based on this assumption, the increased covalency at B -site would suggest an increase of effective charge around A , favoring thus the coordination sphere that maximizes the Coulomb attraction force.

To further examine how the nature of the octahedral cations influences the structure symmetry in some double perovskites, we have studied the system $Ba_2Sr_{1-x}Ca_xWO_6$. Interest in these compounds is twofold. Firstly, the structures reported for the end members, i.e., Ba_2SrWO_6 ($x = 0$) and Ba_2CaWO_6 ($x = 1$), are quite controversial. Kovba et al. [10] described Ba_2SrWO_6 being monoclinic at room temperature with the lattice parameters $a = 6.109 \text{ \AA}$, $b = 6.028 \text{ \AA}$, $c = 8.548 \text{ \AA}$, $\beta = 91.57^\circ$. Cox et al. [11] has, using synchrotron X-ray diffraction, determined the space group of Ba_2SrWO_6 to be $I2/m$, without giving the atomic positions. However, Khalyavin et al. [12] has defined it lately to be triclinic and refined the structure in the space group $F\bar{1}$ with the lattice parameters: $a = 8.5409 \text{ \AA}$, $b = c = 8.5860 \text{ \AA}$, $\alpha = 89.35^\circ$, $\beta = \gamma = 90.31^\circ$. Similarly, Ba_2CaWO_6 was reported by Steward and Rooksby [13], Filip'ev et al. [14] and Chi and Bauer [15] to be double cubic ($Fm\bar{3}m$). Very recently, Yamamura et al. [16] described it as tetragonal at room temperature with the space group $I4/m$. Secondly, Ca is smaller in size than Sr; substituting Sr by Ca will gradually increase the tolerance factor. Consequently, one may anticipate the occurrence of either rhombohedral structure ($a^-a^-a^-$) or tetragonal one ($a^0a^0c^-$) in $Ba_2Sr_{1-x}Ca_xWO_6$ with certain intermediate compositions. However, Ca is more electronegative than Sr. Substitution of Sr by Ca will increase the covalency of $M-O$ bonds. In addition, the high charge W(VI) cation is expected to be more covalent than e.g., Nb(V). Therefore, $Ba_2Sr_{1-x}Ca_xWO_6$ appears to be an interesting system to examine what might be the cause of structural difference observed in $Ba_2MM'O_6$ -type double perovskites. In this communication, we show that the correct space groups of the end members are monoclinic $I2/m$ and cubic $Fm\bar{3}m$, respectively. In particular, we identified the rhombohedral tilt system occurring in certain members with intermediate compositions, which is attributable to a more covalent nature of the $M/M'-O$ bonds.

2. Experimental

Samples of $Ba_2Sr_{1-x}Ca_xWO_6$ were prepared from $BaCO_3$, $SrCO_3$, $CaCO_3$ and WO_3 in alumina crucibles using the standard solid-state reaction. The stoichiometry mixtures were fine ground and were reacted first at 1000°C

over night. The resultant powders were reground and sintered between 1250 and 1350°C for several days, and finally the samples were furnace-cooled to room temperature. All syntheses were carried out in air. X-ray powder diffraction data were collected on a Philips X'Pert diffractometer, equipped with the X'celerator, using the monochromatic $CuK\alpha$ radiation in steps of 0.02° (2θ) and 8 s counting time in the range $15^\circ < 2\theta < 120^\circ$. The calculations were performed by the Rietveld method using the Rietica computer programme [18]. The polynomial function with six parameters was used to fit the background. The profiles were described using a Pseudo-Voigt function.

3. Results

X-ray powder diffraction patterns of $Ba_2Sr_{1-x}Ca_xWO_6$ are easily identified to adopt the perovskite structure (Fig. 1). The noticeable intensities of the super lattice lines at about 18° and 35° (2θ), indexed as (111) and (311), respectively, in a double cubic cell, indicate the ordered arrangement of the $(Sr,Ca)O_6$ and WO_6 octahedra. Since all observed superlattice reflections have the odd–odd–odd indices, only out-of-phase tilts of the octahedra in this system are possible. The space groups that occur in $Ba_2Sr_{1-x}Ca_xWO_6$ can be derived from the splitting of the main reflections, most easily from that of the ($h00$)-type and (hhh)-type reflections. In Fig. 2, an enlarged region containing the basic (222) and (400) reflections for some representative samples is shown. For Ba_2SrWO_6 ($x = 0$), the basic (222) reflection splits in a triplet and that of the (400) in a doublet. This is readily explained by a monoclinic distortion. Since no superlattice reflections associated with any in-phase tilt are present, the logical choice of the space group would be $I2/m$. In contrary to the observation of Yamamura et al. [16], the basic reflections of our

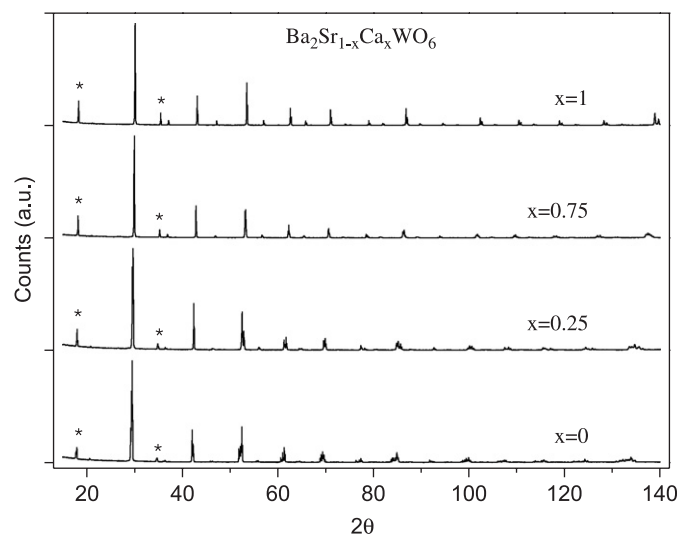


Fig. 1. X-ray powder diffraction pattern of some selected samples in $Ba_2Sr_{1-x}Ca_xWO_6$. Note the significant intensity of the (111) and (311) super lattice reflections as were marked by an asterisk (*).

Ba_2CaWO_6 samples do not show any splitting except the well-resolved $\text{K}\alpha_1$ and $\text{K}\alpha_2$ splitting (Fig. 2). Evidently, Ba_2CaWO_6 adopts the cubic space group $Fm\bar{3}m$ at room temperature. Further, an intermediate phase exists between the monoclinic and cubic phases. For the sample with

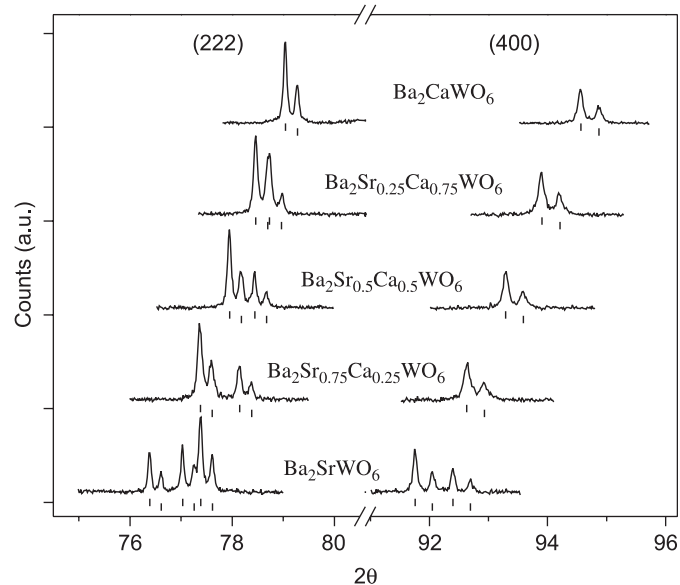


Fig. 2. Enlarged sections showing the evolution of the basic (222) and (400) reflections in $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$. Tick marks below are the positions of Bragg's reflections calculated using the space groups $I2/m$ ($x = 0$), $R\bar{3}$ ($x = 0.25, 0.5$ and 0.75) and $Fm\bar{3}m$ ($x = 1$), respectively.

$x = 0.25$, for example, the doublet of the basic (400) reflection merges to a single peak, and the splitting of the basic (222) reduced to a doublet with the intensity ratio of about 3:1. This is characteristic of a rhombohedral symmetry signifying the space group $R\bar{3}$. Clearly, the tetragonal $I4/m$ structure does not occur in $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$, since, in this case, the splitting of the basic (222) and (400) reflections would just be opposite to that in $R\bar{3}$. The rhombohedral structure persists in a wide composition range, and the cubic structure is seen only at $x \approx 1$.

The structures that occur in $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ were, therefore, modelled in the space groups $I2/m$, $R\bar{3}$ and $Fm\bar{3}m$, respectively. All Rietveld refinements using the X-ray powder diffraction data yielded satisfactory results. In Table 1, we list the refined crystallographic data of some compounds in $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$. The plots of the observed and calculated profiles are shown in Fig. 3. Table 2 gives some selected interatomic distances.

4. Discussion

The present study confirms Ba_2SrWO_6 being monoclinic with the space group $I2/m$ as was originally reported by Cox et al. [11]. This structure is derived from the cubic aristotype by ordering the Sr(II) and W(VI) cations and tilting the SrO_6/WO_6 octahedra about the primitive $[110]_p$ -axis. The tilt system of $a^0b^-b^-$ observed in Ba_2SrWO_6 is consistent with its tolerance factor ($t = 0.929$), which deviates largely from unity. As was mentioned above,

Table 1
Refined lattice parameters and atomic positions of some selected $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ in the space groups $I2/m$, $R\bar{3}$ and $Fm\bar{3}m$, respectively

Ba_2SrWO_6		$\text{Ba}_2\text{Sr}_{0.75}\text{Ca}_{0.25}\text{WO}_6$		$\text{Ba}_2\text{Sr}_{0.25}\text{Ca}_{0.75}\text{WO}_6$		Ba_2CaWO_6	
$I2/m$		$R\bar{3}$				$Fm\bar{3}m$	
a (Å)	6.10676(5)	a (Å)	6.01203(5)	a (Å)	5.95789(5)	a (Å)	8.39405(3)
b (Å)	6.03736(7)	α (deg.)	60.3968(9)	α (deg.)	60.1385 (8)		
c (Å)	8.53990(8)						
β (deg.)	90.4460(6)						
Ba	$4i$ ($x,0.5,z$)	Ba	$2c$ (x,x,x)	Ba	$2c$ (x,x,x)	Ba	$8c$ (0.25,0.25,0.25)
x	0.4955(3)	x	0.2501(1)	x	0.2488(1)	B (Å) ²	0.43(2)
z	0.2504(2)	B (Å) ²	0.60(3)	B (Å) ²	0.20(2)	Ca	$4a$ (0,0,0)
B (Å) ²	0.91(3)	Sr/Ca	$1a$ (0,0,0)	Sr/Ca	$1a$ (0,0,0)	B (Å) ²	0.79(7)
Sr	$2c$ (0.5,0,0)	B (Å) ²	0.52(3)	B (Å) ²	0.40(3)	W	$4b$ (0.5,0.5,0.5)
B (Å) ²	0.47(5)	W	$1b$ (0.5,0.5,0.5)	W	$1b$ (0.5,0.5,0.5)	B (Å) ²	0.09(2)
W	$2b$ (0,0.5,0)	B (Å) ²	0.11(3)	B (Å) ²	0.09(1)	O	$24e$ ($x,0,0$)
B (Å) ²	0.23(3)	O(1)	$6f$ (x,y,z)	O(1)	$6f$ (x,y,z)	x	0.2656(4)
O(1)	$4i$ ($x,0,z$)	x	0.231(1)	x	0.231(1)	B (Å) ²	1.8(1)
x	0.563(2)	y	0.315(1)	y	0.315(1)		
z	0.270(2)	z	0.7083(7)	z	0.7083(7)		
B (Å) ²	1.5(3)	B (Å) ²	1.3(1)	B (Å) ²	1.1(1)		
O(2)	$8j$ (x,y,z)						
x	0.235(1)						
y	0.279(1)						
z	0.034(1)						
B (Å) ² *	1.4(2)						
$R_{\text{wp}} = 11.93\%$, $R_{\text{p}} = 8.69\%$, $R_{\text{B}} = 3.12\%$, $\chi^2 = 2.04$		$R_{\text{wp}} = 8.57\%$, $R_{\text{p}} = 6.66\%$, $R_{\text{B}} = 2.73\%$, $\chi^2 = 2.05$		$R_{\text{wp}} = 8.01\%$, $R_{\text{p}} = 6.28\%$, $R_{\text{B}} = 3.49\%$, $\chi^2 = 1.46$		$R_{\text{wp}} = 10.63\%$, $R_{\text{p}} = 7.71\%$, $R_{\text{B}} = 2.37\%$, $\chi^2 = 3.23$	

Table 2
Selected interatomic distances (Å) in $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$

	Ba_2SrWO_6	$\text{Ba}_2\text{Sr}_{0.75}\text{Ca}_{0.25}\text{WO}_6$	Ba_2CaWO_6
(Sr,Ca)–O(1)	2.461(13) 2 ×	2.361(9) × 6	2.223(4) × 6
(Sr,Ca)–O(2)	2.338(9) 4 ×		
W–O(1)	2.003(13) 2 ×	1.936(9) 6 ×	1.974(4) 6 ×
W–O(2)	1.978(7) 4 ×		
Ba–O(1)	2.705(11) 1 ×	2.791(2) 4 ×	2.9703(2) 12 ×
	3.051(2) 2 ×	2.921(7) 4 ×	
	3.411(11) 1 ×	3.125(7) 4 ×	
Ba–O(2)	2.766(8) 2 ×		
	2.873(13) 2 ×		
	3.232(7) 2 ×		
	3.290(8) 2 ×		

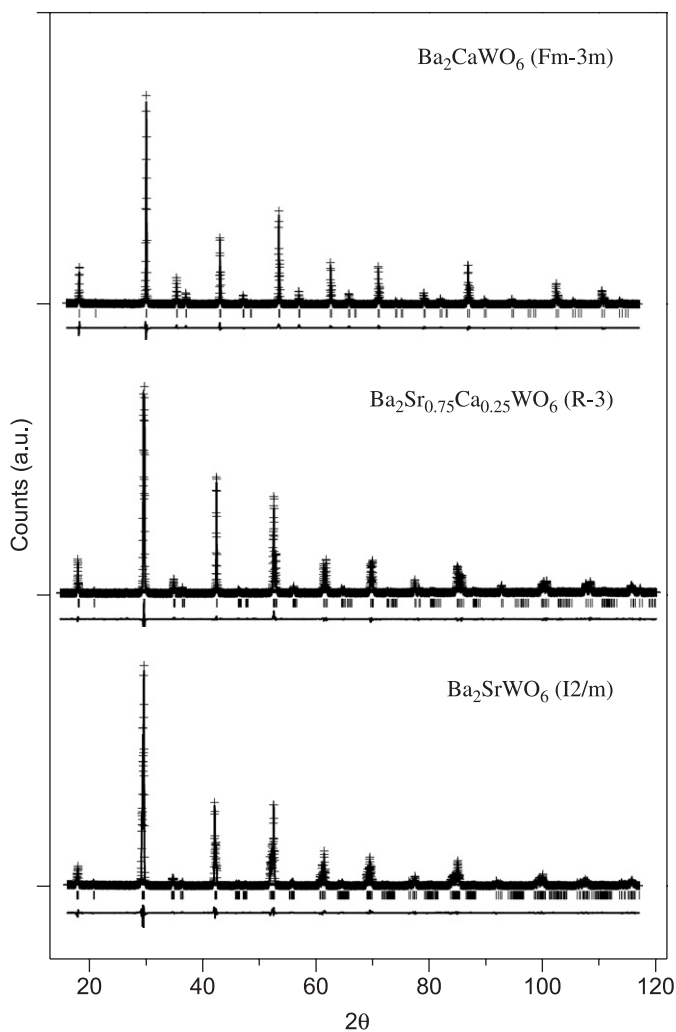


Fig. 3. Observed (crosses) and calculated (continuous line) profiles of $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ in the space group $I2/m$ ($x = 0$), $R\bar{3}$ ($x = 0.25$) and $Fm\bar{3}m$ ($x = 1$). Tick marks indicate the positions of allowed reflections. The difference curves ($I_{\text{obs}} - I_{\text{cal}}$) are shown below.

Khalyavin et al. [12] described Ba_2SrWO_6 as triclinic in the space group $F\bar{1}$. However, their X-ray diffraction pattern is just the same as ours. In particular, the primitive (222) and (400) reflections split into a triplet and a doublet,

respectively. In fact, as their initially assigned space group $I2/a$ is not compatible with two non-equivalent octahedral positions, they have chosen the space group $F\bar{1}$ (tilt system $a^-b^-b^-$) to model the structure. In their refinements, however, the lattice parameters were illogically constrained in such a way that $b = c$ and $\beta = \gamma$. Even so, using this model with 59 structural parameters did not improve the results of our data. Clearly, the assignment of triclinic symmetry is inappropriate for Ba_2SrWO_6 .

In agreement with the earlier studies [13–15], the room temperature structure of Ba_2CaWO_6 is cubic. This result is, in the first place, unexpected given its tolerance factor being appreciably smaller than unity ($t = 0.967$). Nevertheless, the tolerance factor has been found to be somewhat reluctant to account for the cubic symmetry in double perovskites. For example, the cubic structure occurs in some members of $\text{Ba}_2M(\text{III})M'(\text{V})\text{O}_6$ ($M = \text{lanthanides}$ and Y and $M' = \text{Ru, Ir, Sb, and Nb}$) [5–8], all having the t -values of about 0.98. In these compounds, the $M(\text{III})\text{--O}$ bond lengths are actually shorter than those estimated from the sum of the corresponding ionic radii [19], though the $M'(\text{V})\text{--O}$ bond distances agrees well with the sum of the ionic radii. This is also the case in the title system; the averaged Sr--O (~ 2.38 Å) and Ca--O (2.22 Å) bond lengths are approximately 8% and 7.5% shorter than the predicted values (2.58 Å and 2.40 Å). Clearly, in double perovskites the apparent mismatch between $A\text{--O}$ and the averaged $M/M'\text{--O}$ bond lengths, e.g., $t < 1$, can be adjusted by compressing the $M\text{--O}$ bonds without necessarily tilting the $M/M'\text{O}_6$ octahedra.

As was mentioned above, the structure of Ba_2CaWO_6 at room temperature has recently been described by Yamamura et al. [16] to be tetragonal $I4/m$. They also observed Ba_2CaWO_6 undergoing a phase transition below room temperature, and assigned the space group $I2/m$ to the low temperature phase. As their specific heat measurement showed a discontinuous, but finite, change in slope at $T \approx 220$ K, they considered the $I4/m \rightarrow I2/m$ transition to be second order phase transition. However, such description cannot be correct since there is no pathway that allows a continuous change between the tilt systems $a^0a^0c^-$ ($I4/m$) and $a^0b^-b^-$ ($I2/m$); the $I4/m \rightarrow I2/m$ phase transition must be first order from the symmetry consideration [17]. In fact, the low temperature X-ray powder diffraction patterns given in Ref. [16] would rather suggest a rhombohedral distortion than a monoclinic distortion; that is, the basic (222) and (400) reflections are visibly a doublet and a singlet, respectively. It is unclear whether the observed second order phase transition in Ba_2CaWO_6 may actually correspond to the $Fm\bar{3}m \rightarrow R\bar{3}$ transition. The structure of the low temperature phase clearly necessitates further investigation.

The phase sequence in the double perovskites $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$, with increasing the Ca-concentration, is $I2/m \rightarrow R\bar{3} \rightarrow Fm\bar{3}m$. It is interesting to review the observed rhombohedral structure. It is now well established experimentally that the intermediate tilt system of

either $a^0 a^0 c^-$ or $a^- a^- a^-$ occurs between the tilt systems $a^0 b^- b^-$ and $a^0 a^0 a^0$, when the tolerance factor progressively approaches to 1. These observations pointed to the fact that the $a^0 a^0 c^-$ or $a^- a^- a^-$ tilt systems should provide the best energy balance to stabilize a distorted perovskite with small to moderate octahedral tilting. None of them is, however, suitable when larger tilting angle is required, for which the tilt system $a^0 b^- b^-$ or $a^- a^- c^+$ is favoured. A simple question arises: which structural stabilization forces make such preference for one tilt system over the other in perovskites? Although this is a very complicated problem involving the delicate balance among various bonding interactions, some clues may be traced out in Ref. [9]. As was already mentioned, the suitable tilt system in AMO_3 -perovskites has been argued to depend on the ionic contribution of A -cation, i.e., the $a^0 a^0 c^-$ and $a^- a^- a^-$ tilt systems being favoured by divalent and trivalent A -cation, respectively. Such argument may also be applied in double perovskites, as was evidenced by the observations that a large number of the $Sr_2MM'O_6$ double perovskites do adopt the $a^0 a^0 c^-$ tilt system. In the case of $Ba_2MM'O_6$, however, such preference may change as the ionicity of A -cation increases. In addition, since the formal charge of one of the octahedral cation becomes higher, i.e., $>IV$, it will lead to a more covalent interaction with neighbouring oxygen. These could be the reasons why both tetragonal $a^0 a^0 c^-$ and rhombohedral $a^- a^- a^-$ tilt systems occur in $Ba_2Ln(III)M'(V)O_6$; the change-over depends on the subtle difference of the $M'(V)$ -O bond's nature [8]. Following this line of thought, the occurrence of rhombohedral structure in $Ba_2Sr_{1-x}Ca_xWO_6$ seems to be straightforward: both the substitution of Sr by Ca and the high charge of W(VI) increase the covalency of the octahedral M/M' -O bonds. This is in agreement with the earlier suggestion that the covalent M -O bonding stabilizes the rhombohedral symmetry [8].

It is interesting to notice a recent publication of Saines et al. [20], who questioned this idea by referring that the double perovskite Ba_2NdMoO_6 adopts the $I4/m$ structure [21]. They inferred from the electronegativity values of Pauling's [22] scale, showing that Mo has a comparable electronegativity to Ru, Ir and Sb rather than to Nb, that the covalency being the cause of symmetry difference may not be correct. They, therefore, re-examined the Ba_2LnNbO_6 and Ba_2LnSbO_6 systems by using high-resolution powder synchrotron X-ray and neutron diffraction techniques. While the phase sequences across the lanthanides, being $I2/m \rightarrow I4/m \rightarrow Fm\bar{3}m$ and $R\bar{3} \rightarrow Fm\bar{3}m$ for $M = Nb$ and $M = Sb$, respectively, were confirmed, they proposed a different model to explain the structural difference. According to this model, the π -bonding that is formed between the octahedral M -cation and the neighbouring oxygen plays an essential role in determining the structural symmetry. Since in $I4/m$, one-third of the Ln -O- M angles remain 180° and none of them does in $R\bar{3}$, the double perovskite that contains the cation being capable of forming M -O π -bonding should favour the tetragonal

symmetry. This is the case for Nb(V) which has the d^0 -electronic configuration. For Sb(V) with the d^{10} -configuration, however, no π -bonding exists, and the rhombohedral $R\bar{3}$ symmetry is preferred.

Although this explanation may account for the obvious difference between ions with d^0 - and d^{10} -electronic configuration, the model does not make clear why double perovskites that contain d^3 -cation (e.g., Ba_2LaRuO_6) or d^4 -cation (e.g., Ba_2LaIrO_6) also adopt the rhombohedral structure. Instead, they suggested that the boundary of having the stable $I4/m$ and $R\bar{3}$ structures lies between the d^1 - and d^3 -cations [20]. Even so, this proposal does not explain the observed rhombohedral symmetry in Ba_2BiTaO_6 [23] and, now, in $Ba_2Sr_{1-x}Ca_xWO_6$; both compounds do contain d^0 -cations (Ta(V) and W(VI)). Evidently, π -bonding does not hold the keys of structural difference in these double perovskites. In fact, the proposal of Saines et al. based on some geometric difference between the tilt systems $a^0 a^0 c^-$ and $a^- a^- a^-$ without considering the substantial difference between AMO_3 and $AMM'O_6$ and the likely impacts of π -bonding does not seem to be convincing. For example, in metallic AMO_3 perovskites, e.g., $SrMoO_3$, the kinetic energy of the delocalized d -electrons is believed to stabilize structures where the M -O- M bond angles are linear or close to linear [9]; whether this is also true in the insulating $A_2MM'O_6$ remains unclear. In fact, a clear difference of the double perovskites in question is that the transition metal cations are separated by rare earth or alkaline earth cations due to 1:1 ordering. In this case, the π -bonding originating from the overlap between M' t_{2g} -orbitals and the O 2p-orbitals would depend primarily on the O- M' -O bond angles instead of the M -O- M' angles [24]. Since the octahedra remain essentially rigid even with a relatively large tilting angle, the strength of π -bonding of a given ion is not expected to vary significantly in different tilt systems. In other words, it is unlikely that the π -bonding may discriminate between the tilt systems $a^0 a^0 c^-$ and $a^- a^- a^-$, in which the O- M' -O bond angles are either 90° or very close to 90° . Even if the π -bonding does play a role, in a covalent model it will weaken somewhat the overlap of the A -O bonding. Considering that the first coordination spheres of oxygen around A -cation are coplanar in $a^- a^- a^-$ and non-coplanar in $a^0 a^0 c^-$ [9], it follows that a weakening of the covalent overlap of A -O bonding should be in favor of the rhombohedral structure rather than the tetragonal one, since the decrease of covalent energy around A is less in rhombohedral tilt system. Apparently, such a conclusion based on the covalent model is similar to that based on the ionic model mentioned in the introduction.

It should be pointed out that the suspicion of Saines et al. on the idea of covalency is conducted from the electronegativity values of Pauling's [22] scale. This scale indeed shows that Mo ($\chi = 2.16$) has a comparable electronegativity to Ru ($\chi = 2.20$) and Ir ($\chi = 2.20$) rather than to Nb ($\chi = 1.6$) and it has even higher value than those of Sb ($\chi = 2.05$) and Bi ($\chi = 2.02$). Given that the

double perovskites of $\text{Ba}_2\text{Ln(III)M(V)O}_6$ for some specific Ln are tetragonal with $M = \text{Nb, Mo}$ and are rhombohedral with $M = \text{Ru, Ir, Sb, Bi}$, one may naturally concluded the electronegativity being not the cause of this difference in symmetry. However, Pauling's electronegativity scale has been criticized for not providing the adequate values to account for the chemical behaviour of the elements. This is particularly true that many of his transition metal χ 's are even higher than those of the metalloids, violating thus the so-called Si rule [25]. On the other hand, there exists more than one valid electronegativity system [26]. Taken an example of the Allred–Rochow scale, one find the following values: $\chi(\text{Nb}) = 1.23$, $\chi(\text{Mo}) = 1.30$, $\chi(\text{Ru}) = 1.42$, $\chi(\text{Ir}) = 1.55$, $\chi(\text{Sb}) = 1.82$ and $\chi(\text{Bi}) = 1.67$. Obviously, these values are more reasonable to account for the systematic change of the electronegativity across the period or down the groups, agreeing with our basic understanding of the periodic properties of the elements. It should also be pointed out that the electronegativity is not an invariant property of an element; it depends on other factors too, e.g. the valence state (hybridization) and the atomic charge [26]. Since not all these values are yet available, it is difficult to quantify them in a complicated compound. Comparing the $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ and $\text{Ba}_2\text{Ln}(\text{Nb,Mo})\text{O}_6$ systems, for example, Ca is considered to be more electronegative than Sr ($\Delta\chi \approx 0.05$), but yet its χ -value is lower than those of lanthanides [26]. On the other hand, the electronegativity of tungsten ($\chi(\text{W}) = 1.40$) is higher than those of niobium and molybdenum (see χ s given above). Therefore, the comparison of bond covalency referring to electronegativity is not straightforward. Nevertheless, the influence of the relative strength of the $M/M\text{--}O$ bond covalency on the structural symmetry in double perovskites is evident as can also be seen from the following pairs of compounds: $\text{Ba}_2\text{GdTaO}_6^1$ ($I4/m$) vs. $\text{Ba}_2\text{BiTaO}_6$ ($R\bar{3}$) [23] and $\text{Ba}_2\text{NdMoO}_6$ ($I4/m$) [21] vs. $\text{Ba}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_6$ (see footnote 1) ($R\bar{3}$). These examples clearly rule out the idea of π -bonding being the determinant force to stabilize the tetragonal structure.

In conclusion, we have studied the crystal structure of the double perovskites $\text{Ba}_2\text{Sr}_{1-x}\text{Ca}_x\text{WO}_6$ using X-ray powder diffraction techniques. Contrary to some recent publications describing the structures of the end members as triclinic ($F\bar{1}$) and tetragonal ($I4/m$), the correct space groups were found to be monoclinic $I2/m$ ($x = 0$) and cubic $Fm\bar{3}m$ ($x = 1$) instead. With increasing the Ca concentration, we observed an intermediate phase existing between the monoclinic and the cubic structures with the phase sequence: $I2/m \rightarrow R\bar{3} \rightarrow Fm\bar{3}m$. This observation proves that the tilt system $a^0 b^- b^-$ transforms to the one of $a^0 a^0 a^0$ via an intermediate system. The occurrence of rhombohedral symmetry confirms the suggestion that the increase of covalency of the octahedral cations favours the tilt system

$a^- a^- a^-$ in double perovskites. It disagrees with the recent proposal that the π -bonding is the first cause of adopting the tetragonal symmetry in preference to the rhombohedral one.

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¹ $\text{Ba}_2\text{GdTaO}_6$ and $\text{Ba}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_6$ have been found by us to adopt tetragonal $I4/m$ and rhombohedral $R\bar{3}$ structure, respectively.