



On the symmetry and crystal structures of Ba₂LaIrO₆

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ABSTRACT

Accurate profile analysis of X-ray diffraction data was carried out to settle recent dispute on the symmetry and crystal structures of the double perovskite Ba₂LaIrO₆. Even through careful comparison of the full-width at half-maximum values, we found no evidence for Ba₂LaIrO₆ adopting either monoclinic (*I2/m*) or mixed rhombohedral (*R3*) and monoclinic (*I2/m*) structures at room temperature, becoming triclinic (*I1*) at below about 200 K. The correct space group is just *R3* at temperatures between 82 and 653 K. Furthermore, the *R3* → *Fm3m* phase transition does occur in Ba₂LaIrO₆, but the transition temperature is found to be much higher than the reported value.

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1. Introduction

Double perovskites with the general formula A₂BB'O₆ have attracted great interest in recent years. This is not due only to their interesting physical properties, such as superconductivity [1,2], dielectricity [3,4] and magnetoresistivity [5], but also because they show a rich variety of structures. For example, depending on the compositions and/or temperature the double perovskites may adopt various tilt systems with different symmetries [6,7]. An interesting property of the double perovskites is that they seem to crystallize in particular tilt systems only: i.e. *a⁰a⁰a⁰* (*Fm3m*), *a⁰a⁰c⁻* (*I4/m*), *a⁻a⁻a⁻* (*R3*), *a⁰b⁻b⁻* (*I2/m*) and *a⁺b⁻b⁻* (*P2₁/n*). In addition, for many double perovskites the deviation from the ideal cubic structure follows either the sequence *Fm3m* → *I4/m* → *I2/m* → *P2₁/n* or the sequence *Fm3m* → *R3* → *I2/m* → *P2₁/n*.

The structures of double perovskites are usually determined from powder diffraction data using profile analysis by the Rietveld method [8]. Although the different tilt systems can be recognized by inspecting diagnostic reflections, this is, in practice, not always straightforward as the sample quality, instrument resolution and the presence of pseudo-symmetry may hinder proper observation. Moreover, while the Rietveld method is a powerful tool for solving crystal structures from powder diffraction data, care should be taken in interpreting the refined results. Wrongly assigned space groups are often seen in the literature. A case in point is the double perovskite system Ba₂LnIrO₆ (Ln=lanthanide and Y). The structure of some members was first described by Wakeshima et al. as monoclinic in the space group *P2₁/n* [9]. Li

and Kennedy studied Ba₂PrIr_{1-x}Ru_xO₆, using high-resolution synchrotron X-ray and neutron powder diffraction data, and concluded that the symmetry of Ir-rich phases is higher than monoclinic. They reported the tetragonal space group *P4/mnc* (tilt system *a⁰a⁰c⁺*) for Ba₂PrIrO₆ [10]. Fu and Ijdo re-investigated Ba₂LaIrO₆ and Ba₂YIrO₆ using X-ray powder diffraction data. They showed, from the characteristic peak splitting as well as the nature of the superlattice reflections, that the actual symmetries are rhombohedral and cubic, respectively [11]. The structures have been refined and can be described adequately in the space groups *R3* and *Fm3m*, respectively. Fu and Ijdo also examined the controversial reports on the structure of Ba₂PrIrO₆ and showed that neither the space group *P2₁/n* nor the space group *P4/mnc* is correct. Ba₂PrIrO₆ is a double cubic perovskite instead [12]. The later finding has been confirmed by Kockelmann et al. using high-resolution time-of-flight neutron powder diffraction data [13]. However, we have noticed a recent paper by Zhou et al. [14] who investigated, once again, the structure of Ba₂LaIrO₆. In their paper they claimed that Ba₂LaIrO₆ crystallizes in *R3* at above about 373 K only: below 373 K the *R3* structure purportedly coexists with the *I2/m* structure. While this conclusion was derived from the Rietveld refinement using the synchrotron data, the authors were unable to refine the room temperature structure from their neutron data using a two phase model, describing the room temperature structure in *I2/m* only. In addition, they also reported the existence of a phase transition in Ba₂LaIrO₆ at below about 200 K, and assigned the triclinic space group *I1* (tilt system *a⁻b⁻c⁻*) to the low temperature phase. Although they inferred from the profile change of the neutron diffraction pattern as well as the absence of any super reflections associated with the in-phase tilting that cooling induces the transition to *I1*, no real evidence for a triclinic distortion has been provided as yet by high-resolution diffraction data.

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Table 1
Characteristics of the splitting of the basic (*hhh*)- and (*h00*)-type reflections in some tilt systems of the double perovskites.

Space group		$Fm\bar{3}m$	$R\bar{3}$	$I4/m$	$I2/m$	$I\bar{1}$
<i>(hhh)</i> -type reflection	Number of reflections	1	2	1	3	4
	Intensity ratio	–	~3:1	–	~1:1:2	~1:1:1:1
<i>(h00)</i> -type reflection	Number of reflections	1	1	2	2	3
	Intensity ratio	–	–	~1:2	~2:1	~1:1:1

To settle these contradictions, we carried out an accurate profile analysis of X-ray powder diffraction data of Ba_2LaIrO_6 recorded between 82 and 723 K. In addition, differential thermal analysis (DTA) was performed. For the purpose of comparison we also examined some compounds in the related $Ba_{2-x}Sr_xNdIrO_6$ system. In this paper, we show that the symmetry of Ba_2LaIrO_6 is rhombohedral at temperatures between 82 K and below about 653 K. At higher temperatures the structure becomes cubic. Neither the monoclinic ($I2/m$) nor the triclinic ($I\bar{1}$) structure could be identified at any temperature above about 82 K.

2. Experimental

Samples of Ba_2LaIrO_6 and $Ba_{2-x}Sr_xNdIrO_6$ were prepared from $BaCO_3$, $SrCO_3$, La_2O_3 , Nd_2O_3 , and Ir metal powder in alumina crucibles using the standard solid-state reaction. The La_2O_3 and Nd_2O_3 powder was preheated at 950 °C overnight before use. The thoroughly ground mixtures were first heated at 900 °C for 15 h. The resultant powders were then reground and sintered at 1250 °C for a few days with intermediate grindings. All syntheses were carried out in air and all samples were furnace cooled to room temperature.

X-ray powder diffraction experiment was performed on a Philips X'Pert diffractometer, equipped with the X'celerator, using $CuK\alpha$ radiation. For non-ambient X-ray diffraction, an Anton Paar TTK 450 chamber was used with direct sample cooling/heating in the temperature range between 80 and 723 K and a temperature stability of ~0.1 K. The data were collected in steps of 0.02° (2θ) and 10 sec counting time in the range $15^\circ < 2\theta < 140^\circ$. The model refinements were performed by the Rietveld method using the Rietica computer program [15]. The Chebyshev-polynomial function with 6 or 12 parameters was used to fit the background. The profiles were described by a Pseudo-Voigt function.

Thermal analysis was performed with a Setaram TAG24 Thermal analyzer in the temperature range of 273–623 K.

3. Results

The space groups reported thus far for Ba_2LaIrO_6 are $P2_1/n$ (at room temperature) [9], $R\bar{3}$ (at room temperature or between 373 and 473 K) [11,14], $I2/m$ (at room temperature) [14], $I\bar{1}$ (at below about 200 K) [14] and $Fm\bar{3}m$ (at above about 473 K) [14]. Since neither X-ray [11] nor neutron diffraction data [14] showed superlattice reflections associated with the in-phase tilting, the space group $P2_1/n$ is ruled out from further consideration. Clearly, the remaining space groups contain only out-of-phase tilting ($R\bar{3}$, $I2/m$ and $I\bar{1}$) or non-tilting ($Fm\bar{3}m$) resulting in similar superlattice reflections with the Miller indices of odd-odd-odd when indexed with a double cubic cell. The recognition of these space groups is easy by examination of the peak splitting of the basic (*hhh*) and (*h00*)-type reflections. In Table 1, the characteristics of these reflections in different space groups are summarized.

Fig. 1 shows the room temperature X-ray diffraction pattern of Ba_2LaIrO_6 with the insert showing the enlarged sections

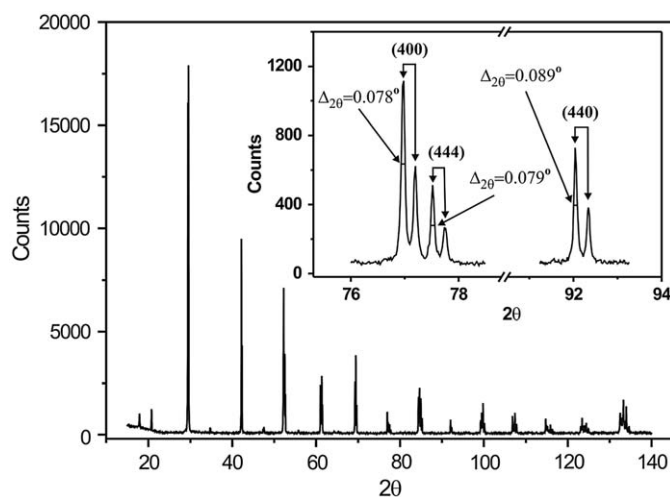


Fig. 1. X-ray powder diffraction pattern of Ba_2LaIrO_6 at room temperature. Insert shows enlarged sections containing the basic (222) and (400) reflections, which are indexed with the rhombohedral setting. Note that peak splitting due to $K\alpha_1$ and $K\alpha_2$ radiations is indicated by arrows. The fitted FWHM-values using pseudo-Voigt function are also given.

containing the basic (222) and (400) reflections. Clearly, the characteristics of the basic (222) and (400) reflections, i.e. appearing as a doublet and a singlet, indicate a rhombohedral distortion as was observed previously [11]. To see whether the observed profiles deviate from the rhombohedral symmetry, we closely examined the values of the full-width at half-maxima (FWHM) by fitting the experimental data with the pseudo-Voigt function. The fitted values¹ ($\Delta_{2\theta}$) of the doublet are 0.078° and 0.079° (see also Fig. 1), respectively, indicating that the basic (222) reflection splits indeed into two reflections. On the other hand, the $\Delta_{2\theta}$ -value of the basic (400) reflection (0.089°) is in agreement with the angle dependence of FWHMs showing that it is not split.

To see whether the $R\bar{3} \rightarrow I2/m$ (via a two phase region of $R\bar{3} + I2/m$) and the $I2/m \rightarrow I\bar{1}$ phases transitions occur in Ba_2LaIrO_6 at below about 373 and 200 K, respectively [14], we closely examined the profiles of the basic (222) and (400) reflections as function of temperature (see Fig. 2). On heating, no anomalies of FWHMs of these reflections could be detected across 373 K; the fitted $\Delta_{2\theta}$ -values of the doublet and singlet at $T=323, 348, 373, 423$ and 473 K are 0.076(2)°, 0.079(1)° and 0.087(2)°, respectively. The fact that the $R\bar{3} \rightarrow I2/m$ phase transition is unlikely to exist in Ba_2LaIrO_6 can also be seen from the thermal analysis: no DTA signal was observed in the measured temperature range, suggesting a first order phase transition does not occur. On the other hand, the separation of the doublet becomes smaller with increasing temperature, and it merges to a single reflection at above about 633 K (Fig. 2a). At this temperature, however, the structure does not become cubic as the FWHM-values of the basic

¹ These are the values of $K\alpha_1$ lines; $K\alpha_2$ lines show the same FWHM-values.

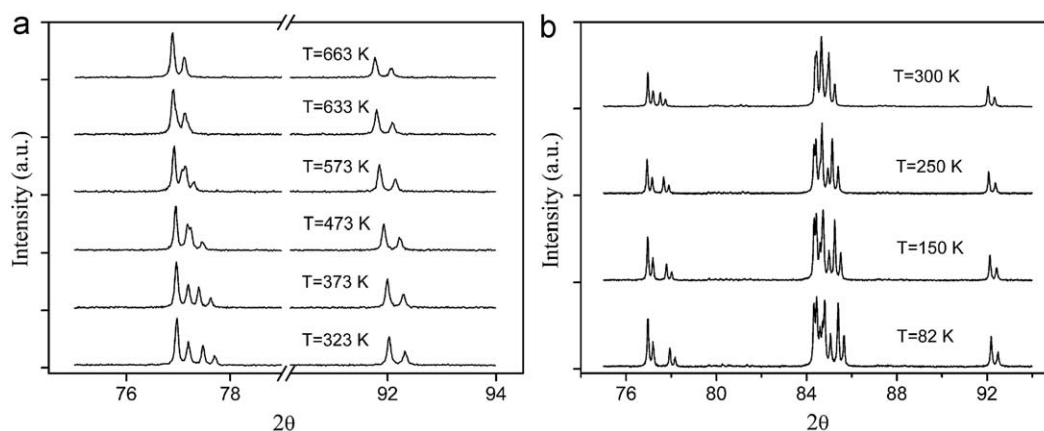


Fig. 2. Enlarged sections showing the evolution of the basic (222) and (400) reflections in $\text{Ba}_2\text{LalrO}_6$ as function of temperature. In (b) the basic (321) reflection ($2\theta \approx 85^\circ$) is also shown. Note that the profile of the basic (321) reflection changes significantly on cooling though the symmetry remains unchanged.

Table 2

Refined lattice constants and atomic positions of $\text{Ba}_2\text{LalrO}_6$ at some selected temperature and $\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$ at room temperature.

$\text{Ba}_2\text{LalrO}_6$					$\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$			
<i>T</i>	82 K	300 K	573 K	663 K	<i>x</i> =0	<i>x</i> =0.25	<i>x</i> =0.5	
S.G.	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$Fm\bar{3}m$	$Fm\bar{3}m$	$R\bar{3}$	$I2/m$	
<i>a</i> (Å)	6.02488(2)	6.04370(2)	6.06304(3)	8.58420(3)	8.49004(3)	5.98269(3)	5.99863(4)	
<i>b</i> (Å)							5.96558(5)	
<i>c</i> (Å)							8.43633(7)	
α (deg)	60.5277(5)	60.2984(5)	60.0849(6)			60.1252(8)		
β (deg)							90.1691(7)	
γ (deg)								
Ba	2c (<i>x,x,x</i>)	2c (<i>x,x,x</i>)	2c (<i>x,x,x</i>)	8c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)	Ba/Sr	8c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)	2c (<i>x,x,x</i>)	4i ($x, \frac{1}{2}, z$)
<i>x</i>	0.2522(1)	0.2515(1)	0.2505(2)		<i>x</i>		0.2494(3)	0.4956(4)
					<i>z</i>			0.2493(3)
La	1a (0,0,0)	1a (0,0,0)	1a (0,0,0)	4a (0,0,0)	Nd	4a (0,0,0)	1a (0,0,0)	2c ($\frac{1}{2}, 0, 0$)
Ir	1b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	1b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	1b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	4b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	Ir	4b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	1b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	2b ($0, \frac{1}{2}, 0$)
O	6f (<i>x,y,z</i>)	6f (<i>x,y,z</i>)	6f (<i>x,y,z</i>)	24e (<i>x,0,0</i>)	O(1)	24e (<i>x,0,0</i>)	6f (<i>x,y,z</i>)	4i (<i>x,0,z</i>)
<i>x</i>	0.2253(12)	0.2307(14)	0.2373(22)	0.2735(6)	<i>x</i>	0.2663(5)	0.2331(14)	0.5447(22)
<i>y</i>	0.3146(11)	0.3067(13)	0.2987(21)		<i>z</i>		0.3106(13)	0.2681(20)
<i>z</i>	0.7111(14)	0.7028(14)	0.6931(18)		O(2)		0.7376(24)	8j (<i>x,y,z</i>)
					<i>x</i>			0.2355(17)
					<i>y</i>			0.2715(19)
					<i>z</i>			0.0340(9)
<i>B</i> (Å) ^{2a}	0.02(1)	0.23(1)	0.46(1)	0.46(1)	<i>B</i> (Å) ^{2a}	0.473(9)	0.31(1)	0.481(9)
	$R_{\text{wp}}=10.97\%$	$R_{\text{wp}}=10.57\%$	$R_{\text{wp}}=10.98\%$	$R_{\text{wp}}=11.85\%$		$R_{\text{wp}}=8.64\%$	$R_{\text{wp}}=8.97\%$	$R_{\text{wp}}=7.56\%$
	$R_{\text{p}}=8.43\%$	$R_{\text{p}}=8.36\%$	$R_{\text{p}}=7.96\%$	$R_{\text{p}}=9.00\%$		$R_{\text{p}}=6.71\%$	$R_{\text{p}}=6.76\%$	$R_{\text{p}}=5.63\%$

^a An overall thermal parameter is used in the refinement.

(222) reflection ($\Delta_{2\theta}=0.107^\circ$) is significantly larger than that of the basic (400) reflection ($\Delta_{2\theta}=0.088^\circ$). The structure of $\text{Ba}_2\text{LalrO}_6$ becomes truly cubic at above about 663 K since the FWHMs do not show abnormal values ($\Delta_{2\theta}=0.078^\circ$ and 0.086° for the basic (222) and (400) reflections). On cooling the appearance of the basic (222) and (400) reflections remain unchanged except the separation of the doublet becomes larger (Fig. 2b). Neither the peak shapes nor the FWHM-values show triclinic distortion at below about 200 K [14]. Therefore, the structures of $\text{Ba}_2\text{LalrO}_6$ at $82 \leq T \leq 653$ K and at $T \geq 663$ K can be described in the space groups $R\bar{3}$ and $Fm\bar{3}m$, respectively.

Identifying the space groups in $\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$ was carried out a similar manner. The basic (222) and (400) reflections are seen as singlet–singlet ($x=0$), doublet–singlet ($x=0.25$) and triplet–doublet. The corresponding space groups are thus $Fm\bar{3}m$, $R\bar{3}$ and $I2/m$, respectively.

All Rietveld refinements using X-ray powder diffraction data yielded satisfactory results. In Table 2, we listed the refined crystallographic data of $\text{Ba}_2\text{LalrO}_6$ at some representative

temperatures and $\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$ for three typical compositions. The plots of the observed and calculated profiles of the critical region are shown in Figs. 3 and 4.

4. Discussion

The present investigation shows that $\text{Ba}_2\text{LalrO}_6$ is rhombohedral in the temperature range of 82–653 K. The observed rhombohedral space group $R\bar{3}$ is the one expected given its tolerance factor ($t=0.967$). The same space group has recently been observed in a number of the related double perovskites with comparable t -values: e.g. $\text{Ba}_2\text{BiSbO}_6$ ($t=0.961$) [17], $\text{Ba}_2\text{LnSbO}_6$ ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}$) ($t=0.960$ – 0.971) [18] and $\text{Ba}_2\text{LaRuO}_6$ ($t=0.968$) [19]. On the other hand, some double perovskites of this type which adopt the monoclinic $I2/m$ space group all have significantly lower t -values. Examples are $\text{Ba}_2\text{Bi(III)Bi(V)O}_6$ ($t=0.927$) [20,21], $\text{Ba}_2\text{NdBiO}_6$ ($t=0.937$) [22], $\text{Ba}_2\text{LaNbO}_6$ ($t=0.952$) [23], $\text{Ba}_2\text{LaTaO}_6$ ($t=0.952$) [24], Ba_2SrWO_6 ($t=0.929$) [16].

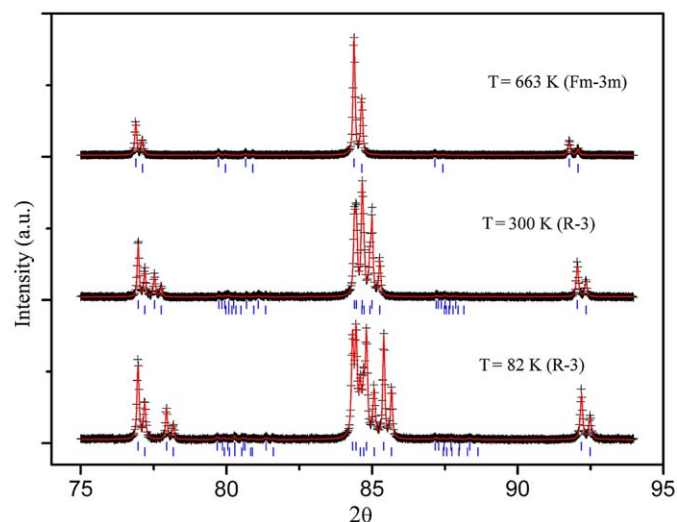


Fig. 3. Observed (crosses) and calculated (continuous line) profiles of $\text{Ba}_2\text{LalrO}_6$ at some selected temperature showing the region containing the basic (222), (321) and (400) reflections. Tick marks below indicate the positions of the allowed Bragg's reflections.

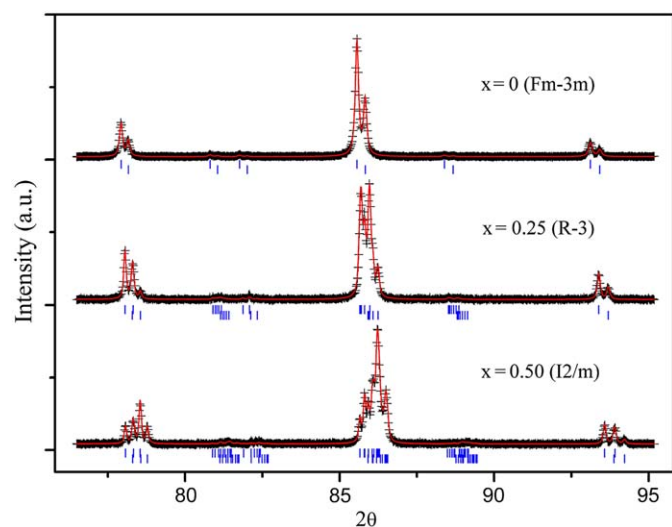


Fig. 4. Observed (crosses) and calculated (continuous line) profiles of $\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$ for some selected compositions showing the region containing the basic (222), (321) and (400) reflections. Tick marks below indicate the positions of the allowed Bragg's reflections. Note the clear difference of profiles between the rhombohedral ($x=0.25$) and the monoclinic ($x=0.5$) phases.

Zhou et al. reported that $\text{Ba}_2\text{LalrO}_6$ is a mixture of the $R\bar{3}$ and $I2/m$ phases at below 373 K [14]. They came to this conclusion because their room temperature synchrotron data can only be fitted adequately with a two phase model. Although the existence of a two-phase region has been unambiguously observed in some double perovskites [16,24], there is no evidence such as extra reflections or abnormal peak broadening suggesting the same thing happens in $\text{Ba}_2\text{LalrO}_6$ too. As a matter of fact, the failure of fitting their room temperature neutron data clearly indicates the inadequacy of the two-phase model. To further illustrate why $\text{Ba}_2\text{LalrO}_6$ cannot be rhombohedral at room temperature, they showed the neutron data of the wavelength 2.439 Å, revealing the splitting of the double cubic (440) reflection into a doublet [14]. However, this cannot be the evidence justifying their proposition since the cubic (440) reflection, i.e. the basic (220) reflection, splits just into doublet in the space group $R\bar{3}$. Clearly, the present

X-ray diffraction data show no evidence that the symmetry of $\text{Ba}_2\text{LalrO}_6$ deviates from the rhombohedral in the temperature range of $82 \leq T \leq 653$ K. Both the a -axis and the α -angle vary smoothly and quasi-linearly with the temperature (Fig. 5).

As was mentioned above, the monoclinic distortion of the space group $I2/m$ should split the basic (222) and (400) reflections into a triplet and a doublet with the intensity ratio of roughly 1:1:2, and 2:1, respectively (Table 1). In the tilt system ($a^-a^-c^0$), the tilting of octahedra around a diad axis of the parent perovskite, which is equivalent to the b -axis of the monoclinic supercell, results in the a -axis being slightly longer than the b -axis. The Miller indices of the triplet are $(40\bar{4})$, (404) and (044) , and those of the doublet are (440) and (008) , respectively. This is a logical consequence of the octahedral tilting. It is seen in all well defined monoclinic double perovskites to date (see examples listed in Table 3). Even if the monoclinic distortion is small, e.g. $\beta \approx 90^\circ$, the triplet is reduced virtually to a doublet with the intensity ratio of about 1:1, but the doublet would, in principle, remain unchanged. Given that both X-ray (Fig. 1) [11] and synchrotron data [14] show just the doublet (with the intensity ratio of $\sim 3:1$) and a singlet of the basic (222) and (400) reflections, it seems as if the space group $I2/m$ cannot account for a pattern obviously showing rhombohedral symmetry. Close examination of the refined lattice parameters given by Zhou et al., $a=6.0481(3)\text{Å}$, $b=6.0664(3)\text{Å}$, $c=8.5634(5)\text{Å}$, $\beta=90.256(3)^\circ$, has shown a reversal of axis lengths, i.e. $a < b$. Curiously, these values allow the (044) and (008) reflections to almost perfectly overlap with the $(40\bar{4})$ and (440) reflections, leading to an apparent doublet and a singlet. Although, the lattice parameters reported by Zhou et al. could be a physical possibility, whether they explain the true symmetry of $\text{Ba}_2\text{LalrO}_6$ is questionable. First, all well defined monoclinic double perovskites containing Ba show the characteristic $a > b$ (Table 3). Second, it is unexpected that a monoclinic distortion, as was proposed for $\text{Ba}_2\text{LalrO}_6$, may adjust the lengths of axes in such a way that the (044) and (008) reflections always perfectly overlap with the $(40\bar{4})$ and (440) reflections across a temperature span of ~ 300 K.

The problem here is likely the one of lattice metric singularities discussed some years ago by Mighell [26]. He showed that metric singularity may yield two (or more) unit cells of different symmetries with identical d -values. In the example discussed in his paper, he indicated that any rhombohedral cell has a derivative monoclinic subcell, both of which result in the same set of d -values. He advised, therefore, that if a unit cell of lower symmetry is found, it is critical to recognize that the other may exist as well. In the present case, taking the refined rhombohedral lattice parameters at room temperature, $a=6.04370\text{Å}$ and $\alpha=60.2984^\circ$, it is easy to show that the monoclinic cell of $a=6.03898\text{Å}$, $b=6.06621\text{Å}$, $c=8.55975\text{Å}$, $\beta=90.365^\circ$ may account for all observed reflections. These values are obviously close to the lattice constants reported by Zhou et al. [14].

It should be pointed out that the non-cubic double perovskites containing Ba generally show large distortions (Table 3). This is in contrast to some double perovskites containing Sr, which show pseudo symmetry. To exclude the possibility that pseudo symmetry may cause an unusual appearance of profiles, we compared $\text{Ba}_2\text{LalrO}_6$ with $\text{Ba}_{2-x}\text{Sr}_x\text{NdIrO}_6$. In a previous publication [12], we mentioned that the double perovskite $\text{Ba}_2\text{NdIrO}_6$, having a slightly higher t -value (0.978), already adopts the cubic symmetry. It is anticipated that, if Ba is substituted by Sr, the $I2/m$ structure should occur via an intermediate structure of either $R\bar{3}$ or $I4/m$. This is indeed the case: the symmetries of the $x=0.25$ and $x=0.5$ phases are rhombohedral ($R\bar{3}$) and monoclinic ($I2/m$), respectively (see Table 2 and Fig. 3). Critically, the diagnostic reflections of the monoclinic phase are seen as triplet and doublet, respectively. Given their closely chemical and structural

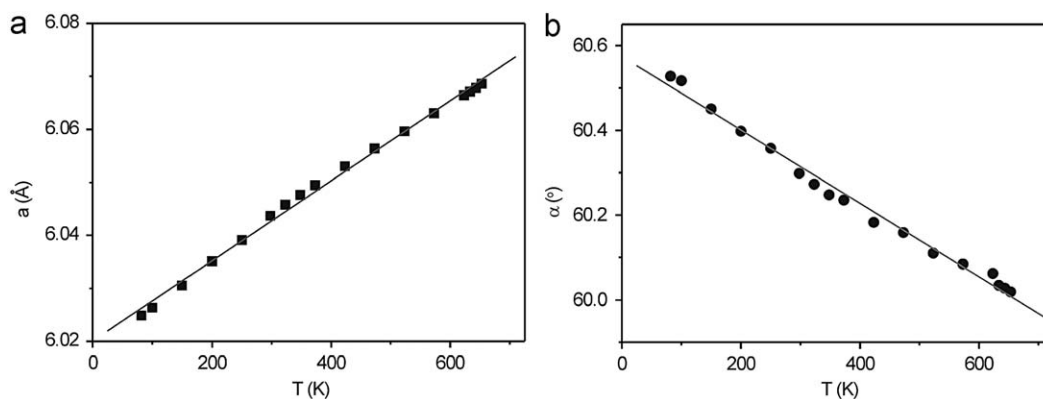


Fig. 5. The variation of lattice constants of $\text{Ba}_2\text{LaIrO}_6$ in the rhombohedral region as function of temperature. Lines are the linear fit to the refined values of the a -axis (a) and α -angle (b).

Table 3

Refined lattice constants of some well defined monoclinic double perovskites.

Compounds	Lattice constants				Ref.
	a (Å)	b (Å)	c (Å)	β (deg)	
$\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$	6.18505(7)	6.13219(7)	8.6585(1)	90.229(1)	[21]
$\text{Ba}_2\text{PrBiO}_6$	6.2011(2)	6.1583(2)	8.6968(3)	89.922(5)	[22]
$\text{Ba}_2\text{NdBiO}_6$	6.1776(2)	6.1366(2)	8.6686(3)	89.801(2)	[22]
$\text{Ba}_2\text{LaNbO}_6$	6.14448(8)	6.09131(9)	8.6040(1)	90.348(1)	[23]
$\text{Ba}_2\text{PrNbO}_6$	6.0940(1)	6.0546(2)	8.5521(2)	90.178(2)	[25]
$\text{Ba}_2\text{NdNbO}_6$	6.07918(9)	6.04547(9)	8.5391(1)	90.134(1)	[23]
$\text{Ba}_2\text{LaTaO}_6$	6.1486(1)	6.0964(1)	8.6109(2)	90.345(1)	[24]
Ba_2SrWO_6	6.0677(6)	6.03732(8)	8.5399(1)	90.4457(7)	[16]

similarities, the pseudo symmetry does not seem to be the reason for the observed profiles in $\text{Ba}_2\text{LaIrO}_6$.

In their paper Zhou et al. also reported the triclinic $\bar{1}\bar{1}$ structure for $\text{Ba}_2\text{LaIrO}_6$ at below about 200 K [14]. Although the obvious profile changes in the neutron diffraction pattern occurred on cooling, neither did they specify the reflections undergoing such changes nor had they shown if those changes are indeed due to triclinic distortion. Further, no high-resolution synchrotron data were provided to confirm the suggested symmetry. As was shown above, our low temperature X-ray data of $\text{Ba}_2\text{LaIrO}_6$ do not reveal any deviation from rhombohedral symmetry down to above about 82 K, though the appearance of some reflections, e.g. the basic (321) reflection, do change considerably (see Fig. 2b and Fig. 3). To see whether the proposed space group $\bar{1}\bar{1}$ is compatible with the observed profiles at low temperature, we simulated the X-ray diffraction pattern by using the crystallographic data reported in Ref. [14]. Fig. 6 shows the region of the calculated pattern containing diagnostic reflections (Fig. 6a). It does not match the observed diffraction data at 82 K (Fig. 6b). Even if the actual pattern may differ to some extent, as only 11 K structural data are available, the lack of any resemblance of the profiles does not support the idea that $\text{Ba}_2\text{LaIrO}_6$ is triclinic at below about 200 K.

At this point, it is necessary to consider whether the space group $\bar{1}\bar{1}$ may indeed occur in double perovskites. Although the space group $\bar{1}\bar{1}$ was once assigned to $\text{Ba}_2\text{LaRuO}_6$ [27], a recent investigation disproved this and showed the correct space group to be $R\bar{3}$ [19]. In fact, the well investigated double perovskites show the structural changes following the sequences of either $Fm\bar{3}m \rightarrow I4/m \rightarrow I2/m \rightarrow P2_1/n$ or $Fm\bar{3}m \rightarrow R\bar{3} \rightarrow I2/m \rightarrow P2_1/n$. Thus, it does not seem appropriate to select an uncommon tilt system, such as $(a^-b^-c^-)$, without providing solid evidence. A similar case has occurred in the related $\text{Ba}_2\text{PrIrO}_6$: instead of $P4/mnc$ [10], the correct space group is found to be $Fm\bar{3}m$ [12,13]. Clearly, one

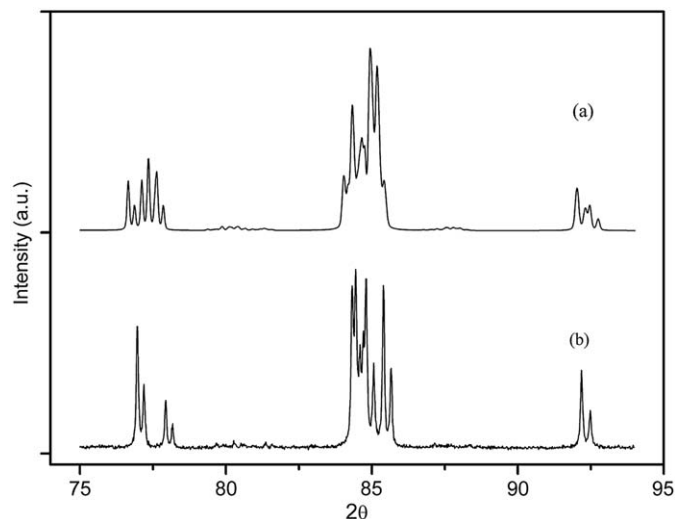


Fig. 6. Part of the calculated X-ray diffraction profiles of $\text{Ba}_2\text{LaIrO}_6$ in the space group $\bar{1}\bar{1}$ (a) [14] as compared to the observed profiles at 82 K (b) of the present work.

cannot rely on the Rietveld refinement only without a critical look at the results obtained.

It should be also mentioned that Zhou et al. did point out that their attempts to refine the structure in $R\bar{3}$ using the room temperature synchrotron data were unsuccessful, and, particularly, the fit to the basic (321) reflection was less than optimal [14]. While these problems were not occurring in the present investigation (see Table 2 and Fig. 3), we did notice that the refinement in the space group $R\bar{3}$ using the Rietica program may become unstable if the initial parameters, in particular the lattice constants, are not chosen properly. In this case, the refinement may terminate without reaching the lowest R 's.

Finally, we want to point out that the $R\bar{3} \rightarrow Fm\bar{3}m$ phase transition in $\text{Ba}_2\text{LaIrO}_6$ is confirmed. However, the transition temperature is found to be much higher than the one reported, i.e. ~ 663 vs. ~ 473 K [14]. The reason for such a large discrepancy is unclear, however, it may be due to the magnitude of peak splitting of the samples and the analysis method applied. Zhou et al. apparently pinpointed the phase transition by the first disappearance of peak splitting of the basic (222) reflection.

In conclusion, we have re-investigated the crystal structure of the double perovskites $\text{Ba}_2\text{LaIrO}_6$ using X-ray powder diffraction techniques in the temperature range between 82 and 663 K. Careful profile analysis has shown that $\text{Ba}_2\text{LaIrO}_6$ adopts the rhombohedral

space group $R\bar{3}$ and only becomes cubic at above about 663 K. Neither the space group $I2/m$ nor the space group $I\bar{1}$ was found to exist in Ba_2LaIrO_6 at the temperature range investigated.

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References

- [1] A.W. Sleight, J.L. Gillson, P.E. Bierstedt, *Solid State Commun.* 17 (1975) 27.
- [2] D.E. Cox, A.W. Sleight, in: R.M. Moon (Ed.), *Proceedings of the Conference on Neutron Scattering*, National Technical Information Service, Springfield, VA, Gatlinburg, 1976, p. 45.
- [3] M.A. Akbas, P.K. Davies, *J. Am. Ceram. Soc.* 81 (1998) 670.
- [4] I.M. Reaney, E.L. Colla, N. Setter, *Jpn. J. Appl. Phys.* 33 (1994) 3984.
- [5] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, Y. Tokura, *Nature (London)* 395 (1998) 677.
- [6] P.M. Woodward, *Acta Crystallogr. B* 53 (1997) 32.
- [7] C.J. Howard, B.J. Kennedy, P.M. Woodward, *Acta Crystallogr.* 59 (2003) 463.
- [8] H.M. Rietveld, *Acta Crystallogr.* 22 (1967) 151.
- [9] M. Wakeshima, D. Harada, Y. Hinatsu, *J. Alloys Compd.* 287 (1999) 130–136.
- [10] L. Li, B.J. Kennedy, *J. Solid State Chem.* 177 (2004) 3290.
- [11] W.T. Fu, D.J.W. Ijdo, *J. Alloys Compd.* 394 (2005) L5.
- [12] W.T. Fu, D.J.W. Ijdo, *J. Solid State Chem.* 178 (2005) 1312.
- [13] W. Kockelmann, D.T. Adroja, A.D. Hillier, M. Wakeshima, Y. Izumiyama, Y. Hinatsu, K.S. Knight, D. Visser, B.D. Rainford, *Phys. B Condens. Mater.* 378 (2006) 543.
- [14] Q.D. Zhou, B.J. Kennedy, M. Avdeev, L. Giachini, J.A. Kimpton, *J. Solid State Chem.* 182 (2009) 3195.
- [15] C.J. Howard, B.A. Hunter, *A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns*, Lucas Heights Research Laboratories, 1998.
- [16] W.T. Fu, Y.S. Au, S. Akerboom, D.J.W. Ijdo, *J. Solid State Chem.* 181 (2008) 2523.
- [17] W.T. Fu, *Solid State Commun.* 116 (2000) 461.
- [18] W.T. Fu, D.J.W. Ijdo, *J. Solid State Chem.* 178 (2005) 2363.
- [19] W.T. Fu, D.J.W. Ijdo, *Solid State Commun.* 136 (2005) 456.
- [20] D.E. Cox, A.W. Sleight, *Solid State Commun.* 19 (1976) 969.
- [21] B.J. Kennedy, C.J. Howard, K.S. Knight, Z. Zhaoming, Z. Qingdi, *Acta Crystallogr. B* 62 (2006) 537.
- [22] W.T.A. Harrison, K.P. Reis, A.J. Jacobson, L.F. Schneemeyer, J.V. Waszczak, *Chem. Mater.* 7 (1995) 2161.
- [23] W.T. Fu, D.J.W. Ijdo, *J. Solid State Chem.* 179 (2006) 1022.
- [24] P.J. Saines, J.R. Spencer, B.J. Kennedy, M. Avdeev, *J. Solid State Chem.* 180 (2007) 2991.
- [25] P.J. Saines, B.J. Kennedy, B. Johannessen, S. Poulton, *J. Solid State Chem.* 181 (2008) 2994.
- [26] A.D. Mighell, *Powder Diffr.* 15 (2000) 82.
- [27] P.D. Battle, J.B. Goodenough, R. Price, *J. Solid State Chem.* 46 (1983) 234.