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On the space group of the double perovskite Ba_2PrIrO_6

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Abstract

The structure of the double perovskite Ba_2PrIrO_6 has been re-examined by profile analysis of X-ray diffraction data. It has been shown that neither the monoclinic $P2_1/n$ nor the tetragonal $P4/mnc$ space group correctly describes its structure. Ba_2PrIrO_6 has cubic symmetry, space group $Fm\bar{3}m$, cell parameter $a = 8.40135(6)$ Å. In agreement with earlier observations, Ba_2PrIrO_6 is an ordered perovskite containing the valence pair Pr(IV)/Ir(IV).
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1. Introduction

In ABO_3 perovskites, the octahedrally coordinated B-cation can be substituted partially by other suitable ions. A simple case is the so-called double perovskite of the formula $A_2BB'O_6$, in which half of the octahedrally coordinated B-cation is replaced. Ordering between B and B'-cations may occur. If an ordered arrangement occurs, the symmetry and the size of the unit cell are changed.

One important factor determining the structure of the double perovskites $A_2BB'O_6$ is the tolerance factor, $t = (r_A + r_B)/\sqrt{2}(\bar{r}_{(B,B')} + r_O)$, where $\bar{r}_{(B+B')}$ is the averaged ionic radius of the B and B'-cations. T indicates the matching between the A–O and B–O/B'–O bond distances. Ideal matching occurs for $t \approx 1$, when the structure is cubic with the lattice parameter double that of the primitive cubic perovskite, the space group is $Fm\bar{3}m$. For $t > 1$ or $t < 1$, the structures of double perovskites are distorted and have lower symmetry. Just as for normal ABO_3 perovskites, the most commonly occurring distortion is due to tilting of the $BO_6/B'O_6$ octahedra. Woodward, based on Glazer's description of

the tilt systems for perovskites [1,2], has considered cation ordering and octahedral tilting occurring simultaneously, deriving 13 possible space groups for ordered double perovskites $A_2BB'O_6$ [3]. Recently, Howard et al. undertook a group-theoretical analysis of the problem, identifying 12 space groups under the same conditions of octahedral tilting and cation ordering [4].

In the past few years, the structural and magnetic properties of the double perovskites Ba_2MIrO_6 (M = lanthanide, Sc, Y) have been reported [5–8]. They almost all contain an ordered arrangement of MO_6 and IrO_6 octahedra with the valence pair of M(III)/Ir(V). Exceptions are Ba_2CeIrO_6 and Ba_2PrIrO_6, in which the oxidation states were found to be Ce(IV) and Pr(IV).

The structure of Ba_2PrIrO_6 was first described, together with other Ba_2MIrO_6 (M = lanthanide, Sc, Y) perovskites, by Wakeshima et al. [8] as monoclinic in the space group $P2_1/n$ (tilt system $(a^+b^-b^-)$). However, they have provided no real evidence of either super lattice diffraction lines associated with the in-phase tilting of octahedra or of peak splitting (broadening) that might suggest monoclinic symmetry. In fact, the monoclinic space group $P2_1/n$ is often found for double perovskites $A_2BB'O_6$ when the A-cation is relatively small, e.g. A = Sr; the structures reported in this space group containing the larger Ba may have higher

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symmetry since the mismatch in the sizes of the A-cation and that of the octahedral cavity of the $BO_3/B'O_3$ network is, in general, small. Recently, Li et al. [9] have investigated the $Ba_2PrRu_{1-x}Ir_xO_6$ system using high-resolution powder synchrotron X-ray and neutron diffraction techniques. They have reported a tetragonal space group $P4/mnc$ (tilt system ($a^+b^0c^0$)) for Ba_2PrIrO_6. Although they inferred from the Le Bail analysis carried out that the symmetry of Ir-rich phases are higher than monoclinic, no real proof has been given of Ba_2PrIrO_6 being truly tetragonal. From the refined oxygen positions obtained by Li et al. a tilting angle of the PrO_6/IrO_6 octahedra of about $4.7°$ around the primitive $[001]_p$-axis can be calculated. However, the expansion of the c-axis is insignificant. The c/a ratio of the reduced lattice parameter is just 1.0001 suggesting a cubic metric rather than a tetragonal one. Clearly, the space group $P4/mnc$ contains only in-phase tilting of octahedra around the primitive four-fold axis; such a tilting scheme has not yet been found for other known ordered double perovskites [4].

In a recent X-ray powder diffraction study on Ba_2MIrO_6 (M = La, Y) [10], we showed that the lower symmetry ($P2_1/n$) once reported for these compounds is actually incorrect; Ba_2LaIrO_6 and Ba_2YIrO_6 are rhombohedral ($R\bar{3}$) and cubic ($Fm\bar{3}m$), respectively. Considering that the tolerance factor of Ba_2PrIrO_6 ($t = 0.996$, assuming the valence pair of Pr(IV)/Ir(IV)) is just about equal to that of Ba_2YIrO_6 ($t = 0.997$) and that the phase sequence $R\bar{3} \rightarrow P4/mnc \rightarrow Fm\bar{3}m$ does not seem to be logical one[1] [4], we suspected that both the monoclinic and the tetragonal space groups reported for the title compound are wrong. Therefore, we have re-examined the structure of Ba_2PrIrO_6 and found that it is actually double cubic. In this communication, we report our results obtained from X-ray powder diffraction data.

2. Experimental

Samples of Ba_2PrIrO_6 were prepared from $BaCO_3$, Pr_6O_{11} and Ir metal in platinum crucibles using the standard solid-state reaction. The well-ground mixtures were first reacted at $900°C$ for a few hours. The resultant powders were then sintered at $1250°C$ for several days, accompanied by frequent intermittent regrinding, and finally the samples were furnace-cooled to room temperature. All synthesises were carried out in air.

X-ray diffraction patterns were collected with a Philips PW1050 diffractometer using the monochro-

matic Cu-$K\alpha$ radiation in steps of $0.02°$ (2θ) and $15\,s$ counting time in the range $15° < 2\theta < 116°$. The calculations were performed by the Rietveld method using the Rietica computer program [11]. A polynomial function with six parameters was used to fit the background. The profiles have been fitted using a Pseudo-Voigt function.

3. Results

The X-ray powder diffraction pattern of Ba_2PrIrO_6 at room temperature is shown in Fig. 1. It is dominated by the strong lines characteristic of a primitive perovskite cell and a few weak super lattice diffraction lines. In particular, the noticeable intensities of the super lattice lines at about $18.3°$ and $35.4°$ (2θ) (indicated by asterisks in Fig. 1), which are indexed as (111) and (311) respectively in a double cubic cell, suggest an ordered arrangement of the PrO_6 and IrO_6 octahedra. To identify the possible space group for Ba_2PrIrO_6, we have examined the occurrence of the super lattice diffraction lines as well as the splitting of diffraction peaks corresponding to the basic cubic perovskite cell. We considered the combined octahedral tilting and cation ordering [3,4]. As can be seen easily from Fig. 2(a), the space groups $P2_1/n$ and $P4/mnc$, which allow the in-phase tilting of the adjacent octahedra around the primitive $[001]_p$-axis, are inconsistent with the observed X-ray diffraction patterns. No lines associated with the in-phase tilting can be seen, even at a counting level exceeding 20 000 counts for the strongest reflection. On the other hand, all the observed super lattice lines must be indexed in terms of a double cubic cell, all with odd indices. This suggests that only out-of-phase tilting between the adjacent octahedra is possible if it exists at all. Considering further that octahedral tilting occurs around one of the principle axes, i.e. $[001]_p$, $[110]_p$ and $[111]_p$-axis of the primitive cubic cell, an ordered perovskite structure would have one of the following possible space groups: $I4/m$ ($a^0a^0c^-$), $I2/m$ ($a^0b^-b^-$) and
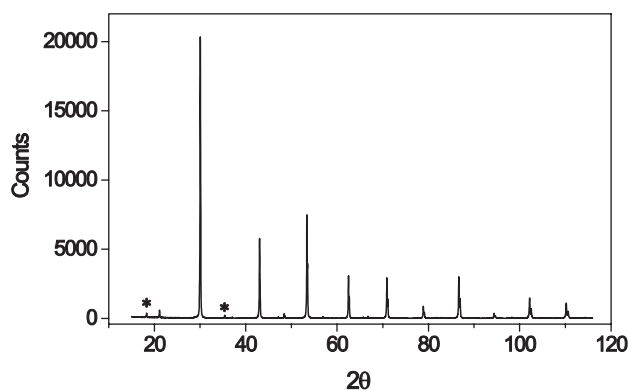

Fig. 1. X-ray powder diffraction pattern of Ba_2PrIrO_6. Peaks marked by an asterisk (*) are the (111) and (311) superlattice reflections.

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[1] Our recent but unpublished work has shown that Ba_2NdIrO_6 ($t = 0.978$) adopts double cubic at room temperature with the cell parameter $a = 8.49014(5)$ Å.
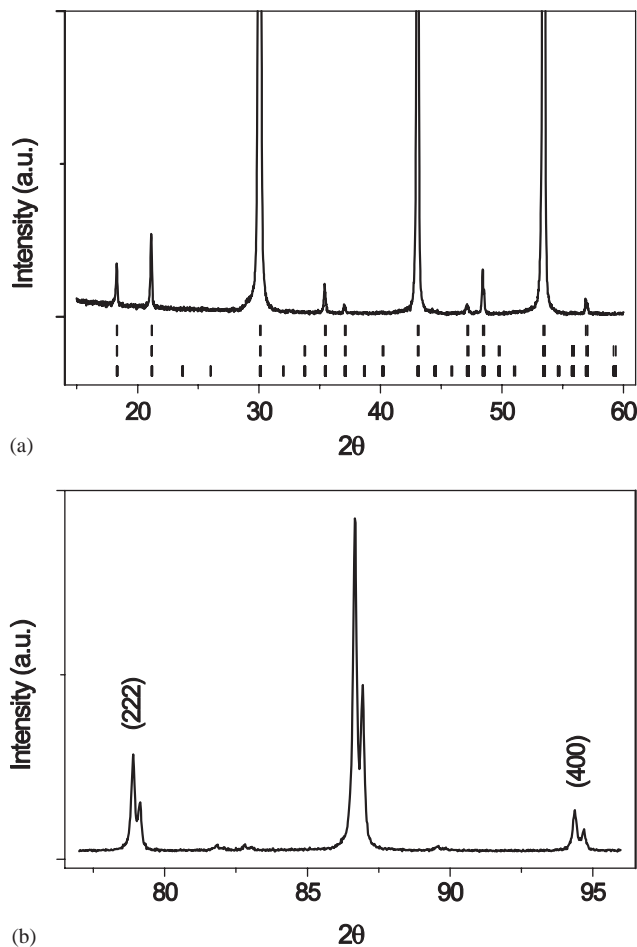
Fig. 2. (a) Is an enlarged section showing the weak super lattice reflections with tick marks indicating the positions of allowed reflections in the space groups $Fm\bar{3}m$ (upper), $P4/mnc$ (middle) and $P2_1/n$ (lower). (b) Shows the basic (222) and (400) diffractions. The splitting of these peaks due to lowering of symmetry is discussed in the text.

$R\bar{3}$ $(a^-a^-a^-)$ including the one without tilting, $Fm\bar{3}m$ $(a^0a^0a^0)$ [3,4]. However, close examination of the main peak splitting has ruled out the possibility of octahedral tilting in Ba_2PrIrO_6. For example, the basic (222) reflection (see Fig. 2(b)) is allowed to split in either $R\bar{3}$ and $I2/m$, but splitting does not occur. On the other hand, the basic (400) diffraction would split in two in both $I4/m$ and $I2/m$ and again it remains as one single peak; only $K\alpha_1$ and $K\alpha_2$ splitting is visible. In fact, we did not observe any peak splitting associated with lower symmetry in the high 2θ-angle part of our X-ray diffraction patterns. Consequently, the likely space group for Ba_2PrIrO_6 is the cubic one, $Fm\bar{3}m$.

Rietveld refinements using the X-ray powder diffraction data of Ba_2PrIrO_6 carried out in $Fm\bar{3}m$ yielded satisfactory results. On convergence, the agreement factors are $R_{wp} = 15.31\%$ ($R_p = 10.23\%$) with a refined cell parameter of $a = 8.40135(6)$ Å. To further justify

our choice of the cubic $Fm\bar{3}m$ model, we refined a model in both $P2_1/n$ and $P4/mnc$, space groups proposed earlier. These models did not refine at all well. For example, the refinement of the monoclinic angle in $P2_1/n$ causes the system to be unstable, this was also observed by Li et al. [9]. On the other hand, the refined cell parameters in $P4/mnc$, $a = 5.9404(2)$ Å and $c = 8.4025(5)$ Å, are not really different from that of the cubic model ($c/a = 1.0002(5)$). In addition, the refined oxygen positions all showed relatively larger standard deviations and their thermal parameters also appeared to be unusual, e.g. $B_{(O1)}$ becomes negative (see Table 1). We concluded, therefore, that the cubic space group $Fm\bar{3}m$ is consistent with the present X-ray diffraction data, correctly describing the crystal structure of Ba_2PrIrO_6.

Table 1 lists the refined atomic positions and thermal parameters. Table 2 gives some selected interatomic distances. The plots of the observed and calculated profiles are shown in Fig. 3.

4. Discussion

The crystal structure of Ba_2PrIrO_6 is of the simple face centred cubic $(NH_4)_3FeF_6$-type, consisting of regular PrO_6 and IrO_6 octahedra in a 1:1 ordering scheme on alternate (111) planes (Fig. 4). Compared to the ideal cubic perovskite, the oxygen atoms are shifted away from Ir atoms along the pseudo-cubic $[100]_p$-axis, resulting in Pr–O and Ir–O bond lengths of 2.142 and 2.058 Å, respectively (Table 2). Using the sum of ionic radii given by Shannon [12], these values are closer to those expected for the valence pair Pr(IV)/Ir(IV) (2.25 and 2.025 Å) compared to the valence pair of Pr(III)/Ir(V) (2.39 and 1.97 Å).

The double cubic structure of Ba_2PrIrO_6 is the one expected given the systematic change of the match between the Ba–O and the averaged (Ln,Ir)–O (Ln = lanthanide) bond lengths. The tolerance factor of Ba_2LaIrO_6 is $t = 0.967$, indicating that the Ba atoms are somewhat too small to fit in the cavity formed by the LaO_6 and the IrO_6 octahedra. Tilting of the octahedra about the primitive $[111]_p$-axis, resulting in the space group $R\bar{3}$, reduces the size of the cavity by reducing some of the cation–anion distances [10]. On the other hand, the tolerance factor of Ba_2PrIrO_6 is very close to unity ($t = 0.996$) and no such bond-length mismatch exists. This is in agreement with the fact that a number of known ordered perovskites which do adopt the cubic space group $Fm\bar{3}m$, e.g. Ba_2TlSbO_6 ($t = 0.993$) [13], Ba_2YSbO_6 ($t = 0.99$), Ba_2HoSbO_6 ($t = 0.99$) [14] and Ba_2YIrO_6 ($t = 0.997$) [10], all have tolerance factors close to unity. We have noticed too that Hinatsu et al. [15] have corrected their earlier description of the structure as monoclinic in the case of Ba_2HoMO_6

Table 1
Refined atomic positions, thermal parameters and lattice constants of Ba_2PrIrO_6 in the space group $Fm\bar{3}m$

$Fm\bar{3}m$					$P4/mnc$				
Atom	x	y	z	$B(\mathring{A})^2$	Atom	x	y	z	$B(\mathring{A})^2$
Ba (8c)	0.25	0.25	0.25	0.59(2)	Ba (4d)	0.5	0.25	0.25	0.66(2)
Pr (4a)	0	0	0	0.35(3)	Pr (2a)	0	0	0.5	0.48(3)
Ir (4b)	0.5	0.5	0.5	0.28(2)	Ir (2b)	0.5	0.5	0.5	0.32(2)
O (24e)	0.2550(7)	0	0	0.54(10)	O1 (4e)	0	0	0.255(10)	−0.4(19)
					O2 (8h)	0.246(8)	0.736(6)	0	1.3(12)

$a = 8.40135(6)$ Å

$R_{wp} = 15.31\%$, $R_p = 10.23\%$, $\chi = 1.80$

$a = 5.9404(2)$ Å and $c = 8.4025(5)$ Å

$R_{wp} = 15.39\%$, $R_p = 10.33\%$, $\chi = 1.81$

The refined values in the space group $P4/mnc$ are also listed for comparison.

Table 2
Selected interatomic distances (Å) in Ba_2PrIrO_6

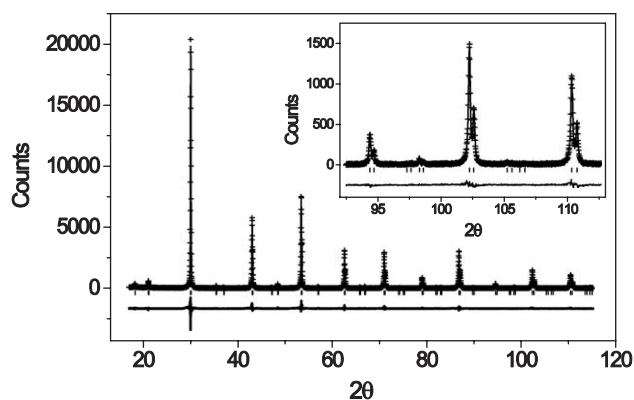| Pr–O	$2.142(6) \times 6$
Ir–O	$2.058(6) \times 6$
Ba–O	$2.9706(1) \times 12$

Fig. 3. Observed (crosses) and calculated (continuous line) profiles of Ba_2PrIrO_6 in the space group $Fm\bar{3}m$. Insert shows the section of high 2θ-angle part. Tick marks indicate the positions of allowed reflections. A difference curve $(I_{obs.}-I_{cal.})$ is shown at the bottom.

Fig. 4. Schematic representation of the crystal structure of Ba_2PrIrO_6 showing the PrO_6 (dark shaded) and IrO_6 (light shaded) octahedra and the Ba atoms (black).

($M =$ Ru, Ir). However, they did not comment on the other double perovskites Ba_2LnMO_6 ($Ln =$ lanthanide; $M =$ Ru and Ir). Both compounds were found to have the cubic space group $Fm\bar{3}m$, as is expected from their respective tolerance factors ($t = 0.998$ and 0.997).

As was mentioned above, neither the space group $P2_1/n$ nor the space group $P4/nmc$ is consistent with the observed X-ray diffraction pattern of Ba_2PrIrO_6. In the crystal structure study of the $Ba_2PrRu_{1-x}Ir_xO_6$ system [9], Li et al. did show the presence of a small peak at $2\theta \approx 19.1°$ in their synchrotron X-ray diffraction data of Ba_2PrRuO_6 (Fig. 3 in Ref. [9]). Since this diffraction peak is allowed in the space groups $P2_1/n$ or $P4/nmc$ and not in the space group $I4/m$, which may be used to
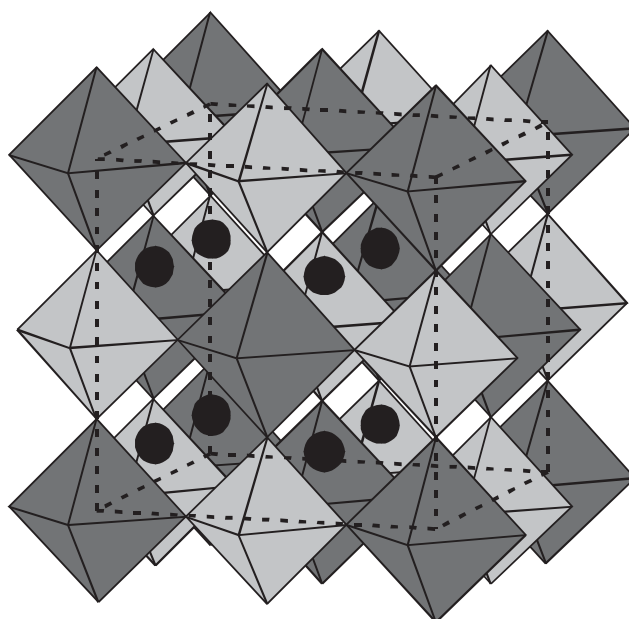
describe structures containing the out-of-phase octahedral tilting, they have modeled their diffraction data of the Ir-rich phase in $Ba_2PrRu_{1-x}Ir_xO_6$ with the tetragonal $P4/nmc$ space group. However, the authors showed also that the intensity of the same diffraction line is rapidly weakened upon Ir-substitution, and it is no longer observable when the Ir concentration is above about 40% (Fig. 4 in Ref. [9]). Consequently, it does not seem to be logical to assign the space group $P4/nmc$ to Ba_2PrIrO_6. It is also noticed that their neutron powder diffraction data of $Ba_2PrRu_{0.7}Ir_{0.3}O_6$ at 100 K, which is assumed to crystallize in the tetragonal space group $P4/nmc$, shows no in-phase octahedral tilting (the tilting angle is merely $0.2(2)°$), the refined oxygen positions are just those expected in the space group $Fm\bar{3}m$ within the standard deviations.

It is interesting to consider the structure of the related double perovskite Ba_2PrRuO_6 once more. This compound has been described previously as monoclinic in the space group $P2_1/n$ [9,16]. In the light of the present investigation, such a description is doubtful. Compared to Ba_2PrIrO_6, the tolerance factor of Ba_2PrRuO_6, $t = 0.977$, assuming the valence pair of Pr(III)/Ru(V), deviates somewhat more from unity; but the value lies between those of rhombohedral Ba_2LaIrO_6 ($R\bar{3}$) and cubic Ba_2PrIrO_6 ($Fm\bar{3}m$). In fact, the published neutron [16] and synchrotron X-ray powder diffraction data [9] of Ba_2PrRuO_6 showed the presence of only one weak diffraction peak, indexed as (321) in a double edge cubic cell. This reflcection is not allowed in the space groups derived from out-of-phase octahedral tilting or the absence of any tilting at all. Although the position of this peak coincides with an allowed diffraction line in the space group $P2_1/n$ (or $P4/mnc$), the idea of it originating from the in-phase octahedral tilting seems questionable. For example, considering that octahedral tilting is nearly rigid, it is rather unusual that the (321) diffraction is the strongest as well as the only visible super lattice reflection in both neutron and X-ray diffraction data. In fact, using the refined atomic positions given in Refs. [9,16], the simulated neutron and X-ray diffraction pattern should show the presence of other superlattice diffractions with comparable intensity. In particular, the model given by Li et al. suggested that the intensity of the supperlattice reflections at $2\theta \approx 15.3°$ and $21.1°$, indexed respectively as (221) and (410) reflections in a double cubic cell, should be 4 and 5 times higher than that of the (321) reflection ($2\theta \approx 19.1°$). Therefore, we suspect that the observed weak peak may be due to a contamination, e.g. the hollandite-type $BaRu_6O_{12}$ [17,18], though a complete identification appeared to be difficult due to extremely low intensity of this reflection and limited regions given in the literatures. Clearly, the structure of Ba_2PrRuO_6, as well as the structure of $Ba_2PrRu_{1-x}Ir_xO_6$, necessitates further investigation.

In conclusion, we have studied the crystal structure of Ba_2PrIrO_6 using X-ray powder diffraction techniques. It is an ordered double perovskite containing the valence pair of Pr(IV)/Ir(IV). Contrary to the previously reported structure, no octahedral tilting was found to occur in Ba_2PrIrO_6, and the corresponding space group is $Fm\bar{3}m$.

Acknowledgments

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