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Crystal structure of Ba_2InTaO_6 as determined by the Rietveld refinement

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Rietveld profile analysis of X-ray diffraction data was carried out to determine the symmetry and crystal structures of the double perovskite Ba_2InTaO_6. Contrary to a recent study of Raman spectroscopy, we find no evidence that Ba_2InTaO_6 adopts the tetragonal space group $P4/mnc$ of the tilt system $a^0a^0c^+$. Instead, it has cubic symmetry with the space group $Fm\bar{3}m$ in the temperature range 82–723 K. In Ba_2InTaO_6 the ordering between In(III) and Ta(V) cations is a difficult process requiring prolonged heat treatment at high temperature.

1. Introduction

In the past years the crystal structures of double perovskites with the formula $Ba_2Ln(III)M(V)O_6$, in which Ln is a trivalent lanthanide or Y and M is a pentavalent metal cation, have been extensively studied. The relationship between the structure and the tolerance factor (t), defined as

$$t=\frac{(r_{Ba}+r_O)}{\sqrt{2}(\bar{r}_{(Ln,M)}+r_O)}$$

with $\bar{r}_{(Ln,M)}$ being the averaged ionic radius of the Ln and M cations, follows the trends: (i) The cubic $Fm\bar{3}m$ (tilt system $a^0a^0a^0$) structure occurs with the tolerance factor t being above about 0.98. (ii) When t is approximately between 0.96 and 0.98, the double perovskites adopt either the rhombohedral $R\bar{3}$ (tilt system $a^-a^-a^-$) or the tetragonal $I4/m$ (tilt system $a^0a^0c^-$) structure. (iii) With even lower t, the monoclinic $I2/m$ structure (tilt system $a^0b^-b^-$) is found. (iv) At room temperature all tilt systems occurred in Ba_2LnMO_6 contain only the out-of-phase tilting of the octahedra about the two-, three- and four-fold axis of the cubic aristotype.

Several other tilt systems have also been reported for the $Ba_2Ln(III)M(V)O_6$-type double perovskites. One particular example is the tilt system $a^0a^0c^+$ of the space group $P4/mnc$, first reported for Ba_2PrIrO_6 [1]. In contrast to the commonly observed tilt system $a^0a^0c^-$ ($I4/m$), the $P4/mnc$ structure contains in-phase tilting between the adjacent octahedra about the four-fold axis of the cubic aristotype. However, the re-examination of the crystal structure of Ba_2PrIrO_6 using X-ray powder diffraction data [2] disproved this assignment showing that it is a double cubic perovskite instead. The same result has also been observed by a recent investigation using high-resolution time-of-flight neutron powder diffraction technique [3].

Similarly, Ba_2InTaO_6, with a tolerance factor $t=1.004$, was previously reported to be cubic having the space group $Fm\bar{3}m$ [4,5]. However, a recent paper by Dias et al. [6], using Raman spectroscopy, shows that Ba_2InTaO_6 is not cubic since the Raman spectrum presents more than four Raman-active modes predicted by the space group $Fm\bar{3}m$. Therefore, they assigned the space group $P4/mnc$ for this compound, and fitted the observed Raman spectrum with 14 Lorentzian lines. Although the fit they show may seem to account for the observed Raman data, doubts are cast on the validity of their assignment. First, the choice of the space group $P4/mnc$ is somewhat arbitrary; no systematic comparison among the other possible tilt systems is given except for the tilt system $a^0a^0c^-$ ($I4/m$). Second, it is questionable whether the diffuse-like Raman spectrum between 130 and 310 cm^{-1} can be described in terms of six phonon modes whereas the similar kinks, e.g. at ~425 and ~600 cm^{-1}, etc., are neglected. Third, while Raman spectroscopy may be sensitive to (local) symmetry, it does not provide full description of the crystal structure. It is uncommon to determine the space group of a compound based on the Raman spectroscopy alone.

The structural details of the double perovskites Ba_2LnTaO_6 (Ln=lanthanide and Y) have recently been reported [7]. At room temperature, three structures were identified*: monoclinic $I2/m$ for Ln=La–Nd ($t=0.952$–0.962); tetragonal $I4/m$ for Ln=Eu–Dy ($t=0.97$ to -0.978); cubic $Fm\bar{3}m$ for Ln=Ho–Lu and Y (0.981–0.99).

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* Ba_2SmTaO_6 ($t=0.968$) was found to be a mixture of the $I2/m$ and $I4/m$ phases at room temperature [7].

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Further, the cubic phase, e.g. Ba_2YTaO_6 [8] and Ba_2HoTaO_6 [9], undergoes the phase transition to the tetragonal $I4/m$ structure at low temperature ($T=253$ and 260 K, respectively). The ionic radius of In(III) (0.80 Å) is somewhat smaller than that of Lu(III) (0.861 Å), but the tolerance factor of Ba_2InTaO_6 ($t=1.004$) is just about equal to the unity. Therefore, it is an interesting question of whether the reported tetragonal space group $P4/mnc$ indeed occurs in this compound, and, if it does, the phase sequence in the Ba_2LnTaO_6 series would be $I2/m \rightarrow I4/m \rightarrow Fm\overline{3}m \rightarrow P4/mnc$ with decreasing the size of trivalent cations. Furthermore, the tetragonal Ba_2InTaO_6 is expected to become cubic at high temperature. The phase transition, $P4/mnc \rightarrow Fm\overline{3}m$, is then different from the one observed in Ba_2YTaO_6 and Ba_2HoTaO_6 ($I4/m \rightarrow Fm\overline{3}m$) with increasing temperature. To clear these questions, we carried out a detailed analysis of X-ray powder diffraction data recorded in the temperature range between 82 and 723 K. In this paper, we confirm that the symmetry of Ba_2InTaO_6 is cubic. No evidence has been found that it adopts the tilt system $a^0a^0c^+$ at the temperature range investigated.

2. Experimental

Samples of Ba_2InTaO_6 were prepared from $BaCO_3$, In_2O_3 or $In(OH)_3$ and Ta_2O_5 in alumina crucibles using the standard solid-state reaction. The thoroughly ground mixtures were first heated at 900 °C overnight. The resultant powders were then reground and sintered at 1400 °C for 24 h. However, an initial X-ray diffraction has shown the ordering lines are quite diffuse with weak intensity. The sintering temperature was raised to 1500 °C and the samples were kept at this temperature for several cycles of 12 h, with intermediate grindings, until the intensity of the ordering lines no longer changes. All synthesises were carried out in air and the samples were furnace cooled to room temperature with cooling rate of about 5 °C/min.

X-ray powder diffraction data were collected with a Philips X'Pert diffractometer, equipped with the X'celerator, using Cu$K\alpha$ radiations, in steps of 0.02° (2θ) and 10 s counting time in the range $15^\circ < 2\theta < 140^\circ$. 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 model refinements were performed by the Rietveld method using the Rietica computer program [10]. The Chebyshev-polynomial function with 12 parameters was used to fit the background. The profiles were described by a Pseudo-Voigt function.

3. Results

X-ray powder diffraction pattern of Ba_2InTaO_6 at room temperature is shown in Fig. 1. It is easily recognized as an ordered perovskite from the substantial intensity of the ordering lines (indicated by arrows). However, the degree of order between octahedral site cations depends on both the sintering temperature and the sintering time. The inset in Fig. 1 shows the evolution of the superlattice line at $2\theta \approx 18.5^\circ$, indexed as (111) in a double cubic cell, as compared with the basic (100) reflection ($2\theta \approx 21.5^\circ$). The intensity of the superlattice reflection increases with both the sintering temperature and time, suggesting that the cation ordering is controlled by kinetics rather than thermodynamics. The similar phenomenon has been observed previously in the related double perovskite Sr_2AlTaO_6 [11].

The space groups reported thus far for Ba_2InTaO_6 are $Fm\overline{3}m$ [4,5] and $P4/mnc$ [6], respectively. To identify the correct one, we have examined the splitting of some reflections which are sensitive to the crystal symmetry. In Fig. 2, we plotted the basic (222) and (400) reflections. If $P4/mnc$ is the true space group, these reflections should appear as singlet and doublet, respectively. It is not the case: both reflections are seen as single line except the obvious $K\alpha_1$ and $K\alpha_2$ splitting. In fact, none of the measured reflections shows apparent splitting. To see whether the non-observable peak splitting might be due to a too small tetragonal distortion, we closely examined the values of the full-width at half-maxima (FWHM) by fitting the experimental data with the pseudo-Voigt function. This analysis does not reveal any deviation from a cubic symmetry. For example, the fitted FWHM-values ($\Delta_{2\theta}$) for the basic (310) ($2\theta \approx 72^\circ$), (222) ($2\theta \approx 80^\circ$), (321) ($2\theta \approx 88.5^\circ$) and (400) ($2\theta \approx 96.4^\circ$) reflections are 0.084°, 0.092°, 0.098° and 0.106°, respectively. In the space group $P4/mnc$, those reflections would be seen as triplet, singlet, triplet and doublet. The quasi linear behavior of $\Delta_{2\theta}$ as function of 2θ is typically the angle-dependent FWHMs showing that the basic reflections are not split. The fact that Ba_2InTaO_6 is unlikely to adopts the space group $P4/mnc$ can also be seen from the X-ray diffraction data taken at non-ambient temperature. Suppose that Ba_2InTaO_6 is tetragonal at room temperature [6], the distortion is expected to be larger at low temperature and becomes smaller or eventually disappears at high temperature [8,9]. The evolution of the basic (222) and (400) reflections as function of temperature is shown in Fig. 2 as inset. Clearly, their profiles remain unchanged on cooling and on heating. The fitted FWHM-values are 0.0924(3)°

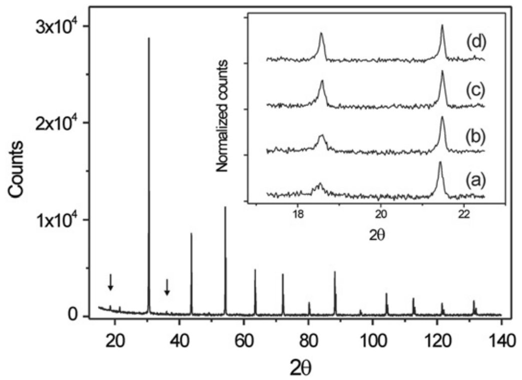

Fig. 1. X-ray powder diffraction pattern of Ba_2InTaO_6 at room temperature. Arrows indicate the superlattice reflections due to B-cation ordering. Inset shows the evolution of the ordering line at $2\theta \approx 18.5^\circ$ as compared to the basic (100) reflection ($2\theta \approx 21.5^\circ$). The sintering conditions are (a) 1400 °C, 24 h; (b) 1400 °C, 24 h+1500 °C, 12 h; (c) 1400 °C, 24 h+1500 °C, 24 h; (d) 1400 °C, 24 h+1500 °C, 36 h.

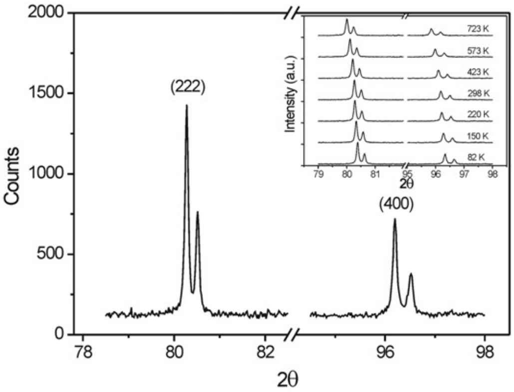

Fig. 2. Enlarged sections showing the basic (222) and (400) reflections of Ba_2InTaO_6 at room temperature. Insert shows the evolution of these reflections as function of temperature.

Table 1
Refined crystallographic data of Ba_2InTaO_6 at some selected temperature.

Ba_2InTaO_6 ($Fm\overline{3}m$)					
T (K)	82	150	300	423	723
a (Å)	8.27460(2)	8.27678(2)	8.28279(3)	8.29040(3)	8.30262(3)
Ba	8*c* (0.25,0.25,0.25)				
B (Å)^2	0.17(1)	0.23(1)	0.43(2)	0.48(2)	0.83(2)
In	4*a* (0,0,0)				
B (Å)^2	0.04(2)	0.05(2)	0.05(3)	0.09(2)	0.30(3)
Ta	4*b* (1/2,1/2,1/2)				
B (Å)^2	0.14(2)	0.15(2)	0.16(3)	0.13(2)	0.41(2)
O	24*e* (*x*,0,0)				
x	0.2568(5)	0.2572(5)	0.2565(7)	0.2568(6)	0.2578(6)
B (Å)^2	0.35(6)	0.56(6)	0.57(7)	0.61(6)	1.02(7)
	$R_{wp}=8.60\%$ $R_p=6.52\%$ $\chi^2=1.77$	$R_{wp}=8.53\%$ $R_p=6.50\%$ $\chi^2=1.75$	$R_{wp}=8.09\%$ $R_p=5.98\%$ $\chi^2=1.81$	$R_{wp}=8.32\%$ $R_p=6.38\%$ $\chi^2=1.65$	$R_{wp}=7.91\%$ $R_p=5.90\%$ $\chi^2=1.50$

Table 2
Interatomic distances at some selected temperatures in Ba_2InTaO_6.

	T=82 K	*T*=300 K	*T*=723 K
Ba–O (Å)	2.92593(7) × 12	2.9288(1) × 12	2.9362(1) × 12
In–O (Å)	2.118(4) × 6	2.115(6) × 6	2.141(5) × 6
Ta–O (Å)	2.020(4) × 6	2.026(6) × 6	2.010(5) × 6

and 0.109(5)°, respectively, indicating that the symmetry of Ba_2InTaO_6 does not change in this temperature range.

Rietveld refinements in the space group $Fm\overline{3}m$ yielded satisfactory results. The refined cell parameter at room temperature is $a=8.28279(3)$ Å, and the agreement factors are $R_{wp}=8.09\%$ and $R_p=5.98\%$ with goodness of fit $\chi^2=1.81$. The attempt to refine the occupancy factors of two *B*-sites resulted in following values: 0.988(7)/0.012(7). Since these values are not truly significant, the final refinement is carried out in the model with full cation ordering. To further justify our choice of the cubic $Fm\overline{3}m$ model, we also refined a model in the space group $P4/mnc$ as was suggested by Raman spectroscopy [6]. While the similar agreement factors were obtained ($R_{wp}/R_p=8.27\%/6.22\%$ with $\chi^2=1.89$), the refined cell parameters, $a=5.85640(7)$ Å and $c=8.28396(18)$ Å, do not really differ from cubic symmetry. The ratio between *c*- and *a*-axis, when using the values corresponding to the primitive cell, is $c/a=1.0002$. In addition, the refined oxygen positions, $x_{O(2)}=0.2479(34)$, $y_{O(2)}=0.7327(40)$ and $z_{O(1)}=0.2534(62)$, all showed relatively larger standard deviations and their thermal parameters become abnormal, e.g. $B_{O(1)}=9.2(9)$ Å^2 and $B_{O(2)}=-1.4(2)$ Å^2. Clearly, the space group $P4/mnc$ fails to describe the structure of Ba_2InTaO_6. Table 1 shows the refined crystallographic data of Ba_2InTaO_6 at some selected temperatures. Table 2 gives some selected interatomic distances. The plots of the observed and calculated profiles are shown in Fig. 3.

4. Discussion

The present investigation shows that Ba_2InTaO_6 is cubic in the temperature range 82–723 K. It consists of rock salt ordering of In(III) and Ta(V) cations in alternate (111) planes. The oxygen atoms are slightly shifted away from Ta along the pseudo-cubic $[100]_p$-axis, resulting in two distinct InO_6 and TaO_6 octahedra. The In–O and Ta–O bond lengths at room temperature are 2.115(6) and 2.026(6) Å, respectively (Table 2), which are very close to the values of the sum of Shannon's ionic radii of the corresponding ions (2.20 and 2.04 Å) [12]. The Ba–O bond distance, 2.9288(1) Å, is also in agreement with the sum of the ionic radii (3.01 Å).

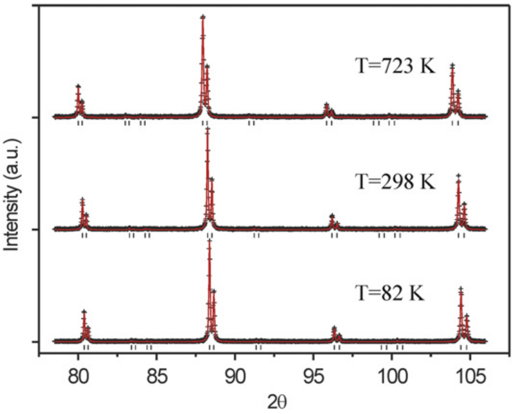

Fig. 3. Observed (crosses) and calculated (continuous line) profiles of Ba_2InTaO_6 in the space group $Fm\overline{3}m$ at some selected temperature. Only the reflections at high diffraction angle part are shown. Tick marks below indicate the positions of the allowed Bragg's reflections.

The observed space group $Fm\overline{3}m$ for Ba_2InTaO_6 is the one expected given the systematic change of ionic radii in Ba_2LnTaO_6. For larger trivalent *Ln*, e.g. *Ln*=La–Dy, the tolerance factors, $t=0.952$–0.978, are significantly smaller than the unity, leading to a large mismatch between the Ba–O and the averaged (*Ln*, Ta)–O bond lengths. Since Ba is undersize, tilting of the octahedra occurs that reduces the size of the cavity by reducing some of the Ba–O distances. As the *Ln* becomes smaller, e.g. *Ln*=Ho–Lu and Y, the tilting of the octahedra is no longer necessary and the double perovskite adopts the cubic space group $Fm\overline{3}m$. The tolerance factor of Ba_2InTaO_6 ($t=1.004$) would suggest a perfect match between the cuboctahedral and octahedral ions in perovskite structure. In fact, several known cubic double perovskites of this type all have tolerance factors close to unity. Examples are Ba_2TlSbO_6 ($t=0.993$) [13], Ba_2YSbO_6 ($t=0.99$), Ba_2HoSbO_6 ($t=0.99$) [14], Ba_2YIrO_6 ($t=0.997$) [15], Ba_2YNbO_6 ($t=0.981$) [16,17] and Ba_2YTaO_6 ($t=0.981$) [7,18].

Dias et al. reported that the symmetry of Ba_2LaIrO_6 at room temperature and below is not cubic but tetragonal due to the in-phase tilting of the adjacent $(In/Ta)O_6$ octahedra [6]. They came to this conclusion because their Raman spectrum at room temperature shows more than four Raman-active modes being allowed by the space group $Fm\overline{3}m$. They fitted, therefore, the Raman spectrum in terms of 14 Lorentzian peaks predicted by the space group $P4/mnc$. Although this approach is common to Raman spectroscopists, the validity of their assignment is questionable. For example, many of the additional lines in the wavenumbers between 120 and 310 cm^{-1} are too defuse to be considered as true Raman peaks. In addition, some small kinks at about 425, 500, 600 and 670 cm^{-1} exist as well which are, nevertheless, ignored in their analysis. Further, while no phase transition to lower symmetry was concluded, the Raman doublet in the spectra interval 750–900 cm^{-1} show visibly split at low temperature. Since the possible Raman modes have not been assigned to any of those peaks, the Raman fit described by Dias et al. is merely mathematic rather than crystallographic.

As was mentioned above, the X-ray diffraction data taken at various temperatures do not support the tetragonal symmetry reported for Ba_2InTaO_6. Generally speaking, varying temperature has a similar, but opposite, effect as changing the ionic radii. In other words, the structural distortion from cubic symmetry due to octahedral tilting is expected to be larger at low temperature and becomes smaller or eventually disappears at elevated temperature. This is not the case; the FWHM-values of the basic (400) reflection remain virtually constant in the temperature span of more than 600 K (Fig. 2). It should be pointed out that the laboratory X-ray diffractometer may provide sufficient resolution to identify even small distortions if the quality of samples is high. This is the case of the present double perovskite Ba_2InTaO_6. Assuming that the observed FWHM-value of the basic (400) reflection at room temperature ($\Delta_{2\theta}=0.106^\circ$) corresponds to the cubic symmetry (Fig. 4(a)), a simple simulation, using the same profile parameters, shows that this reflection should visibly split in the space group $P4/mnc$ if the c/a ratio is just 1.001 (Fig. 4 (c)). Even if the c/a ratio is 1.0005, the change of the FWHM-value, being from 0.106° to 0.137°, should be recognizable from the diffraction pattern (Fig. 4 (b)). Clearly, such a detection limit is sufficient for tetragonal distortion usually observed in this type of double perovskites: Ba_2HoTaO_6 ($c/a=1.0036$ at 200 K) [9], Ba_2GdNbO_6 ($c/a=1.0043$ at 298 K) [17], Ba_2YTaO_6 ($c/a=1.0030$ at high pressure) [18] and Ba_2EuNbO_6 ($c/a=1.0045$ at 298 K) [19].

It is well known that Raman spectroscopy alone cannot provide full description of a crystal structure. However, it is site sensitive, and thus a suitable probe for local structure and lattice dynamics. Often, Raman spectrum shows additional lines than those calculated from the factor group analysis which may be due to various reasons such as impurity phases [20], second-order Raman scattering [21], electronic transition [22], etc. It is unclear what the additional Raman lines observed in Ba_2InTaO_6 may signify [6]. We noticed, however, that Dias et al. prepared the sample in a relatively short time, and their X-ray diffraction pattern shows apparently no visible reflection at $2\theta \approx 36^\circ$ arising from the B-site ordering. Indeed, the anti-site disorder has been observed in some our samples shown in Fig. 1. For example, the refined occupancy factors of samples (a) and (b) are 0.826(6)/0.174(6) and 0.880(5)/0.120(5), respectively. Those samples have also slightly larger lattice constants, being 8.28800(5) and 8.28602(4) Å for samples (a) and (b), than the fully ordered sample. On the other hand, the Raman spectra reported for Ba_2YTaO_6 [21] and Ba_2YbTaO_6 [23] also show the similar (diffuse) lines. Interestingly, many of the additional lines have been attributed to the infrared-active mode (F_{1u}) as due to disorder induced Raman activity. Whether this may account for the observed Raman spectra of Ba_2InTaO_6 requires further investigation; but even so, the local symmetry due to disorder cannot be described in terms of space group such as $P4/mnc$, which depicts the cooperative octahedral tilting in perovskites.

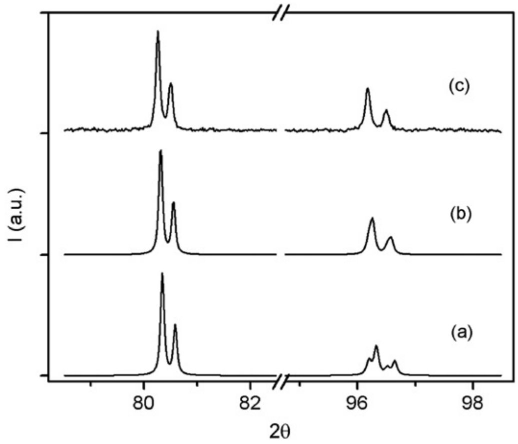

Fig. 4. Part of the calculated X-ray diffraction profiles of Ba_2InTaO_6 in the space group $P4/mnc$ using c/a ratio of 1.001 (a) and 1.0005 (b), respectively, as compared with the observed profiles (c). Note that the split of basic (400) reflection is clearly visible in (a).

In conclusion, we have investigated the crystal structure of the double perovskite Ba_2InTaO_6 using X-ray powder diffraction techniques in the temperature range between 82 and 723 K. Careful profile analysis shows that Ba_2InTaO_6 adopts the cubic space group $Fm\overline{3}m$. The reported tetragonal space group $P4/mnc$ from Raman spectroscopy study has not been confirmed at the temperature range investigated.

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