Crystal structure of Ba_2InTaO_6 as determined by the Rietveld refinement

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ABSTRACT

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 $Fm\overline{3}m$ 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.

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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

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

with $\overline{r}_{(Ln,M)}$ being the averaged ionic radius of the Ln and M cations, follows the trends: (i) The cubic $Fm\overline{3}m$ (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 $R\overline{3}$ (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 $Fm\overline{3}m$ [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 $Fm\overline{3}m$. 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 $Fm\overline{3}m$ 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].

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 $15° < 2\theta < 140°$. 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 $\sim$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 $2\theta \approx 18.5°$, indexed as (111) in a double cubic cell, as compared with the basic (100) reflection ($2\theta \approx 21.5°$). 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
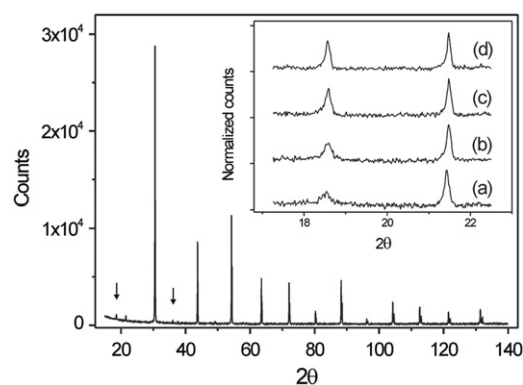

Fig. 1. X-ray powder diffraction pattern of Ba_2InTaO_6 at room temperature. Arrows indicate the superlattice reflections due to B-cation ordering. Inset shows the evolution of the ordering line at $2\theta \approx 18.5°$ as compared to the basic (100) reflection ($2\theta \approx 21.5°$). The sintering 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.
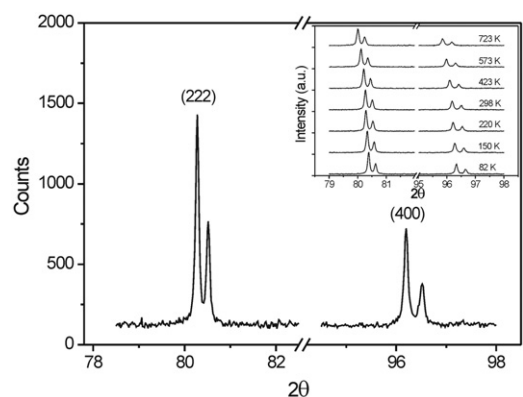

Fig. 2. Enlarged sections showing the basic (222) and (400) reflections of Ba_2InTaO_6 at room temperature. Insert shows the evolution of these reflections as function of temperature.

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) ($2\theta \approx 72°$), (222) ($2\theta \approx 80°$), (321) ($2\theta \approx 88.5°$) and (400) ($2\theta \approx 96.4°$) 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)°