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High-temperature structural studies of $\text{PbBi}_2\text{M}_2\text{O}_9$ ($\text{M} = \text{Nb}$ and Ta)

Rene Macquart¹, Brendan J Kennedy¹, Brett A Hunter² and
Christopher J Howard^{2,3}

¹ The Centre for Heavy Metals Research, School of Chemistry, The University of Sydney,
New South Wales 2006, Australia

² ANSTO PMB 1 Menai, New South Wales 2234, Australia

³ School of Physics, The University of Sydney, New South Wales 2006, Australia

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Abstract

A high-resolution synchrotron diffraction study of the temperature dependence of the structures of the two layered Bi oxides $\text{PbBi}_2\text{Ta}_2\text{O}_9$ (PBT) and $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBN) is reported. The transition from the low-temperature orthorhombic ferroelectric structure to the high-temperature tetragonal paraelectric structure in PBN involves an intermediate orthorhombic paraelectric phase. We conclude that this has the same *Amam* structure as observed in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and its Bi-rich analogue. Identifying the sequence of phase transitions in PBT is more challenging since above 200 °C the structure is metrically tetragonal within the resolution of the synchrotron diffraction measurements. By contrast, neutron diffraction measurements suggest that PBT remains orthorhombic to above the Curie temperature ≈ 430 °C. The possible identity of the intermediate space group is discussed.

1. Introduction

The Aurivillius-type phases are a family of layered bismuth oxides [1] that are based on a structural motif of a regular stacking of $[\text{Bi}_2\text{O}_2]^{2+}$ slabs and perovskite-like $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ blocks. Although these types of oxide have been known for over 50 years there has been a recent resurgence of interest in their structures since their ferroelectric properties make them attractive candidates for use in nonvolatile memory chips [2]. In general the dielectric constants of the Aurivillius oxides show a broad maximum at the Curie temperature and it has been postulated that this is a consequence of disorder between Bi from the $[\text{Bi}_2\text{O}_2]^{2+}$ layers and the perovskite-like A-type cations [3]. Consequently, considerable effort has been directed towards the identifying and understanding the factors that influence the extent of cation disorder in the $n = 2$ compounds, that is, in the oxides of the type $\text{ABi}_2\text{M}_2\text{O}_9$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ and $\text{M} = \text{Nb}, \text{Ta}$) [4–7]. In this respect we have found that the extent of cation disorder

is greatest in $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBN)[4] due to the similar stereochemical requirements of the isoelectronic Pb^{2+} and Bi^{3+} cations. Replacing the Pb with an alkaline-earth cation (Ca, Sr or Ba) considerably reduces the extent of cation disorder, although it does not totally eliminate it [5, 6]. The persistence of cation disorder in these oxides reflects the local bonding effects between the perovskite-like slabs and the $[\text{Bi}_2\text{O}_2]^{2+}$ layers.

The structures of the ferroelectric Aurivillius oxides are derived from a non-polar high-temperature tetragonal structure (space group $I4/mmm$). The most commonly observed orthorhombic structure (SG $A2_1am$) is obtained from the high-temperature prototype by a combination of displacement of the perovskite-type B cations and tilting of the BO_6 octahedral units. Of the various Aurivillius-type oxides studied in recent times two $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and its Bi-rich analogue $\text{Sr}_{0.85}\text{Bi}_{2.1}\text{Ta}_2\text{O}_9$, have attracted the most attention [8, 9]. Variable-temperature high-resolution powder neutron diffraction studies of both these oxides have demonstrated the existence of an intermediate paraelectric phase that is described in SG Amm [8, 9].

As part of our ongoing studies of the structures and phase transitions in perovskite-type oxides we have examined the structure of the two oxides PBN and $\text{PbBi}_2\text{Ta}_2\text{O}_9$ (PBT) from room temperature up to 750°C using high-resolution synchrotron x-ray diffraction methods. Neutron diffraction methods have also been used in the study of both oxides, the room temperature measurements on PBN being reported earlier [4], and the neutron study on PBT being presented here.

2. Experimental details

The polycrystalline samples PBN and PBT were prepared using published methods [4]. Variable-temperature synchrotron x-ray diffraction patterns were recorded on the Debye-Scherrer diffractometer at beamline 20B, The Australian National Beamline Facility [10], at the Photon Factory in Japan, using a custom-built furnace. For the x-ray measurements, samples were loaded into 0.3 mm quartz glass capillaries, and data were recorded at $\lambda = 0.6508 \text{ \AA}$ over the angular range $5^\circ \leq 2\theta \leq 45^\circ$ using a single image plate. This wavelength is just below the Nb L edge and well above the Pb and Bi edges. Powder neutron diffraction patterns were collected at a wavelength of 1.88 \AA on the high-resolution powder diffractometer at ANSTO's HIFAR reactor [11]. The PBT sample was housed in a 10 mm diameter steel can for the measurements. Structures were refined using the Rietveld method implemented in the program Rietica [12]. Although the oxides exhibit considerable Pb-Bi disorder [4] no attempt was made to refine this since the scattering factors for Pb and Bi at 0.6508 \AA are essentially equal. Likewise the neutron scattering lengths of Pb and Bi are sufficiently similar to preclude useful estimates of the extent of cation disorder.

3. Results and discussion

Portions of the synchrotron diffraction pattern of PBN at room temperature and 750°C are shown in figure 1. The well resolved splitting of the (315) and (513) reflections near $2\theta = 22.6^\circ$ evident in the diffraction pattern recorded at room temperature demonstrates that PBN is orthorhombic at this temperature. This was confirmed by examination of the powder neutron diffraction pattern, figure 2, which showed a (213)-type reflection indicative of rotations of the NbO_6 . As found previously [4], refinement of the room temperature structure of PBN in space group $A2_1am$ provided a satisfactory fit to the observed synchrotron and neutron diffraction data. As the temperature is increased the splitting between the (315) and (513) reflections seen

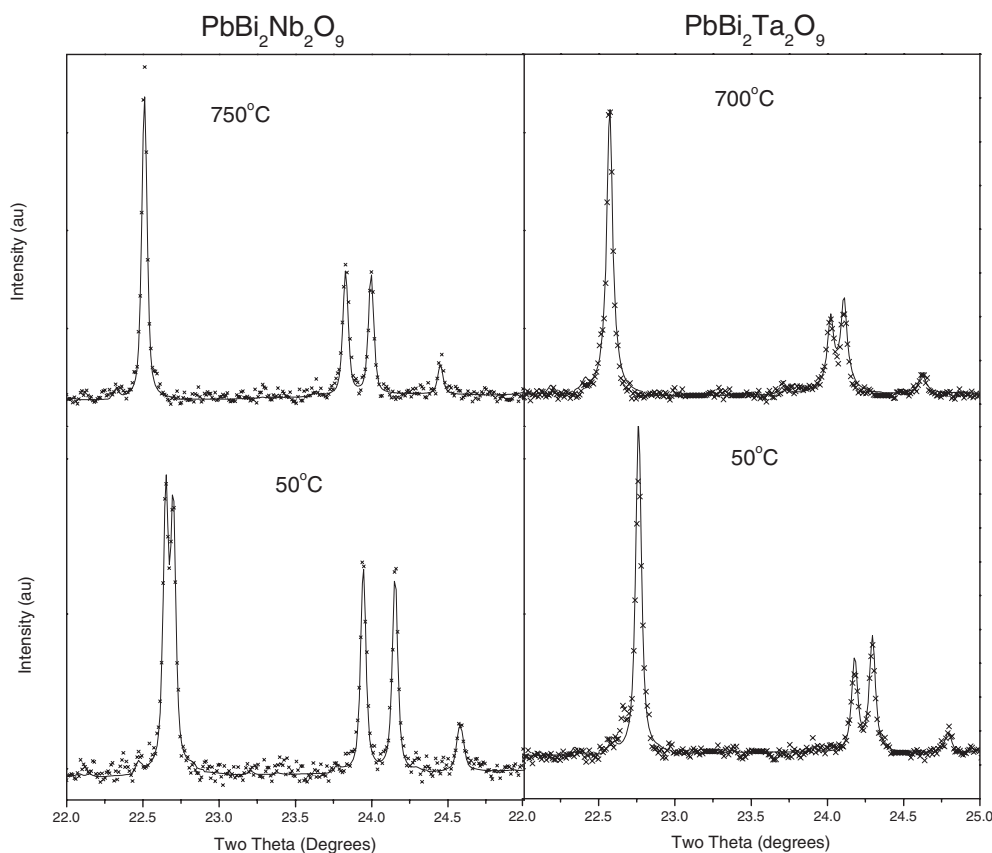
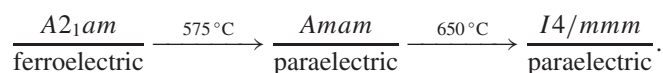


Figure 1. Portions of the observed and calculated synchrotron diffraction patterns for PBN and PBT. The splitting of the (315)/(513) reflections near $2\theta = 22.6^\circ$ is indicative of orthorhombic symmetry. The regions near $2\theta = 23.2^\circ$, 23.5° and 24.4° in PBT contained very weak spurious peaks from an unidentified phase and were excluded from the Rietveld refinements.

in the synchrotron diffraction profiles, and that between the a - and b -parameters gradually diminishes until at 625°C the pattern suggests the material is tetragonal. The variation in the c -parameter is more informative; figure 3. From room temperature to 575°C there is an almost linear increase in the c -parameter. The rate of increase with temperature is reduced for temperatures between 575°C and 650°C and then above this the c -parameter again shows an almost linear increase with temperature, but at a rate greater than at the lower temperatures. The change in gradient near 575°C coincides with the ferroelectric Curie temperature of PBN, which is reported [4] to be 560°C , indicating that the ferroelectric-to-tetragonal paraelectric phase transition involves an intermediate orthorhombic phase. This sequence is just that observed in SBT [8, 9] so we conclude that the sequence of transitions in PBN is the same as that found in SBT, that is



In the case of PBT the (315)/(513) doublet in the room temperature synchrotron diffraction profile was unresolved, figure 1, although the half-width of this peak ($\Gamma = 0.053^\circ$) was greater than that of the nearby (1 1 15) reflection ($\Gamma = 0.049^\circ$) which is not expected to be split in

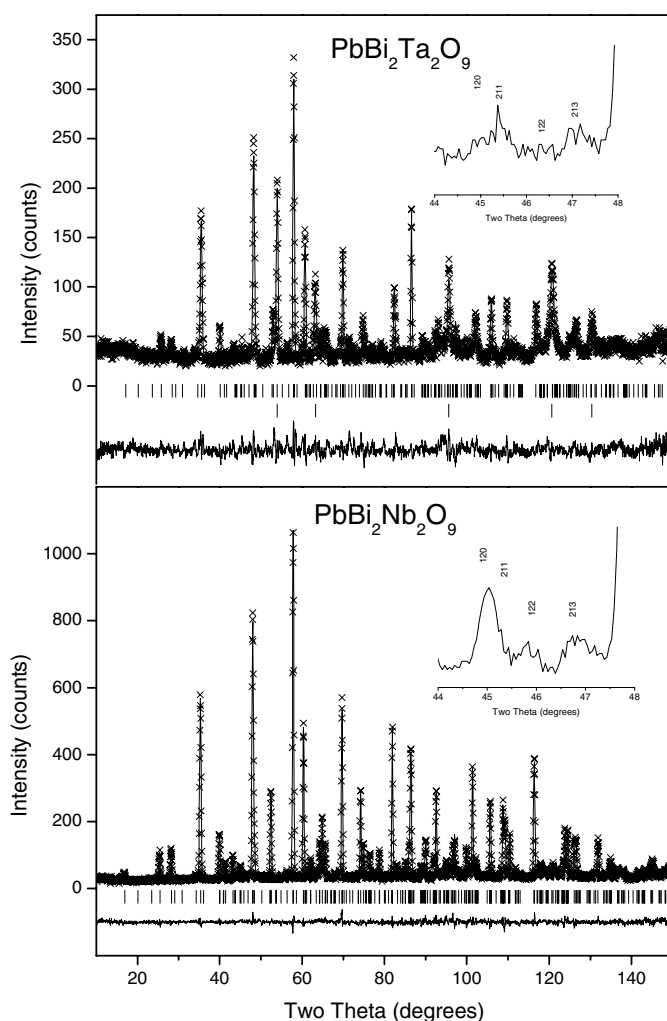


Figure 2. Observed calculated and difference neutron profiles for PBN and PBT at room temperature. The data for the Ta compound were obtained with the sample in an iron can and the lower set of reflection markers show the positions of the Bragg reflection for this phase. The insets show the presence of the (213) reflections near $2\theta = 47^\circ$ indicative of orthorhombic symmetry.

either orthorhombic or tetragonal symmetry. Higher-resolution measurements, possible using an analyser crystal, might be expected to resolve the orthorhombic (315)/(513) splitting, although in general such measurements are considerably more time consuming than those presented here. That PBT is orthorhombic at room temperature was clearly established from the room temperature powder neutron diffraction pattern, figure 2, which showed reflections indicative of a $\sqrt{2}a \times \sqrt{2}b$ superstructure arising from tilting of the TaO_6 octahedra. It was concluded that PBT and PBN are isostructural at room temperature, and Rietveld refinements in space group $A2_1am$ from the RT diffraction patterns were satisfactory. No attempt was made to quantify the extent of Pb/Bi disorder or its temperature dependence, although such disorder appears to influence the physical properties of these types of oxide [4].

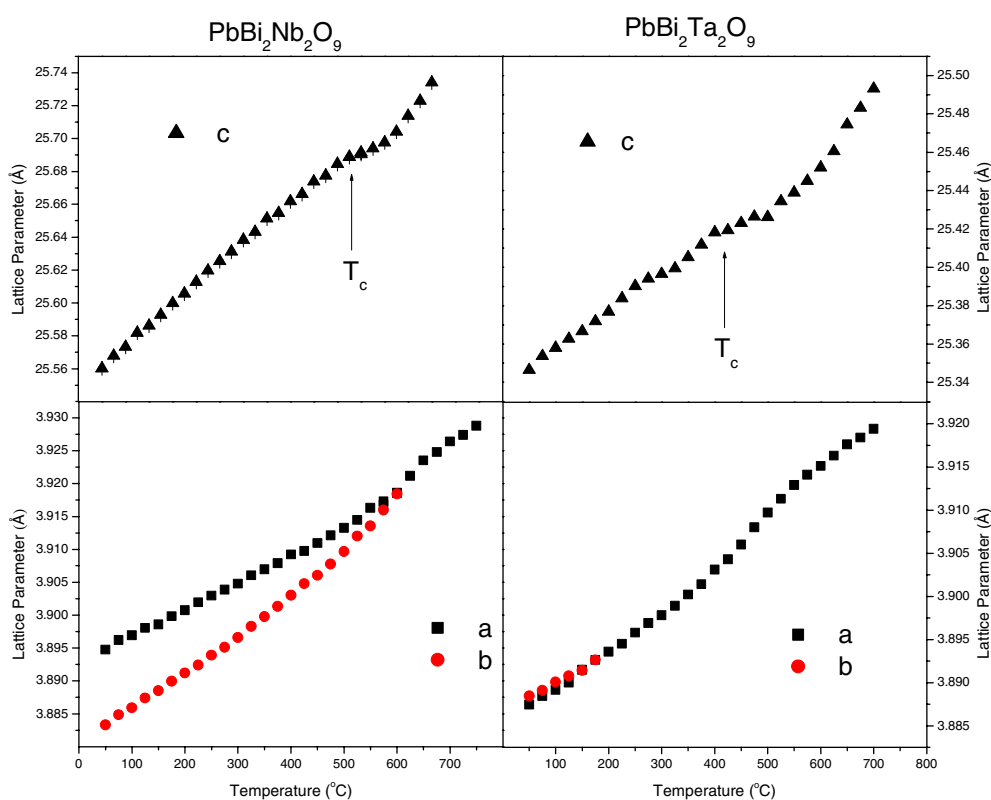
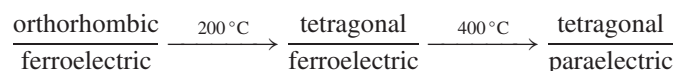


Figure 3. The temperature dependence of the lattice parameters for PBN and PBT. In both cases the orthorhombic values have been divided by $\sqrt{2}$ to make them comparable to the tetragonal values. The Curie temperatures (T_c) for both oxides are marked.

(This figure is in colour only in the electronic version)

As the sample of PBT was heated the width of the unresolved (315)/(513) doublet at $2\theta = 22.5^\circ$ progressively decreased until at 200°C the width of this peak was comparable to that of neighbouring reflections. Within the resolution of the present synchrotron diffraction patterns, PBT was metrically tetragonal at all temperatures above 200°C .

The dielectric measurements of PBT, however, showed that this compound becomes paraelectric near 400°C , that is some 200°C above the apparent transition to tetragonal. In principle, this could be indicative of the sequence of transitions



where, from the lattice parameter data, it would appear both transitions should be continuous. If, however, the orthorhombic ferroelectric and tetragonal paraelectric phases are taken to be the known structures in space groups $A2_1am$ and $I4/mmm$ respectively, no suitable tetragonal intermediate can be found. In addition, the temperature-dependent variation of the cell parameters suggests that there is another structural phase transition near 525°C , figure 3, which is not accounted for in the sequence shown above.

To help resolve this conundrum, additional high-temperature neutron diffraction patterns were collected for PBT. Although these were collected at relatively coarse temperature intervals

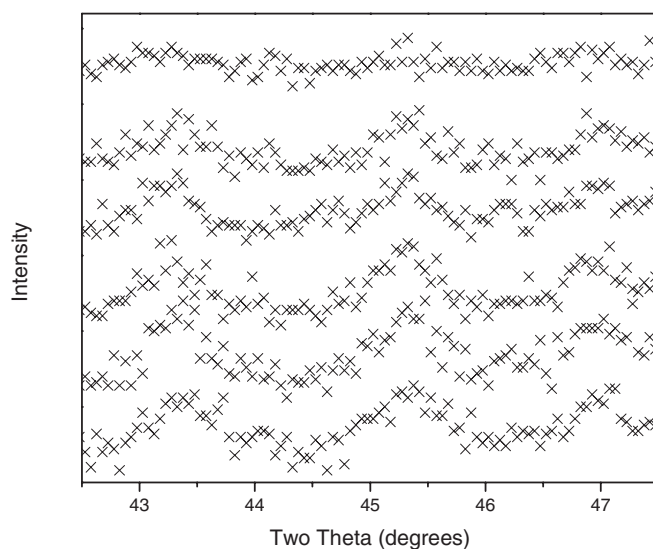


Figure 4. Portions of the powder neutron diffraction profiles for PBT. The patterns were recorded at (from bottom to top) 100, 200, 300, 400, 500 and 600 °C. Note the loss of the (211) and (213) reflections near $2\theta = 45^\circ$ and 47° respectively as the sample is heated.

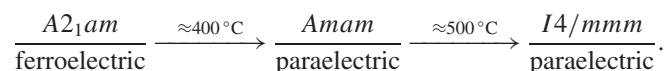
and have limited signal-to-noise ratios, they show that the (213) reflection persists up to at least 400 °C, figure 4, that is into the temperature region where the synchrotron diffraction patterns suggest that the material is tetragonal. Considering both the neutron and synchrotron diffraction patterns we conclude that PBT is orthorhombic up to 400 °C; however, in the region 200–400 °C the a - and b -parameters are effectively equal. This high degree of pseudo-symmetry is similar to that observed in SrZrO₃ at high temperature [13].

The fact that PBT remains orthorhombic up to 400 °C and that the dielectric measurements show the Curie temperature to be approximately 400 °C imply that the first change in slope in the lattice parameter plot, near 400 °C, corresponds to the ferroelectric-to-paraelectric phase transition, and that the ferroelectric phase remains in SG $A2_1am$ up to this temperature. As indicated above, and is seen in figure 3, there is evidence for a second structural phase transition near 500 °C. The synchrotron and neutron diffraction patterns demonstrate that PBT is tetragonal above 500 °C and all such patterns could be fitted to a model in the paraelectric space group $I4/mmm$. Whilst the temperature intervals are somewhat crude, even in the synchrotron diffraction study (25 °C steps) the temperature variation of the lattice parameters suggest that the transition near 500 °C is continuous.

Examination of the possible pathways for a continuous transition from the ferroelectric and orthorhombic $A2_1am$ structure to the paraelectric and tetragonal $I4/mmm$ structure using the computer program ISOTROPY [14] suggest that there are only two possible paraelectric intermediate phases, $Amam$ or $I\bar{4}2m$ (the latter space group, though non-centrosymmetric, cannot support ferroelectricity [15]).

Rietveld analysis of the powder neutron diffraction patterns collected from PBT at 450 °C assuming structures in $A2_1am$, $Amam$ and $I\bar{4}2m$ all gave comparable fits (R_p : 8.16, 8.33 and 8.22; and χ^2 : 3.68, 3.46 and 3.89 respectively). Given the different number of variables in these three space groups it is not possible to unambiguously distinguish between these on the basis of the observed diffraction data. In the absence of studies on PBN and the related Sr-containing compounds [8, 9] it could be concluded that the intermediate paraelectric phase is

tetragonal in space group $I\bar{4}2m$. However, we suggest by analogy the same sequence in PBT as observed in PBN and SBT. The analogy with PBN is particularly close since the chemical and physical properties of Ta^V and Nb^V are extremely similar as a consequence of their similarity in ionic size [16] arising from the lanthanide contraction. That is, we suggest that PBT also follows the sequence



The fact that the orthorhombic structure in $Amam$ is metrically tetragonal is acceptable since the same is true of the orthorhombic structure in $A2_1am$ in advance of the transition to this phase. An attractive feature of the sequence $A2_1am \rightarrow Amam \rightarrow I4/mmm$ is that it is consistent with the commonly accepted views on the origins of the distortions in the $A2_1am$ structure. This structure can be thought of as being derived from the tetragonal parent by a combination of rotation of the BO_6 octahedra and displacement of the B-type cation [17]. The intermediate $Amam$ phase allows for the tilting of the octahedra whereas the alternative $I\bar{4}2m$ phase does not. Using similar arguments, the suggestion by Kim *et al* [18] for an intermediate $Aba2$ phase in SBT can also be discounted.

4. Summary and conclusions

In summary, we have shown that an intermediate paraelectric phase exists between the low-temperature orthorhombic ferroelectric phase and the high-temperature tetragonal paraelectric phase in both PBT and PBN. High-resolution synchrotron diffraction studies have shown that this intermediate phase has orthorhombic symmetry in PBN. We conclude that this has the same $Amam$ structure as observed in SBT and its Bi-rich analogue [8, 9]. Identifying the sequence of phase transitions in PBT is more challenging since above 200°C the structure is metrically tetragonal within the resolution of the present synchrotron diffraction measurements. Neutron diffraction measurements have indicated that PBT remains orthorhombic to at least the Curie temperature of $\approx 430^\circ\text{C}$. Although it is possible to fit the diffraction patterns of the intermediate paraelectric phase in PBT to models in both the tetragonal, $I\bar{4}2m$, and orthorhombic, $Amam$, space groups we believe that the orthorhombic model is most likely to be correct. The recent observation [19] of an intermediate paraelectric phase in the $n = 4$ Aurivillius oxide $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ suggests that this may be a common transition pathway in these types of oxide and further studies in this area are planned.

Although our studies of these Aurivillius phases are not yet complete, we have indications that PBN, PBT and SBT all show similar behaviour. At elevated temperatures, they are all tetragonal paraelectrics in SG $I4/mmm$. Lowering the temperature induces first a tilting around the [110] direction (in the parent) of octahedra in the perovskite-like blocks, to form a structure in $Amam$, then cation displacements parallel to this axis of octahedral tilting to form a ferroelectric structure in $A2_1am$. On the other hand, the larger A-site cation in BBN ($\text{BaBi}_2\text{Nb}_2\text{O}_9$) inhibits octahedral tilting, so the structure remains tetragonal, and the cation displacements occur along the [001] direction to give a ferroelectric structure in $I4mm$ [20]. There are indications of the same behaviour in BBT ($\text{BaBi}_2\text{Ta}_2\text{O}_9$).

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