First 14-Layer Twinned Hexagonal Perovskite Ba$_{14}$Mn$_{1.75}$Ta$_{10.5}$O$_{42}$: Atomic-Scale Imaging of Cation Ordering

Fengqiong Tao, † Cécile Genevois, ‡§ Fengqi Lu, † Xiaojun Kuang, *† Florence Porcher, † Liangju Li, † Tao Yang, † Wenbo Li, # Di Zhou, † and Mathieu Allix†‡§

† Guangxi Ministry-Province Jointly-Constructed Cultivation Base for State Key Laboratory of Processing for Nonferrous Metal and Featured Materials, Guangxi Universities Key Laboratory of Non-ferrous Metal Oxide Electronic Functional Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China
‡ UP3079 CEMHTI, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France
§ Université d’Orléans, Faculté des Sciences, Avenue du Parc Floral, 45067 Orléans Cedex 2, France
* CEA Saclay, Laboratoire Léon Brillouin, F-91191 Gif Sur Yvette, France
† College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, P. R. China
§ Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi’an Jiaotong University, Xi’an 710049 Shaanxi, P. R. China

Supporting Information

ABSTRACT: Formation of hexagonal perovskite with mixed cubic and hexagonal stacking of AO$_3$ layers becomes more and more difficult when the number of layers in the stacking repeating unit increases. So far, the highest number of layers reported for twinned hexagonal perovskite is 12, with alternative 5 consecutive cubic layers and one hexagonal layer in the (ccccch)$_2$ sequence. Here, we present the unexpected formation of a 14-layer twinned hexagonal perovskite with a stacking sequence (ccccch)$_2$ for the BaO$_3$ layers on the Ba$_{14}$Mn$_{1.75}$Ta$_{10.5}$O$_{42}$ (Ba$_8$MnTa$_6$O$_{24}$) composition, the first example of twinned hexagonal perovskite with a periodicity exceeding 12-layers. The B-cation and vacancy distributions are characterized by multiple efficient and complementary techniques including neutron and synchrotron powder diffraction, scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) imaging, and electron energy loss spectroscopy (EELS) and X-ray energy dispersive spectroscopy (EDS) elemental mapping. Atomic-resolution STEM-HAADF imaging and EELS/EDS elemental mapping enables direct observation of high-spin d$^5$ Mn$^{2+}$ cation ordering in the d$^5$ Ta$^{3+}$ host, thus demonstrating the great potential of this technique for probing cation ordering and performing structure determination. Moreover, atomic mapping allows for the observation of local defect structure variants, which can be a powerful tool for future new material design. The large high-spin Mn$^{2+}$ cation and Ta-vacancy pair formation in face-sharing octahedral sites play key roles on both the stabilization of this 14-layer twinned hexagonal perovskite structure and the Mn$^{2+}$ ordering in the central corner-sharing octahedral (CSO) positions within the five-consecutive CSO layers. Compared with the 8-layer twinned Ba$_8$ZnTa$_6$O$_{24}$ material, the low quality factor in microwave frequency and enhanced ultraviolet and visible light absorption of Ba$_{14}$Mn$_{1.75}$Ta$_{10.5}$O$_{42}$ as well as the photocatalytic activity on water splitting are discussed in terms of the presence of high-spin Mn$^{2+}$ cations in the structure.

INTRODUCTION

Metal oxide materials based on the ABO$_3$ perovskite family are of great importance in current solid state chemistry and physics given their structural diversity and their technologically relevant physical properties, e.g., superconductivity, ferromagnetism, ionic motion, low dielectric loss, etc. The cubic ABO$_3$ perovskite structure is built up from cubic-close-packed AO$_3$ layers with B cations occupying the octahedral sites between the AO$_3$ layers. Similarly, hexagonal perovskite oxides contain the same building units of close-packed AO$_3$ layers but arranged with hexagonal or mixed cubic-hexagonal close packing. These structures are interesting prototypes to be exploited for structural chemistry and physical properties in order to provide a deeper understanding of the fundamental chemistry and physics of materials in the cubic perovskite family and possibly to further discover potential new materials.

The most two common types of hexagonal perovskites are twinned and shifted structures where the stacking of AO$_3$ layers shows an alternation of single and two consecutive hexagonal AO$_3$ layers. Schematically, the structures of stoichiometric...
ABO₃ twinned and shifted hexagonal perovskites are provide in Figure 1. The twinned structures have the \((c_nh_2)\) stacking sequence of AOX layers: (a) 4-layer, \(n = 1\); (b) 6-layer, \(n = 2\); (c) 8-layer, \(n = 3\); (d) 10-layer, \(n = 4\); and (e) 12-layer, \(n = 5\). While the shifted hexagonal perovskite structures have the \((c_nh_2)\) stacking sequence of AOX layers: (f) 9-layer, \(n = 1, m = 3\); (g) 12-layer, \(n = 2, m = 3\); (h) 5-layer, \(n = 3, m = 1\); (i) 18-layer, \(n = 4, m = 3\); (j) 21-layer, \(n = 5, m = 3\); (k) 8-layer, and \(n = 6, m = 1\). The large green, small cyan, and red spheres denote A and B cations and O anions, respectively.

Figure 1. Schematic plots for the (a–e) twinned and (f–k) shifted hexagonal perovskite structures. The twinned structures have the \((c_nh_2)\) stacking sequence of AOX layers: (a) 4-layer, \(n = 1\); (b) 6-layer, \(n = 2\); (c) 8-layer, \(n = 3\); (d) 10-layer, \(n = 4\); and (e) 12-layer, \(n = 5\). While the shifted hexagonal perovskite structures have the \((c_nh_2)\) stacking sequence of AOX layers: (f) 9-layer, \(n = 1, m = 3\); (g) 12-layer, \(n = 2, m = 3\); (h) 5-layer, \(n = 3, m = 1\); (i) 18-layer, \(n = 4, m = 3\); (j) 21-layer, \(n = 5, m = 3\); (k) 8-layer, and \(n = 6, m = 1\). The large green, small cyan, and red spheres denote A and B cations and O anions, respectively.

ABO₃ twinned and shifted hexagonal perovskites are provide in Figure 1. The twinned structures have \((c_nh_2)\) stacking sequences of AOX layers, which can form 4-, 6-, 8-, 10-, and 12-layer structures (referred to as 4H-, 6H-, 8H-, 10H-, and 12H-twinned structures, respectively in Figure 1a–e). The twinned hexagonal perovskite structure can be described as perovskite blocks assembled in a zigzag manner with each perovskite block sharing a single h-BaO₃ layer with the adjacent blocks, thus forming two face-sharing octahedral (FSO) layers. Similarly, shifted structures have \((c_nh_2)\) stacking sequences of AOX layers: (a) 4-layer, \(n = 1\); (b) 6-layer, \(n = 2\); (c) 8-layer, \(n = 3\); (d) 10-layer, \(n = 4\); and (e) 12-layer, \(n = 5\). While the shifted hexagonal perovskite structures have the \((c_nh_2)\) stacking sequence of AOX layers: (f) 9-layer, \(n = 1, m = 3\); (g) 12-layer, \(n = 2, m = 3\); (h) 5-layer, \(n = 3, m = 1\); (i) 18-layer, \(n = 4, m = 3\); (j) 21-layer, \(n = 5, m = 3\); (k) 8-layer, and \(n = 6, m = 1\). The large green, small cyan, and red spheres denote A and B cations and O anions, respectively.

In this work, we report the synthesis, structure determination, and physical properties of a 14-layer twinned hexagonal perovskite structure, namely, Ba₁₄Mn₁.₇₅Ta₁₀.₅O₄₂ (Ba₈MnTa₆O₂₄). This material is the first example of a twinned hexagonal perovskite with a periodicity exceeding 12 layers. Hexagonal perovskite tantalates and niobates based materials have recently attracted growing interest because of their high permittivity and low dielectric loss performance in microwave frequency and their interesting structural variants.

Our initial interest in the Ba₈MnTa₆O₂₄ composition was motivated by the search of a new 8-layer phase analogue to the twinned 8-layer tantalates Ba₈MnTa₆O₂₄ (M = Zn, Ni, Co), which demonstrated high-Q performance comparable to that of the well-known complex perovskite dielectric resonators Ba₃ZnTa₂O₉ and Ba₃MgTa₂O₉. Surprisingly, instead of the expected 8-layer structure, the Ba₈MnTa₆O₂₄ composition forms a longer-periodicity corresponding to a 14-layer twinned hexagonal perovskite structure (\(n = 7\) member of the twinned structure), demonstrating long-range Mn²⁺ cationic ordering in the purely corner-sharing octahedral (CSO) Ta host and partial ordering of B-site vacancies along the ab-plane. The unexpected stabilization of the 14-layer twinned structure from the nominal Ba₈MnTa₆O₂₄ composition demonstrates the complexity of the mechanism controlling the stacking periodicity of hexagonal and cubic AOX layers in twinned structures. It also implies the great potential of the further discovery of new twinned or shifted structures with longer periodicities. More significantly, efficient and complementary methods are presented here to solve the structure on this 14-layer twinned hexagonal perovskite structure. Synchrotron and neutron powder diffraction, electron diffraction, scanning transmission electron microscopy—high angle annular dark field (STEM-HAADF) imaging, electron energy loss spectroscopy (EELS), and X-ray energy dispersive spectroscopy (EDS) elemental mapping are...
combined to give a precise description of the structure via direct observation on the cation ordering at an atomic scale.

**EXPERIMENTAL SECTION**

Polycrystalline Ba$_2$Mn$_{1.75}$Ta$_{10.5}$O$_{42}$ (BMT) samples were synthesized by a traditional solid-state reaction in air with starting materials of BaCO$_3$ (99.9%, Aladdin), MnCO$_3$ (99.9%, Aladdin), and Ta$_2$O$_5$ (99.9%, Aladdin). The starting materials were weighed according to the correct stoichiometry and mixed in ethanol with an agate mortar and pestle. The dried mixtures were calcined at 1473 K for 8 h in alumina crucibles, then ground and pressed into pellets under a pressure of 330 MPa. These pellets were fired at 1773 K for 12 to 24 h with heating and cooling rates of 5 K/min. A Ba$_2$Mn$_{1.75}$Ta$_{10.5}$O$_{42}$ sample of around 10 g was prepared for neutron powder diffraction according to the procedure described above with a final firing at 1773 K for 24 h. The pellets were ground into fine powder for diffraction characterization. The BMT pellets for microwave dielectric property measurement were synthesized using the following procedure: the precalcined powders were mixed with a 5% poly(vinyl alcohol) (PVA) solution as an organic binder and then pressed into pellets under a pressure of 330 MPa, and finally sintered at 1773 K for 14 h with a heating and cooling rate of 5 °C/min. The estimated densities of the pellets were calculated by using the geometric sizes (diameters and thickness) and the masses of the pellets.

The phase formation of BMT was investigated by powder X-ray diffraction (XRD), which was performed on a Pye Unicam XPERT PRO diffractometer with Cu Kα radiation equipped with an Anton Parr HTK 1200N high temperature attachment. High quality laboratory XRD data for Rietveld refinement were collected over the 10–120° 2θ range. Variable temperature (VT) XRD data were collected from room temperature (RT) to 1373 K with a 25 K temperature step. High-intensity and high-resolution synchrotron powder diffraction (SPD) data were collected on an 11BM diffractometer at the Advanced Photon Source (Argonne National Laboratory, US). The sample powder was loaded in a 0.3 mm diameter glass capillary, and data were collected at RT over the 0.5–60° 2θ range using a step size of 0.001° and a dispersion of 1 eV/channel.

The atomic resolution EDS mapping was acquired on a JEOL transmission electron microscope. The sample was thinned by ion milling, and the X-ray energy dispersive spectroscopy (EDS) from a FEI/Inspect FEG scanning electron microscope (SEM). Transmission electron microscopy (TEM) was used to characterize the structure. The selected area electron diffraction (SAED) was performed on a Philips CM200 transmission electron microscope. The sample was first crushed in ethanol, and a drop of the solution with the small crystallites in suspension was deposited onto a carbon coated copper grid. High resolution STEM-HAADF imaging and atomic resolution EELS and EDS mapping were realized on a JEOL transmission electron microscope (JEM-ARM200CF) cold FEG operating at 200 keV and TEM/STEM double spherical aberration (Cs) corrector equipped with a Centurio EDS and a GIF Quantum (Gatan Imaging Filter). The STEM-HAADF images were acquired with a 0.1 nm camera length and a 0.13 nm probe size. The atomic resolution EDS mapping was acquired using the same 0.13 nm probe size and a 0.02 nm step size. The EELS mapping was acquired with a collection angle near 80 mrad, a step size of 0.06 nm, and a dispersion of 1 eV/channel.

Hydrogen-reduction thermogravimetric analysis (TGA) was employed to determine the oxygen content of the as-prepared material via the mass loss related to the reduction of Mn cations. The TGA experiment was carried out on a STA8800 thermal analysis instrument, for which the baseline was calibrated using Al$_2$O$_3$ as a standard material. The 14-layer sample was placed in an alumina crucible and heated in a 5% H$_2$-95% N$_2$ flow with an ∼20 mL/min flow rate from room temperature up to 1473 K with a heating rate of 5 K/min. AC impedance spectroscopy measurements were carried out over a temperature range from room temperature to 1173 K by using a Solartron 1260A impedance/gain-phase analyzer with a frequency range from 10$^{-2}$ Hz to 10$^{3}$ Hz. Prior to measurements, the pellet was coated with platinum paste and fired at 1073 K for 40 min in order to remove the organic components to form electrodes. The microwave dielectric properties were measured by the Hakki–Coleman dielectric resonance method with the TE$_{011}$ mode using an Agilent 8720ES network analyzer. The temperature coefficient of resonant frequency ($\tau_f$) values were measured from 298 to 358 K.

Magnetization measurements were carried out using a PPMS-9 QUANTUM physical property measurement system. Magnetization versus temperature curves were measured between 5 and 300 K in field-cooled (FC) and zero-field-cooled (ZFC) modes with applied fields of 300 Oe. Ultraviolet and visible (UV–vis) light absorption spectra of the dry-pressed disk sample was measured by a UV3600 UV–vis spectrometer fitted with an integrating sphere with BaSO$_4$ as standard material in the wavelength region of 200–1200 nm with a resolution of 0.1 nm.

The photocatalytic performance on water reduction was checked on a gas-closed circulation system equipped with a CEL-SPH2N vacuum line, a 150 mL Pyrex glass reactor, and a gas sampling port directly connected to a Techcomp-GC7900 gas chromatograph employing N$_2$ gas as carrier for H$_2$ detection. During the photocatalytic evaluation, the powder samples (∼50 mg) with and without cocatalyst loading were dispersed via magnetic stirring in 20 vol% methanol aqueous solution (∼50 mL) in a 278 K cycling water bath to keep the reaction vessel at a constant temperature; then the vessel was exposed to ultraviolet (CEL-M500, Hg-lamp) or visible (CEL-HXF300, Xe-lamp) light. Cocatalyst loading (in the weight percentage of 1%) proceeded as described below in order to enhance the photocatalytic activity of BMT. Typically, ∼80 mg BMT powder together with 0.56 mL of H$_2$PtCl$_6$·6H$_2$O (1.48 mg Pt/mL) were mixed in 50 mL of distilled water in a 100 mL beaker under an ultrasonic treatment for 20 min. An appropriate amount of diluted K$_2$HPO$_4$ aqueous solution (7.4 mmol/L) was added into the beaker drop-by-drop. Finally, the cocatalyst-loaded powder was extensively washed by water and dried at 60 °C prior to the photocatalytic testing. For other metal loading, the used sources are RuCl$_3$·3H$_2$O, AgNO$_3$, HAuCl$_4$·3H$_2$O, and PdCl$_2$.
1650 °C did not show any obvious evolution of the ratio between the simple cell and the triple cell forms, indicating the possible occurrence of an equilibration between the simple and tripled phases.

EDS measurements realized from a SEM on the 14-layer phase show an average composition of $\text{Ba}_4\text{Mn}_{4.5(1)}\text{Ta}_{10.3(1)}$. This composition lies close to the nominal $\text{Ba}_{14}\text{Mn}_{1.75}\text{Ta}_{10.5}$ composition given the usual uncertainty related to the technique, except for the Mn content. However, the accuracy on the Mn content is relatively low given its much lighter mass compared with that of Ba and Ta atoms. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K. However, the accuracy on the Mn content is relatively low given its much lighter mass compared with that of Ba and Ta atoms. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K. However, the accuracy on the Mn content is relatively low given its much lighter mass compared with that of Ba and Ta atoms. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K. However, the accuracy on the Mn content is relatively low given its much lighter mass compared with that of Ba and Ta atoms. No apparent mass reduction/gain was observed during the hydrogen-reduction TGA experiment up to 1473 K.

Structure Determination. The structure determination of the 14-layer BMT material was initially carried out considering the simple 14-layer structure only, for which a twinned hexagonal perovskite model was built up in the $P\bar{6}_3/mmc$ space group according to a $(\text{cba})$ $(\text{c}<\text{c}>\text{c})$ stacking sequence for the close-packed BaO$_3$ layers (Figure 3a). This structural model was first refined against laboratory powder XRD data, which confirmed the 14-layer twinned structure for $\text{Ba}_4\text{Mn}_{1.75}\text{Ta}_{10.5}\text{O}_{42}$. The simple 14-layer hexagonal perovskite structure contains three CSO B-sites (B1–B3) and one FSO B-site (B4). The refinement revealed a strong preference for Mn cations to occupy the central octahedral sites (B2 sites in green in Figure 3a) in the consecutive 5-layer CSO block between the FSO dimers and the location of B-cationic vacancies in the FSO sites B4 only.

The simple 14-layer structure was then first converted into a triple superstructure in the $P\bar{6}_3/mcm$ space group, and then, a two-phase Rietveld refinement including both the simple 14-layer structure and the triple superstructure was performed against combined SPD and NPD data. The refinement converged to $R_{wp} \sim 16.1\%$ on SPD data and 4.58% on NPD data and gave mass percentages of the simple and triple 14-layer phases, respectively, as $\sim 36\%$ and $\sim 64\%$, although there has to be a consequent uncertainty on this quantification result obtained from two-phase Rietveld analysis of the partially ordered sample. This phase quantification seems in good agreement with the TEM (SAED) observations performed on numerous crystallites which clearly showed the presence of more triple phase than simple phase. Further reducing the symmetry for the triple superstructure to the acentric $P\bar{6}_3c2$ space group because the FSO sites within each FSO dimer are shared by Ta atoms and vacancies. In b, the FSO B8 site is empty; thus, the B8O$_6$ octahedra are not shown.

The refined overall cationic compositions for the simple 14-layer phase are $\text{Ba}_{14}\text{Mn}_{2.01(8)}\text{Ta}_{10.35(4)}$, close to the nominal composition $\text{Ba}_{14}\text{Mn}_{2.01(8)}\text{Ta}_{10.35(4)}$, and showing a slightly larger discrepancy between the refined and expected Mn contents than for the

![Figure 2. SAED patterns of BMT recorded along (a) [010] and (b) [110] directions. The reflection spots marked by arrows are due to double diffraction. The indexations were performed using the simple 14-layer hexagonal perovskite cell. In b, the weaker reflection columns ((1/3) (1/3) (1/3)) and ((2/3) (2/3) (2/3)) between the main reflection columns arise from the triple superstructure formation.](image1)

![Figure 3. Representations of (a) the simple 14-layer twinned hexagonal perovskite structure described using the $P\bar{6}_3/mmc$ space group and (b) the corresponding triple superstructure in the acentric $P\bar{6}_3c2$ space group. The octahedral sites in green are occupied by Mn and Ta atoms; the other octahedral sites in blue are occupied by Ta atoms, and the FSO sites in pale blue are shared by Ta and vacancies. In b, the FSO B8 site is empty; thus, the B8O$_6$ octahedra are not shown.](image2)
Figure 4. (a) STEM-HAADF image of $\text{Ba}_4\text{Mn}_{1.75}\text{Ta}_{10.5}\text{O}_{42}$ along the [010] orientation. The EELS atomic maps for Ba, Mn, and Ta are shown in b, c, and d, respectively. (e) Overlaid STEM-HAADF and EELS images. (f) [010] projection of structure for the simple 14-layer phase obtained from Rietveld refinement: the CSO sites in green are shared by Mn and Ta atoms, the other CSO sites in blue are occupied by Ta, and the FSO sites are shared by Ta and vacancies.

refined and expected Ta contents. Nevertheless, the refined cationic ratio for the triple 14-layer phase, $\text{Ba}_4\text{Mn}_{1.7\pm0.2}\text{Ta}_{10.5\pm0.2}$, is in excellent agreement with the nominal composition. This two-phase refinement reproduced the preference of Mn cation on the central octahedral sites in the CSO blocks between the FSO dimers in both phases: the refined Mn occupancies in the other sites are found no higher than 6%.

At the next stage, STEM-HAADF and EELS techniques were employed to image this new 14-layer twinned hexagonal perovskite structure with atomic resolution in order to observe the local cationic distribution of Mn and Ta. Regarding the STEM-HAADF image and considering the constant thickness through the observed area, the intensity is proportional to the density of the sample and the atomic number of the elements ($\approx Z^{1.75}$). By consequence, in these “Z-contrast” images, the Mn atomic columns ($Z_{\text{Mn}} = 25$) appear less bright than the Ba ($Z_{\text{Ba}} = 56$) and Ta ($Z_{\text{Ta}} = 73$) atomic columns. The EELS elemental mapping of Ba, Ta, and Mn enables atomic-resolution position identification from the STEM-HAADF image (Figure 4). The positions of large Ba cations (Figure 4b) are consistent with the stacking sequence of $(cccccccch)_2$ for BaO$_3$ layers in the 14-layer structural model. The Mn atoms formed complete ordering in the central octahedral sites within the CSO blocks between the FSO dimers forming single octahedral layers that are mostly composed by MnO$_6$ (Figure 4c,e,f), consistent with the B-site occupancy refinement from the Rietveld analysis showing strong preference of the Mn cation on the central octahedral sites within the CSO blocks. It should be noted here that this STEM-HAADF image was recorded along the [010] direction, from which the simple and triple structures are not distinguishable. However, several observations performed on different crystallites showed the same information, validating these observations for both the simple and triple structures. Unfortunately, the [110] direction, suitable for simple/triple structure distinction, is not adapted for atomic imaging and mapping as projected interatomic distances along this direction are much shorter (see Figure 2), thus rendering complex the observation and discussion of cation ordering along this direction.

With the STEM-HAADF imaging and the EELS elemental mapping taken into consideration, all Mn atoms were placed on the central CSO sites in the CSO blocks between the FSO dimers in both the simple and triple 14-layer structures, and the Ta occupancies over the six FSO sites were refined without any constraints during the two-phase refinement for BMT. Such rearrangement only slightly increased the reliability factors to $R_p = 12.5\%$ on SPD data and 3.98% on NPD data. The final Rietveld plots of NPD and SPD data for $\text{Ba}_4\text{Mn}_{1.7\pm0.2}\text{Ta}_{10.5\pm0.2}\text{O}_{42}$ are given in Figure 5, and their enlarged views are provided in Figures S6,7. The final refined structural parameters and bond lengths for the simple and triple 14-layer phases are listed in Tables 1 and 2 and Tables S1 and 2, respectively. Table 1 and Table S1 also provide calculated BVSs for the simple and triple BMT phases, respectively. The BVSs of Mn$^{2+}$ on the mixed Ta/Mn sites are ~2.36–2.40, agreeing well with the ordering of Mn$^{2+}$ on these sites, although they are slightly larger than 2, owing to the mixed occupation of smaller Ta$^{5+}$ (BVSs ~3.35–3.41). The fully occupied Ta sites exhibit BVSs values close to 5 in both phases except for a lower value ~4.26 for the Ta7 site in the tripled phase. While most of the partially occupied Ta sites in both phases have small BVSs within 2.6–3.6 due to the partial occupation (~22–54%) except for the ~78% occupied Ta10 site shows overbonding (BVS ~5.5) in the tripled phase. Overall, the calculated BVSs are reasonably consistent with the ordered B-cationic distribution proposed from the STEM-HAADF imaging and the EELS elemental mapping results given the complexity of the structures reported here.

Magnitization Data. The oxidation state of Mn in the 14-layer BMT was further investigated by magnetism susceptibility measurements. Magnetization data of BMT measured on zero-field cooled (ZFC) and field cooled (FC) runs display no difference over the measured temperature regions (Figure 6). The Curie–Weiss law fit of the inverse magnetic susceptibility in the high temperature region between 150 and 300 K (inset
in Figure 6) shows an effective moment of $5.59(1) \mu_B$ per Mn and antiferromagnetic Weiss constant $-32.8(4)$ K. This result is in agreement with the high spin ($S = 5/2$) configuration for Mn$^{2+}$ cations (the spin-only effective moment of high-spin Mn$^{2+}$ is 5.9 $\mu_B$) and isolated MnO$_6$ octahedra without apparent Mn–O–Mn superexchange interaction, consistent with the ordered single MnO$_6$ layers in the 14-layer twinned hexagonal perovskite.

Electrical Properties. The complex impedance plot of the BMT pellet at 405 °C consists of one large and one small semicircular arcs (Figure 7). The large arc displays a capacitance of $\sim 3$ pF/cm, indicative of the bulk response with a permittivity of $\sim 30$. The small arc has a capacitance with a magnitude of $\sim 10^{-10}$ F/cm, attributable to the response from the thinner grain boundary regions. The bulk conductivity varied within $10^{-9}$–$10^{-3}$ S/cm in the temperature region 473–1173 K, giving an activation energy 0.76(2) eV (inset in Figure 7). Microwave dielectric property measurement on the BMT

Table 1. Structural Parameters for the Simple 14-Layer Hexagonal Perovskite of BMT$^a$ from the Combined Refinement on Both SPD and NPD Data

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
<th>$B_{iso}(\text{Å}^2)$</th>
<th>BVS$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.10831(9)</td>
<td>1</td>
<td>0.92(3)</td>
<td>2.45</td>
</tr>
<tr>
<td>Ba2</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.81408(8)</td>
<td>1</td>
<td>2.09(4)</td>
<td>2.23</td>
</tr>
<tr>
<td>Ba3</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.03521(9)</td>
<td>1</td>
<td>1.80(3)</td>
<td>2.14</td>
</tr>
<tr>
<td>Ba4</td>
<td>2c</td>
<td>2/3</td>
<td>1/3</td>
<td>0.92862(5)</td>
<td>1</td>
<td>1.09(4)</td>
<td>1.94</td>
</tr>
<tr>
<td>Ta1</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.92862(5)</td>
<td>1</td>
<td>0.66(2)</td>
<td>4.70</td>
</tr>
<tr>
<td>Ta2</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.125</td>
<td>0.03(5)</td>
<td>3.35</td>
</tr>
<tr>
<td>Mn2</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0875</td>
<td>0.03(5)</td>
<td>2.36</td>
</tr>
<tr>
<td>Ta5</td>
<td>4f</td>
<td>2/3</td>
<td>1/3</td>
<td>0.64351(6)</td>
<td>1</td>
<td>0.60(2)</td>
<td>4.65</td>
</tr>
<tr>
<td>Ta6</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.21461(9)</td>
<td>0.541(2)</td>
<td>0.42(3)</td>
<td>3.58</td>
</tr>
<tr>
<td>O1</td>
<td>12k</td>
<td>0.660(1)</td>
<td>0.83000(5)</td>
<td>0.17440(9)</td>
<td>1</td>
<td>1.42(4)</td>
<td>1.94</td>
</tr>
<tr>
<td>O2</td>
<td>6h</td>
<td>0.333(1)</td>
<td>0.1667(6)</td>
<td>1/4</td>
<td>1</td>
<td>1.74(5)</td>
<td>1.74</td>
</tr>
<tr>
<td>O3</td>
<td>12k</td>
<td>1/2</td>
<td>0</td>
<td>0.3941(1)</td>
<td>1</td>
<td>1.26(3)</td>
<td>2.00</td>
</tr>
<tr>
<td>O4</td>
<td>12k</td>
<td>0.1687(4)</td>
<td>0.8313(4)</td>
<td>0.9613(1)</td>
<td>1</td>
<td>1.27(4)</td>
<td>1.97</td>
</tr>
</tbody>
</table>

$^a a = 5.818857(7)$ Å, $c = 33.43938(9)$ Å, and $V = 980.548(4)$ Å$^3$. Space group: $P6_3/mmc$, $Z = 1$. $^b$The BVSs for the oxygen sites were calculated with the mixed and partial occupancies of the B-sites taken into consideration.

Table 2. Bond Lengths for the Simple 14-Layer Twinned Hexagonal Perovskite of BMT

<table>
<thead>
<tr>
<th>bond</th>
<th>length (Å)</th>
<th>bond</th>
<th>length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba1–O1(x3)</td>
<td>2.797(5)</td>
<td>Ba4–O1(x6)</td>
<td>3.017(4)</td>
</tr>
<tr>
<td>Ba1–O3(x6)</td>
<td>2.9108(2)</td>
<td>Ba4–O2(x6)</td>
<td>2.9094(2)</td>
</tr>
<tr>
<td>Ba1–O4(x3)</td>
<td>2.883(4)</td>
<td>Ta1–O3(x3)</td>
<td>2.034(2)</td>
</tr>
<tr>
<td>Ba2–O1(x6)</td>
<td>2.9350(5)</td>
<td>Ta1–O2(x2)</td>
<td>1.988(4)</td>
</tr>
<tr>
<td>Ba2–O2(x3)</td>
<td>2.722(4)</td>
<td>Ta2/Mn–O4(x6)</td>
<td>2.136(4)</td>
</tr>
<tr>
<td>Ba2–O3(x3)</td>
<td>3.166(4)</td>
<td>Ta3–O1(x3)</td>
<td>1.943(5)</td>
</tr>
<tr>
<td>Ba3–O3(x3)</td>
<td>2.894(3)</td>
<td>Ta3–O3(x3)</td>
<td>2.103(2)</td>
</tr>
<tr>
<td>Ba3–O4(x9)</td>
<td>2.9118(1)</td>
<td>Ta4–O1(x3)</td>
<td>2.178(5)</td>
</tr>
<tr>
<td>Ba4–O2(x3)</td>
<td>2.055(5)</td>
<td>Ta4–O2(x3)</td>
<td>2.055(5)</td>
</tr>
</tbody>
</table>
ceramics (~90% of the X-ray theoretical density) showed that the material exhibits modest ε, ~ 29–31, low quality factor Qf ~ 8630–9588 GHz, and positive temperature coefficient of resonant frequency T ∼ 24–29 ppm/°C.

**Photocatalytic Activity.** Figure 8 displays the UV–vis absorption spectrum of BMT. Here, the 8-layer twinned Ba8ZnTa6O24 containing d-shell fully filled (d10) Zn2+ cation was also measured for comparison with BMT. As indicated in the inset, BMT shows a band gap of ∼ 3.08 eV. In fact, there is a broad absorption band within the visible light range for BMT. Therefore, the photocatalytic activity on water splitting was tested on BMT with methanol as sacrificial agent, while a gentle H2 generation rate (∼ 0.78 μmol/h/g, roughly 1 order of magnitude higher than that of the host compound. Moreover, the bimetallic loading of Pt–Ag or Ru–Ag (1 wt % in total) shows an even higher activity in comparison with the loading of a single cocatalyst, probably due to some synergetic effect. Overall, such an increase is beneficial from the superficial modification, validating the intrinsic photocatalytic ability of BMT. The BMT powders were examined by XRD after the photocatalytic testing. No apparent change was observed on the XRD patterns of the BMT powders, indicating that BMT is stable during the photocatalytic testing.

**DISCUSSION**

It is well-known that the electrostatic repulsion between the FSO B-cations owing to the short B-B distances is an important factor affecting the stabilization of the hexagonal perovskite structures. In B-cationic deficient compositions, the distribution of the B-cationic vacancies over the FSO sites may reduce the FSO cationic repulsion and so further stabilize the hexagonal perovskite structures. The B-site vacancies in the B-site deficient hexagonal perovskites display either partial ordering in the FSO dimers in the twinned structures, e.g., Ba8MTa6O24 (M = Zn, Ni, Co), or completely long-range ordering between two consecutive hexagonal layers in the shifted structures, e.g., Ba8MNb6O24 (M = Co, Zn). The vacancy ordering in the shifted structure leads to single empty octahedral layers in the central octahedral position of the FSO trimers and avoids the formation of short FSO B−B pairs. Similarly to the other B-site deficient twinned hexagonal perovskites, the B-site vacancies in BMT are found to be located in FSO sites. In the simple 14-layer phase, the Ta and vacancies (€) are disordered in the FSO site with the refined Ta content just above 50%. Therefore, the formation of local Ta-€ pairs in the FSO dimers is expected to reduce the strong FSO cationic repulsion. In the triple superstructure, the FSO sites demonstrate partial ordering of Ta and vacancies along the ab-plane of the simple 14-layer phase, and there is short-range ordering of Ta and vacancies within each FSO dimer. Two kinds of FSO B-cationic dimers are formed in the triple superstructure: one is the B7−B8 dimer, where the B7 site is fully occupied by Ta, and the B8 site is empty; the other one is the B9−B10 dimer, where the B9 site contains ~0.22 Ta and ~0.78 €, while the B10 sites contain ~0.78 Ta and ~0.22 €. Such FSO cationic and vacancy ordering confirms the formation of FSO Ta-€ pairs. Therefore, Ba8Mn1.75Ta10.5O42 can be viewed as the n = 14 member of the B-site deficient twinned Abm2O3 family, half of which are FSO sites are empty to avoid the formation of FSO B−B pairs to eliminate the FSO B−B repulsion, i.e., there are very few FSO B−B pairs in the 14-layer B14Mn1.75Ta10.5O42.

The 14-layer hexagonal perovskite structure of BMT features remarkable long-range cationic ordering of Mn2+ in the central octahedral sites of the CSO perovskite blocks between the FSO blocks, as directly demonstrated by the combined STEM-HAADF imaging and EELS elemental mapping. Given the very
little presence of FSO B–B pairs in the 14-layer $A_{8n}B_{10n}O_{24n}$-type
$B_{14n}M_{1.75n}Ta_{10.5n}O_{42n}$ material, Mn$^{2+}$ cationic ordering in the 14-
layer twinned hexagonal perovskite $B_{14}M_{1.75}Ta_{10.5}O_{42}$ is
taking place essentially in the purely CSO Ta host network
that is disrupted by the insertion of single hexagonal BaO3
layers. The single octahedral Mn$^{2+}$ layers are separated apart by
$\sim 1.7$ nm. This case is similar to the shifted 8-layer hexagonal
perovskites $Ba_8M_{Nb6}O_{24}$ ($M = Co, Zn$), containing
ordered Co/Zn layers separated by $\sim 1.9$ nm. It is worth
noting here that the STEM-HAADF imaging and EDS
elemental mapping have also highlighted some minor structural
defects in the 14-layer twinned hexagonal perovskite
$B_{14}M_{1.75}Ta_{10.5}O_{42}$ (Figure 9). This defected structure exhibits
the stacking of two MnO6 octahedral layers which are separated
by one TaO6 layer in addition to the regular separation of
MnO6 layers apart by $\sim 1.7$ nm.

As demonstrated in Figures 4 and 9, the combination of
STEM-HAADF imaging and EELS elemental mapping enables
direct atomic-scale observation of cationic distribution in the
14-layer twinned structure. These results are of great interest in
order to perform the structure determination of new materials
and particularly demonstrate strong applicability on probing the
cation ordering in widely structural types. Cation order
− disorder plays important role in controlling the physical
properties, such as in the well-known complex perovskites $Ba_8M_{Nb6}O_{24}$ ($M = Zn, Mg$) dielectric resonators where
the 2:1 B-cation ordering significantly lowers the dielectric loss in microwave frequency. Direct visualization of ordered
− disordered cationic distribution at atomic resolution is of great
importance for deep insight into the composition−structure−
property relationships in order to tailor the properties for device
applications. Moreover, the observation of local defects such as
the new stacking structure presented above (Figure 9) may
provide ideas of new structures on which the composition is
provided by EDS. Atomic-resolution STEM-HAADF imaging
and EELS/EDS elemental mapping then appears to be a
powerful tool to further drive the development of innovative
materials.

In BMT, the central octahedral sites (B2 site in the simple
structure or B3 and B4 sites in the triple superstructure) in the
CSO blocks have essentially centrosymmetric coordinate
environments, while the other sites have acentric (out-of-
center) coordinate environments (Figure 10). These distinct
coordinate environments perfectly match the chemical bonding
preference of Mn$^{2+}$ and Ta$^{5+}$, respectively. The $d^5$ Mn$^{2+}$
cations have centrosymmetric oxygen bonding preference. Meanwhile,
the empty $d$ shell in Ta$^{5+}$ results in second order Jahn–
Teller (SOJT) distortion for TaO6 octahedra showing
various bonding distances with oxygen. Locating the highly
charged Ta$^{5+}$ in the FSO sites or the edge octahedral site within
the CSO block next to the empty octahedra is necessary for
stabilizing the oxygen atoms via the out-of-center distortion
forming three short bonds with the oxygen atoms in the empty
octahedra. Therefore, both distribution of B-cation vacancies
in the FSO sites and the bonding preferences of Mn$^{2+}$ and Ta$^{5+}$
contribute to the long-range Mn cationic ordering in the 14-
layer twinned hexagonal perovskite structure, similarly to the 8-
layer shifted hexagonal perovskites $Ba_8M_{Nb6}O_{24}$ ($M = Co, Zn$).

The ordering of Mn$^{2+}$ cations in the 14-layer twinned
structure BMT is also driven by the differences between the
cationic sizes and charges of Ta$^{5+}$ and Mn$^{2+}$. Mn$^{2+}$
cations, which exhibit a high-spin $d^5$ configuration as revealed by the
magnetization measurements, have an ionic radius of 0.83 Å.
This is much larger than that for Ta$^{5+}$ (0.64 Å) and even larger...
than those of the divalent cations Mg$^{2+}$ (0.72 Å), Zn$^{2+}$ (0.74 Å), Ni$^{2+}$ (0.69 Å), and Co$^{2+}$ (0.745 Å) for high-spin, 0.65 Å for low-spin), which are commonly found in hexagonal perovskites. The Mn$^{2+}$ cation ordering in the CSO blocks in the 14-layer hexagonal perovskite structure differs from the twinned 8-layer Ba$_8$MnTa$_6$O$_{24}$ (M = Zn, Ni, Co)\textsuperscript{16,17} and 10-layer Ba$_{10}$M$_{0.25}$Ta$_{7.9}$O$_{30}$ (M = Mg, Co)\textsuperscript{27} hexagonal perovskites, where the Mn$^{2+}$ cations are confined within the FSO sites forming FSO Ta$^{5+}$-M$^{2+}$ pairs which help to reduce the FSO cationic electrostatic repulsion in the FSO dimers in comparison with the FSO Ta$^{5+}$-Ta$^{5+}$ pairs.\textsuperscript{16,17,27} Compared with other divalent cations such as Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ in Ba$_8$MnTa$_6$O$_{24}$ (M = Zn, Ni, and Co) and Ba$_8$M$_{0.25}$Ta$_{7.9}$O$_{30}$ (M = Mg and Co) compositions, the large high-spin Mn$^{2+}$ cations in the FSO sites could induce stronger electrostatic repulsion in the FSO dimers thus destabilizing the 8-layer twinned structure on Ba$_8$MnTa$_6$O$_{24}$ composition (i.e., Ba$_{14}$Mn$_{1.75}$Ta$_{8.5}$O$_{42}$). Forming the 14-layer twinned A$_5$B$_{15}$O$_{48}$-type perovskite phase free of FSO B-B pairs is energy-favorable for the Ba$_8$MnTa$_6$O$_{24}$ composition, although establishing the longer-periodicity for Mn$^{2+}$ cations and B-site vacancies is suspected to cost extra energy.\textsuperscript{18} The formation of the 14-layer twinned structure in Ba$_8$MnTa$_6$O$_{24}$, though a shorter-periodicity 8-layer twinned structure is observed for Ba$_{10}$M$_{0.25}$Ta$_{7.9}$O$_{30}$ (M = Mg, Co) compositions, the large high-spin Mn$^{2+}$ cations in the FSO sites could induce stronger electrostatic repulsion in the FSO dimers thus destabilizing the 8-layer twinned structure on Ba$_8$MnTa$_6$O$_{24}$ composition, suggesting a 14-layer structure. Compared with the 8H-twinned Ba$_8$MnTa$_6$O$_{24}$ (M = Zn, Ni, Co)\textsuperscript{10,16} and the 10H-twinned Ba$_{10}$(Mg/Co)$_{0.5}$Ta$_{7.5}$O$_{30}$\textsuperscript{27} structures, the 14-layer twinned BMT ceramics presented here possess rather poor quality factors. Low quality factors frequently occur in Mn$^{2+}$-containing compounds (e.g., complex perovskite Ba$_8$MnNb$_2$O$_{24}$\textsuperscript{28,29} and columbite MnNb$_2$O$_6$\textsuperscript{30,31} containing high-spin Mn$^{2+}$ cations) when compared with the Mg$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ analogues. In general, the compounds containing transitional metal cations with partially filled 3d shells have higher dielectric loss than the Mg$^{2+}$/Zn$^{2+}$ analogues, implying an important role of 3d electron number or d shell configuration on controlling the dielectric loss.\textsuperscript{32} Electronic structure calculation of Ba$_8$MnNb$_2$O$_6$ and Ba$_8$NiNb$_2$O$_6$ indicates that the half-filled t$_{2g}$ orbitals in Mn$^{2+}$ and fully filled t$_{2g}$ orbitals in Ni$^{2+}$ are responsible for the difference between their lattice vibration modes: the half-filled Mn t$_{2g}$ orbitals soften infrared modes and increase lattice vibration inharmonicity and therefore the intrinsic loss.\textsuperscript{32} The 3d electronic configuration of the high-spin d$^5$ Mn$^{2+}$ cations may also explain the origin of the high dielectric loss of the 14-layer twinned BMT material. However, the dielectric loss is generally highly sensitive to the processing which significantly impacts the extrinsic loss associated with the porosity, cationic order, and secondary phase formation.\textsuperscript{33,34}

The BMT powder shows gray color, suggesting mild absorption over the visible light range, which could be ascribed to the d electron transition t$_{2g}$ → e$_g$ in Mn$^{2+}$ atoms, although they are in high-spin configuration, which places spin-forbidding constrain, thus lowering the probability of the d electron transition. The broad absorption band within the visible light range for BMT confirms the occurrence of d electron transition within the d shell in the Mn$^{2+}$ atoms. Because of the existence of Mn$^{2+}$ in the 14-layer twinned structure, BMT has a narrower band gap of ∼3.08 eV compared with the extra wide band gap ∼4.45 eV of the 8-layer twinned Ba$_{8}$ZnTa$_{5}$O$_{24}$. This makes BMT perform higher UV-light absorption within 250–400 nm, beneficial to photocatalytic activity under UV radiation. Although tantalum oxide and tantalates are a large group of photocatalyst, not only for water splitting but also for the degradation of environmental organic pollutants,\textsuperscript{34,35} there are relatively few investigations on the photocatalytic properties of hexagonal perovskite tantalate compounds except for the 5-layer shifted A$_5$Ta$_{4}$O$_{15}$ (A = Sr, Ba) compounds, which display interesting photocatalytic activity.\textsuperscript{36,37} The photocatalytic activity on the water splitting demonstrated on BMT, although relatively weak, may stimulate further exploitation of new photocatalysts from the large hexagonal perovskite families particularly with compositions containing transitional metal cations with partially filled d shells.

**CONCLUSIONS**

The nominal Ba$_8$MnTa$_6$O$_{24}$ composition forms a 14-layer Ba$_8$Mn$_{7.5}$Ta$_{10.5}$O$_{42}$ twinned hexagonal perovskite structure, instead of an 8-layer structure analogue to the 8H-twinned Ba$_{8}$ZnTa$_{5}$O$_{24}$. Ba$_8$Mn$_{7.5}$Ta$_{10.5}$O$_{42}$ presents the first example with the stacking sequence (ccccc)\_2 for the BaO$_3$ layers showing long periodicity exceeding the 12H-twinned structure. The STEM-HAADF imaging and EELS/EDS elemental mapping directly demonstrate high-spin d$^5$ Mn cation ordering in the d$^5$ Ta host and local defect structure variant at atomic resolution in BMT. Both the large high-spin Mn$^{2+}$ cation and the FSO Ta-vacancy pair formation contribute to the stabilization of this 14-layer twinned hexagonal perovskite structure and the Mn$^{2+}$ ordering in the central CSO positions within the five consecutive CSO layers in BMT. Analysis of SAED, SPD, and NPD data reveals the coexistence of the simple 14-layer structure with its triple superstructure arising from partial ordering of the vacancies among the FSO sites in BMT sample. Compared with the 8-layer twinned Ba$_{8}$ZnTa$_{5}$O$_{24}$, BMT possesses a low quality factor in microwave frequency. Moreover, its narrow band gap with enhanced UV–vis light absorption owing to the high-spin Mn$^{2+}$ cations leads to photocatalytic activity on water splitting for BMT under UV radiation.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b01566.

XRD data, temperature dependency of the cell parameters, and hydrogen-reduction TGA data of BMT; schematic view for the cell tripling of the simple 14-layer hexagonal perovskite; structural parameters and bond lengths for the triple 14-layer phase of BMT; and photocatalytic H$_2$ evolution for BMT loaded with various cocatalysts under UV light irradiation (PDF)

Simple and triple phases of 14-layer twinned hexagonal perovskite BMT (CIF)

**AUTHOR INFORMATION**

*Corresponding Authors

*(X.K.) E-mail: kuangxi@glut.edu.cn.

*(M.A.) E-mail: mathieu.allix@cnrs-orleans.fr