ABSTRACT: Significant oxide ion conductivity has previously been reported for the Ba$_3$M$'$$'$$'$$'$M$'$$''$$''$$''$$''$O$_{8.5}$ family (M$'$$'$$'$$'$ = Nb$^{5+}$, V$^{5+}$; M$'$$''$$''$$''$$''$ = Mo$^{6+}$, W$^{6+}$) of cation-deficient hexagonal perovskite derivatives. These systems exhibit considerable structural disorder and competitive occupation of two distinct oxygen positions (O3 site and O2 site), enabling two-dimensional (2D) ionic conductivity within the ab plane of the structure; higher occupation of the tetrahedral O3 site vs the octahedral O2 site is known to be a major factor that promotes oxide ion conductivity. Previous chemical doping studies have shown that substitution of small amounts of the M$'$$'$$'$$'$ or M$'$$''$$''$$''$$''$ ions can result in significant changes to both the structure and ionic conductivity. Here, we report on the electrical and structural properties of the Ba$_3$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ series ($x =$ 0.00, 0.025, 0.050, 0.100). AC impedance measurements show that substitution of Nb$^{5+}$ with Ta$^{5+}$ leads to a significant increase in low-temperature (<500 °C) conductivity for $x =$ 0.1. Analysis of neutron and X-ray diffraction (XRD) data confirms that there is a decrease in the M1O$_3$/M1O$_2$ ratio upon increasing x from 0 to 0.1 in Ba$_3$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$, which would usually coincide with a lowering in the conductivity. However, neutron diffraction results show that Ta doping causes an increase in the oxide ion conductivity as a result of longer M1–O3 bonds and increased polyhedral distortion.

INTRODUCTION

Solid-state oxide ion conducting materials play an important role as electrolytes in electrochemical conversion devices such as solid oxide electrolyzer cells (SOECs) and solid oxide fuel cells (SOFCs). One of the main limiting factors of these devices is the low ionic conductivity of the electrolyte at room temperature. To achieve the sufficiently high oxide ion conductivities required for real-world operation (>10$^{-2}$ S cm$^{-1}$), temperatures of between 500 and 1000 °C are currently necessary. However, such high operating temperatures result in long start-up times, reduced efficiency, and lower operational lifetimes. Therefore, research into intermediate temperature (300–600 °C) solid electrolytes has become a prominent field, leading to the development of highly conductive material families such as LAMOX (La$_3$Mo$_2$O$_{12}$) and BIMEVOX (Bi$_3$V$_2$O$_{11}$), as well as doped lanthanum gallates (LSGM) and sodium bismuth titanates (NBT). A structural motif common to these ionic conductors is a flexible lattice, in which the cations are distorted from their ideal positions and oxygen defects (vacancies and interstitials) are present. Although these materials possess substantially higher ionic conductivities, the presence of easily reduced species such as Mo$^{6+}$ and Bi$^{3+}$ precludes their use in fuel cells due to the required operating conditions (low oxygen partial pressures) at the fuel electrode. In addition, large-scale production of LSGM and NBT is hindered by the formation of poorly conducting secondary phases and precise stoichiometric requirements, respectively. Furthermore, the increasing demand for low-carbon energy generation solutions may pose future supply risks for elements commonly used in solid electrolyte production; much like the proliferation of electric vehicles is massively increasing the demand for lithium, so too could widespread fuel cell adoption cause many of the required rare-earth elements see demand rise beyond supply. This necessitates the diversification of energy production and storage technologies, ideally using materials composed of earth-abundant elements.

Hexagonal perovskite derivatives have recently been shown to exhibit significant oxide ion and/or proton conductivity. Ba$_3$NbMoO$_{8.5}$ exhibits a bulk conductivity of 2.2 × 10$^{-3}$ S cm$^{-1}$ at 600 °C and good stability over a wide range of oxygen partial pressures, similar to commercial solid-state oxide ion conductors such as YSZ. Ba$_3$NbMoO$_{8.5}$ crystallizes in a hybrid of the 9R perovskite (A$_3$B$_2$O$_6$) and palmierite (A$_3$B$_2$O$_9$) structures. The 9R perovskite consists of nine AO$_3$ layers stacked along the c-axis in the order (hhc)$_3$, with trimers of face-sharing BO$_6$ octahedra connected via corner-sharing. The palmierite structure is a cation-deficient derivative of the 9R perovskite, arising from the replacement of the cubic AO$_3$ layers with oxygen-deficient AO$_2$ layers, thereby forming isolated tetrahedral units separated by empty octahedral sites.

Received: November 8, 2022
Published: January 17, 2023
The average hybrid model of Ba$_2$NbMoO$_{8.5}$ is shown in Figure 1. Nb$^{5+}$ and Mo$^{6+}$ are distributed across two crystallographic sites, M1 and M2. A single-crystal X-ray diffraction (XRD) study highlighted that the M1 and M2 positions are partially occupied due to their close proximity to one another (∼1.6 Å), thus making simultaneous occupation unfavorable. Hence, only two cation sites per hybrid stack may be occupied at once. The 1:1 ratio of Nb$^{5+}$ to Mo$^{6+}$ leads to a nonstoichiometric oxygen content, where partial occupation of the O2 and O3 sites within the palmierite-like layers (of average composition [BaO$_{2}$]) creates a variable coordination environment surrounding the M1 site (M1O$_{x}$); a recent pair distribution function (PDF) study has confirmed the existence of local 4-, 5-, and 6-fold M1 geometries. The resulting disordered distribution of intrinsic oxygen vacancies and available oxygen sites creates an uninterrupted two-dimensional pathway for the migration of oxide ions along the palmierite-like layers.

The flexibility of the M1 site for multiple coordination environments is a key structural motif; the highest ionic conductivity is observed where tetrahedral M1O$_{4}$ environments is a key structural motif; the highest ionic conductivity and/or stability of several crystal systems and significantly increase their resilience to reducing atmospheres.

Here, we report the electrical and structural properties of the Ba$_2$Nb$_{1-x}$Ta$_{x}$MoO$_{8.5}$ series (x = 0.00, 0.025, 0.050, 0.100).

**EXPERIMENTAL SECTION**

Ba$_2$Nb$_{1-x}$Ta$_{x}$MoO$_{8.5}$ (x = 0.00, 0.025, 0.050, 0.100) compounds were prepared by solid-state reaction of stoichiometric amounts of BaCO$_3$ (99.999%, Sigma-Aldrich), Nb$_2$O$_5$ (99.98%, Sigma-Aldrich), Ta$_2$O$_5$ (99.98%, Sigma-Aldrich), and MoO$_3$ (99.98%, Sigma-Aldrich). These starting materials were ground using a mortar and pestle until homogeneous. The resulting powders were pressed into a pellet and calcined in an alumina crucible at 900 °C for 12 h to decarbonate. The pellets were then re-ground, re-pelleted, and heated at 1100 °C for 48 h before being cooled to room temperature at a rate of 5 °C min$^{-1}$. The latter grinding and heating step was repeated until phase-pure products were obtained.

Room-temperature X-ray powder diffraction (XRD) patterns were collected on a PANalytical Empyrean powder diffractometer equipped with a Cu Kα tube. Data were recorded in the range 10° < 2θ < 100°, with a step size of 0.013°.

Time-of-flight (TOF) neutron powder diffraction data were collected at 20 °C on the Polaris diffractometer at the ISIS Neutron and Muon Source, U.K. A 5 g sample of Ba$_2$Nb$_{0.9}$Ta$_{0.1}$MoO$_{8.5}$ was loaded into a cylindrical vanadium can of 8 mm diameter, and data were collected for a total of 2 h. Rietveld refinement was performed using the GSAS/EXPGUI package.

Scanning electron microscopy (SEM) images were collected using a Carl Zeiss GeminiSEM 300 with an XMax 80 detector and an AZtecHK EBSD analysis system with a Nordlys Nano EBSD camera (Oxford Instruments Ltd.). Energy-dispersive X-ray (EDX) spectroscopy data were mapped using the Oxford INCA X-ray microanalysis software to identify the elemental composition of the sample. Samples were mounted on a stub and coated with a thin layer of carbon.

The PIEFACE software package was used to fit the distorted coordination polyhedra using the minimum bounding ellipsoid method. The standard deviation, σ(R), of the three principal ellipsoid radii ($R_1$ ≥ $R_2$ ≥ $R_3$) was used to quantify the polyhedral.
distortion of the system. The value $S$ quantifies the degree to which the ellipsoid is prolate ($1 \geq S > 0$), spherical ($S = 0$), or oblate ($0 > S \geq -1$).

The electrical properties of the Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.00, 0.025, 0.050, 0.100$) series were measured by AC impedance spectroscopy using a Solartron 1260 impedance analyzer in the frequency range of 0.1 Hz to 1 MHz with an applied alternating voltage of 0.1 V. Measurements were performed on platinum-coated pellets of approximately 1 mm thickness and 10 mm diameter possessing a density 95% of the theoretical density. Measurements were taken every 15 °C (allowing 2 h of equilibration at each temperature step) upon cooling from 600 °C in a sealed tube furnace. Measurements were taken in a dry gaseous atmosphere ($p_{H_2O} < 10^{-4}$ atm), obtained by flowing compressed air through a column of a commercial desiccant (Drierite).

## RESULTS AND DISCUSSION

**Characterization of Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.00, 0.025, 0.050, 0.100$).** Laboratory powder X-ray diffraction (XRD) confirmed all of the as-prepared Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.00, 0.025, 0.050, 0.100$) samples to be phase-pure. All phases could be indexed to the unit cell with space group $R3mI$, in agreement with previous reports. The average stoichiometry of each sample was confirmed by EDX measurements (Table S1). SEM micrographs showed irregular shaped grains with sizes ranging from $\sim 5$ to 10 μm (Figure S1) with a similar microstructure to the Ba$_n$MoO$_{3x}$ phases reported previously. Synthesis of the composition $x = 0.125$ and higher $x$ was attempted but could not be made phase-pure (the impurity was identified as Ba$_n$MoO$_{13.5}$), suggesting this is the limit of the solid solution.

Using high-resolution XRD data, Rietveld refinement of the $R3m$ $H$ model for the Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ series was performed to investigate the structural changes effected by Ta substitution. The model of the parent compound Ba$_n$MoO$_{3x}$ refined from neutron diffraction data was used as the starting point for each composition of the Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.00, 0.025, 0.050, 0.100$) solid solution. This model places oxygen atoms at three different Wyckoff positions: O1 at $18h$, O2 at $9c$, and O3 at $36i$. The barium atoms, Ba1 and Ba2, were placed at the 6c and 3a sites, respectively. Nb$^{5+}$ and Mo$^{6+}$ were distributed across both 6c Wyckoff positions (M1 and M2), in a 1:1 ratio on each site. The Ba and O1 fractional occupancies refined to within ±1% of full occupancy, so were fixed at 1.0. Due to the low atomic number of oxygen, XRD is not able to model the oxygen atoms in the structure with the same accuracy and precision as the metal atoms. Therefore, the fractional occupancies of the O2 and O3 site were fixed at their initial values. The atomic displacement parameters, $U$, were modeled isotropically ($U_{iso}$) for all atoms; anisotropic modeling ($U_{aniso}$) resulted in the divergence of the refinement.

For the refinement of the Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.025, 0.050, 0.100$) model of the parent compound Ba$_n$MoO$_{3x}$, tantalum was incorporated into the model. Initially, Ta$^{5+}$ was distributed equally across the M1 and M2 sites (as Ta1 and Ta2, respectively), in place of Nb$^{5+}$, e.g., for $x = 0.10, 0.05$ was substituted on the M1 site and 0.05 on the M2 site. The M1 and M2 fractional occupancies ($g$) were refined using a $g(M1) = -g(M2)$ constraint. However, the occupancy of Ta2 refined to either zero or negative values. Therefore, all refinements were repeated with the Ta$^{5+}$ placed exclusively on the Ta1 site, with its fractional occupancy fixed. In further corroboration, if the Ta was distributed equally on the M1 and M2 sites for Ba$_n$Nb$_{0.9}$Ta$_{0.1}$MoO$_{8.5}$, $\chi^2$ and $R_{WP}$ were equal to 3.336 and 10.71%, respectively. Upon refining the Ta occupancy (where Ta is observed to occupy the M1 site only), $\chi^2$ and $R_{WP}$ are reduced to 3.299 and 10.65%, respectively.

A good Rietveld fit was obtained for all compositions, as evidenced by the statistical parameters reported in Table S2. The Rietveld refinement fit to the XRD pattern of Ba$_n$Nb$_{0.9}$Ta$_{0.1}$MoO$_{8.5}$ is displayed in Figure 2; the Rietveld refinement fits for the rest of the series can be found in the Supporting Information (Figure S2). All diffraction patterns could be fitted using the same hexagonal space group $R3mH$, and no change in symmetry was observed upon Ta doping. An overall increase in the unit cell parameters is observed with increasing Ta content (Table S2), although there is no clear trend with $x$.

Ta substitution increases the total occupancy of the M1 site and hence causes a decrease in the M2 occupancy. It was not possible to determine the average number of tetrahedra in the structure because the oxygen site occupancies were fixed, as discussed earlier. Significant anisotropic peak broadening was observed in the X-ray diffraction patterns for all $x$. This broadening is caused by strain in the lattice. A good fit was obtained using the method previously reported by Stephens where anisotropic broadening of the diffraction peaks is modeled by refining the two independent microstrain covariance parameters, $S_{400}$ and $S_{202}$. The electrical properties of the Ba$_n$Nb$_{1-x}$Ta$_x$MoO$_{8.5}$ ($x = 0.00, 0.025, 0.050, 0.100$) series were measured using AC impedance spectroscopy. The resulting complex impedance plots resemble those previously reported for the parent compound, Ba$_n$NbMoO$_{3x}$, two arcs at high ($10^5$ Hz) and intermediate ($10^3$ Hz) frequencies represent the bulk ($10^{-12}$ F cm$^{-1}$) and grain boundary ($10^{-11}$–$10^{-8}$ F cm$^{-1}$) responses, respectively. At higher temperatures, a Warburg electrode response in the low-frequency region is characteristic of ionic diffusion in a material with partially blocking electrodes (Figure 3).

The grain boundary arc becomes increasingly depressed as the Ta content increases and all compositions show very poor
resolution between the bulk ($\sim 1 \times 10^{-11}$ F cm$^{-1}$) and grain boundary ($\sim 6 \times 10^{-11}$ F cm$^{-1}$) responses due to their similar time constants ($\tau = RC$). A pronounced Warburg response is observed for all compositions. Furthermore, the $x = 0.1$ composition exhibits an additional feature between the grain boundary arc and the Warburg response, which can be attributed to charge transfer to and from the oxide ions at the electrode–ceramic interface, as previously reported for V-doped Ba$_3$NbMoO$_{8.5}$.

Total resistivity values ($R_{b} + R_{gb}$) were extracted from the low-frequency intercept of the grain boundary arc and the resulting total conductivity values are presented in the Arrhenius plot in Figure S3. Compared to the parent compound, the Ta-doped compositions with $x = 0.025$ and $0.050$ show slightly lower total conductivities, whereas the composition with $x = 0.1$ exhibits an increase in total conductivity; at 600 $^\circ$C, the total conductivity of Ba$_3$Nb$_{0.9}$Ta$_{0.1}$MoO$_{8.5}$ is $8.4 \times 10^{-4}$ S cm$^{-1}$, while Ba$_3$NbMoO$_{8.5}$ has a total conductivity of $5.4 \times 10^{-4}$ S cm$^{-1}$.

Resistivity and capacitance values were extracted from the impedance data using equivalent circuit fitting. A resistor in parallel with a constant phase element can be used to model the response of a material to an applied voltage. The overall material response was modeled using multiple RC elements in series to account for the individual responses, i.e., the bulk, grain boundary, charge transfer, and electrode responses. Figure 3 displays the three distinct equivalent circuits that were used to model the data at different temperatures. RC elements for the bulk ($R_{b}$-CPE$_{b}$), grain boundary ($R_{gb}$-CPE$_{gb}$), and electrode ($R_{el}$-CPE$_{el}$) responses were used to model the low-temperature data. At 422 $^\circ$C, a feature associated with charge transfer to and from the oxide ions at the electrode–ceramic interface appears between the grain arc and the Warburg response. This was modeled with the RC element $R_{ct}$-CPE$_{ct}$.

For temperatures above 436 $^\circ$C, the bulk signal moves outside the frequency range of the scan; therefore in Figure 3c, the RC element for the bulk response was substituted by a resistor in series. The goodness of fit was evaluated by the match between the calculated and observed spectra, and the physical plausibility of the fitting parameters. As presented in the Arrhenius plot (Figure 3d), the addition of Ta$^{5+}$ ($x = 0.025$) initially causes a decrease in conductivity in comparison to the parent compound. This conductivity increases upon further Ta$^{5+}$ doping ($x = 0.050$) and becomes larger than the parent
compound for \( x = 0.100 \). A comparison of the bulk conductivity of \( \text{Ba}_2\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) with \( \text{Ba}_2\text{Nb}_{0.9}\text{V}_{0.1}\text{MoO}_{8.5} \) and other members of the \( \text{BaM}^+\text{M}^{6+}\text{O}_{8.5} \) family is shown in Figure S4. At lower temperatures (<500 °C), the bulk conductivity of \( \text{Ba}_2\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) is higher than the parent compound; at 300 °C, it exhibits a bulk conductivity (3.8 × 10^{-7} S cm⁻¹) 4 times that of the parent (9.4 × 10^{-7} S cm⁻¹), with this disparity decreasing as temperature increases so that at 600 °C, both \( \text{Ba}_2\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) and \( \text{Ba}_2\text{Nb}_{0.9}\text{MoO}_{8.5} \) present a bulk conductivity of ∼2.0 × 10^{-7}. This convergence is the result of a lowering of activation energies above 500 °C, in accordance with the more favorable oxide ion conduction pathways generated by the loss of water and subsequent oxygen population rearrangement. The same behavior is observed for the \( \text{Ba}_2\text{Mo}_{1-x}\text{Nb}_{x}\text{O}_{8.5-x/2} \) series, where the conductivities of the solid solution converge at higher temperatures, suggesting that the thermal structural rearrangement results in comparable ratios of tetrahedra/octahedra between the compositions.²⁵

**Structure Refinement of \( \text{Ba}_3\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) by Neutron Powder Diffraction.** XRD is unsuitable for accurately determining the location of oxygen atoms within the structure and hence to determine why the \( x = 0.1 \) composition presents a higher low-temperature conductivity to \( x = 0.0 \) neutron diffraction data were collected. The same model used for refinement from the XRD data was used as a starting model for the Rietveld refinement from time-of-flight neutron powder diffraction data of \( \text{Ba}_3\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \). Again, Nb⁵⁺ and Mo⁶⁺ were distributed across both 6c Wyckoff positions (M1 and M2), in a 1:1 ratio on each site. In accordance with the X-ray refinement, the Ta⁵⁺ was only added to the M1 site (Ta1). The M1 and M2 fractional occupancies (g) were refined using a g(M1) = g(M2) constraint, while O2 and O3 used a g(O2) = −0.25g(O3) constraint. Ba and O1 fractional occupancies refined to within 1% of full occupancy and were therefore fixed at 1.0. The atomic displacement parameters, \( U_{iso} \), were modeled anisotropically (\( U_{aniso} \)) for all atoms except the highly disordered O3 position which was modeled isotropically (\( U_{iso} \)). The \( U \) parameters for the M1 and M2 sites were constrained together to prevent unwanted divergence. A structural model with M2 on a split 6c Wyckoff position was employed.¹⁹

An excellent fit was achieved between the calculated and observed histograms (Figures 4 and S4) in the space group \( R\bar{3}m\bar{H} \) as reported for other members of the \( \text{BaM}^+\text{M}^{6+}\text{O}_{8.5} \) family (\( \text{M}' = \text{Nb}^{5+}, \text{V}^{5+}; \text{M}'' = \text{Mo}^{6+}, \text{W}^{6+} \)).¹⁶,¹⁷,²⁶ The statistical parameters obtained were \( \chi^2 = 4.005, R_g = 1.90\%, \) \( R_p = 1.21\% \). The refined atomic parameters are shown in Table 1. The unit cell parameters \( a = 5.92266(6) \) Å and \( c = 21.08858(2) \) Å match up well with the results from the Rietveld refinement from XRD data for the corresponding \( x = 0.1 \) composition (Table S2), and both neutron and X-ray refinements show larger unit cell parameters than the corresponding parent compound.

The Ta-doped material shows an increase in overall M1 site occupancy (which agrees with the trend observed for the X-ray series) but a decrease in occupancy of the tetrahedra-forming O3 site (0.092 to 0.083), causing the percentage of tetrahedra to fall from 54.2% to 49.8%. This suggests that Ta doping leads to more octahedra on the M1 site, in accordance with the preference of Ta⁵⁺ ions for octahedral coordination.²⁸ The ratio of O2/O3 site occupancies and hence percentage of tetrahedra in the structure is regarded as an important factor dictating the conductivity of the \( \text{BaM}^+\text{M}^{6+}\text{O}_{8.5} \) phases (\( \text{M}' = \text{Nb}^{5+}, \text{V}^{5+}; \text{M}'' = \text{Mo}^{6+}, \text{W}^{6+} \)).¹⁶,¹⁷,²⁶ as a higher proportion of MIO₄ tetrahedra provides an increased amount of favorable pathways for oxide ion conduction. However, this is only true if other supplementary factors remain equal; M1–O3 distance, polyhedral distortion, and M2 site occupancy are also key to achieving high ionic conductivity. Therefore, the higher conductivity but lower proportion of tetrahedra in the \( x = 0.1 \) sample suggests that there are other factors that must be considered.

Table S3 shows a comparison of the bond lengths of \( \text{Ba}_3\text{NbMoO}_{8.5}, \text{Ba}_3\text{Nb}_{0.9}\text{V}_{0.1}\text{MoO}_{8.5} \), and \( \text{Ba}_3\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \). The bond angles are shown in Table S4. The M1–O3 bond, in particular, is significantly longer for \( \text{Ba}_3\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) than all of the other \( \text{BaM}^+\text{M}^{6+}\text{O}_{8.5} \) phases. The distance between the M1 position and the mobile oxygen species is known to influence ionic conduction and commonly occurs due to the out-of-center displacement (D) of the M1 atom away from the O2/O3 sites. The PIEFACE software package was employed to analyze the minimum bounding ellipsoid (i.e., the smallest volume ellipsoid able to contain all atoms of the coordination polyhedron). For further elaboration, see the Supporting Information. It was observed that the value of D remains relatively unchanged for the M1 site (for both tetrahedra and octahedra) upon Ta doping, whereas the M2 site sees a shift toward the center of the polyhedra (Table S5). Therefore, the longer M1–O3 bond length for \( \text{Ba}_3\text{Nb}_{0.9}\text{Ta}_{0.1}\text{MoO}_{8.5} \) is not a result of displacement.

Polyhedral distortion can also result in significant changes in bond length and was therefore quantified using PIEFACE. The minimum bounding ellipsoid has three radii (\( R_m, R_p, \) and \( R_e \)) with a mean value of R. The standard deviation, \( \sigma(R) \), is equal to \( \sqrt{\sigma^2(R)} \), where \( \sigma^2(R) \) is the variance, i.e., the average of the squared differences from the mean. Therefore, the standard deviation is used as a measure of the polyhedral distortion. The \( \sigma(R) \) value of the MIO₄ tetrahedra is significantly higher in the Ta-doped material than the parent compound, increasing from 0.05362 to 0.06486 Å, showing that the tetrahedra become.
octahedra is most likely also the origin of the lattice expansion, more distorted with Ta doping. The M2O₆ octahedra become more distorted (with \( \sigma(R) \) increasing from 0.12934 to 0.13204 Å), but the M1O₆ octahedra remain unchanged; the Ta-doped structure is more distorted overall than the parent compound. Therefore, the longer M1–O3 bond observed in Ba₃NbO₅TaₐMoO₆.5 is most likely a consequence of the larger distortion of the MO₆ polyhedra as a result of the greater polarizability of Ta⁵⁺ compared to Nb⁵⁺.⁴¹ Increasing the distance between the M1 and O2/O3 sites has previously been shown to decrease the energy barrier to migration by lowering the motional enthalpy required for the movement of oxide ions.²⁴ Therefore, the increase in M1–O3 bond length with Ta doping supports the enhanced conductivity that is observed. The increased distortion of the M1O₆ and M2O₆ octahedra is most likely also the origin of the lattice expansion, which is observed upon substitution of Ta⁵⁺ for Nb⁵⁺.

The shape of the variable coordination polyhedra can be described using the ellipsoid shape parameter, S (Table S5). In addition to being more distorted, the ellipsoid defined for the M1O₆ tetrahedra becomes more prolate (axially stretched, \( 1 \geq S > 0 \)), which correlates with the increased M1–O3 bond length. Both M1O₆ and M2O₆ octahedra remain relatively unchanged (but still oblate i.e., axially compressed, \( 0 > S \geq -1 \)).

These results suggest there are competing factors influencing the overall bulk ionic conductivity of Ba₃M’M’’O₈.₅ phases. As Ta is introduced into the structure, we see a decrease in the number of tetrahedra and an associated drop in conductivity. Table S3 also shows that the O2–O2 and O2–O3 distances increase with lattice expansion. Given that \( x = 0.025 \) and \( x = 0.050 \) have larger cell volumes than \( x = 0.100 \), it is likely that the O2–O2 and O2–O3 distances are longer, which would also explain the reduced oxide ionic conductivity.

However, as the proportion of Ta increases, the M1–O3 bond elongates and the conductivity increases with \( x \) until it surpasses that of the parent compound for \( x = 0.1 \). This suggests that once the M1–O3 bond length reaches a critical point, it facilitates a net increase in the overall conductivity, even though the ratio of tetrahedra:octahedra has decreased with respect to the parent compound and the O2–O2 and O2–O3 distances are longer. The seemingly diminished role of the tetrahedra:octahedra ratio is not unprecedented; in the recent work on Ba₃VWO₆.₅,¹⁵ the structure is shown to have an extraordinarily high number of highly distorted tetrahedra, but it exhibits relatively low levels of ionic conductivity due to the lack of an occupied M2 site. This disrupts the three-dimensional (3D) network within the structure, thereby preventing conduction along the c-axis between the two-dimensional palmiter-like layers.

**CONCLUSIONS**

In summary, we have shown that the low-temperature (<500 °C) ionic conductivity of Ba₃NbMoO₈.₅ can be significantly enhanced by substituting Nb⁵⁺ with Ta⁵⁺. Ba₃Nb₀.₅Ta₀.₅MoO₆.5 exhibits the highest low-temperature ionic conductivity among the Ba₃Nb₁₋ₓTaₓMoO₆.₅ (\( x = 0.00, 0.025, 0.050, 0.100 \)) series. It may be possible to increase the conductivity further if higher Ta⁵⁺ doping levels could be achieved. The results indicate that a combination of factors are needed to realize the highest ionic conductivity in the Ba₃M’M’’O₈.₅ family. These include a large unit cell with long M1–O3 bonds, an occupied M2 site, disordered polyhedra (\( \sigma(R) > 0.06 \)), and a sufficiently high ratio of tetrahedra/octahedra. Co-doping strategies such as the substitution of both V⁵⁺ and Ta⁵⁺ for Nb⁵⁺ could result in even higher oxide ion conductivities than reported to date.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c03943. Rietveld refinement fits, scanning electron microscopy images, and minimum bounding ellipsoid data (PDF)

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Table 1. Refined Atomic Parameters from Rietveld Fit to the Crystallographic Model of Ba₃Nb₀.₅Ta₀.₅MoO₆.5 from Time-of-Flight Neutron Powder Diffraction Data

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<td>0.39832(4)</td>
<td>0.0093(2)</td>
<td>0.0324(4)</td>
</tr>
<tr>
<td>Mo1</td>
<td>6c</td>
<td>0.4447(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.39832(4)</td>
<td>0.0093(2)</td>
<td>0.0324(4)</td>
</tr>
<tr>
<td>Ta1</td>
<td>6c</td>
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<td>0</td>
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<td>0.0324(4)</td>
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<tr>
<td>Nb2</td>
<td>6c</td>
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<td>0</td>
<td>0</td>
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<td>0.5242(2)</td>
<td>0.0093(2)</td>
<td>0.0324(4)</td>
</tr>
<tr>
<td>Mo2</td>
<td>6c</td>
<td>0.0553(4)</td>
<td>0</td>
<td>0</td>
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<td>0.5242(2)</td>
<td>0.0093(2)</td>
<td>0.0324(4)</td>
</tr>
<tr>
<td>O1</td>
<td>18h</td>
<td>1</td>
<td>0.17313(4)</td>
<td>0.82686(4)</td>
<td>0.10389(2)</td>
<td>0.0246(2)</td>
<td>0.0223(3)</td>
<td>0.0185(2)</td>
</tr>
<tr>
<td>O2</td>
<td>9e</td>
<td>0.503(2)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.0248(5)</td>
<td>0.0371(9)</td>
<td>0.0280(5)</td>
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<tr>
<td>O3</td>
<td>36i</td>
<td>0.0831(4)</td>
<td>0.0929(4)</td>
<td>0.0784(7)</td>
<td>0.3202(1)</td>
<td>0.030(1)^a</td>
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</tr>
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</table>

\(^a\)\( U_{xx} \) (Å²). \(^b\)\( U_{13} \). \(^c\)\( U_{23} \). \(^d\) \( U_0 \) (in Å²) represents anisotropic displacement parameters.
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