Epitaxial antiperovskite/perovskite heterostructures for materials design

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Engineered heterostructures formed by complex oxide materials are a rich source of emergent phenomena and technological applications. In the quest for new functionality, a vastly unexplored avenue is interfacing oxide perovskites with materials having dissimilar crystallochemical properties. Here, we propose a unique class of heterointerfaces based on nitride antiperovskite and oxide perovskite materials as a previously unidentified direction for materials design. We demonstrate the fabrication of atomically sharp interfaces between nitride antiperovskite Mn3GaN and oxide perovskites (La0.3Sr0.7)(Al0.65Ta0.35)O3 and SrTiO3. Using atomic-resolution imaging/spectroscopic techniques and first-principles calculations, we determine the atomic-scale structure, composition, and bonding at the interface. The epitaxial antiperovskite/perovskite heterointerface is mediated by a coherent interfacial monolayer that interpolates between the two antistructures. We anticipate our results to be an important step for the development of functional antiperovskite/perovskite heterostructures, combining their unique characteristics such as topological properties for ultralow-power applications.

INTRODUCTION
Complex oxide materials and in particular heterostructures formed from them are a rich source of emergent phenomena and technological applications (1–3). Interfacing oxide perovskites with materials having dissimilar crystallochemical properties and functionalitites (4) are likely to vastly expand the range of interfacing phenomena and applications. However, stabilizing such heterostructures with the chemical and structural quality required to promote the desired functionality is challenging when the constituting materials are non-isotropiical, having large geometrical and chemical strains (5, 6). We propose a unique class of heterointerfaces based on nitride antiperovskite and oxide perovskite materials as a new direction for materials design.

Antiperovskite materials are intermetallic compounds with perovskite crystal structure (space group Pm3m, no. 221) but with anion and cation positions interchanged in the unit cell (7). Like their oxide perovskite counterparts, antiperovskite materials show a variety of tunable physical properties, including superconductivity, itinerant antiferromagnetism, giant magnetoresistance, large magnetovolume effects, and topological electronic behavior (8–15). Among antiperovskite materials, transition metal (TM)-based nitride compounds (M3XN; M: TM; X: metallic or semiconducting element) are particularly interesting as their physical behaviors are remarkably sensitive to external perturbations such as magnetic fields, temperature, or pressure (14–20). This is mainly due to the strong spin-lattice coupling characteristic of M3XN compounds. With such a correlated physical background, the development of epitaxial M3XN heterostructures provides an ideal platform for tuning the properties of M3XN with the proper choice of materials and design. In this context, ABO3 oxide perovskites are unrivaled material systems to interface with M3XN nitride antiperovskites as both compounds have analogous perovskite-type crystal structure with comparable lattice constants, affording good epitaxial match along any common crystallographic direction, which should thus promote epitaxial growth. This enables the use of strain engineering to tune the behavior of M3XN materials. In addition, the wide variety of physical properties of ABO3 compounds can be used as external triggers to tune the functionality of antiperovskite materials, allowing the development of multifunctional artificial materials and devices, such as recently proposed for heterostructures between Mn3GaN and oxide ferroelectric and piezoelectric perovskites (16–19).

To exploit this potential, it is first necessary to understand at the atomic level the interfacial structure and chemistry between nitride antiperovskite and oxide perovskite materials to promote a bridging structure allowing for epitaxy. From the crystallographic perspective, the atomic configuration at the interface between these two antistructures is not obvious. As illustrated in Fig. 1A, M3XN antiperovskite and ABO3 perovskite compounds show reversed anion and cation positions in the unit cell. This distinctive difference leads to different considerations for interfaces between M3XN and ABO3 materials than that between two perovskite or two antiperovskite materials (Fig. 1B). The ABO3 perovskite structure can be described as alternating mixed cation-anion AO and BO2 layers along the [001]perovskite ([001]p) direction of the unit cell, and only two trivial interfacial configurations are physically stable for interfaces formed between two different ABO3 and A′O2B′O3 compounds: A′O/BO2 and B′O2/AO (Fig. 1C). Using the same analogy, nitride M3XN antiperovskites can be viewed as a stacking of alternating MX and M3N layers along the [001]p direction. As illustrated in Fig. 1D, the number of hypothetical simplest

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possible interfacial configurations between $M_3XN$ antiperovskite and $ABO_3$ perovskite materials doubles to four depending on the termination of the $ABO_3$ perovskite: $M_2N/BO_2$, $MX/BO_2$, $M_2N/O$, and $MX/O$. However, a fundamental subsequent consideration is the chemical bonding at the interface between nitride antiperovskite and oxide perovskite materials. Contrary to oxide perovskites, which have predominantly ionic bonding, nitride antiperovskites generally show metallic/covalent chemical bonding. In this context, developing a strategy to properly interface nitride antiperovskites with oxide perovskite materials can facilitate the emergence of interfacial hybridization interactions and hence interfacial properties and functionalities not achievable in more conventional oxide/oxide interfaces, opening a new path in the search for emergent behavior linked to interfacial phenomena (4).

Sparked by the quest for fundamental understanding of the nitride antiperovskite/oxide perovskite interface, we fabricated high-quality epitaxial Mn$_3$GaN films on (001)-oriented (La$_{0.3}$Sr$_{0.7}$)$_2$O$_3$ (LSAT) and SrTiO$_3$ single-crystal substrates as paradigms of $M_3XN$/$ABO_3$ interfaces. Using a combination atomic-resolution scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), energy-dispersive x-ray spectroscopy (EDS) techniques, and density functional theory study, we studied the interfacial structure of Mn$_3$GaN/LSAT and Mn$_3$GaN/SrTiO$_3$ on an atomic scale. We investigated both the stability and the mechanism of nucleation of the observed interface using first principles calculations. For simplicity, the manuscript focuses on the Mn$_3$GaN/LSAT interface. Additional information, including experimental data regarding the Mn$_3$GaN/SrTiO$_3$ interface and materials and methods, is presented in the Supplementary Materials.

RESULTS

Figure 2 summarizes the x-ray diffraction (XRD) structural characterization for a 60-nm-thick Mn$_3$GaN film grown on a (001) LSAT substrate. The epitaxial growth and single-phase structure of the films were monitored using in situ reflection high-energy electron diffraction (RHEED) and confirmed through symmetric θ-2θ XRD measurements by the observation of only the (00l) reflections (Fig. 2A). In Fig. 2B, a representative θ-2θ XRD scan taken around the (002) LSAT substrate peak is shown. The presence of Kiessig fringes surrounding the Mn$_3$GaN (002) reflection indicates the high crystalline quality of the film and a pristine interface, corroborated by the narrow 0.035° full width at half maximum (FWHM) value of the rocking curve for Mn$_3$GaN (002) (Fig. 2C). Decreasing film thickness results in an improvement of the crystallinity, reaching films with FWHM values as low as 0.023°. An in-plane cube-on-cube epitaxial relationship between Mn$_3$GaN and substrate was confirmed by off-axis azimuthal φ-scan around the (022) reflection (Fig. 2D). From x-ray reciprocal space mapping (RSM) measurements centered in the asymmetrical (−113) LSAT peak (Fig. 2E), the out-of-plane ($a_x$) and in-plane ($a_l$) lattice constants were determined at $a_x = 3.90 ± 0.01$ Å and $a_l = 3.92 ± 0.01$ Å, close to the bulk lattice constant of $a = 3.898$ Å (21).

To investigate the structure and chemical composition of the Mn$_3$GaN/LSAT interface, we used a combination of atomic-resolution
STEM, EELS, and EDS techniques. For additional analyses, including data for the Mn$_3$GaN/SrTiO$_3$ interface, please see the Supplementary Materials. In Fig. 3A, we show an atomic-resolution high-angle annular dark-field (HAADF)–STEM image taken along the [100] zone axis of LSAT. The image displays an atomically sharp interface and further corroborates the high crystalline quality of the films. In Fig. 3B, a magnified HAADF-STEM image close to the epitaxial Mn$_3$GaN/LSAT interface is shown, overlaid with the cation positions, as determined by this study. The atomic-resolution EDS and EELS analyses (figs. S1 and S2) and HAADF-STEM intensity profiles (Fig. 3C) demonstrate that the LSAT substrate termination is (Al$_{0.65}$Ta$_{0.35}$)O$_2$ (BO$_2$ termination) and thus implies that the Mn$_3$GaN termination at the interface is expected to be Mn$_2$N. However, we noticed that the first Mn$_2$N interfacial monolayer (labeled as layer 1 in Fig. 3C) exhibits a pattern of alternating bright and dark spots, indicative of compositional and/or structural reconfigurations at the interface.

We performed atomic-resolution EDS and EELS measurements to determine the atomic composition of the first monolayer above the LSAT substrate (see figs. S1 and S2). The Mn intensity measured at the first Mn$_2$N layer at the interface was found to be notably lower compared to Mn$_3$N layers far from the interface. This difference in Mn intensity, together with the observed alternating pattern of bright and dark spots in the HAADF-STEM image, points to a lower relative Mn concentration in every other atomic position (dark-contrast spots) along the [100] direction in the interfacial monolayer. We quantified the Mn concentration at the interfacial monolayer with HAADF-STEM image simulations (xHREM software, HREM Research Inc., Japan), changing the Mn occupancy for the best fit (fig. S3). The simulations are compatible with an approximately 80% Mn deficiency in the atomic positions, corresponding to a darker contrast in the HAADF-STEM data. Thus, the combination of simulations and structural and chemical analyses indicates that the transition from the LSAT substrate to the Mn$_3$GaN film is mediated by a sharp interfacial Mn$_x$N monolayer with $x \approx 1.2$.

To unequivocally determine the atomic structure of the Mn$_x$N interfacial monolayer, we performed additional STEM and EDS analyses along the [110] zone axis (fig. S4). In Fig. 4, we show the schematic of the proposed Mn$_3$GaN/LSAT interface based on analyses along the [100] and [110] zone axes. This model is also consistent with STEM analyses that we performed in epitaxial Mn$_3$GaN films grown on (001)-oriented SrTiO$_3$ (see the Supplementary Materials). Indistinguishable projections of the Mn$_x$N monolayer along the [100] and [010] directions indicate that the ordering of Mn and N atoms constitutes a two-dimensional periodic structure with C$_4$ rotational symmetry. Considering $x = 1$ for simplicity, the ideal MnN monolayer would be arranged as depicted in Fig. 4 (B and C), with the N atoms located above (Al/Ta) atoms of LSAT and the Mn atoms over the interstice of the (Al/Ta)O$_2$ layer of LSAT. The illustration shows that the ideal MnN interfacial monolayer has an analogous structure.
as a perovskite AO layer, with A being Mn and N being O. Moving away from the interface, a MnGa puckered layer is observed occurring on top of the MnN interfacial layer (Fig. 3B), with the Mn cations displaced toward the interface. A gradual decrease of the interplanar distances along the [001] direction within the first five layers of above the interface is also apparent. Above the fifth layer, the interplanar distance reaches the bulk value.

We performed first-principles calculations to study the stability of the interfacial model derived from the atomic-resolution experiments. Because of the complex crystal structure of LSAT, $\text{AlO}_2$-terminated $\text{LaAlO}_3$ was used to mimic $\text{BO}_2$-terminated LSAT. $\text{Mn}_3\text{GaN}/\text{LaAlO}_3$ with two different interfaces, $\text{MnN}/\text{AlO}_2$ and $\text{Mn}_2\text{N}/\text{AlO}_2$, were simulated, as shown in Fig. 5A. Specifically, their formation energies $\Delta E$ were calculated to test for stability. As shown in Table 1, the calculated
results indicate that both interfaces have negative $\Delta E$, which implies that both are energetically stable. However, $\Delta E = -2.265$ eV for the Mn$_2$N interface is appreciably lower than that of the observed MnN interface, $\Delta E = -0.058$ eV. The lower $\Delta E$ for the Mn$_2$N interface can be understood from the chemical bonding at the interface. As shown in Fig. 5 (B and C), the charge density between Mn and O (or N) at the MnN interface is notably smaller than that of the Mn$_2$N interface, corresponding to a stronger Mn—O and Mn—N bonding at a Mn$_2$N interface, thus resulting in a more cohesive and energetically stable interface.

The apparent discrepancy between the interfacial models derived from the experimental and theoretical studies can be explained by considering the onset of Mn$_3$GaN growth in the presence of an energy barrier, preventing the system from relaxing from the local to the global energy minimum. To explore this hypothesis, the formation energies for Mn/LaAlO$_3$ were calculated using two different Mn configurations, Mn(1) and Mn(2), as shown in Fig. S10. Mn(1) and Mn(2) correspond to the positions of Mn in the MnN and Mn$_2$N interfaces, respectively, as described in Fig. 5D. The Mn/LaAlO$_3$ supercell with the Mn atom located in the Mn(1) site had a lower energy than that of the Mn atom at the Mn(2) position (Table 1). An analogous behavior was observed by calculations using the non-polar SrTiO$_3$ surface, which indicates that the Mn(1) site is the most energetically favorable position for Mn on both polar and nonpolar ABO$_3$ perovskite surfaces. While Mn(1) is surrounded by four O$^{2-}$ anions, in the vicinity of Mn(2), there is one O$^{2-}$ and two B cations. The strong local coulomb repulsion between Mn(2) and the B cations accounts for the higher formation energy of the Mn(2)/ABO$_3$ supercells. In addition, the more positive the B cation, the higher energy of the Mn(2) site. As shown in Table 1, the calculated energy difference between Mn(1)/SrTiO$_3$ and Mn(2)/SrTiO$_3$ (0.452 eV) is larger than that of Mn(1)/LaAlO$_3$ and Mn(2)/LaAlO$_3$ (0.155 eV), mainly due to Ti$^{4+}$ being more positive than Al$^{3+}$. Thus, the Mn(2) site in the Mn(2)/LSAT system will hence be more unstable because of the Ta$^{5+}$ cations in the LSAT terminating layer.

Therefore, our combination of experimental and theoretical studies indicates that, during the initial growth of Mn$_3$GaN, Mn ions arriving at the B-terminated ABO$_3$ layer sit on the Mn(1) positions and then coordinate with N, forming a Mn$_x$N monolayer as determined by the STEM studies. This interfacial monolayer works as a structural bridge between the ABO$_3$ substrate and Mn$_3$GaN film and establishes heteroepitaxy between the two nonisostructural materials with different chemical composition and bonding. Moreover, the experimentally observed puckered GaMn layer can be related to the strong out-of-plane Ga—Mn bonding due to the strong charge density overlap between Mn in the first interfacial layer and Ga in layer 2 (Fig. 5B and fig. S11).

**DISCUSSION**

The realization of an atomically sharp bridging structure allowing an epitaxial interface structure and bonding between nitride antiperovskites and oxide perovskites manifests a critical step in the development of a new class of epitaxial heterostructures based on materials with dissimilar crystallochemical properties. The ability to engineer such novel heterointerfaces from chemically divergent constituents brings a new dimension to the mature field of complex oxides and provides a playground for the manipulation of the interfacial physical properties and the establishment of new states of matter. In particular, Mn-based nitride antiperovskites with non-collinear $\Gamma^5\gamma$ triangular antiferromagnetic structures are ideal systems to interface with piezoelectric or ferroelectric oxide compounds to induce piezomagnetic or magnetoelectric effects in the antiperovskite, as recently proposed theoretically (16–19) and demonstrated experimentally (22). In addition, materials showing geometrically frustrated antiferromagnetic spin structures are the source of intriguing physical

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**Fig. 5. Theoretical calculations for different interfacial configurations.** (A) Sections of the relaxed Mn$_3$GaN/LaAlO$_3$ supercell with the MnN/LaAlO$_3$ interface and the Mn$_2$N/LaAlO$_3$ interface. (B) Charge density plots around the MnN interface in the (100) and (110) planes. (C) Charge density plots around the Mn$_2$N interface in the (100) and (200) planes. (D) Illustration of the two possible deposited positions of Mn atoms Mn(1) and Mn(2) (purple dashed circles) onto the AlO$_2$ plane. (E) Schematic diagram of energies of MnN interface and Mn$_2$N interface, showing that the MnN interface is in a local energy minimum.
behavior, including large anomalous Hall (23, 24) and Nernst effects, large magnetoresistance, spin transfer torque, and spin Hall effect (25–28). Given the potential of these materials for antiferromagnetic spintronics (29), the rational design of epitaxial heterostructures of Mn-based nitride antiperovskites and ABO₃ perovskites is of great importance for property tuning and functional device design. We expect our study to trigger the investigation and development of functional antiperovskite/perovskite heterostructures, opening a new and exciting avenue for materials design.

**MATERIALS AND METHODS**

**Sample growth and x-ray characterization**

Thin-film heterostructures were grown by DC reactive planar magnetron sputtering using a Mn₃Ga stoichiometric target (99.9% purity) at 50 W. The films were deposited at a substrate temperature of 550°C in an Ar [50 standard cubic centimeters per minute (scm)]/N₂ (5.2 scm) atmosphere of 9.5 mtorr. The sample-to-target distance was fixed to 4 inches. Before deposition, the vacuum chamber was evacuated until a base pressure of 10⁻⁷ torr was achieved. X-ray characterization of the samples was performed at room temperature by using a four-circle x-ray diffractometer equipped with Cu-Kα radiation.

**HAADF-STEM imaging and atomic-resolution EDS and EELS**

Because of the delicate bonding between antiperovskite nitride and perovskite oxide, samples for STEM observation should be carefully prepared. Focused ion beam sampling or prolonged exposure to ion milling caused the interface to collapse, and the damaged area looks dark with a few nanometers thickness along the interface. Therefore, samples were prepared via the conventional way. Samples were mechanically ground to a thickness of less than 50 μm (EM TXP, Leica, Germany), dimpled to a thickness of ~5 μm (Dimple Grinder II, Gatan, USA), and thinned for electron transparency by Ar ion-beam milling with LN₂-cooling stage (Precision Ion Polishing System II, Gatan, USA). HAADF-STEM images were taken in a STEM (JEM-2100F, JEO) at 120 kV, with a spherical aberration corrector (CEOS GmbH). The optimum size of the electron probe was ~1.2 Å. The collection semi-angles of the HAADF detector were adjusted from 70 to 240 mrad. The obtained raw images were band-pass–filtered to reduce background noise (HREM Filters Pro, HREM research, Japan). To identify the interfacial chemistry, electron-energy-loss spectra were obtained in JEM-2100F (JEO) at 120 kV using an EEL spectrometer (GIF Quantum ER, Gatan, USA). Because Ga, Sr, Ta, and Al species are not detectable via EELS, the further chemistry at the interface was understood via the atomic-level EDS with a 100-mm² detector (X-max³, Oxford, UK).

**Computational details**

First-principles calculations were performed with the projector augmented-wave method (30) implemented in Vienna Ab initio Simulation Package (31) using unconstrained noncollinear magnetic structures (32, 33). The exchange and correlation effects were treated within the generalized gradient approximation (34). We used the plane-wave cutoff energy of 550 eV and 16 × 16 × 16 and 12 × 12 × 1 k-point meshes in the irreducible Brillouin zone for bulk and interface structures, respectively. Two supercells of Mn₃GaN/LaAlO₃ with the formula Mn₁₂Ga₄N₅La₅Al₅O₁₄ for MnN phase and Mn₁₄Ga₄N₅La₄Al₅O₁₄ (for MnN phase) were used to simulate the interfacial structure (Fig. 5A). Since previous reports showed that magnetism strongly influences the calculated lattice constant in Mn₃GaN (16), when optimizing the lattice structure, we assumed a noncollinear magnetic order in bulk Mn₃GaN, while the interfacial MnN layer was set to be antiferromagnetically aligned with the neighboring GaMn layer. The in-plane lattice constant of the interface supercell was constrained to the calculated lattice constant of bulk cubic Mn₃GaN (a = 3.867 Å). The internal coordinates and the c lattice constant were relaxed until the force on each atom was less than 0.001 eV/Å. When evaluating the stability of Mn/ABO₃, we used the symmetric supercells (with the formula Mn₃Al₃B₃O₁₄) made by an ABO₃ slab, Mn monolayers, and a vacuum layer over ~1 Å, as shown in fig. S10.

The formation energies were evaluated as follows (35)

\[ \Delta E_{\text{Mn/ABO}_3} = (E_{\text{supercell}} - 4E_{\text{MnGaN}} - 4E_{\text{LaAlO}_3} - E_{\text{Al}} - E_N - 2E_O)/2 \]

where \( E_{\text{MnGaN}}, E_{\text{LaAlO}_3}, E_{\text{Al}}, E_N, \) and \( E_O \) are the total energies of the related bulk material, and \( E_N \) and \( E_O \) are the half of the total energies of the related molecule.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/30/eaba4017/DC1

**REFERENCES AND NOTES**


Acknowledgment

Funding: This work was supported by the NSF under DMREF grant no. DMR-1629270 and the Army Research Office through Grant W911NF-17-1-0462. Transport measurement at the University of Wisconsin-Madison was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under award number DE-FG02-06ER46327. S.-Y.C. acknowledges the support of the Global Frontier Hybrid Interface Materials of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2013M3A6B1078872) and POSTECH-Samsung Electronics Industry-Academia Cooperative Research Center. Research at University of Nebraska-Lincoln was partly supported by the NSF Materials Research Science and Engineering Center (MRSEC) under grant no. DMR-1420645. K.S acknowledges an NRF grant funded by the Korean government (NRF-2018R1A2B6008258) and the Fundamental Research Program of the Korea Institute of Materials Science (PNK66410). Research at the University of California-Irvine was supported by the Department of Energy (DOE), Office of Research, Office of Basic Science (BES), under grant DE-SC0014430. Author contributions: C.-B.E., S.-Y.C., and M.S.R. supervised the experiments. E.Y.T. supervised theoretical calculations. C.X.Q. and T.N. fabricated and characterized thin-film samples. N.C. and M.S.R. carried out electrical transport measurements. K.S. and S.-Y.C. carried out STEM work including the atomic-scale EELS and EDS analyses. L.X. and X.P. carried out the preliminary STEM work. D.-F.S., T.R.P., and E.Y.T. performed theoretical calculations. All authors took part in the analysis. C.X.Q., T.T., S.-Y.C., and C.-B.E. wrote the manuscript. C.-B.E. directed the overall research. Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 30 November 2019
Accepted 10 June 2020
Published 24 July 2020
10.1126/sciadv.aba4017

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Sci Adv 6 (30), eaba4017.
DOI: 10.1126/sciadv.eaba4017