Epitaxial Stabilization of Metastable 3C BaRuO₃ Thin Film with Ferromagnetic Non-Fermi Liquid Phase

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Thin films of perovskite ruthenates of the general formula ARuO₃ (A = Ca and Sr) are versatile electrical conductors for viable oxide electronics. They are also scientifically intriguing, as they exhibit nontrivial electromagnetic ground states depending on the A-site element. Among them, realization of the cubic perovskite (3C) BaRuO₃ in thin film form has been a challenge so far, because the 3C phase is metastable with the largest formation energy among the various polymorph phases of BaRuO₃. In this study, 3C BaRuO₃ thin films are successfully prepared employing epitaxial stabilization. The 3C BaRuO₃ thin films show itinerant ferromagnetism with a transition temperature of \( T_{\text{c}} \approx 48 \) K and a non-Fermi liquid phase. The epitaxial stabilization of the 3C BaRuO₃ further enables to make a standard comparison of perovskite ruthenates, thereby establishing the importance of the Ru-O orbital hybridization in understanding the itinerant magnetic system.

The epitaxial stabilization of transition metal oxides grants us access to metastable structural phases with fascinating emergent properties. Therodynamically, epitaxial stabilization is determined by the competition between the surface diffusion and nucleation energy during thin film growth.[9] Therefore, interestingly, there are also cases in which the epitaxial stabilization of metastable phases in thin-film form is possible even when a fully strained state is not achieved, including domain matching epitaxy in oxides such as B-phase VO₂ thin films on STO substrates.[10–11] Even without the coherent chemical bonding at the interface owing to a large lattice mismatch, a relaxed thin film would still be able to maintain the same structural surface symmetry of the substrate. Several examples, including TiO₂/YSZ, LiNbO₃/STO, Sr₂RuO₄/LaAlO₃ (thin film/substrate) systems have been reported.[5,12,13]

Within this context, BaRuO₃ (BRO) is an excellent model system for the verification of symmetry stabilization because it possesses various polymorph phases with small differences in their formation energy. The most stable BRO phase is a nine-layered rhombohedral (9R, space group: R-3m) structure with three face-sharing RuO₆ octahedra connected by corner-sharing along the out-of-plane direction.[14] When bulk material is synthesized at pressure greater than 3 GPa, the structure of BRO becomes four-layered hexagonal (4H), six-layered hexagonal (6H), or cubic perovskite (3C).[15,16] The different crystal structures of BRO induce substantially distinct electronic and magnetic ground states. BRO with 9R, 4H, or 6H phase is known to be a paramagnetic metal with short-range antiferromagnetic fluctuations,[17] whereas 3C BRO, which consists solely of 3D corner-shared RuO₆ octahedra, is known to be a ferromagnetic metal (Figure S1, Supporting Information).[16] So far, most studies on the BRO polymorphs have focused on bulk samples. The fabrication of epitaxially stabilized 3C BRO thin film has been known to be challenging because of the natural formation of polycrystalline and/or mixed polymorph phases. A

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systematic study of 3C BRO using epitaxial stabilization would facilitate our understanding and ensure the controllability of the intriguing polymorph system. Moreover, the realization of 3C BRO in thin film form would enable a systematic investigation of the 4d perovskite Ruthenate thin films (A\text{RuO}_3, A = \text{Ca}, \text{Sr}, \text{and Ba}) with nontrivial electromagnetic ground states that depend on the A-site ion.

In this study, we successfully realized epitaxially stabilized ferromagnetic metallic 3C BRO thin films using pulsed laser deposition (PLD). We present the structural, optical, electric, and magnetic properties of 3C BRO thin film to complement existing knowledge of the perovskite Ruthenate family comprising of CaRuO_3 (CRO), SrRuO_3 (SRO), and BRO. Not only did the 3C BRO thin film exhibited a clear ferromagnetic hysteresis with a transition temperature of \( \approx 48 \) K, but its behavior resembled that of a non-Fermi liquid (NFL). A systematic comparison with the other perovskite Ruthenates led to a correlation between the p–d hybridization strength and the ferromagnetic ordering of the spins.

To verify the idea of epitaxial stabilization in cubic perovskites, we deposited BRO thin films on an STO (001) substrates with the square surface symmetry as an extension of “cube-on-cube” epitaxy (Figure 1). We controlled the growth parameters of PLD to optimize the stabilization, as shown in Figure 1a. Notably, by fine-tuning the oxygen partial pressure \( P(\text{O}_2) \) and temperature \( T_g \) during film growth, we obtained BRO thin films with various polymorph crystalline phases. Particularly, the \( P(\text{O}_2) \) largely modified the plume dynamics during growth, resulting in dramatic changes in the resultant thin films. [18,19] The growth parameter mapping of the polymorph BRO thin films on STO substrates (Figure 1a) indicates that at high \( P(\text{O}_2) \) (>10 mTorr), the thin films have multiple phases that are not affected by the surface symmetry of the substrate. Depending on \( T_g \), we not only succeeded in obtaining the 9R phase, which is the most stable phase in bulk, but also the 6H and 4H phases. On the contrary, the 3C BRO thin films were preferentially stabilized when grown at low \( P(\text{O}_2) \) (≤10 mTorr). The 3C BRO films were stable across a wide range of \( T_g \), namely, 650 °C ≤ \( T_g < 750 \) °C. The region marked in yellow on the growth parameter map in Figure 1a represents the growth window of 3C BRO. Figure 1b shows the X-ray diffraction (XRD) \( \theta-2\theta \) scans for BRO thin films grown at \( P(\text{O}_2) = 300 \) and 1 mTorr (indicated
Table 1. Comparison of ARuO₃ (A = Ca, Sr, and Ba) materials in the bulk and thin film forms on (001) SrTiO₃ substrates. For bulk ARuO₃, the A-site ionic radius, crystal structure, lattice constant, and <A—O> bond length were obtained from the literature.²⁶ The information of the thin film was obtained from experiments conducted in the current study, including the symmetry-stabilized 3C BaRuO₃.

| Material | A-site ionic radius [Å] | Bulk crystal structure | Pseudo-cubic lattice constant [Å] | Thin Film (≈30 nm on STO substrate) | Pseudo-tetragonal lattice constant [Å] | Pseudo-cubic unit cell volume [Å³] |
|----------|-------------------------|------------------------|-----------------------------------|------------------------------------|--------------------------------------|----------------------------------|
| CRO      | 1.00                    | Orthorhombic           | a = 5.36                          | Tensile 1.70% (fully strained)     | a = 5.32                            | 56.92                            |
|          |                         |                        | b = 5.54                          |                                    | c = 7.64                            |                                  |
|          |                         |                        | c = 7.85                          |                                    |                                     |                                  |
| SRO      | 1.18                    | Orthorhombic           | a = 5.57                          | Compressive 0.64% (fully strained) | a = 5.60                            | 60.70                            |
|          |                         |                        | b = 5.55                          |                                    | c = 7.81                            |                                  |
| 3C BRO   | 1.36                    | Cubic                  | a = b = c = 4.00                  | Compressive 2.46% (partially strained) | a = b = c = 3.99 | 64.00                            |
|          |                         |                        |                                    |                                    |                                     |                                  |

Table 1. Comparison of ARuO₃ (A = Ca, Sr, and Ba) materials in the bulk and thin film forms on (001) SrTiO₃ substrates. For bulk ARuO₃, the A-site ionic radius, crystal structure, lattice constant, and <A—O> bond length were obtained from the literature.²⁶ The information of the thin film was obtained from experiments conducted in the current study, including the symmetry-stabilized 3C BaRuO₃.

The successful epitaxial stabilization of the 3C BRO thin film enabled us to make a standard comparison of the three members of the perovskite Ruthenate family complementing our understanding of the materials system in its entirety. The structural parameters of the perovskite Ruthenates are summarized in Table 1. In the bulk form, CRO and SRO have orthorhombic structures with GdFeO₃-type tetrahedral distortion, whereas 3C BRO has a simple cubic structure without any distortions. On the contrary, the ARuO₃ thin films (=30 nm) grown on the (001) STO substrates, depending on the degree of strain, can be represented as having tetragonal structures. In both cases, the overall lattice parameters and (pseudo-cubic) unit cell volumes increase as the ionic radius of the A-site ion increases, as expected. The pseudo-cubic unit cell volumes of the CRO, SRO, and 3C BRO thin films are 58.25, 60.23 and 66.23 Å³, respectively, a striking 13.7% increase when comparing 3C BRO with CRO. This wide tunability of the unit cell volume in the perovskite Ruthenates provides an essential opportunity to customize the structure-related physical properties. For example, as a consequence of Ba doping in bulk Srₓ₋₁BaₓRuO₃, the Ru—O bond is stretched, becoming longer than the A—O bond in the cubic phase.²⁴,²⁵

The change in the lattice structures of the perovskite ARuO₃ thin films naturally leads to changes in their electronic structures and consequently their magnetic properties. Figure 2a shows the real part of the optical conductivity (σ(ω)) of a 3C BRO thin film obtained by spectroscopic ellipsometry. The σ(ω) of CRO and SRO thin films on (001) STO substrates are also shown for comparison (Figure S7, Supporting Information).²⁹ All of the perovskite ARuO₃ thin films show qualitatively similar σ(ω) spectra, which originate from the common Ru⁴⁺ orbital state and its interaction with oxygen, that is, Drude absorption and four interband transitions, manifesting the correlated metallic nature. Note that the other polymorph phases of BRO with Ru—Ru bond exhibit entirely different σ(ω) spectra, and hence, a distinctive
The electronic structure of the perovskite BaRuO$_3$ thin films commonly exhibit two d–d transition peaks at 1.6–1.9 (α) and 4.3–4.5 eV (β), and two charge transfer transition peaks at 3.0–3.3 (A) and >6 eV (B). These peaks (α, β, A, and B) are routinely attributed to the optical transitions between the orbital states of Ru 4d, and O 2p → Ru 4d and Ru 4d ε$^\prime$, O 2p → Ru 4d ε$^\prime$, and O 2p → Ru 4d ε$^\prime$ respectively. To quantitatively compare the optical transitions among the BaRuO$_3$ thin films, the $\sigma_i(\omega)$ values were fitted using Drude–Lorentz oscillators.

Table 2 summarizes the values of the optical transition energy and spectral weight ($W_i = \int \sigma_i(\omega) d\omega$) for each thin film. Among them, $W_A$, $W_B$, $W_\alpha$, and $W_\beta$ exhibited a maximum for the SRO. $W_B$ could not be quantitatively analyzed as peak B extended beyond our experimental spectral range of 5.5 eV. The charge transfer transitions (peak A and B) are essential for describing the p–d hybridization strength between the O 2p and Ru 4d orbital states and therefore, the magnetic exchange interaction in an itinerant magnetic system. Hence, we estimated the relative contribution of $W_A$ from the total $W$ ($W_{\text{tot}}$) of each thin film, as shown in Figure 2c. The relative contribution of $W_A$ to the total optical transitions was the least for the CRO and the most for the SRO and was intermediate for the 3C BRO thin films. This tendency follows the trend of the ferromagnetic transition temperature ($T_c$), which is discussed as follows (Figure 2c). We note that the hybridization strength determining the magnetic ground state can be further applied to other Ba–Ru–O systems in addition to the various BaRuO$_3$ polymorphs.

The epitaxially stabilized 3C BRO thin film shows itinerant ferromagnetic behavior resembling that of the SRO thin film (Figure S8, Supporting Information). Figure 3 shows the magnetic properties of a 3C BRO thin film on the STO substrate. The contribution from the substrate was carefully subtracted (Figure S9, Supporting Information). The zero-field-cooled (ZFC) and field-cooled (FC) temperature-dependent magnetization, $M(T)$, for the 3C BRO thin film are obtained along the out-of-plane and in-plane directions, as shown in Figure 3a and Figure S10 (Supporting Information), respectively. The 3C BRO thin film exhibits a ferromagnetic transition with a clearly discernible $T_c$ of ~48 K, as is evident from the $dM/dT$ curves for both the out-of-plane and in-plane directions (insets of Figure 3a and Figure S10a (Supporting Information)). In the bulk form, 3C BRO is ferromagnetic with $T_c = 60$ K. However, under pressure, the $T_c$ decreases dramatically to 39 K.

Table 2. Parameters of the deconvoluted Lorentzian peaks including the optical transition energy and spectral weight for the BaRuO$_3$ thin films.}

|                  | Optical transition energy [eV] | Optical conductivity | Spectra weight [eV$^2$] |
|------------------|-------------------------------|----------------------|-------------------------|
|                  | α    | A    | β    | B    | Drude | $W_\alpha$ | $W_A$ | $W_B$ | $W_\alpha$ | $W_B$ |
| CRO              | 1.89 | 3.03 | 4.27 | 5.94 | 10.70 | 6.76      | 12.76 | 8.02  | 56.45      |
| SRO              | 1.70 | 3.25 | 4.20 | 6.00 | 13.71 | 3.73      | 19.38 | 6.53  | 48.60      |
| 3C BRO           | 1.60 | 3.11 | 4.45 | 6.00 | 9.10  | 2.23      | 12.28 | 3.36  | 47.16      |
above 4 GPa, a trend that is consistent with our result for the partially strained, epitaxially stabilized 3C BRO thin film.\cite{35} We also note a considerable \(M\) remaining above \(T_c\), possibly owing to magnetic fluctuation that survives up to a higher \(T_c\). The magnetic field-dependent magnetization, \(M(H)\), shows a clear hysteresis loop opening below \(T_c\) (Figure 3b; Figure S10b Supporting Information). The saturation \(M(0.5 \mu_B/\text{Ru})\) of the thin film is slightly smaller than that of the bulk 3C BRO (0.8 \(\mu_B/\text{Ru})\).\cite{36} Even though we observed somewhat larger out-of-plane \(M\) than in-plane \(M\), the ferromagnetism in the 3C BRO thin film is more isotropic than that in SRO thin films, possibly owing to its original cubic symmetry.

The magnetic ordering of the perovskite Ruthenates thin films, that is, paramagnetism in CRO, and ferromagnetism in SRO \((T_c \approx 150 \text{ K})\)\cite{16} (Figure S8, Supporting Information) and BRO \((T_c \approx 50 \text{ K})\) (Figure 3), could be collectively understood in terms of the magnitude of the orbital hybridization. As previously discussed, the optical charge transfer transition determines the strength of the p–d hybridization. This facilitates the exchange interaction between Ru ions connected via O ions, a result that is supported by those of a band calculation study.\cite{31,36} Indeed, when \(T_c\) was plotted along with \(W_A/W_{\text{stot}}\), as shown in Figure 2c, the same A-site dependency is clearly demonstrated, thereby validating the importance of the hybridization strength in understanding the itinerant magnetism in perovskite Ruthenates.

To further explore the itinerant nature of the magnetism of 3C BRO, the transport properties of the thin film were measured, as shown in Figure 4. The metallic \(T\)-dependent resistivity \((\rho(T))\) of the 3C BRO thin film is similar to that of the CRO thin film. On the other hand, it also shows an anomaly at 48 K, signifying the \(T_c\), as in the case of SRO thin film (Figure S11, Supporting Information). The resistivity values of 3C BRO are smaller than those of the reported bulk sample, probably owing to the phase purity of our thin film. However, the \(\rho(T)\) was still larger than those of the SRO thin film across the experimental temperature range.\cite{19,26,30} The low temperature \(\rho(T)\) was further fitted using the power law \(\rho(T) = \rho_0 + T^\alpha\) (where \(\rho_0\) is the residual resistivity and \(\alpha\) is a scaling exponent), to reveal a NFL phase with \(\alpha = -1.4\) below \(-25 \text{ K}\) (Figure S12, Supporting Information).
Information). In a pressure-depended study of the bulk 3C BRO, the value of \( \alpha \) was \( \approx 1.4 \) under the pressure of 8 GPa, which is consistent with our observation.\[35\]

The magneto-transport results of the 3C BRO thin film provide additional support for the existence of the NFL phase. Figure 4b shows the magnetic field-dependent Hall resistivity \( \rho_{xy}(H) \). The 3C BRO thin film exhibits nonlinear behavior in \( \rho_{xy} \) (anomalous Hall term), which is induced by the ferromagnetic order at low temperature. Note that the normalized \( \rho_{xy}(H) \) curve qualitatively coincides with the normalized \( M(H) \) curve (Figure S13, Supporting Information), except for the hysteresis loop opening, of which the origin is not clear at the moment. Figure 4c shows the magnetoresistance (MR) at different temperatures. By scaling the MR and zero-field resistivity, we drew Kohler’s plot, as shown in the inset of Figure 4c. Based on Kohler’s rule, if the carrier density of the system is robust to temperature variation, the MR curves measured at different temperatures can be scaled into a single curve. Because Kohler’s rule is based on the linearity of the Boltzmann equation with the electron scattering lifetime, any deviation from the rule presents as evidence for NFL behavior.\[37\] As shown in the inset of Figure 4c, the scaled MR curves violate Kohler’s rule, thus supporting the NFL behavior of 3C BRO, in addition to the fact that the scaling exponent \( \alpha \) deviates from 2. On the other hand, the positive MR observed in the ferromagnetic phase of 3C BRO thin film is rather unusual. While there are several mechanisms reported for the observation of positive MR in various ferromagnetic materials,\[38\] the small \( M \) and possible magnetic fluctuation above \( T_c \) might be attributed to the positive MR in 3C BRO thin film.

In summary, we successfully prepared epitaxially stabilized 3C BRO thin films to complement the perovskite phases of Ruthenate thin films. The 3C BRO thin films grown under optimal conditions revealed a tetragonal structure with a fourfold symmetry, indicative of the surface epitaxial stabilization. The variation in the lattice structures within the family of perovskite ARuO\(_3\) thin films naturally leads to changes in the electronic structures, and consequent magnetic properties. Indeed, we confirmed the strong correlation between the ferromagnetism of the perovskite Ruthenates and the orbital hybridization strength. The epitaxially stabilized 3C BRO thin film showed itinerant ferromagnetism with a transition temperature of \( \approx 48 \) K. A clear magnetic hysteresis loop was presented with a saturation magnetic moment of \( \approx 0.5 \mu_B/Ru \). Furthermore, \( d \)c and magneto-transport results indicate that the 3C BRO thin film behaves like a NFL at low temperatures. Our study provides a fundamental understanding of the systematic evolution of the physical properties within cubic perovskite Ruthenate thin films.

**Experimental Section**

**Thin Film Growth and Structural Characterization:** High-quality epitaxial BaRuO\(_3\) (BRO) thin films were grown on atomically flat SrTiO\(_3\) (STO) (001) single crystalline substrates using Pulsed Laser Deposition at 750 °C. Laser (248 nm; Lightmachinery, IPEX 864) fluence of 1.0 J cm\(^{-2}\) and a repetition rate of 5 Hz was used. The vertical distance between the target and the substrate was fixed to 65 mm. In order to successfully prepare 3C BRO, the films were grown under various oxygen partial pressure conditions, ranging from 0.3 to 10\(^{-3}\) Torr. The atomic structure, crystal orientations, and the epitaxial relation of BRO thin films were determined using high resolution x-ray diffraction, in-plane \( \phi \)-scan, and reciprocal space map. The thickness of all the BRO thin films was \( \approx 30 \pm 1 \) nm from X-ray reflectometry. Cross-sectional transmission electron microscopy specimens were prepared by ion milling at the LN\(_2\) temperature after conventional mechanical polishing. High-angle annular dark field scanning transmission electron microscopy (HAADF STEM) measurements were performed on Nion UltraSTEM200 operated at 200 kV. The microscope was equipped with a cold field emission gun and a corrector of third- and fifth-order aberration for sub-angstrom resolution. The collection inner and outer half-angles for HAADF STEM were 65 and 240 mrad, respectively.

**Ellipsometry:** The optical properties of the BRO thin films were investigated using spectroscopic ellipsometers (VASE and M-2000, J. A. Woollam Co.) at room temperature. The optical spectra were obtained between 0.74 and 5.5 eV for the incident angles of 65°. Two-layer model (BRO thin film on STO substrate) was sufficient for obtaining physically reasonable spectroscopic dielectric functions of BRO.

**Resistivity and Magnetization Measurements:** \( \rho(T) \) were measured using established closed-cycle refrigerator. The measurements were performed from 300 to 10 K, using Van der Pauw method with In electrodes and Au wires. Magnetotransport measurements were performed in magnetic fields up to 9 T and temperatures down to 2 K in a quantum design physical properties measurement system. \( M(T) \) were measured using Magnetic Property Measurement System (MPMS, Quantum Design). The measurements were performed from 300 to 2 K under 1000 Oe of magnetic field along the in-plane and out-of-plane direction.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

3C BaRuO\(_3\), epitaxial stabilization, ferromagnetism, hybridization control, non-Fermi liquids, ruthenates
