Epitaxial stabilization of ultra thin films of high entropy perovskite

Cite as: Appl. Phys. Lett. 116, 071601 (2020); https://doi.org/10.1063/1.5133710
Submitted: 25 October 2019 • Accepted: 30 January 2020 • Published Online: 18 February 2020

Ranjan Kumar Patel, Shashank Kumar Ojha, Siddharth Kumar, et al.

ARTICLES YOU MAY BE INTERESTED IN

The emergent field of high entropy oxides: Design, prospects, challenges, and opportunities for tailoring material properties
APL Materials 8, 040912 (2020): https://doi.org/10.1063/5.0003149

Magnetic properties of rare-earth and transition metal based perovskite type high entropy oxides
Journal of Applied Physics 127, 185109 (2020): https://doi.org/10.1063/5.0004125

Dielectric properties and electrocaloric effect of high-entropy (Na_{0.2}Bi_{0.2}Ba_{0.2}Sr_{0.2}Ca_{0.2})TiO_3 ceramic
Applied Physics Letters 115, 223901 (2019); https://doi.org/10.1063/1.5126652

APL Quantum
CALL FOR APPLICANTS
Seeking Editor-in-Chief
Epitaxial stabilization of ultra thin films of high entropy perovskite

Cite as: Appl. Phys. Lett. 116, 071601 (2020); doi:10.1063/1.5133710
Submitted: 25 October 2019 · Accepted: 30 January 2020 ·
Published Online: 18 February 2020

Ranjan Kumar Patel,1 Shashank Kumar Ojha,1 Siddharth Kumar,1 Akash Saha,2 Prithwijit Mandal,1 J. W. Freeland,3 and S. Middey1,a)

AFFILIATIONS
1Department of Physics, Indian Institute of Science, Bengaluru 560012, India
2Undergraduate Programme, Indian Institute of Science, Bengaluru 560012, India
3Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
4Electronic mail: smiddiey@iisc.ac.in

ABSTRACT
High entropy oxides (HEOs) are a class of materials, containing equimolar portions of five or more transition metal and/or rare-earth elements. We report here about the layer-by-layer growth of HEO [(La0.2Pr0.2Nd0.2Sm0.2Eu0.2)NiO3] thin films on NdGaO3 substrates by pulsed laser deposition. The combined characterizations with in situ reflection high energy electron diffraction, atomic force microscopy, and x-ray diffraction affirm the single crystalline nature of the film with smooth surface morphology. The desired +3 oxidation of Ni has been confirmed by an element sensitive x-ray absorption spectroscopy measurement. Temperature dependent electrical transport measurements revealed a first order metal-insulator transition with the transition temperature very similar to the undoped NdNiO3. Since both these systems have a comparable tolerance factor, this work demonstrates that the electronic behaviors of A-site disordered perovskite-HEOs are primarily controlled by the average tolerance factor.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5133710

Finding ways to tune materials’ properties is essential for fulfilling the demand of the constantly evolving modern technology. Transition metal oxides show various fascinating electronic and magnetic phenomena such as metal-insulator transition, superconductivity, colossal magnetoresistance, multiferroicity, skyrmions, etc., which have a lot of potential for technological applications. Furthermore, transition metal (TM) based high entropy oxides (HEOs) have been explored in recent years to achieve tunable properties in unexplored parts of the complex phase diagram. In general, the configurational entropy of a multi-component solid solution can be enhanced by mixing a large number of cations in equiatomic proportions and a single structural phase is formed if the entropy contribution overcomes enthalpy driven phase separation ($\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$; $\Delta G_{mix}$, $\Delta H_{mix}$, $\Delta S_{mix}$ are the Gibbs free energy, enthalpy, and entropy of mixing, respectively). After the report of the first HEO (MgCu2Al2ZnO4 with a rock salt structure) by Rost et al., HEOs with other structural symmetries such as perovskite and spinel have also been synthesized. However, this promising field of HEO is at a very early stage and most of the aspects of HEOs are yet to be explored experimentally. For example, it is still unknown whether the strong disorder or the average tolerance factor ($t_{avg}$) determines the electronic and magnetic behaviors of perovskite HEOs.

As a prototypical example of perovskite (ABO3) series, RENiO3 (RE= La, Pr, Nd, Sm, Eu…Lu) exhibits an interesting phase diagram as a function of tolerance factor ($t = \frac{R_{RE} + R_{O}}{\sqrt{2}(R_{Ni} + R_{O})}$, where $R_{RE}$, $R_{Ni}$, $R_{O}$ are the ionic radii of RE, Ni, and O, respectively). LaNiO3, the least distorted member of this series, remains metallic and paramagnetic down to the lowest temperature. Bulk PrNiO3 and NdNiO3 (NNO) show temperature driven simultaneous transitions from an orthorhombic, paramagnetic, and metallic phase to a monoclinic, antiferromagnetic, and insulating phase, respectively [see Fig. 1(a)]. The insulating phase is also characterized by a checkerboard type charge ordering. In the case of more distorted members, such as SmNiO3, EuNiO3, etc., the magnetic transition gets decoupled from the other three simultaneous transitions, resulting in an intermediate paramagnetic, insulating, and charge ordered phase. The quest to understand the origin of these transitions has led to remarkable progress in epitaxial stabilization of the RENiO3 family (see Refs. 25 and 26 and literature cited therein), and thin films of RENiO3 with RE = La, Pr, Nd, Sm, and Eu have been stabilized so far. This further provides a
In this Letter, we report layer-by-layer growth of (La0.2Pr0.2Nd0.2Sm0.2Eu0.2)NiO3 [(LPNSE)NO] thin films on a single crystalline NdGaO3 (NGO) substrate by pulsed laser deposition (PLD). The variation in bulk lattice constants together with the pseudo-cubic lattice constants of several members of the RENiO3 series is shown in Table I. Since the average of t of RENiO3 with RE = La, Pr, Nd, Sm, Eu [indicated by a vertical line in Fig. 1(a)] is comparable to NNO, the electronic behavior of [(LPNSE)NO] thin films has also been compared with that of NNO films. Several characterization techniques including in situ RHEED (reflection high energy electron diffraction) and ex-situ atomic force microscopy (AFM), x-ray diffraction (XRD), and x-ray absorption spectroscopy (XAS) confirmed high structural quality of these (LPNSE)NO thin films with a proper oxidation state of Ni. Transport measurements and XAS experiments further revealed that in-spite of having a strong structural disorder, the electronic behaviors of the (LPNSE)NO sample are very similar to a single A site cation NNO film.

(LPNSE)NO films with thicknesses of 15 uc, 30 uc, and 45 uc (uc = unit cell in pseudocubic notation) and the NNO film with a thickness of 15 uc were grown on NGO (110) or (001)pc substrates (here, or and pc denote the orthorhombic and pseudocubic setting) by a PLD system at 735 °C under a dynamic oxygen pressure of 100–150 millitorr. The details of the target preparation can be found in the supplementary material. A KrF excimer laser, operating with 4 Hz and an energy density of 1.5 J/cm², was used for the deposition. The layer by layer growth was monitored by using a high pressure RHEED system. The films were post-annealed at the growth temperature under an oxygen pressure of 500 Torr for 30 min and cooled to room temperature at the same oxygen pressure. A Park system AFM was used to check the morphology of these films. X-ray diffraction patterns were recorded using a Rigaku Smartlab x-ray diffractometer. Temperature dependent resistivity was measured by using the Van der Pauw geometry in a Quantum Design PPMS (physical property measurement system). XAS spectra at Ni-L3,2 and O-K edges were collected in bulk-sensitive (probing depth ~20 nm) TFY (total fluorescence yield) mode at the 4-ID-C beamline of the Advanced Photon Source, Argonne National Laboratory.

The time dependent intensity of the specular reflection of the RHEED pattern [Fig. 1(b)], recorded during the deposition, shows very prominent oscillations, confirming the layer-by-layer growth of the (LPNSE)NO film. The inset of Fig. 1(b) shows a RHEED image of a (LPNSE)NO film, taken after cooling to room temperature. The streaky pattern of specular (0 0) and off-specular (0 1), (0–1) Bragg reflections is a characteristic of smooth surface morphology. Akin to the RHEED pattern of the NNO film on the NGO substrate,41 (LPNSE)NO films also have half-order spots: (0 1/2) and (0 –1/2) (denoted by the arrows), indicating orthorhombic/monoclinic symmetry at room temperature.42 The inset of Fig. 2(a) shows the AFM image of the 45 uc (LPNSE)NO film, and the roughness is found to be ~1.8 Å well below cpc, further testifying excellent surface morphology of the film.

In order to check the structural quality of the samples and to detect the presence of any impurity phase, we have recorded 20-ω diffraction scan for (LPNSE)NO films using Cu Kα radiation. Such a long scan XRD for the 45 uc (LPNSE)NO film [Fig. 2(a)] consists of broad film peaks in the vicinity of sharp substrate peaks, confirming the single crystalline nature of the film. Most importantly, the absence of any impurity peaks (within the detection limit of XRD) infers the growth conditions used in this work is able to stabilize the multicomponent system into a single phase. XRD patterns around the (0 0 2)pc peak for 15 uc, 30 uc, and 45 uc (LPNSE)NO films are shown in Figs. 2(b)–2(d), respectively. The very close proximity between the film peak and the substrate peak [Fig. 2(b)] in the case of the 15 uc (LPNSE)NO film prohibits a reliable estimation of the out-of-plane lattice constant (cpc). cpc values for 30 uc and 45 uc films are found to be 3.792 Å and 3.784 Å, respectively. The presence of thickness fringes in the vicinity of the film peaks further supports the excellent flatness.

TABLE I. Lattice parameters (a, b, and c) of few rare earth nickelates. Pseudo cubic lattice constants a pc, b pc, and c pc are also listed. For orthorhombic systems, a pc = b pc = \( \sqrt{a^2 + b^2} \) and c pc = 2c2.

| Compound | a (Å) | b (Å) | c (Å) | a pc = b pc (Å) | c pc (Å) | References |
|----------|-------|-------|-------|-----------------|----------|------------|
| LaNiO3   | 5.457 | 5.457 | 13.146| 3.838           | 3.838    | 38         |
| PrNiO3   | 5.419 | 5.380 | 7.626 | 3.818           | 3.813    | 38         |
| NdNiO3   | 5.389 | 5.382 | 7.610 | 3.808           | 3.805    | 38         |
| SmNiO3   | 5.327 | 5.432 | 7.565 | 3.804           | 3.782    | 39         |
| EuNiO3   | 5.294 | 5.458 | 7.537 | 3.802           | 3.769    | 39         |
of the film-substrate interface. Rocking curve XRD further supports extremely high quality of the film, and φ scan XRD establishes the same in-plane orientation of the (LPNSE)NO film and NGO substrate (see the supplementary material). The thickness of the films calculated from the position of the fringes (e.g., ~17.3 nm for 45 uc film) are close to the value expected from the RHEED oscillations. The cpc value of the 15 uc NNO film is found to be 3.845 Å (XRD pattern not shown). Complimentary experiments like synchrotron based x-ray diffraction and extended x-ray absorption fine structure (EXAFS) experiments will be required to understand the difference in cpc between (LPNSE)NO and NNO films.

After confirming the high structural and morphological quality, we have investigated the electrical transport of the films. As reported earlier, the 15 uc NNO thin film on the NGO substrate undergoes first order MIT [upper panel of Fig. 3(a)]. The transition temperature in the cooling run (TMIT ~ 160 K) and in the heating run (TMIT ~ 180 K) is lower compared to the bulk NNO and is related to the epitaxial strain and finite thickness. Surprisingly, the resistivity (ρ) of the 15 uc (LPNSE)NO film at 300 K is very similar to that of the 15 uc NNO film in spite of having a strong disorder on the A site. It further exhibits a MIT with strong thermal hysteresis (TMIT ~ 175 K, TMIT ~ 185 K). However, the transition is more sluggish and the resistivity of the insulating phase is also lower than that of the 15 uc NNO film. With the increase in the film thickness, TMIT becomes approximately 200 K [upper panel of Fig. 3(b)], which is very close to the transition temperature expected for the corresponding f of the (LPNSE)NO phase from the bulk phase diagram [Fig. 1(a)]. This finding clearly establishes that the average tolerance factor controls TMIT for this HEO, rather than the disorder at the A-site.

All RENiO3 with an insulating phase also hosts E-type antiferro-magnetic ordering. The magnetic transition temperature (Tc) can be approximately estimated from the d(lnρ)/dT(T) vs T plot, as demonstrated recently for NNO films and EuNiO3/LaNiO3 superlattices. Such resistivity analysis of the heating run data [lower panel of Figs. 3(a) and 3(b)] provides a Tc value of 170 K for both 15 uc NNO and 15 uc (LPNSE)NO samples, 185 and 190 K for 30 uc and 45 uc (LPNSE)NO films, respectively. This suggests simultaneous electronic and magnetic transitions in these (LPNSE)NO films. Soft x-ray resonant scattering experiments can further confirm this.

The required high +3 oxidation state of Ni makes RENiO3 based systems very susceptible to oxygen nonstoichiometry. In order to further understand the electronic and chemical structures of these films, we have measured XAS spectra on the Ni L3,2 edge and O-K edge at 300 K and 85 K (much below TMIT). Due to the strong overlap of the L4 edge with Ni L3 for the (LPNSE)NO film, we discuss here only the L2 edge. First of all, the XAS line shape of both 15 uc NNO and 15 uc (LPNSE)NO films at 300 K [Fig. 4(a)] is consistent with Ni3+ in the metallic phase of nickelates, affirmin the stabilization of the desired oxidation state of Ni. Further, the appearance of strong multiplet structures (around 870.05 eV) in the insulating phase of the (LPNSE)NO film is also consistent with the observation of the NNO film [Fig. 4(a)] and the insulating phase of other nickelates. Similar to the high Tc cuprates, RENiO3 also contains ligand holes, which can be observed as a pre-peak around 528 eV in the O-K edge XAS spectrum due to the hole in the oxygen 1s core state and L2 corresponds to a hole in the O 2p state. While the intensity of the pre peak is reduced in the (LPNSE)NO film at 300 K, the position and FWHM (full width at half maxima) are very similar for both samples. The measurements at 85 K have found lowering of the peak width in both samples (not shown), which is expected due to the band narrowing across the MIT. Thus, transport and XAS measurements conclude that the overall electronic structure effect across the MIT of the (LPNSE)NO film is very similar to that of the NNO film.

To summarize, we have grown high quality epitaxial films of multicomponent (LPNSE)NO in a layer-by-layer fashion by pulsed laser deposition. RHEED, XRD, AFM, XAS, and transport measurements have been carried out to investigate the structure and the electronic behavior of these films. In spite of having multi elements and strong disorder at the RE site, the average tolerance factor determines...
the electronic transition temperature. However, the microscopic details, e.g., nucleation of the insulating/metallic phase around the transition temperature, charge transfer between Ni and RE sites, conductivity noise, etc., may depend on the details of the RE composition and need to be explored further. Stabilization of such a multi-site or both the sites can be studied in the future to explore disorder driven physics in strongly correlated systems.

See the supplementary material for the details of target preparation, results of the rocking curve, and phi scan in XRD.

This work was funded by a DST Nanomission Grant (No. DST/EMR/2018/246) and a SERB Early Career Research Award (No. ECR/2018/001512). The authors acknowledge AFM and XRD facilities at the Department of Physics, IISc Bangalore. RKP and SM thank the Department of Science and Technology, India (No. SR/NM/07/2015) for the financial support to conduct the synchrotron experiment at the Advanced Photon Source and Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) for managing the project. This research used resources of the Advanced Photon Source, a U.S. Department of Energy Office of Science User Facility operated by the Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

REFERENCES

1. M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
2. Y. Tokura, Rep. Prog. Phys. 69, 797 (2006).
3. Z. Yang, C. Ko, and S. Ramanathan, Annu. Rev. Mater. Res. 41, 337 (2011).
4. G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, Rev. Mod. Phys. 84, 119 (2012).
5. M. Lorenz, M. R. Rao, T. Venkatesan, E. Fortunato, P. Barquinha, R. Branquinho, D. Salgueiro, R. Martins, E. Carlos, A. Liu et al., J. Phys.: D: Appl. Phys. 49, 433001 (2016).
6. J. Matsuno, J. Fujioka, T. Okuda, K. Ueno, T. Mizokawa, and T. Katsufuji, Sci. Technol. Adv. Mater. 19, 899 (2018).
7. M. Rost, E. Sachet, T. Borman, A. Moballeghi, E. C. Dickey, D. Hou, J. L. Jones, S. Curtarolo, and J.-P. Maria, Nat. Commun. 6, 8485 (2015).
8. D. Béradan, S. Franiger, A. Meena, and N. Dragoe, J. Mater. Chem. A 4, 9536 (2016).
9. C. M. Rost, Z. Rak, D. W. Brenner, and J.-P. Maria, J. Am. Ceram. Soc. 100, 2732 (2017).
10. C. M. Rost, Z. Rak, D. W. Brenner, and J.-P. Maria, J. Am. Ceram. Soc. 100, 2732 (2017).
11. A. Sarkar, R. Djenadic, N. I. Usbharani, K. P. Sanghvi, V. S. Chakravadhanula, A. S. Gandhi, H. Hahn, and S. S. Bhattacharya, J. Eur. Ceram. Soc. 37, 747 (2017).
12. R. Djenadic, A. Sarkar, O. Clemens, C. Loho, M. Botros, V. S. Chakravadhanula, C. Kübel, S. S. Bhattacharya, A. S. Gandhi, and H. Hahn, Mater. Res. Lett. 5, 102 (2017).
13. S. Jiang, T. Hu, J. Gild, N. Zhou, J. Nie, M. Qin, T. Harrington, K. Vecchio, and J. Luo, Sci. Mater. 142, 116 (2018).
14. G. Anand, A. P. Wynn, C. M. Handley, and C. L. Freeman, Acta Mater. 146, 119 (2018).
15. A. Sarkar, L. Velasco, D. Wang, Q. Wang, G. Talasila, L. de Biasi, C. Kübel, T. Brezesinski, S. S. Bhattacharya, H. Hahn et al., Nat. Commun. 9, 3400 (2018).
16. V. Sharma, B. L. Musico, X. Gao, C. Hua, A. F. May, A. Herklotz, A. Rastogi, D. Mandrus, J. Yan, H. N. Lee et al., Phys. Rev. Mater. 2, 060404 (2018).
17. J. D. Krockova, M. Styr, D. M. Knapik, K. Mróczka, W. T. Jochman, M. Danielewski, and M. Martin, Mater. Lett. 216, 32 (2018).
18. R. Witte, A. Sarkar, R. Kruk, B. Eggert, R. A. Brand, H. Wende, and H. Hahn, Phys. Rev. Mater. 3, 034406 (2019).
19. A. Sarkar, Q. Wang, A. Schiele, M. R. Chellali, S. S. Bhattacharya, D. Wang, T. Brezesinski, H. Hahn, L. Velasco, and B. Breitung, Adv. Mater. 31, 1806236 (2019).
20. Y. Zhang, J. Yan, S. Calder, Q. Zheng, M. A. McGuire, D. L. Abernathy, Y. Ren, S. H. Lapidus, K. Page, H. Zheng et al., Chem. Mater. 31, 3705–3711 (2019).
21. P. Meisenheimer, T. Kratofil, and J. Heron, Sci. Rep. 7, 13344 (2017).
22. Y. Sharma, Q. Zheng, A. R. Mazza, E. Fortunato, T. Heitmann, Z. Gai, B. Musico, P. F. Miceli, B. C. Sales, V. Keppens et al., preprint arXiv:1909.05019 (2019).
23. M. L. Medarde, J. Phys.: Condens. Matter 9, 1679 (1997).
24. G. Catalan, Phase Trans. 81, 729 (2008).
25. U. Staeb, G. I. Meier, F. Faub, R. Allesspanck, J. G. Bednorz, J. Karpinski, S. M. Kazakov, L. Paolasini, and F. d’Acapito, Phys. Rev. Lett. 88, 126402 (2002).
26. S. Middey, J. Chakhalian, P. Mahadevan, J. W. Freeland, A. J. Mills, and D. D. Sarma, Annu. Rev. Mater. Res. 46, 305 (2016).
27. S. Catalan, M. Gilbert, J. Fowle, J. Íñiguez, M.-J. Triscione, and J. Kreisel, Rep. Prog. Phys. 81, 046501 (2018).
28. S. D. Ha, M. Otaki, R. Jaramillo, A. Podpirka, and S. Ramanathan, J. Solid State Chem. 190, 233 (2012).
29. J. Liu, M. Kargarian, M. Kaveev, B. Gray, P. J. Ryan, A. Cruz, N. Tahir, Y.-D. Chuang, J. Guo, J. M. Rondinelli, J. W. Freeland, G. A. Fiete, and J. Chakhalian, Nat. Commun. 4, 2714 (2013).
30. L. Feigl, B. Schultz, S. Olyas, D. Ouellette, A. Kozhanov, and C. Palmstrøm, J. Cryst. Growth 366, 501 (2013).

FIG. 4. (a) Ni L$_{2,3}$-edge and (b) O-K edge XAS for 15 uc NNO and 15 uc (LPNSe)NO films on the NGO substrate. Ni L$_{2,3}$ edge data has been moved vertically for visual clarity. In the O-K edge XAS spectra, the pre-peak around 528 eV is related to the transition from O 1s to the Ni 3d-0 2p hybridized states. The lower intensity of this pre-peak for the LPNSeNO film compared to NNO is likely to be related to the structural disorder. 44 $^{4s}$ and 5$d$ hybridized states of rare earth (RE) ions, present in the sample and substrate, result in the peak around 534–535 eV. Ni 4$s$ and 4$p$ also hybridized with O 2$p$, resulting in the peaks around 540–545 eV.
35. D. Meyers, S. Middey, M. Kareev, M. van Veenendaal, E. J. Moon, B. A. Gray, J. Liu, J. W. Freeland, and J. Chakhalian, Phys. Rev. B 88, 075116 (2013).

36. E. Miheev, A. J. Hauser, B. Himmetoglu, N. E. Moreno, A. Janotti, C. G. Van de Walle, and S. Stemmer, Sci. Adv. 1, ea1500797 (2015).

37. M. Hepting, M. Minola, A. Frano, G. Cristiani, G. Logvenov, E. Schierle, M. Wu, M. Bluschke, E. Weschke, H.-U. Habermeier, E. Benckiser, M. L. Tacon, and B. Keimer, Phys. Rev. Lett. 113, 227206 (2014).

38. R. Scherwitzl, S. Gariglio, M. Gabay, P. Zubko, M. Gibert, and J.-M. Triscone, Phys. Rev. Lett. 106, 246403 (2011).

39. Y. Bruno, K. Z. Ruschanski, S. Valencia, Y. Dumont, C. Carrétero, E. Jacquet, R. Abrudan, S. Blügel, M. Letzai, M. Bipes, and A. Barthelémy, Phys. Rev. B 88, 195108 (2013).

40. P. King, H. Wei, Y. F. Nie, M. Uchida, C. Adamo, S. Zhu, X. He, I. Bozović, D. G. Schlom, and K. M. Shen, Nat. Nanotechnol. 9, 443 (2014).

41. A. S. Disa, D. Kumah, J. Ngai, E. D. Specht, D. Arena, F. J. Walker, and C. H. Ahn, APL Mater. 1, 032110 (2013).

42. S. Catalano, M. Gibert, V. Bisogni, O. E. Peil, F. He, R. Sutarto, M. Viret, P. Zubko, R. Scherwitzl, A. Georges, G. A. Sawatzky, T. Schmitt, and J.-M. Triscone, APL Mater. 2, 116110 (2014).

43. J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre, and J. B. Torrance, Phys. Rev. B 46, 4414 (1992).

44. J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, M. A. G. Aranda, and M. T. Fernández-Díaz, J. Am. Chem. Soc. 121, 4754 (1999).

45. J.-S. Zhou, J. Goodenough, and B. Dabrowski, Phys. Rev. B 67, 202404 (2003).

46. S. K. Ojha, S. Ray, T. Das, S. Middey, P. Mahadevan, Z. Wang, Y. Zhu, X. Liu, M. Kareev, and J. Chakhalian, Phys. Rev. B 99, 235153 (2019).

47. S. Middey, D. Meyers, R. Kumar Patel, X. Liu, M. Kareev, P. Shafer, J.-W. Kim, P. J. Ryan, and J. Chakhalian, Appl. Phys. Lett. 113, 081602 (2018).

48. J. L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Phys. Rev. B 50, 978 (1994).

49. V. Scagnoli, U. Staub, A. M. Mulders, M. Janousch, G. I. Meijer, G. Hammerl, J. M. Tonnerre, and N. Stojic, Phys. Rev. B 73, 100409 (2006).

50. S. Middey, D. Meyers, M. Kareev, Y. Cao, X. Liu, P. Shafer, J. W. Freeland, J.-W. Kim, P. J. Ryan, and J. Chakhalian, Phys. Rev. Lett. 120, 156801 (2018).

51. S. Middey, D. Meyers, M. Kareev, X. Liu, Y. Cao, J. W. Freeland, and J. Chakhalian, Phys. Rev. B 98, 045115 (2018).

52. S. Lafuente, G. Subias, J. García, S. D. Matteo, J. Blasco, V. Cuartero, and C. R. Natoli, J. Phys.: Condens. Matter 23, 325601 (2011).

53. D. H. Douma, R. Cipriani, A. Lamperti, P. Lupo, E. Cianci, D. Sangalli, F. Casoli, L. Nasi, F. Albertini, P. Torelli, and A. Debernardi, Phys. Rev. B 90, 205201 (2014).

54. M. Medarde, A. Fontaine, J. L. García-Muñoz, J. Rodríguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi, and P. Lacorre, Phys. Rev. B 46, 14975 (1992).

55. J. Liu, M. Kareev, B. Gray, J. W. Kim, P. Ryan, B. Dabrowski, J. W. Freeland, and J. Chakhalian, Appl. Phys. Lett. 96, 233110 (2010).

56. M. Wu, E. Benckiser, P. Audenh, E. Goering, P. Wochner, G. Christiani, G. Logvenov, H.-U. Habermeier, and B. Keimer, Phys. Rev. B 91, 195130 (2015).

57. S. Middey, P. Rivero, D. Meyers, M. Kareev, X. Liu, Y. Cao, J. W. Freeland, S. Barraza-Lopez, and J. Chakhalian, Sci. Rep. 4, 6819 (2014).

58. J. W. Freeland, M. van Veenendaal, and J. Chakhalian, “Special issue: Electronic structure and function from state-of-the-art spectroscopy and theory,” J. Electron Spectrosc. Relat. Phenom. 208, 56 (2016).

59. D. Meyers, J. Liu, J. W. Freeland, S. Middey, M. Kareev, J. Kwon, J. M. Zuoz, Y.-D. Chuang, J. W. Kim, P. J. Ryan et al., Sci. Rep. 6, 27934 (2016).

60. K. Post, A. McLeod, M. Hepting, M. Bluschke, Y. Wang, G. Cristiani, G. Logvenov, A. Charnukha, G. Ni, P. Radhakrishnan et al., Nat. Phys. 14, 1056 (2018).

61. H. Upton, Y. Choi, H. Park, J. Liu, D. Meyers, J. Chakhalian, S. Middey, J.-W. Kim, and P. J. Ryan, Phys. Rev. Lett. 115, 036401 (2015).

62. G. N. Daptary, S. Kumar, M. Kareev, J. Chakhalian, A. Bid, and S. Middey, Phys. Rev. B 100, 125105 (2019).

63. J. H. Park, J. M. Coy, T. S. Kastirga, C. Huang, Z. Fei, S. Hunter, and D. H. Cobden, Nature 500, 431 (2013).