Overcoming synthetic metastabilities and revealing metal-to-insulator transition & thermistor bi-functionalities for d-band correlation perovskite nickelates

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Effective synthesis of meta-stable materials challenging the thermodynamic limits will play a significant role in broadening the horizon in material designs and further explorations of their functionalities. Although d-band correlated rare-earth nickelate perovskites (ReNiO$_3$) have achieved promising applications, e.g., metal-to-insulator transition, artificial intelligence, and memory/ logical devices, the thermodynamic instability and high vacuum-dependence in material synthesis have largely caused bottlenecks in these applications. Herein we demonstrate a vacuum-free and low cost chemical route to effectively synthesize single-crystalline ReNiO$_3$ thin films that further promote their device applications. It achieves high flexibility and convenience by adjusting the A-site compositions within the perovskites via single (i.e. Nd, Sm, Eu, and Gd), binary (i.e., $\text{Sm}_x\text{Nd}_{1-x}$, $\text{Sm}_x\text{Eu}_{1-x}$, and $\text{Sm}_x\text{Nd}_{1-x}$), and triple (i.e. $\text{Sm}_x\text{Nd}_{1-x}\text{Eu}_{1-x}$ and $\text{Sm}_x\text{Nd}_{1-x}\text{Gd}_{1-x}$) rare-earth elements. The respective regulations in electronic structures, as probed via X-ray absorption fine structure analysis, result in sharper metal-to-insulator transitions within a broad temperature range of 400 K, compared with their reported performances. Furthermore, we discover an overlooked thermistor transport behavior of ReNiO$_3$ within the binary A-site elements, which exhibits large temperature coefficients of resistance (> 2%) across a broad range of temperatures (5–470 K). By overcoming the bottlenecks in material synthesis of ReNiO$_3$, the present work profoundly paves the way for device fabrication.

Challenging thermodynamic limits and synthesizing materials at their meta-stable states can largely broaden the horizons in designing the next-generation new materials, such as ultra-strong metals, multi-functional oxides, semiconductors with irregular orbital configurations, and ultralight structural materials. One of the most notable meta-stable material families is the perovskite structured rare-earth nickelates (ReNiO$_3$) with d-band electron correlations. It is well known that ReNiO$_3$...
exhibits metal-to-insulator transitions (MITs) that can be triggered by variations in temperature, and this enriches electrical, optical and magnetic functionalities beyond conventional semiconductors.\textsuperscript{7–15} The orbital configurations and electronic band structures of ReNiO\textsubscript{3} are largely determined by the bond angle of Ni–O–Ni within the NiO\textsubscript{6} octahedron.\textsuperscript{10–13} Owing to the coupling between the electronic structure and structures in ReNiO\textsubscript{3}, their metal to insulator transition temperature (T\textsubscript{MIT}) can be effectively regulated within a broad range of temperature from 100 to 600 K continuously, by simply varying the rare-earth composition.\textsuperscript{11–13} This distinguished feature can be potentially applied in thermal or temperature driven devices,\textsuperscript{11–13} competing with vanadium oxides. In addition, ReNiO\textsubscript{3} also exhibits complex electronic phase diagrams that are exceptionally sensitive to other parameters, such as electrostatic polarizations,\textsuperscript{7,9} lattice distortions,\textsuperscript{11} and orbital occupancy.\textsuperscript{8} Utilizing a static electronic field or hydrogenation to regulate the orbital configurations in ReNiO\textsubscript{3} results in other interesting applications, such as memory devices,\textsuperscript{7,8} solid state energy conversion devices,\textsuperscript{16} biological sensing,\textsuperscript{17} and neuron-spin logical devices.\textsuperscript{18} These recent demonstrations promote further explorations of new generation electronic and optoelectronic devices based on the electron correlated perovskite systems.\textsuperscript{7,8,15–19}

Nevertheless, the present ineffectiveness in the thin film growth of ReNiO\textsubscript{3} with a high thermodynamic instability, i.e., Re = Sm, Eu or Gd, remains a vital bottleneck for their further device applications. In contrast to the conventional oxide materials, the crystallization and material growth of ReNiO\textsubscript{3} via the conventional chemical reactions under usual conditions is restricted, owing to their positive formation free energy (ΔG).\textsuperscript{11–14} To date, the thin film growth of ReNiO\textsubscript{3} is heavily dependent on vacuum-based approaches, such as pulsed laser deposition (PLD),\textsuperscript{6,15–18,20,21} magnetic sputtering or magnetic sputtering followed by high pressure annealing\textsuperscript{7,8,14–18,29} and metal-organic chemical vapor deposition (MOCVD).\textsuperscript{19} Performing these vacuum depositions relies on vacuum systems, such as a vacuum chamber and pumps, and this elevates the cost and complexity in the deposition of ReNiO\textsubscript{3}. Therefore, the effectiveness of the thin film growth of ReNiO\textsubscript{3} is expected to be improved if the vacuum deposition can be replaced by a chemical solution based spin coating procedure.

Here we developed a low-cost and vacuum-free approach based on wet-chemical and high-pressure solid-state reaction processes, to effectively grow ReNiO\textsubscript{3} thin films with single crystallinity and extensively adjustable rare-earth compositions, including Nd, Sm, Eu, Gd, Sm\textsubscript{1–x}Nd\textsubscript{x}, Sm\textsubscript{1–y}Eu\textsubscript{y}, Sm\textsubscript{1–x–y}Nd\textsubscript{x}Eu\textsubscript{y} and Sm\textsubscript{1–x}NdGd\textsubscript{x}. Sharp and widely tunable MIT properties were observed within a broad range of temperature from 100–500 K, by regulating the Re compositions and film/substrate interfacial strains. The respective variations in electronic structures of ReNiO\textsubscript{3} were further investigated assisted by near edge X-ray absorption fine structure (NEXAFS) analysis. In addition to their metal to insulator transitions, an additional functionality associated with the thermistor transportation was discovered within the insulating phase of highly metastable ReNiO\textsubscript{3} with a small size of the rare-earth element. The achieved temperature coefficient of resistance (TCR) exceeds 2% across a broad temperature range (5–480 K), shedding light on applying the as-grown ReNiO\textsubscript{3} as a Joule sensor for the detection of temperature and thermal perturbations.

The main challenge that impedes synthesizing the perovskite structured ReNiO\textsubscript{3} (Re ≠ La) via the conventional chemical processes is associated with their positive formation free energies (ΔG).\textsuperscript{11–14} The LaNiO\textsubscript{3} is known to be the only thermodynamically stable one within the family of ReNiO\textsubscript{3}, and further reducing the radius of Re enhances the positive magnitude of ΔG and elevates the metastability.\textsuperscript{14} This is demonstrated in Fig. 1a, where the relative elevation in ΔG compared to that of LaNiO\textsubscript{3} is calculated for ReNiO\textsubscript{3} and plotted as a function of the size of the rare-earth elements. In this work, the element transfer of Re and Ni to the substrate for the thin film growth of ReNiO\textsubscript{3} was achieved by spin coating a chemical solution that contains precursors of Re(NO\textsubscript{3})\textsubscript{3} and Ni(CH\textsubscript{3}COO)\textsubscript{2} dissolved in ethylene glycol monomethyl ether (EGME), as illustrated in Fig. 1b. The rare-earth compositions in the as-grown ReNiO\textsubscript{3} can be easily adjusted by varying the types and combinations of the Re(NO\textsubscript{3})\textsubscript{3} chemical precursor. The crystallization of ReNiO\textsubscript{3} from the chemical precursors is illustrated at the bottom of Fig. 1b. From the thermodynamic perspective, the ΔG is reduced via a heterogeneous nucleation of ReNiO\textsubscript{3} onto the lattice template of the perovskite structured substrate,\textsuperscript{10,13,20,21} combined with the utilization of high oxygen pressures.\textsuperscript{11–14} From the kinetic perspective, elevating the synthetic temperature promotes the migration of the lattice atoms during the thin film growth.

The proposed approach was first applied to the thin film growth of SmNiO\textsubscript{3} on single crystalline perovskite substrates, such as LaAlO\textsubscript{3} (LAO), SrTiO\textsubscript{3} (STO) and (La,Sr)(Al,Ta)O\textsubscript{3} (LSAT), with an orientation of (001). The lattice constants of LAO, STO and LSAT are 3.79 Å, 3.905 Å, and 3.87 Å, respectively, and these numbers are similar to the half magnitude of the phase diagonal of SmNiO\textsubscript{3} (3.807 Å). Therefore, a heterogeneous film growth of SmNiO\textsubscript{3} on these substrates is expected that reduces the formation free energy. The X-ray diffraction (XRD) patterns and reciprocal space mapping (RSM) of the as-grown SmNiO\textsubscript{3} on various substrates are shown in Fig. 1c and d, respectively. In XRD, the diffraction peak associated with the film mainly appears besides the ones for the substrates, indicating a similar cross-plane orientation to that of the as-grown SmNiO\textsubscript{3} with the three perovskite substrates (see XRD patterns at a broader scanning range in Fig. S1, ESI\textsuperscript{1}). The state of interferential strain between the as-grown SmNiO\textsubscript{3} and the perovskite substrates is further indicated by their RSM results as shown in Fig. 1d. For SmNiO\textsubscript{3}/LAO, a similar in-plane reciprocal lattice vector (Q\textsubscript{||}) is observed for the film and the substrate, which indicates that the in-plane lattice of SmNiO\textsubscript{3} is locked by the one of LaAlO\textsubscript{3} and the as-grown thin film is under bi-axially compressive distortion. In contrast, the diffraction patterns associated with the films observed for SmNiO\textsubscript{3}/STO and SmNiO\textsubscript{3}/LSAT are elongated. This indicates that the interferential strain between the film and the substrate is relaxed, in which case no effective tensile distortion is imparted upon the film material. Fig. 1e further shows the cross-section morphology of the SmNiO\textsubscript{3}/LAO.\textsuperscript{10,13,20,21}
interface, which demonstrates a coherent growth of single crystalline SmNiO$_3$ on the surface of the LAO substrate. This differs from the cross-section morphology observed in SmNiO$_3$/STO (see Fig. S2, ESI†), in which case the lattice coherency is largely destroyed owing to strain relaxation.

The MIT behavior of the as-grown SmNiO$_3$ on various substrates was characterized by measuring the resistivity as a function of temperature ($R$–$T$ tendency) via both heating up and cooling down processes as shown in Fig. 1f. It can be seen that all samples exhibit a pronounced transition behavior across the transition temperature ($T_{\text{MIT}}$), while their $R$–$T$ tendency measured via heating up and cooling down overlaps well with each other. Compared to the strain relaxed SmNiO$_3$/LSAT or SmNiO$_3$/STO, the compressively distorted SmNiO$_3$/LAO exhibits a sharper MIT behavior and a lower $T_{\text{MIT}}$, as demonstrated by their temperature dependence of TCR in Fig. 1g. These observations are in agreement with the previous reports that the compressive distortion enhances the relative stability in the metallic phase of ReNiO$_3$.7–15 It is worth noticing that the usage of high oxygen pressure and the lattice template effect are both important to achieve a sharp MIT behavior for the as-grown SmNiO$_3$ (see more discussions in the ESI†).

The above synthetic approach was further extended to the growth of ReNiO$_3$ thin films with more combinations of...
rare-earth compositions, including NdNiO$_3$, EuNiO$_3$, GdNiO$_3$, Sm$_{0.75}$Nd$_{0.25}$NiO$_3$, Sm$_{0.5}$Nd$_{0.5}$NiO$_3$, Sm$_{0.25}$Nd$_{0.75}$NiO$_3$, Sm$_{0.75}$Eu$_{0.25}$NiO$_3$, Sm$_{0.5}$Eu$_{0.25}$Nd$_{0.75}$NiO$_3$, and Sm$_{0.5}$Gd$_{0.25}$Nd$_{0.25}$NiO$_3$, on LAO (001). In this work, this was achieved by simply varying the composition and combination of the as-used Re(NO$_3$)$_3$ precursors within the solution, and therefore effective regulations in their $T_{\text{MIT}}$ within a broad range of temperature were expected. Fig. S3 and S4 (ESI†) show the XRD patterns of the presently grown ReNiO$_3$/LAO with single and binary rare-earth compositions, respectively, while their representative RSM results are demonstrated in Fig. S5 (ESI†). It is worth noting that all the as-grown ReNiO$_3$ films exhibit the same in-plane diffraction vector on the LAO substrate, indicating their coherent epitaxy and quasi-single crystallinity.

As their $R$–$T$ tendencies are shown in Fig. 2a, the presently grown ReNiO$_3$/LaAlO$_3$ samples exhibit MIT behavior with comparable transition sharpness and adjustable $T_{\text{MIT}}$ similar to the previously reported ones observed in the vacuum-grown ReNiO$_3$.7–13

![Fig. 2](image-url)
Simply varying the relative ratio of different Re elements can achieve a continuous adjustment in $T_{\text{MIT}}$ within a broad range of temperature from 100–500 K, which is in agreement with the previous reports on multi-element rare-earth nickelates.\textsuperscript{11,13,30} It is also interesting to note that a pronounced hysteresis in $T_{\text{MIT}}$ was observed for NdNiO$_3$ and Nd$_{0.75}$Sm$_{0.25}$NiO$_3$ when heating up compared to cooling down. In contrast, the $R$–$T$ measured via heating up or cooling down nearly overlap with each other for ReNiO$_3$ with smaller rare-earth elements occupying the A-site of the perovskite structure. In Fig. 2b and c, we further summarize the $T_{\text{MIT}}$ and the variation in resistivity across the transition ($R_{\text{Insul}}/R_{\text{metal}}$), respectively. It clearly demonstrates a reducing tendency in $T_{\text{MIT}}$ when enlarging the average radius of the rare-earth elements, which is in agreement with the previous reports.\textsuperscript{11,13,30} For ReNiO$_3$ with a single elemental rare-earth composition, a more significant variation in the resistivity during MIT was observed for the compositions with larger Re. In addition, the magnitude of $R_{\text{Insul}}/R_{\text{metal}}$ is observed to be smaller when mixing various Re within ReNiO$_3$. The widely tunable metal to insulator transitions as achieved in ReNiO$_3$ cater to further electronic applications, such as temperature switches and suppression of the inrush current.

From the perspective of electron orbital configuration and band structure, reducing the size of Re was known to twist the NiO$_6$ octahedron more and bend the Ni–O–Ni bonds, which splits a wider energy gap within the hybridized O-2p and Ni-3d.\textsuperscript{11–14} As a result, the orbital configurations associated with the insulating states (denoted as Ni$^{3+}$) are strengthened, as compared to the ones for the metallic states (denoted as Ni$^{2+}$), leading to an elevation in the energy associated with the hybridized Ni-3d and O-2p orbital configurations.\textsuperscript{22–25} Therefore, NEXAFS analysis was further performed to investigate the O: K-edge and Ni: L-edge of ReNiO$_3$ with various compositions of Re, and the results are shown in Fig. 2d and e, respectively. Following the previous argument, a larger proportion of the metallic orbital configurations compared to the insulating one is expected for ReNiO$_3$ with a larger size of the rare-earth elements that more straightened the Ni–O–Ni bonds.\textsuperscript{11–14} Comparing the O: K-edge EXAFS spectra of GdNiO$_3$ and SmNiO$_3$ to that of Sm$_{0.5}$Nd$_{0.5}$NiO$_3$ (with an increased rare-earth size) in Fig. 2d, we can clearly see an increased pre-peak (marked as A) in the spectrum for ReNiO$_3$ with a larger Re. In their O: K-edge spectrum, the pre-peak A is largely related to the Ni$^{3+}$ (d$L^5$) configuration, while peaks B and C are associated with the Ni$^{2+}$ (d$L^6$) configuration.\textsuperscript{22,25} The enhanced proportion in the ground state of Ni$^{3+}$ as compared to Ni$^{2+}$ indicates a more strengthened metallic phase as compared to the insulating phase, which is in agreement with the reduction in their $T_{\text{MIT}}$ as shown in Fig. 2a. Further consistency was observed from variations in their Ni: L$_1$ spectrum, which originates from the Ni-2p $\rightarrow$ Ni-3d transition and splits into peaks A and B (see Fig. 2e). The proportion of the $t_{2g}^3e_{g}^2$ (Ni$^{3+}$) orbital configurations compared to the $t_{2g}^3e_{g}^2$ (Ni$^{2+}$) one is known to be indicated from the relative height of peak B split from peak A in the Ni: L$_3$ NEXAFS spectrum.\textsuperscript{23–24} Comparing the Ni: L$_3$-edge NEXAFS spectrum as shown in Fig. 2e, an increasing tendency in peak B is clearly observed when increasing the average radius of Re.

The enhanced effectiveness in growing meta-stable ReNiO$_3$ thin films of single crystallinity further paves the way for exploring their practical applications in emerging electronic devices. Apart from their abrupt orbital transitions near $T_{\text{MIT}}$ as known previously, we highlight the temperature sensitivities in electrical transportations observed in the insulating phase of ReNiO$_3$ owing to gradual orbital transitions covering a broader range of temperatures. In the conventional semiconductors, elevating the temperature results in a thermally intrinsic (or extrinsic) activation of carriers from the valence band (or dopant band) to the conduction band, as illustrated in Fig. 3a. The resultant $R$–$T$ tendency follows $R \propto T^{-3/2} \exp\left(\frac{E_g}{k_B T}\right)$, and the as-achieved magnitude of TCR does not exceed $-2\% \, K^{-1}$, as estimated in Fig. S6 (ESI†) for various magnitudes of the band gap ($E_g$).

In contrast to the conventional semiconductors, the transport properties associated with the orbital configuration and the band structure of ReNiO$_3$ are closely coupled to the structure of the NiO$_6$ octahedron and the Ni–O bond angles.\textsuperscript{11–13} The most typical example is the MIT behavior observed when reducing the temperature across $T_{\text{MIT}}$, in which case an abrupt straightening of the bond angle of Ni–O–Ni occurs that opens a band gap to trigger an electronic transition from the metallic phase to the insulating phase.\textsuperscript{13} This was also comprehended previously as a charge disproportionation of the transition metal (2Ni$^{3+} \rightarrow$ Ni$^{3+}$ + Ni$^{2+}$) accompanied by a Jahn–Teller distortion within the NiO$_6$ octahedron to reduce the Coulomb repulsion energy associated with the hybridized Ni-3d and O-2p orbital configurations.\textsuperscript{31} By elevating the temperature even without reaching $T_{\text{MIT}}$, the system’s Coulomb energy is expected to be accumulated within the insulating phase of ReNiO$_3$ to result in a gradual orbital transition. This is also revealed by the temperature varied Ni–O vibration modes as previously observed in the insulating phase of SmNiO$_3$ via temperature dependent Raman spectroscopy,\textsuperscript{32} showing that the structure of the NiO$_6$ octahedron largely determines the orbital configuration and the band structure. Therefore, a more susceptible band structure to temperature is expected for the insulating phase of ReNiO$_3$ compared to the conventional semiconductors (as illustrated in the right of Fig. 3a), which enlarges the $R$–$T$ tendency and the magnitude of TCR.

The above understandings are supported by the low temperature $R$–$T$ tendencies observed in the representative ReNiO$_3$ with single or binary rare-earth compositions. As shown in Fig. 3b, a continuous reducing tendency in the resistivity is observed for the insulating phases of SmNiO$_3$, EuNiO$_3$ and Nd$_{0.5}$Sm$_{0.5}$NiO$_3$ across a broad range of low, mid-low and room temperatures. In Fig. S7 (ESI†), the presently observed $R$–$T$ tendencies were fitted by $R(T)/R_{\text{metal}} = \exp\left(\frac{E_g}{k_B T}\right)$, which describes the transportations for conventional thermistors with a negative temperature coefficient of resistance (NTCR).
In contrast to the conventional semiconductors, the activation energy ($E_a$) calculated for the present ReNiO$_3$ samples is temperature dependent (see Fig. S7c, ESI†), implying their temperature varied orbital configurations and band gaps. Compared to SmNiO$_3$ or NdNiO$_3$ with a single Re composition, the Nd$_{0.25}$Sm$_{0.75}$NiO$_3$ with a binary Re composition exhibits a larger magnitude of TCR exceeding 2% across a broad range of temperatures from 40 to 340 K, as shown in Fig. 3c. This performance is comparable to the best negative temperature coefficient thermistor at a similar wide range of working temperatures. Near room temperature, the as achieved TCR in Nd$_{0.2}$Sm$_{0.8}$NiO$_3$ further increases up to $\sim$4%, and this performance is comparable to that of VO$_2$ which is presently applied in the non-cooling detection of infrared rays (IR).26–28

The large TCR within a broad range of temperatures achieved in the insulating phase of the ReNiO$_3$ materials indicates their thermistor functionality that can be used to sense the temperature or incident thermal perturbations via their resultant variations in resistivity. This further sheds light on their thermistor applications such as temperature detection and sensing, temperature compensation, and infrared ray detection.26–28 Fig. S8 (ESI†) illustrates one such example associated with the detection of temperature and thermal perturbations via ReNiO$_3$. Similar to their MIT, the range of working temperatures when using the insulating phase of ReNiO$_3$ as a thermistor is widely adjustable via the rare-earth compositions to cater for the practical requirements. For example, enhancing the Nd substitution concentration within Nd$_{0.5}$Sm$_{0.5}$NiO$_3$ can effectively extend the lower limit of the applicable range down to 5 K via EuNiO$_3$.

In summary, we developed a vacuum-free approach combining spin coating and high oxygen pressure solid state reactions to efficiently grow quasi-single crystalline ReNiO$_3$ (Re = Nd, Sm, Eu, Gd, Sm$_{1-x}$Nd$_x$, and Sm$_{1-x}$Eu$_x$Nd$_x$ with a binary Re composition) thin films, overcoming their high thermodynamic metastability. The metal to insulator transition performance achieved in the as-grown ReNiO$_3$ is comparable to the ones reported for the vacuum deposited samples. By simple regulation of the composition and combinations of rare-earth elements, effective regulation of $T_{MIT}$ was achieved within a broad range of temperatures from 100–500 K. Results from NEXAFS further demonstrated the consistency in the variation of orbital configurations associated with the metallic and insulating states when varying the rare-earth compositions. In addition to the already known MIT behavior of ReNiO$_3$ driven by the abrupt orbital transitions across $T_{MIT}$, we also highlight the presence of a gradual orbital transition within their insulating phase over a much broader range of temperatures. This results in a thermistor transportation behavior with a large magnitude and a widely tunable temperature coefficient of the resistance, the performance of which is comparable to the best thermistors at a similar range of working temperatures. By overcoming the bottlenecks in material synthesis, it profoundly paves the way for further applying both the metal to insulator transition and thermistor functionalities of ReNiO$_3$ in electronic devices.

**Author contributions**

JC planned for the present work and analysed the data; HH grew the thin films and characterized their transportation...
property; JC and XK performed structural analysis; HD and BG contributed to the TEM experiment; JW contributed to the EXAFS experiment; and JC wrote the manuscript, assisted by NC, YJ and YT. All authors discussed the results and commented on the manuscript.

Conflicts of interest

We declare no competing financial interest.

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