Synthesis and properties of La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$

Mengwu Huo(霍梦五), Zengjia Liu(刘增家), Hualei Sun(孙华蕾), Lisi Li(李历斯), Hui Liu(刘晖), Chaoxin Huang(黄潮欣), Feixiang Liang(梁飞翔), Bing Shen(沈冰), and Meng Wang(王猛)*

Center for Neutron Science and Technology, Guangdong Provincial Key Laboratory of Magnetoelectric Physics and Devices, School of Physics, Sun Yat-Sen University, Guangzhou 510275, China

(Rceived 29 April 2022; revised manuscript received 8 June 2022; accepted manuscript online 18 June 2022)

Superconductivity has been realized in films of La$_{1-x}$Sr$_x$NiO$_3$. Here we report synthesis and characterization of polycrystalline samples of La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$ (0 ≤ x ≤ 0.2). Magnetization and resistivity measurements reveal that La$_{1-x}$Sr$_x$NiO$_3$ are paramagnetic metal and La$_{1-x}$Sr$_x$NiO$_2$ exhibit an insulating behavior. Superconductivity is not detected in bulk samples of La$_{1-x}$Sr$_x$NiO$_2$. The absence of superconductivity in bulk La$_{1-x}$Sr$_x$NiO$_2$ may be due to the generation of hydroxide during reduction, a small amount of nickel impurity, or incomplete reduction of apical oxygen. The effect of interface in films of La$_{1-x}$Sr$_x$NiO$_2$ may also play a role for superconductivity.

Keywords: nickel oxide, superconductivity

PACS: 74.70.-b, 74.25.fc, 74.62.Dh

DOI: 10.1088/1674-1056/ac7a1a

The discovery of superconductivity in film samples of Nd$_0.8$Sr$_0.2$NiO$_2$ has drawn much attention on nickel oxide materials. [*] In fact, LaNiO$_3$ was studied in 1983 before the discovery of superconductivity in copper oxide materials. La$_{2-x}$Sr$_x$NiO$_3$ were investigated because of the structural similarity to the high temperature superconducting (SC) cuprate perovskites La$_2$-Sr$_x$CuO$_4$. Superconductivity has also been predicted in nickelate heterostructures like LaNiO$_3$/LaMnO$_3$ ([M is a trivalent cation, like Al or Ga] superlattices,[2,3] while unconventional superconductivity has not been realized in nickel oxide materials with the oxidation states of Ni$^{3+}$ and Ni$^{2+}$.[4-6] It was suggested that superconductivity may exist in low spin oxidation state of Ni$^{1+}$ with a square coordination with O$^{2-}$ ions.[7-9] However, the lowest valent state of nickel is difficult to stabilize through conventional high-temperature-solid state reaction synthesis method.[10,11]

Tuning the valent states of Ni ions in nickelate thin film heterostructures by combining CaH$_2$ reductant and carrier doping greatly stimulated scientists to explore superconductivity and other novel properties in nickel-based oxides.[11,12-21] Infinite layer RNiO$_2$ (R = Nd, La, and Pr) is isomorphous to La$_2$CuO$_4$ with two-dimensional NiO$_2$ planes stacking as NiO$_2$-R-NiO$_2$-R layers as shown in Fig. 1. La$_2$CuO$_4$ is one of the parent compounds of high-temperature superconductors. Through hole-doping the antiferromagnetic (AF) order can be suppressed and superconductivity emerges in (Ca$_{1-x}$Sr$_x$)$_1$-CuO$_{2-δ}$ with the maximum SC transition temperature of $T_c = 110$ K.[22,23] Furthermore, the spin configuration of Ni$^{3+}$ 3d$^9$ is similar to that of Cu$^{2+}$ in cuprates. SC domes were observed in films of R$_{1-x}$Sr$_x$NiO$_2$ (R = La, Nd, and Pr)[13-15,24] La$_{1-x}$Ca$_x$NiO$_2$[25] and Nd$_{1-x}$Ni$_x$O$_2$[17] AF spin fluctuations were revealed and unconventional mechanism of superconductivity was proposed.[16,26-28] While the superconductivity observed in nickel-based oxides is all in the form of thin film samples,[1,13-15,17,24,29-32] it is worthwhile to explore superconductivity in bulk samples. Recently bulk samples $R_{1-x}$Sr$_x$NiO$_2$ (R = Sm, Nd)[33-35] and La$_{1-x}$Ca$_x$NiO$_3$[36] were synthesized whereas superconductivity was not detected. So far, electrical and magnetic properties of Sr doped bulk samples of La$_{1-x}$Sr$_x$NiO$_3$ have not been reported, where superconductivity has been observed in film samples.

In this paper, we report synthesis and systematic studies of the bulk samples of La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$ with normal compositions of 0 ≤ x ≤ 0.4. The actual doping level is around 0 ≤ x ≤ 0.2 determined from inductively coupled plasma measurements. La$_{1-x}$Sr$_x$NiO$_3$ are synthesized using molten KOH as flux. La$_{1-x}$Sr$_x$NiO$_2$ are obtained via a topochemical reduction process from La$_{1-x}$Sr$_x$NiO$_3$ using CaH$_2$ as a reducing agent. Measurements of resistivity, magnetization, and heat capacity are carried out to explore the magnetic and electrical properties. Results of electronic transport show that La$_{1-x}$Sr$_x$NiO$_3$ (0 ≤ x ≤ 0.2) are good metals, while La$_{1-x}$Sr$_x$NiO$_2$ exhibit insulating behavior and no superconductivity is observed.

La$_{1-x}$Sr$_x$NiO$_3$ with nominal 0 ≤ x ≤ 0.4 were synthesized using KOH as the flux.[37] La$_2$O$_3$ was preheated at 1100 °C for one day to remove water then weighed in a glove box filled with argon. Stoichiometric ratios of powders of NiO (99.99%), La$_2$O$_3$ (99.9%), and SrCO$_3$ (99.99%) were mixed and heated at 1200 °C for one day. The flux of KOH was heated at 450 °C for 12 h to form O$_2$ via the reaction of $3O_2 + 4OH^- ⇄ 4O_2^− + 2H_2O$ [38] followed by the mixture of the nickelate oxide powders and dwelled at 450 °C for 10 h. KOH was removed from powders of La$_{1-x}$Sr$_x$NiO$_3$ by deion-
izing water. Thereafter the powders were dried at 120 °C. Finally, dark powders of La$_{1-x}$Sr$_x$NiO$_3$ were obtained. The topotactic reduction process was demonstrated in Fig. 1. The process was as follows: La$_{1-x}$Sr$_x$NiO$_3$ were placed in a crucible and CaH$_2$ was wrapped with an aluminum foil. They were sealed in an evacuated silica tube at a molar ratio of 1:4. La$_{1-x}$Sr$_x$NiO$_2$ were obtained after heating the mixture at 350 °C for 12 h.

Crystal structures of the samples were investigated by x-ray diffraction (XRD, Empyrean) at 300 K. The diffraction data were refined by the Rietveld method.[39] The cation contents in powder samples of La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$ were measured by the inductively coupled plasma (ICP, Atomic Emission Spectrometry, Optima8300). An isotometric titration method was performed to evaluate the content of oxygen in La$_{1-x}$Sr$_x$NiO$_3$.[40] The powder samples were dissolved in HCl with KI (0.1 mol/L) solution. The Ni$^{3+}$ ions will be reduced to Ni$^{2+}$ and iodine is generated during the process. The content of iodine could be determined by Na$_2$S$_2$O$_3$ (0.01 mol/L) using starch solution as an indicator. Magnetization and resistivity in the temperature range of 3–300 K and heat capacity measurements in the range of 3–200 K were conducted on a physical property measurement system (PPMS, Quantum Design). The electrical resistivity was measured on a pressed bar sample using a standard 4-probe technique.

The crystal structures of La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$ are shown in Fig. 1. XRD patterns of the two compounds are depicted in Figs. 2(a) and 2(b), respectively. The XRD patterns of LaNiO$_3$ can be indexed as a rhombohedral unit cell and LaNiO$_2$ as a tetragonal unit cell as reported previously.[41–44] The XRD patterns for Sr doped compounds indicate that the powder samples are a single phase for La$_{1-x}$Sr$_x$NiO$_3$ with 0 ≤ x ≤ 0.15 and La$_{1-x}$Sr$_x$NiO$_2$ with 0.05 ≤ x ≤ 0.4. To simplify the description, the nominal x is used to present samples with distinct compositions in the article. NiO is identified in La$_{1-x}$Sr$_x$NiO$_3$ for x = 0.2, 0.3, and 0.4. Reflection peaks associated with La$_2$O$_3$ can be observed in the XRD pattern of LaNiO$_2$, as shown in Fig. 2. Ni impurity can be observed in La$_{1-x}$Sr$_x$NiO$_2$ with x = 0.3. Variation of the lattice parameters as a function of the Sr contents is not obvious because the sizes of La$^{3+}$ and Sr$^{2+}$ are similar.[35,45]

The refined structural parameters are shown in Table 1.

![Fig. 1. Structures of La$_{1-x}$Sr$_x$NiO$_3$ (left) and La$_{1-x}$Sr$_x$NiO$_2$ (right). Upon low temperature reduction with CaH$_2$ as a reducing agent, the powder samples undergo a topotactic transition from the perovskite phase to the infinite-layer phase.](image)

![Fig. 2. Ambient powder XRD patterns of (a) La$_{1-x}$Sr$_x$NiO$_3$ and (b) La$_{1-x}$Sr$_x$NiO$_2$ with nominal compositions of 0 ≤ x ≤ 0.4 with corresponding Rietveld fitting results by using the R-3c space group and P4/mmm, respectively. The black dots represent the observed data, the red lines represent the fitting curves, and the blue lines illustrate the differences between the data and fitting. The olive short vertical lines mark the Bragg positions. For comparison the data are shifted vertically. The positions of reflections related to NO$_3$, La$_2$O$_3$, and Ni are indicated.](image)

| Compound | LaNiO$_3$ | LaNiO$_2$ |
|----------|-----------|-----------|
| Space group | R-3c | P4/mmm |
| Unit-cell parameters | a = 5.4443(1) Å, c = 13.1569(3) Å | a = 3.9559(2) Å, c = 3.3901(2) Å |
| Atomic parameters | Ni (0, 0, 0) | La (0, 0, 0.25) |
| Rietveld R-factors | Rp: 0.19, Rp: 0.23 | Rp: 0.14, Rp: 0.16 |
| Rp: 0.06 | Rp: 0.10 |
| Goodness-of-fit on F$^2$ | 5.92 | 2.55 |

To check the real compositions of the as grown and oxygen removed compounds, we show the actual x verse the nominal x in Fig. 3(a). The relations of the actual and nominal contents of Sr follow the same trend, revealing half of the Sr is successfully doped to the samples. For the nominal x = 0.4 compounds, the actual values are x = 0.21 and 0.19 for La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$, respectively. The big error of the actual x in La$_{0.85}$Sr$_{0.15}$NiO$_3$ may be due to inhomogeneity of the two samples we measured. The contents of
oxygen are further investigated through the iodometric titration method. In this way, the oxygen content is determined from the ratio of Ni$^{3+}$ and Ni$^{2+}$. The results as shown in Fig. 3(b) suggest the existence of 12% oxygen vacancies.

![Fig. 3](image_url)

**Fig. 3.** (a) ICP determined actual $x$ in La$_{1-x}$Sr$_x$NiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$. (b) Actual oxygen content of La$_{1-x}$Sr$_x$NiO$_3$ measured via the iodometric titration method. The error bars are the standard deviation of the measured results.

Figure 4 displays the temperature dependence of the physical properties of La$_{1-x}$Sr$_x$NiO$_3$. The resistivity and magnetization of LaNiO$_3$ are consistent with previous reports that reveal LaNiO$_3$ exhibiting a metallic paramagnetic state with large electronic correlations,[46,47] as shown in Figs. 4(a) and 4(b). The upturn in resistivity below 50 K has been observed in bulk LaNiO$_{3-\delta}$ and suggested to result from defect of oxygen during the synthesis process.[48,49] Upon Sr doping, the metallic behavior of La$_{1-x}$Sr$_x$NiO$_3$ is retained, while the magnitude of resistivity changes.

Weak kinks can be identified on magnetization at $\sim$ 22 K in doped compounds. The kink is obvious for La$_{0.8}$Sr$_{0.2}$NiO$_3$ measured with $\mu_0H = 0.1$ T and zero-field cooled (ZFC) mode as shown in Fig. 4(b). The temperatures of the kinks for different compounds locate at the same temperature. To ascertain the origin of the kinks, we carried out measurements of magnetization and specific heat as a function of temperature at various magnetic fields for La$_{0.8}$Sr$_{0.2}$NiO$_3$. The magnetization is gradually suppressed as the magnetic field increases, while the temperature of the anomaly is barely changed [Fig. 4(c)]. We repeated the process of synthesis and measurements. The kinks in magnetization for the doped samples are repeatable. However, an anomaly around 22 K is not observed on specific heat at 0 T and 5 T magnetic fields as shown in Fig. 4(d). The kinks are absent in Nd$_{1-x}$Sr$_x$NiO$_3$[50] and Sm$_{1-x}$Sr$_x$NiO$_3$.[33] It is possible that the abnormal magnetization in La$_{1-x}$Sr$_x$NiO$_3$ at 22 K origins from impurities during the synthesis process.

![Fig. 4](image_url)

**Fig. 4.** (a) Resistivity versus temperature $\rho(T)$ plots of La$_{1-x}$Sr$_x$NiO$_3$ with nominal compositions of $0 \leq x \leq 0.4$. (b) Magnetic susceptibility of La$_{1-x}$Sr$_x$NiO$_3$ with a field of $\mu_0H = 0.1$ T. (c) Magnetization for La$_{0.8}$Sr$_{0.2}$NiO$_3$ in ZFC process for magnetic fields of $\mu_0H = 0$ T, 1 T, and 5 T. (d) Specific heat of La$_{0.8}$Sr$_{0.2}$NiO$_3$ for $3 \leq T \leq 30$ K, and $\mu_0H = 0$ T and 5 T.

To explore the possible superconductivity in the bulk samples of La$_{1-x}$Sr$_x$NiO$_2$, we performed resistivity and magnetization measurements of La$_{1-x}$Sr$_x$NiO$_2$ as shown in Fig. 5. The resistivity versus temperature $\rho(T)$ of La$_{1-x}$Sr$_x$NiO$_2$ in zero applied magnetic field in Fig. 4(a) reveals semiconducting-like behavior. The doped Sr does not affect the electronic properties severally. No superconductivity is observed in the bulk samples. In Fig. 5(b), we
show the fittings by using the activation-energy model $\rho(T) = \rho_0 \exp(E/k_BT)$ through fitting the high temperature resistivity data from 200 K to 300 K, where $\rho_0$ is a prefactor and $k_B$ is the Boltzmann constant. The resultant thermal activation energies are between 35–55 meV, as shown in the inset of Fig. 5(b). (c) To explore the magnetic properties of La$_{1-x}$Sr$_x$NiO$_2$, we show magnetization and magnetoresistance as functions of magnetic field and temperature in Figs. 5(c) and 5(d). The magnetization measured in field cooling (FC) deviates from that of ZFC in a wide temperature range, indicating a spin glass state. Figure 5(d) displays temperature dependence of the magnetoresistance (MR) of LaNiO$_2$. The MR effect changes sign from negative at 3 K, 10 K, and 20 K to positive at 30 K and 50 K, similar to the observation in films of Nd$_{0.8}$Sr$_{0.2}$NiO$_2$. [34] The sign reversal of the MR upon changing temperature suggests the existence of magnetic order or magnetic correlations. Figure 5(e) shows a typical hysteresis of ferromagnetism (FM) vs. magnetic field at various temperatures measured at $T = 3$ K, 50 K, 300 K, and 650 K. The FM is reminiscent of the resident nickel in Sr doped RNiO$_2$. Therefore, magnetic susceptibility is measured from 300 K to 1000 K to verify the existence of Ni. As shown in Fig. 5(f), the ferromagnetic transition of Ni at $T_\text{c} = 627$ K is identified in bulk LaNiO$_2$. However, XRD measurements on powder samples of LaNiO$_2$ did not reveal the existence of Ni, indicating a low content of Ni impurity in the samples. Thus, the spin-glass like behavior may be due to the Ni impurity. Small amount of Ni in the sample would not change the electronic transport properties. The MR effect should be the intrinsic properties of LaNiO$_2$ and induced by magnetic correlations that have been proposed by Raman scattering measurements on NdNiO$_2$ [55] and x-ray magnetic linear dichroism measurements on Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ films. [27]

As theoretical calculations, RNiO$_2$ are metal. However, resistivity measurements reveal that bulk samples of RNiO$_2$ are semiconductors. It has been suggested that the difference between theoretical predictions and experimental observations could be ascribed to hydrogens that take place the apical oxygen sites to reduce the thermodynamical instability. Small size of hydrogen can insert into the samples and form oxide hydride La$_{1-x}$Sr$_x$NiO$_2$H$_x$ which exhibit insulating behavior. This has been observed in NdNiO$_2$H$_x$ ($x \sim 2.3$, $y \sim 0.7$), BaTiO$_3$H$_x$, Sr$_2$CoO$_{4.33}$H$_{0.84}$, and LaSrCoO$_{4.97}$H$_{0.7}$, in addition, impurity and incomplete reduction of the apical oxygens in RNiO$_2$ could also result in large resistivity. It is known that the purity of films is essential for realizing superconductivity in Nd$_{1-x}$Sr$_x$NiO$_2$ films. The absence of superconductivity in bulk samples may be due to the deviation of O$^2-$ ions amount and the existence of Ni impurity. The interfaces between the substrate of SrTiO$_3$ and La$_{1-x}$Sr$_x$NiO$_2$ films may play a role in the magnetic correlations and emergence of superconductivity. Further studies on high quality single crystals of La$_{1-x}$Sr$_x$NiO$_2$ are required.

In conclusion, we synthesized polycrystalline samples La$_{1-x}$Sr$_x$NiO$_2$ and La$_{1-x}$Sr$_x$NiO$_2$ with an actual doping level of $0 \leq x \leq 0.2$ and characterized their properties. The samples of La$_{1-x}$Sr$_x$NiO$_2$ are prepared using KOH as the flux. La$_{1-x}$Sr$_x$NiO$_2$ are synthesized by removing the apical oxygens in Sr content ($x$).

Fig. 5. (a) Resistivity of La$_{1-x}$Sr$_x$NiO$_2$ as a function of temperature from 3 K to 300 K and (b) fits using the activation-energy model $\rho(T) = \rho_0 \exp(E/k_BT)$ from 200 K to 300 K. The inset shows the thermal activation energies against the Sr content. (c) Magnetic susceptibility measured under ZFC and FC conditions for 3 K $\leq T \leq 400$ K and $\mu_0 H = 0.1$ T. (d) Magnetoresistance for LaNiO$_2$ at $T = 3$ K, 10 K, 20 K, 30 K, and 50 K. (e) Magnetization of LaNiO$_2$ at $T = 3$ K, 50 K, 300 K, and 650 K. (f) Magnetic susceptibility of LaNiO$_2$ from 300 K to 1000 K with $\mu_0 H = 0.1$ T.
cal oxygen from La$_{1-x}$Sr$_x$NiO$_3$ using CaH$_2$ as a reducing agent. La$_{1-x}$Sr$_x$NiO$_3$ are good metals as expectation. While La$_{1-x}$Sr$_x$NiO$_2$ exhibit insulating behavior, differing from theoretical calculations. No evidence of superconductivity is observed. The Ni impurity, resident apical oxygens, inserted hydrogens in bulk La$_{1-x}$Sr$_x$NiO$_2$ may mask the fundamental magnetic properties and inhibit the achievement of superconductivity.

Acknowledgements

Work at Sun Yat-Sen University was supported by the National Natural Science Foundation of China (Grant Nos. 12174454, 11904414, 11904416, and U2130101), the Guangdong Basic and Applied Basic Research Foundation (Grant No. 2021B1515120015), the Guangzhou Basic and Applied Basic Research Foundation (Grant No. 202201011123), and the National Key Research and Development Program of China (Grant No. 2019YFA0705702).

References

[1] Li D, Lee K, Wang B Y, et al. 2019 Nature 572 624
[2] Chaloupka J and Khalailullin G 2008 Phys. Rev. Lett. 100 016404
[3] Hansmann P, Yang X, Toschi A, et al. 2009 Phys. Rev. Lett. 103 016401
[4] Zhou G, Jiang F, Zhang J, et al. 2018 ACS Appl. Mater. 10 1463
[5] Klimczuk T, McQueen T M, Williams A J, et al. 2020 Nanotechnology 31 341702
[6] Liu H, Hu X, Guo H, et al. 2022 arXiv:2205.00116
[7] Anisimov V I, Bukhvalov D and Rice T M 1999 Phys. Rev. B 59 7901
[8] Botana A S, Pardo V and Norman M R 2017 Phys. Rev. Mater. 1 021801
[9] Zhang J, Botana A S, Freeland J W, et al. 2017 Nat. Phys. 13 864
[10] Li Q, He C, Zhu X, et al. 2020 Sci. Chin. Phys. Mech. Astron. 63 227411
[11] Liu Z, Sun H, Mao M, et al. 2022 arXiv:2205.00950
[12] Gu Y, Zhu S, Wang X, et al. 2020 Commun. Phys. 3 84
[13] Osada M, Wang B Y, Goodge B H, et al. 2020 Nano Lett. 20 5735
[14] Osada M, Wang B Y, Lee K, et al. 2020 Phys. Rev. Mater. 4 121801
[15] Zeng S, Tang C S, Yin X, et al. 2020 Phys. Rev. Lett. 125 147003
[16] Lu H, Rossi M, Nag A, et al. 2021 Science 373 213
[17] Pan G A, Ferenc Segedin G, LaBollita H, et al. 2022 Nat. Mater. 21 160
[18] Gao J, Peng S, Wang Z, et al. 2021 Natl. Sci. Rev. 8 nwwa218
[19] Hao J, Fan X, Li Q, et al. 2021 Phys. Rev. B 103 205120
[20] Gu Q, Li Y, Wan S, et al. 2020 Nano Lett. 20 6027
[21] Gu Q and Wen H H 2022 Innovation (N Y) 3 160202
[22] Azuma M, Hiroi Z, Takano M, et al. 1992 Nature 356 775
[23] Hiroi Z, Azuma M, Takano M, et al. 1993 Physica C 208 286
[24] Osada M, Wang B Y, Goodge B H, et al. 2022 Adv. Mater. 33 2104083
[25] Zeng S, Li C, Chow L E, et al. 2022 Sci. Adv. 8 eabl9927
[26] Cui Y, Li C, Li Q, et al. 2021 Chin. Phys. Lett. 38 067401
[27] Zhou Z, Zhang X, Yi J, et al. 2022 Adv. Mater. 34 2106117
[28] Zhou T, Gao Y and Wang Z 2020 Sci. Chin. Phys. Mech. Astron. 63 287412
[29] Gao Q, Zhao Y, Zhou X J, et al. 2021 Chin. Phys. Lett. 38 077401
[30] Lee K, Goodge B H, Li D, et al. 2020 APL Mater. 8 041107
[31] Xiang Y, Li Y, Li Y, et al. 2021 Chin. Phys. Lett. 38 047401
[32] Ding X, Shen W, Leng H, et al. 2022 Sci. Chin. Phys. Mech. Astron. 65 267411
[33] He C, Ming X, Li Q, et al. 2021 J. Phys. Condens Matter 33 265701
[34] Li Q, He C, Si J, et al. 2020 Commun. Mater. 1 16
[35] Wang B X, Zheng H, Krivyanke E, et al. 2020 Phys. Rev. Mater. 4 084409
[36] Puphal P, Wu Y M, Fursich K, et al. 2021 Sci. Adv. 7 eabl8091
[37] Shvyakumara C, Hegde M S, Prakash A S, et al. 2003 Solid State Sci. 5 351
[38] Mugavero S J, Gemmill W R, Roof I P, et al. 2009 J. Solid State Chem. 182 1950
[39] Rietveld H M 1969 J. Appl. Crystallogr. 2 65
[40] Lenci F, Turliti G and Ferro P 1997 J. Magn. Magn. Mater. 170 240
[41] Kawai M, Inoue S, Mizumaki M, et al. 2009 Appl. Phys. Lett. 94 082102
[42] Geisler B and Pentcheva R 2021 Phys. Rev. Research 3 013261
[43] Hayward M A, Green M A, Rosseinsky M J, et al. 1999 J. Am. Chem. Soc. 121 8843
[44] Rodríguez E, Álvarez I, López M L, et al. 1999 J. Solid State Chem. 148 479
[45] Alonso J A, Martínez-Lope M J and Hidalgo M A 1995 J. Solid State Chem. 116 146
[46] Guo H, Li Z W, Zhao L, et al. 2018 Nat. Commun. 9 43
[47] Zhou J S, Marshall L G and Goodenough J B 2014 Phys. Rev. B 89 245138
[48] Gayathri N, Raychaudhuri K, Xu X Q, et al. 1998 J. Phys. Condens. Matter 11 2901
[49] Rajeef A T A K P 1999 J. Phys. Condens. Matter 11 3291
[50] Yang H, Wen Z, Zhu J, et al. 2021 Solid State Commun. 336 114420
[51] Yin J, Wu C, Li L, et al. 2020 Phys. Rev. Mater. 4 013405
[52] Sun H, Chen C, Hou Y, et al. 2021 Sci. Chin. Phys. Mech. Astron. 64 118211
[53] Li L, Hu X, Liu Z, et al. 2021 Sci. Chin. Phys. Mech. Astron. 64 287412
[54] Crespin M, Isnard O, Dubois F, et al. 2005 J. Solid State Chem. 178 1326
[55] Fu Y, Wang L, Cheng H, et al. 2020 arXiv:1911.03177
[56] Liu Z, Z, Ren, W, Zhu, et al. 2020 npj Quantum Mater. 5 31
[57] Islam M, Koley S and Basu S 2021 Eur. Phys. J. B 94 187
[58] Krishna J, LaBollita H, Fumeaga A O, et al. 2020 Phys. Rev. B 102 224506
[59] Sl I, Xiao W, Kaufmann J, et al. 2020 Phys. Rev. Lett. 124 166402
[60] Onozuka T, Chikamatsu A, Katayama T, et al. 2016 Dalton Trans. 45 12114
[61] Kobayashi Y, Hernandez O J, Sakaguchi T, et al. 2012 Nat. Mater. 11 307
[62] Helps R M, Rees N H and Hayward M A 2010 Inorg. Chem. 49 11062
[63] Hayward M A, Cussen E J, Claridge B J, et al. 2002 Science 295 1882
[64] Zhou X R, Feng Z X, Qin P X, et al. 2020 Rare Metals 39 368
[65] Bernardino F and Cano A 2020 J. Phys. Matter 3 03
[66] He R, Jiang P, Lu Y, et al. 2020 Phys. Rev. B 102 035118
[67] Ortiz R A, Menke H, Misják F, et al. 2021 Phys. Rev. B 104 165137