Optics Letters

Study of spinel $LiTi_2O_4$ superconductors via near-infrared reflection experiments

YANMIN ZHANG,[1] WEN XU,[2,3] LAN DING,[3] XIA CHEN,[1] JIE ZHANG,[3] CHANGNENG LIANG,[3] HONGYING MEI,[2] YANLI JIA,[4] KUI JIN,[4] CHEN GUAN,[1] TIANDI CHEN,[1] AND SASA ZHANG[1,*]

[1]*School of Information Science and Engineering, Shandong University, Jinan 250100, China*
[2]*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China*
[3]*Yunnan Key Laboratory for Micro/Nano Materials & Technology, Yunnan University, Kunming 650091, China*
[4]*National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
**Corresponding author: sasazhang@sdu.edu.cn*

Received 26 January 2017; revised 12 March 2017; accepted 14 March 2017; posted 16 March 2017 (Doc. ID 285505); published 10 April 2017

We present an optical study on high-quality and single-phase $LiTi_2O_4$ (LTO) superconductor thin films grown on $MgAl_2O_4$ substrates by pulsed laser deposition. The near infrared (NIR) reflectivity is measured for samples with (001) and (111) lattice orientations. The temperature-induced metal-superconductor transition can be observed, and the superconducting transition temperature can be measured for both samples. We find that the NIR reflection experiment can reflect rightly the basic features of LTO superconductor thin films. Furthermore, the results obtained from this simple optical measurement suggest that the photo-induced electronic localization effect can be present in LTO thin films in a metallic state. Such information cannot be obtained directly from conventional transport and magneto-transport measurements. These interesting and important findings demonstrate that the NIR reflection experiment is a powerful optical technique for contactless characterizations and investigations of superconductor materials.

OCIS codes: (120.1880) Detection; (120.5700) Reflection; (310.6860) Thin films, optical properties; (070.4790) Spectrum analysis.

https://doi.org/10.1364/OL.42.001552

It is known that the cubic spinel oxide $LiTi_2O_4$ (LTO) is an interesting superconductor that was discovered by Johnston *et al.* in 1973 [1]. Since then, the considerable experimental and theoretical studies on lithium titanate superconductors have been carried out, and most of the important features of this kind of superconductors have been obtained and discussed [2–5]. Most importantly, it was found that the superconducting transition temperature T_c for LTO thin films is at about 10–12 K, obtained from electrical and magneto transport measurements. Very recently, the anisotropic features of the electronic properties have been examined in understanding the nature of LTO superconductivity [5]. Several bosonic modes have been observed in the (111) and (110) oriented films, but not in (001) oriented films. Moreover, LTO is a metallic material above T_c up to room temperature [3].

For the time being, LTO has been widely studied experimentally via techniques such as the specific heat [2], electrical transport [3], magneto-transport [4], and tunneling spectrum [5]. We notice that less optical study on this interesting superconductor material has been conducted. In 2012, the lithium titanate thin films prepared by a solgel method were studied optically through transmission measurement in UV to visible bandwidth at room temperature [6]. It was found that the characteristic light absorption edge at about a 300 nm wavelength shifts toward a longer wavelength with increasing annealing time for the samples [6], and a transparent superconductor can be achieved in the short wavelength regime. In recent years, it has become possible to prepare high-quality and large-area LTO thin films using pulsed laser deposition (PLD) [7]. Thus, we are able to measure the optical properties of LTO thin films through conventional optical experiments [8,9]. Motivated by our recent achievement in preparing large-size single-crystal LTO thin films with different lattice orientations, in this Letter, we intend to examine the optical properties of LTO superconductors in order to gain an in-depth understanding of superconductivity in LTO thin films and to provide a convenient experimental method for the investigation and characterization of superconductor thin films.

In this Letter, the (001) and (111)-oriented LTO thin films were grown epitaxially on (001) and (111)-oriented $MgAl_2O_4$ (MAO) substrates by PLD in an ultrahigh-vacuum chamber. The size of the MAO substrate is $3 \times 10 \times 0.5\ \mathrm{mm}^3$, and the thickness of LTO epitaxial thin film is 200 nm. The LTO thin film covers the whole xy-plane of the MAO substrate. It has been found that the LTO thin films with (001) and (111) lattice orientations can lead to the anisotropic features of the physical properties such as transport resistances [10] and electronic tunneling spectra [5] due to the corresponding features of anisotropic electron-phonon coupling in the system. Nevertheless, the LTO thin films with different lattice orientations show almost the same superconducting transition temperature $T_c \sim 11 \pm 0.25$ K with a narrow transition width

($\Delta T_c < 0.5$ K), obtained from the Physical Property Measurement System (PPMS, Quantum Design, U.S.). Furthermore, T_c depends very little on the variation of the lattice constant. The X-ray diffraction (XRD) results indicate that the LTO thin films with both (001) and (111) lattice orientations are in a single crystal phase and that the spinel phase reflections are well matched to the spinel single phase of the MAO substrates. Hence, the LTO thin film samples used in this Letter have good lattice orientations and high single crystal quality. The details of the preparation and characterization of LTO thin films have been documented elsewhere [11].

It is known [1] that when LTO thin film is in the metallic phase, the typical electron density is about 3×10^{22} cm^{-3}, and the effective electron mass is 8.11 m_0 with m_0 being the rest electron mass [4]. The resistances measured by the PPMS for our samples are about 71 μΩ cm at 11 K and 500 μΩ cm at 300 K, respectively. Thus, the electronic relaxation time for LTO thin film in metallic phase is of the order of τ ~13.6 fs and τ ~1.9 fs at corresponding temperatures. Because the response of electrons in an electronic system to the external radiation field can be observed markedly when the condition $\omega\tau \sim 1$ is satisfied, with ω being the radiation frequency, the near infrared (NIR) experiment can be applied to measure the optical properties of LTO thin films on top of MAO substrates. It should be noted that the thickness of the MAO substrate is about 0.5 mm, which is much larger than the NIR wavelength. Thus, the strong absorption of the incident NIR light by the substrate can occur. Therefore, the NIR reflection experiment is a good option for studying the optical properties of the LTO thin films on dielectric substrates. Furthermore, because the thickness of the LTO thin film is about 200 nm, which is far away from the NIR light wavelength, the reflection pattern induced by thin-film interference effect can be avoid in the measurements.

In this Letter, the optical reflection (OR) spectrum measurements are carried out in the NIR bandwidths (1.2–1.9 μm in wavelength). The standard deuterium lamp is employed as a broadband NIR incident light source. In the experiments, the incident and emergent light beams are setting at 45° angle to the sample surface as shown in Fig. 1. In this configuration, the incident light field can couple with the electrons in the LTO thin films and, thus, the OR spectrum can carry the information about how electrons in the sample respond to the applied radiation field. The OR spectrum is recorded using an imaging spectrometer (iHR320 HORIBA Jobin Yvon, U.S.) and the InGaAs photodetector is used for the detection of the NIR light beams in a 1.2–1.9 μm wavelength regime. In the experiments, the results for NIR reflection spectra of gold mirror are applied as reference. We measure the reflection spectra for LTO thin films with (001)-orientation [(111)-orientation] from 5 to 150 K (200 K) and for the gold mirror at 300 K, where the variation of temperature is achieved in a liquid-helium cooling system (Oxford, UK).

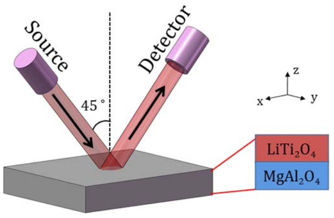

Fig. 1. Schematic diagram of the NIR reflection measurement for LTO thin films.

By definition, the optical reflectivity of a sample is the ratio of the measured light reflection intensities of the sample (LTO thin films) and the reference (gold mirror). The NIR reflectivity spectra for (001)- and (111)-oriented LTO thin film samples are shown in Fig. 2 for different temperatures. As we can see from Fig. 2, within a 1.2–1.9 μm wavelength regime, the intensity of NIR reflection increases monotonically with temperature for the LTO thin films with both (001) and (111) lattice orientations from 7 to 150 K (160 K). We note that in Fig. 2 the curves at 20 and 11 K are almost coincide for (111) LTO thin film. The small peak at about 1563 nm is one of the characteristic lines of the deuterium lamp.

In Fig. 3, we plot the reflectivity as a function of temperature for different radiation wavelengths for LTO thin films with (001) orientation (left) and (111) orientation (right). We notice the following features. (1) The NIR reflectivity for both (001)- and (111)-orientated LTO samples increases almost monotonically with temperature. (2) A sudden drop of the NIR reflectivities for (001)- and (111)-orientated LTO samples can be observed at about 9 K and 11 K, respectively. The insets in Fig. 3 show the $T_{(\mathrm{onset})} = 9$ K (left) and $T_{(\mathrm{onset})} = 11$ K (right) at the fixed radiation wavelength $\lambda = 1.4$ μm, respectively. This implies that a metal-superconductor transition (MST) occurs at corresponding temperatures for different LTO samples. (3) The NIR reflectivity for both (001)- and (111)-orientated samples increases with radiation

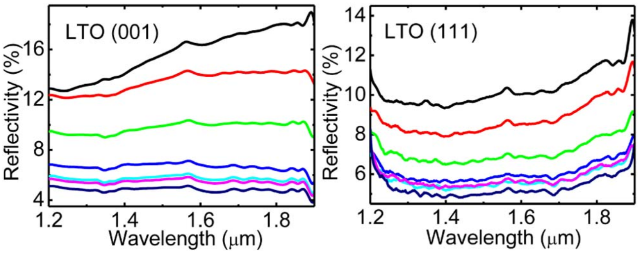

Fig. 2. Spectrum of NIR reflectivity for LTO thin films on MAO substrates at different temperatures. The results are shown for a LTO thin film with (001) orientation (left) at 150, 110, 70, 30, 15, 11, and 7 K, from top to bottom, and with (111) orientation (right) at 160, 120, 80, 40, 20, 11, and 7 K, from top to bottom.

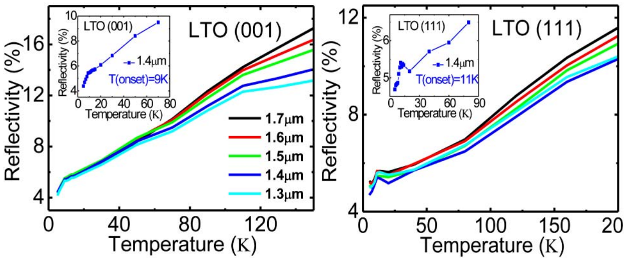

Fig. 3. Reflectivity for (001)-oriented (left) and (111)-oriented (right) LTO thin films as a function of temperature for different radiation wavelengths as indicated. The insets show the results measured around the superconducting transition temperature at a fixed radiation wavelength $\lambda = 1.4$ μm.

wavelength. This effect is more pronounced at relatively high temperatures. (4) The value of the reflectivity in the NIR bandwidth is rather small, less than 20% in the measured wavelength regime.

When an optoelectronic system is subjected to a radiation field, the optical absorption, reflection, and transmission occur simultaneously. The absorptivity A, the reflectivity R, and the transmittance T should satisfy $A + R + T = 1$, required by the energy conservation law. In principle, the optical absorptance (transmittance) is proportional (inversely proportional) to the optical conductivity. When the thickness of a thin film sample is much smaller than radiation wavelength, after ignoring the amplitude attenuation of the light passed, the magnitude of the reflection loss (or optical absorption) is proportional the real part of the complex optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ via

$$A(\omega) \approx \sigma_1(\omega) d/\epsilon_0 cn. \tag{1}$$

Here, c is the speed of light in vacuum, n is the refractive index of the film, d is the film thickness, and ϵ_0 is the permittivity of free space. Moreover, the light transmittance $T(\omega)$ for the thin film in an air/thin-film/substrate structure can be obtained by the Tinkham formula [12]:

$$T(\omega) = |1 + \sigma(\omega) d z_0/(n_{\text{sub}} + 1)|^{-2}. \tag{2}$$

Here, $z_0 = \sqrt{\mu_0/\epsilon_0}$ is the impedance of free space, n_{sub} is the index of refraction for the substrate. Normally, $\sigma(\omega)$ is proportional to $1/\rho_{xx}$ with ρ_{xx} being the DC resistance of the film. These analyses indicate that for an air/thin-film/substrate structure, when the DC resistivity of the thin film is relatively low, the reflectivity of the sample reflects mainly the features of the resistivity.

From the results obtained from our transport measurement (see Fig. 4), the DC resistivity for both (001)- and (111)-orientated LTO samples in the metallic phase is relatively low. This implies a large optical conductivity in the samples in metallic states or at relatively high temperatures. As a result, a strong optical absorption occurs in LTO samples so that the optical transmission is relatively weak. More interestingly, it has been found that in the NIR bandwidth the light transmission depends rather weakly on the wavelength [6]. Therefore, the optical reflectivity in the LTO samples is mainly inversely proportional to the optical conductivity in a metallic regime. In a superconducting phase, the optical transmission for LTO samples is very weak and, thus, the optical reflectivity is more inversely proportional to the optical conductivity. Hence, in the NIR bandwidth, the results obtained from reflectivity for LTO thin films can reflect the features of resistivity. This is one of the main reasons why a relatively small value of the reflectivity for LTO samples can be measured. In a metallic regime, because the DC resistivity in LTO samples increases with temperature, as shown in Fig. 4, the NIR reflectivity also increases with temperature, as shown in Fig. 3. Around the MST temperature, the DC resistivity of the LTO samples drops sharply and, therefore, a sudden drop of the NIR reflectivity can be observed in Fig. 3. In Fig. 3, the non-vanishing NIR reflectivity can be seen for LTO thin films on substrate in a superconducting phase. This is mainly induced by background optical reflection owing to the presence of a superconductor/substrate interface, surface roughness, edge states, etc., in the sample system.

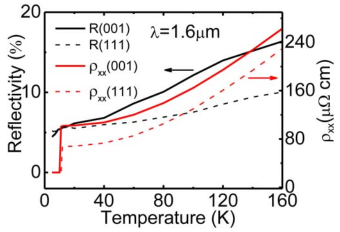

Fig. 4. Optical reflectivity versus temperature for (001) (black solid curve) and (111)-oriented (black dotted curve) LTO thin films at a fixed radiation wavelength $\lambda = 1.6$ μm. The results of the DC resistivity for (001) (red solid curve) and (111)-oriented (red dotted curve) LTO thin films are shown for comparison.

It is interesting to note from Fig. 3 that in the metallic phase, the NIR reflectivity of LTO samples increases with a radiation wavelength, and this effect can be more markedly observed at relatively high temperatures. As we know, the optical conductivity for free electrons in metallic states can be described by the well-known Drude formula which suggests that the real part of optical conductivity should decrease monotonically with increasing $\omega\tau$ [13]; namely, the standard Drude formula can result in an effect that the optical reflectivity decreases with an increasing radiation wavelength, which is contradictory to our experimental findings. In 2001, Smith [13] developed a modified Drude formula in which the light-field-induced backscattering or localization effect has been taken into consideration. In such a case, the complex optical conductivity in an electronic system can be described as [13]

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}\left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega\tau)^n}\right]. \tag{3}$$

Here, the DC conductivity σ_0 is given by $N_e e^2 \tau/m^*$ with the carrier density N_e, the momentum relaxation time τ, and the electron effective mass m^*. Moreover, the coefficient $c_n = [-1, 0]$ describes the fraction of original velocity for an electron after the nth collision event, which reflects the effect of electronic localization. For a nonzero c_n or, in the presence of an electronic localization effect, the optical conductivity can increase with $\omega\tau$ [13]. On the basis of these theoretical analyses and the experimental results shown in Fig. 3, we would like to suggest that the electronic localization effect is present in LTO samples with different lattice orientations in metallic states. Furthermore, with increasing temperature, the DC resistivity increases (see Fig. 4), which implies a decrease in relaxation time τ. Because the term $\omega\tau$ decreases with increasing radiation wavelength and/or decreasing relaxation time, the increase in the reflectivity with an NIR wavelength can be more pronounced, as observed at relatively higher temperatures when the localization effect is present in LTO thin film samples. Thus, we are able to understand the dependence of NIR reflectivity on a radiation wavelength and temperature for LTO superconductor samples with the help of DC resistivity obtained experimentally and of the Drude–Smith formula developed theoretically. We would like to mention further that by employing the state-of-the-art terahertz time-domain spectroscopy, we can measure experimentally and directly the real and imaginary parts of the optical conductivity for an optoelectronic sample and obtain the electronic localization coefficient c_n [14]. Since the NIR reflectivity experiment employed in this Letter can only measure directly the real part of optical conductivity, we are unable to determine easily the value of c_n for LTO samples at present.

The results obtained from electronic transport [10] and tunneling spectrum [5] measurements have demonstrated that the LTO thin films with (001) and (111) lattice orientations can lead to anisotropic features of the physical properties due to the corresponding features of electron-phonon coupling in the system [5]. In Fig. 4, we show the DC resistivity ρ_{xx} (red solid and dotted curves) and optical reflectivity R (black solid and dotted curves) at a fixed radiation wavelength of 1.6 μm versus the temperature for samples with (001) [black and red solid curves] and (111) [black and red dotted curves] lattice orientations. We notice the following features. (1) In the superconducting state, ρ_{xx} is zero, whereas the non-vanishing R can be seen for LTO thin films due to the presence of the background optical reflection in NIR bandwidth. (2) Around the MST transition temperatures, ρ_{xx} approaches rapidly to zero, whereas R drops relatively slowly with decreasing temperature. This is due to the fact that the optical reflectivity not only depends on DC resistivity, but also on radiation frequency, and both the real and imaginary parts of the optical conductivity can contribute to optical reflectivity. Furthermore, when a photo-induced electronic localization effect is taken into consideration, the situation is more complicated. (3) In the metallic state, or when the temperature is above T_c, although both ρ_{xx} and R increase monotonically with temperature, it can be seen obviously from Fig. 4 that the results for temperature dependence of ρ_{xx} and R differ markedly for different measurements. From Fig. 4, we see that ρ_{xx} depends more strongly on the temperature T_e than R does. It was found that in a metallic phase, $d\rho_{xx}/dT_e \sim T_e$, suggesting a Fermi-liquid behavior [15] for LTO thin films. We find dR/dT_e is roughly a constant. From Eq. (3), we see that the temperature dependence of σ_0 and $\sigma(\omega)$ is mainly induced by the electronic relaxation time τ. $\sigma_0 \sim \tau$ so that $\rho_{xx} \sim 1/\tau$. In contrast, $\sigma(\omega)$ is not simply proportional to τ so that R relatively weakly depends on τ due to the presence of term $\omega\tau{\sim}1$ in Eq. (3). Nevertheless, ρ_{xx} and R for LTO sample with (001) orientation are larger than those for sample with (111) lattice orientation. Furthermore, the differences between ρ_{xx} and R for two samples are in the same order of magnitude. The results obtained from other measurements [5,10] indicated that the LTO thin films with (001) and (111) lattice orientations have different optic-phonon modes which result in different electron-phonon scattering strengths. Because the electron-phonon scattering is stronger in the (001) LTO sample than that of the (111) oriented sample, ρ_{xx} and R for (001) the oriented LTO sample are larger than those for the (111) oriented one. Therefore, we further verify the anisotropy features of the physical properties of LTO thin films by the optical experiment.

In this Letter, we have produced large-size and high quality LTO thin films with different lattice orientations synthesized on MAO substrates. The NIR reflectivity spectra for these samples have been measured, and the dependence of the reflectivity upon temperature and radiation wavelength has been examined. We have demonstrated that the temperature-induced metal-superconductor transition in LTO thin films can be detected optically via NIR reflection experiments. The superconducting transition temperature measured optically here agrees with that obtained from an electronic transport measurement. We have analyzed the radiation wavelength dependence of the reflectivity for LTO thin films with the help of the Drude–Smith formula and found that the NIR photo-induced electronic localization effect can be present in LTO thin film samples in a metallic phase. Such information cannot be directly obtained from electronic transport and magneto-transport measurements. This indicates that optical measurement is a powerful experimental method for the investigation of superconductor systems. Moreover, we have found that the NIR reflectivity for an (001) oriented sample in a metallic state is larger than that for the (111) oriented sample, in agreement with the results for the DC resistivity. The optical reflection measurement is a more convenient and realistic option for the investigation of electronic systems which are difficult to make ohmic contact electrodes in order to carry out the transport measurement and/or are with weak light transmission. We believe that the results obtained and discussed in this Letter can help us to gain an in-depth understanding of the physical properties of the LTO thin films with different lattice orientations.

Funding. National Key Basic Research Program of China (2015CB921003); National Natural Science Foundation of China (NSFC) (11574319); Ministry of Science and Technology of the People's Republic of China (MOST) (2011YQ130018); Department of Science and Technology of Yunnan Province (2016FC001).

REFERENCES

1. D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, Mater. Res. Bull. **8**, 777 (1973).
2. C. P. Sun, J.-Y. Lin, S. Mollah, P. L. Ho, H. D. Yang, F. C. Hsu, Y. C. Liao, and M. K. Wu, Phys. Rev. B **70**, 054519 (2004).
3. D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976).
4. K. Jin, G. He, X. Zhang, S. Maruyama, S. Yasui, R. Suchoski, J. Shin, Y. Jiang, H. S. Yu, J. Yuan, L. Shan, F. V. Kusmartsev, R. L. Greene, and I. Takeuchi, Nat. Commun. **6**, 7183 (2015).
5. G. He, Y. L. Jia, X. Y. Hou, Z. X. Wei, H. D. Xie, Z. Z. Yang, J. A. Shi, J. Yuan, L. Shan, B. Y. Zhu, H. Li, L. Gu, K. Liu, T. Xiang, and K. Jin, Phys. Rev. B **95**, 054510 (2017).
6. M. Łapiński, B. Kościelska, and W. Sadowski, J. Alloys Compd. **536**, 30 (2012).
7. A. Kumatani, T. Ohsawa, R. Shimizu, Y. Takagi, and S. Shiraki, Appl. Phys. Lett. **101**, 123103 (2012).
8. J. P. Li and R. K. Y. Chan, Opt. Lett. **35**, 3330 (2010).
9. W. Xu, Q. T. Song, L. J. Zheng, Z. G. Zhang, and W. W. Cao, Opt. Lett. **39**, 4635 (2014).
10. Y. L. Jia, G. He, H. S. Yu, W. Hu, Z. Z. Yang, J. A. Shi, Z. F. Lin, J. Yuan, B. Y. Zhu, K. Liu, L. Gu, H. Li, and K. Jin, "Crystallographic dependent transport properties and oxygen issue in superconducting $LiTi_2O_4$ thin films," arXiv: 1608.06683 (2016).
11. S. Maruyama, J. Shin, X. Zhang, R. Suchoski, S. Yasui, K. Jin, R. L. Greene, and I. Takeuchi, Appl. Phys. Lett. **107**, 142602 (2015).
12. M. Tinkham, Phys. Rev. **104**, 845 (1956).
13. N. V. Smith, Phys. Rev. B **64**, 155106 (2001).
14. C. Zhang, F. H. Su, J. M. Dai, L. Pi, H. Y. Mei, P. Zhang, and W. Xu, Jpn. J. Appl. Phys. **55**, 031101 (2016).
15. H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).