Giant change in IR light transmission in La$_{0.67}$Ca$_{0.33}$MnO$_3$ film near the Curie temperature: promising application in optical devices

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Transport, magnetic, magneto-optical (Kerr effect) and optical (light absorption) properties have been studied in an oriented polycrystalline La$_{0.67}$Ca$_{0.33}$MnO$_3$ film which shows colossal magnetoresistance. The correlations between these properties are presented. A giant change in IR light transmission (more than a 1000-fold decrease) is observed on crossing the Curie temperature (about 270 K) from high to low temperature. Large changes in transmittance in a magnetic field were observed as well. The giant changes in transmittance and the large magneto-transmittance can be used for development of IR optoelectronic devices controlled by thermal and magnetic fields. Required material characteristics of doped manganites for these devices are discussed.

1. INTRODUCTION

It is known that the conductivity of doped manganites increases dramatically at the transition from the paramagnetic to the ferromagnetic state. In the La$_{1-x}$Ca$_x$MnO$_3$ system with doping levels in the range $0.17 < x < 0.5$ this transition occurs simultaneously with an insulator-metal transition. If the manganite samples have fairly good crystalline order, huge temperature changes in light absorption and magneto-absorption can occur at the transition to the metallic ferromagnetic state. These effects open the possibility for use of doped manganites not only as magnetic recording media, but also for developing various optoelectronics devices controlled by magnetic or thermal fields. Previously large temperature changes in light absorption and magneto-absorption near the Curie temperature, $T_c$, have been found in single-crystal (La$_{1-x}$Pr$_x$)$_x$Ca$_{0.33}$MnO$_3$ films ($T_c \approx 185$ K) and single crystal La$_{0.9}$Sr$_{0.1}$MnO$_3$ ($T_c \approx 160$ K). This work reports similar effects in polycrystalline La$_{0.67}$Ca$_{0.33}$MnO$_3$ films with a higher $T_c$, which is only moderately less than room temperature. This may be important in practical use of these effects. This study will also address correlations of other material properties (the structural, transport and magnetic properties) with the optical measurements for this system.

II. EXPERIMENT

The La$_{1-x}$Ca$_x$MnO$_3$ ($x \approx 1/3$) film described in this paper was grown by pulsed-laser deposition (PLD) on a (001) oriented LaAlO$_3$ substrate. A PLD system from Neocera Inc. with a Lambda Physik KrF excimer laser operating at 248 nm was used to ablate the target mater-
the intensity of the reflected light \( \delta = [I(H) - I(0)]/I(0) \), where \( I(H) \) and \( I(0) \) are the intensities of the reflected light in the presence and in absence of a magnetic field respectively, was directly measured in the experiment. Other details of the technique used were described previously.

III. RESULTS AND DISCUSSION

A. Structural, transport and magnetic properties

A \( \Theta-2 \Theta \) scan permits determination of the lattice parameters in the direction perpendicular to the film plane. In the XRD pattern (Fig. 1) only the (001), (002), (003) and (004) reflections from both the substrate and the film are found, indicating a high degree out-of-plane orientation of the film. The XRD pattern for the substrate corresponds to single-crystal LaAlO\(_3\). At fairly high angles the peaks for the substrate are split (having doublets), due to contribution of the K\(_{\alpha1}\) and K\(_{\alpha2}\) radiation. The less intense film peaks are not split. The lattice parameter for the substrate is found to be \( a_s = 0.3789 \pm 0.0002 \) nm. This agrees well with the expected value \( a = 0.37896 \) nm for single-crystal LaAlO\(_3\). The out-of-plane lattice parameter for the film is equal to \( a_f = 0.3838 \pm 0.0002 \) nm which is a little less than that of the target. The surface of the film appears bright and specular. Other films having the same structural, magnetic and transport properties were prepared in the same PLD run. The rms roughness of one of these films was determined to be less than 2 nm in an atomic force microscope. The film studied here is expected to have the same high surface smoothness.

The temperature dependence of the real (\( \chi' \)) and the imaginary (\( \chi'' \)) components of the AC susceptibility are shown in Fig. 2. In the same figure the temperature dependence of the magnetization is presented. The latter is rather noisy due to the small mass of the film. Nonetheless, it is evident from Fig. 2 that the paramagnetic-ferromagnetic transition is quite sharp. From these temperature dependences the Curie temperature, \( T_c \), can be obtained. The value of \( T_c \approx 276 \) K, is found if \( T_c \) is defined as the temperature of the inflection point in the \( \chi' (T) \) curve. It is expected also that \( \chi'' (T) \) should peak at \( T_c \). This temperature is about 273.3 K, which is very close to the \( T_c \) value found from the \( \chi' (T) \) curve.

The temperature dependence of the film resistivity and of the magneto-resistance (MR) are shown in Figs. 3 and 4. As evident from Fig. 3, the resistive transition which accompanies the magnetic one is also sharp (see also the temperature behavior of the temperature coefficient of resistance (TCR) shown in the insert to this Figure). In general, the observed \( \rho(T) \) behavior (as well as the \( \chi' (T) \) curve) reflects the high-quality of the film studied. The temperature, \( T_p \approx 277.5 \) K, where resistance peaks, is very close to \( T_c \), as expected for high quality films.

B. Magneto-optical and optical properties

The spectral dependence of TKE for the film studied (Fig. 5a) is consistent with previous data for doped manganites with similar doping level. There is a large “negative peak” at \( E \approx 2.8 \) eV together with an additional feature near \( E \approx 1.6 \) eV. At \( T = 55 \) K, the peak amplitude near \( E = 2.8 \) eV is about \(-23 \times 10^{-3}\). The temperature dependence of TKE (Fig. 5b) was measured at two incident photon energies (1.8 eV and 2.8 eV), corresponding to the peak positions in TKE spectra (Fig. 5a). These temperature dependences should reflect that of the magnetization. Indeed, the temperature at which an appreciable Kerr effect can be seen, when going from high to lower temperature, is close to the \( T_c \) values obtained from the magnetic and resistance measurements. On the other hand, the temperature dependence curves for TKE recorded at different photon energies, are quite different from each other. It can be seen that temperature dependence of TKE, measured at \( E = 1.8 \) eV, looks quite similar to the M(T) dependence (Fig. 2b). Both curves reveal a sharp increase in magnetization near \( T_c \), but that for \( E = 2.8 \) eV, shows a far slower increase in the TKE signal with decreasing temperature below \( T_c \). This effect is most likely associated with the shifting of the peak to lower energy (“red” region) with increasing temperature (Fig. 5a); whereas the peak at \( E = 1.8 \) eV is not shifted for a wide temperature range. The mechanism of this difference in temperature behavior of the spectral peaks is not clear at present. It is conceivable that this is connected with the different nature of optical transitions responsible for magneto-optical activity in these energy regions. As was shown earlier in the spectral range under study there is an allowed electric-dipole transition in the octahedral complex (MnO\(_6\))\(^{3+}\) at \( E = 3.5 \) eV and spin-resolved \( d-d \) transition in Mn\(^{3+}\) and Mn\(^{4+}\) at lower energies. That is, a large magneto-optical effect in the neighborhood of \( E = 3 \) eV is caused by a charge-transfer transition with an involvement of both Mn and O ions. The temperature dependence of this transition should be more complex than that for Mn ions, as is actually observed in this study. Further studies are necessary, of
course, to clarify this effect. In general, the TKE data obtained correlate well with the results of magnetic and transport measurements and support arguments that this film is of excellent quality and homogeneity.

Let us turn now to the optical properties of the film. An absorption spectrum for the film in the paramagnetic state at \( T = 295 \text{ K} \) is presented in Fig. 6. It can be seen that an increase in wavelength, \( \lambda \), leads to a decrease in absorption, that can be associated with the influence of “tails” of inter-band optical transitions. For a large enough increase in wavelength, the absorption begins to increase. This is determined by the presence of the impurity band, which is usually positioned around \( \lambda = 10 \mu \text{ m} (E = 0.12 \text{ eV}) \) for manganites and associated with Mn\(^{4+}\) ions [34]. Below \( T_c \) a strong increase in absorption has been observed. This is connected with the light absorption by free charge carriers. This phenomena is demonstrated more clearly by the temperature dependence of intensity of light transmitted through the film at a wavelength \( \lambda = 6.4 \mu \text{ m} \) (Fig. 7).

The light intensity is sharply reduced below 270 K in a narrow temperature range (Fig. 7). The giant change in the intensity is more than a 1000-fold decrease. The magnetic field shifts the intensity curve \( I(T) \) to higher temperature. The relative change of transmission under the influence of the magnetic field [magneto-transmittance (MT)], \( \Delta I_H/I_0 = [I_H - I_0]/I_0 \), peaks at 28 \% in a field of 0.8 T at \( T = 265 \text{ K} \) (see insert in Fig. 7). The magneto-transmittance is found to be significant for the film studied in the temperature range 250-280 K. That can be important for possible applications. In previous works [34] this effect was observed at significantly lower temperatures (\( T < 200 \text{ K} \)). It must be emphasized as well that the effect is seen in unpolarized light.

C. Discussion

It is quite clear that the giant decrease in transmission found below \( T_c \) in this study is determined by the transition of the film to the metallic state with fairly high density of free (or quasi-free) charge carriers. In spite of extensive experimental and theoretical efforts, a clear understanding of the metal-insulator transition in doped manganites and the colossal magneto-resistance (CMR) associated with it is not yet available. Several possible explanations can be found in review papers [34]. One of the possible reasons for CMR in homogeneous samples is the shift of the mobility edge induced by a change in temperature or magnetic field [34]. However, it is hard to expect a sufficiently high homogeneity in doped manganites [34]. One of the certain things is that a clear correlation exists between transport properties and magnetization in the mixed-valence manganites [34]. Namely, the resistance \( R \) of manganites in the ferromagnetic state is a function of magnetization and the conductivity increases with enhancement of ferromagnetic order. This, together with the large drop of resistivity and light transmission below \( T_c \), is the source of the huge negative MR and MT in manganites.

The sharp drop in resistance below \( T_c \) in doped manganites can be used for bolometric applications [44]. Actually, the TCR of the film studied is fairly high in the temperature range close to room temperature (see insert in Fig. 3). It has been shown here, however, that changes in the transmission at the magnetic transition are much larger. Indeed, the ratio of resistances at \( T_p \) and 4.2 K, \( R_p/R_{4.2} \), was found to be very high (about 48.6), but the optical transmission exhibits a far larger drop (more than a 1000-fold decrease) below \( T_c \).

The transmission, \( t \), of films is defined as the ratio between intensities of transmitted and incident light. For a film with high absorption, when \( t < 10 \% \), the transmission is related to the absorption coefficient, \( K \), by the equation \( t = (1 - R_1)(1 - R_2)(1 - R_{12}) e^{(-K d)} \), where \( d \) is film thickness, \( R_{12}, R_2, R_1 \) are reflection coefficients at the boundaries of film-substrate, substrate-vacuum, film-vacuum, respectfully. The absorption coefficient is proportional to the DC conductivity (Drude model). It is evident from the foregoing equation that there is no direct proportionality between the transmission and the resistivity, but the temperature dependence of the transmission reflects the \( \rho(T) \) behavior. The change in intensity of the transmitted light through the sample at the transition to the ferromagnetic state is of particular interest for practical use. This change is large for the film studied in comparison with the moderate change in the absorption coefficient. (It can be shown that a 1000-fold decrease in the transmission corresponds to an increase in the absorption coefficient by a factor of 5.6, not taking into account the change in reflectivity.) The decrease in skin depth, \( \delta \), at \( T < 200 \text{ K} \) is responsible for the non-transparency of the film in the ferromagnetic state. This can be estimated with the expression \( \delta = (2\rho/\mu_\mu \omega)^{1/2} \) under the assumption that the magnetic permeability is equal to unity to obtain \( \delta \approx 70 \text{ nm} \) at \( T = 4.2 \text{ K} \), and \( \delta \approx 486 \text{ nm} \) at \( T = T_p \) for light with \( \lambda = 6.4 \mu \text{ m} \). That is, the skin depth is far larger than the film thickness (\( d \approx 150 \text{ nm} \)) in the paramagnetic state, but in the ferromagnetic state it is significantly less than the film thickness. It should be added that the relative change of the intensity of transmitted light in a magnetic field, \( MT = [I_H - I_0]/I_0 \), is certain to be a direct analogue of MR = \( [(R(H) - R(0))/R(0)] \). As in the case of MR, this quantity MT is determined by the ability of an external magnetic field to enhance the magnetic order in the doped manganites.

The high-temperature optical phenomena of magneto-transmittance and the strong temperature dependence of magneto-transmittance near \( T_c \) that has been reported here can be used for development of a number of IR optoelectronic devices, such as light modulators, optical attenuators, light shutters, temperature and magnetic-field indicators, etc. These devices can work in the IR range with \( \lambda \) up to 14 \( \mu \text{ m} \). As far as we know, the number
of materials, which can be used in this energy range as optical control devices, is very limited. High quality and high homogeneity doped manganite films which exhibit a sharp magnetic transition and high conductivity in the ferromagnetic state should be very useful in development of appropriate optical devices.

In conclusion, at a temperature \( T \approx 270 \text{ K} \) not far from room temperature giant temperature changes in light transmittance and large magneto-transmittance has been observed. These effects can be used for IR optoelectronics devices.

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FIG. 2. Temperature dependences of the AC susceptibility (a) and the magnetization (b). The real ($\chi'$) and imaginary ($\chi''$) parts of AC susceptibility were recorded in AC magnetic field $H_{AC} = 0.2$ mT at frequency 125 Hz for field direction parallel to the film plane. $M(T)$ dependence was obtained at $H_{DC} = 2.5$ mT. All dependences were recorded with temperature increasing after the film was cooled in zero field.

FIG. 3. Temperature dependence of the resistivity of the investigated film in zero magnetic field and in fields $H = 2.5$ T and $H = 5$ T. Field $H$ was perpendicular to the film plane. The insert shows the temperature dependence of the temperature coefficient of resistance (TCR) at $H = 0$. 
FIG. 4. Temperature dependence of the magneto-resistance \( [R(H) - R(0)]/R(0) \) at \( H = 2.5 \) T and \( H = 5 \) T. Field \( H \) was perpendicular to the film plane.

FIG. 5. Spectral dependences of TKE at different temperatures (a) and temperature dependences of TKE at different photon energies (b). All dependences were recorded at light incidence angle \( \phi = 68^\circ \).
FIG. 6. The optical absorption spectrum of La$_{0.67}$Ca$_{0.33}$MnO$_3$ film at $T = 295$ K.

FIG. 7. Temperature dependences of the intensity of light transmitted through La$_{0.67}$Ca$_{0.33}$MnO$_3$ film in zero magnetic field and at field $H = 0.8$ T for wavelength $\lambda = 6.4$ $\mu$m. The insert shows the temperature dependence of magneto-transmittance at $H = 0.8$ T for the same wavelength.