Giant change in infrared light transmission in $La_{0.67}Ca_{0.33}MnO_3$ film near the Curie temperature

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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 infrared light transmission (more than a thousand-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 magnetotransmittance 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. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1453496]

I. INTRODUCTION

It is known[1,2] that the conductivity of doped manganites increases dramatically at the transition from the paramagnetic to the ferromagnetic state. In the $La_{1-x}Ca_xMnO_3$ 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.[3] Previously large temperature changes in light absorption and magneto-absorption near the Curie temperature, T_C, have been found in single-crystal $(La_{1-x}Pr_x)_{0.7}Ca_{0.3}MnO_3$ films ($T_C \approx 185$ K)[3] and single-crystal $La_{0.9}Sr_{0.1}MnO_3$ ($T_C \approx 160$ K).[4] 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 $La_{1-x}Ca_xMnO_3$ ($x \approx 1/3$) film described in this article 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 material with a nominal composition $La_{2/3}Ca_{1/3}MnO_3$. The target was prepared by solid-state reaction starting from high purity powders of La_2O_3, $CaCO_3$, and $MnCO_3$. The lattice parameter for the target indexed for a pseudocubic unit cell is found to be $a_p = 0.384\ 35$ nm. The film (about 150 nm thick) was ablated at a substrate temperature of 600 °C in an oxygen atmosphere at pressure $P_{O2} = 250$ mTorr. During deposition the pulse energy was 584 mJ with a repetition rate of 8 Hz. The target–substrate distance was about 7 cm. Time of deposition was about 31 min. After deposition the film was cooled to room temperature in the same oxygen atmosphere. The film was postannealed in flowing oxygen for 25 h at 950 °C.

The film characterization and measurements were done using a variety of experimental techniques. A standard Θ–2Θ scan was used for the x-ray diffraction (XRD) study of the film. The XRD patterns were obtained using a Rigaku model D-MAX-B diffractometer with a graphite monochromator and Cu $K_{\alpha 1,2}$ radiation. The ac susceptibility and dc magnetization were measured in a Lake Shore model 7229 ac Susceptometer/dc Magnetometer. Resistance as a function

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of temperature and magnetic field was measured using a standard four-point probe technique in magnetic fields up to 5 T.

Optical absorption spectra and temperature dependencies of the intensity of the transmitted light (transmission) were investigated in the energy range 0.12–1.0 eV, the temperature range 80–295 K and in magnetic fields up to 0.8 T. The constant magnetic field was applied along the direction of light propagation perpendicular to the plane of the film. The magneto-optical (MO) properties of the film were studied by measurements of the linear transverse Kerr effect (TKE). The TKE was investigated in the energy range 0.5–3.8 eV, the temperature range 10–300 K and in magnetic fields 0.3 T. A dynamic method to record TKE was used. The relative change in the intensity of the reflected light $\delta=[I(H)-I(0)]/I(0)$, where $I(H)$ and $I(0)$ are the intensity 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.[5]

III. RESULTS AND DISCUSSION

A. Structural, transport, and magnetic properties

A Θ–2Θ 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 $LaA1O_3$. At fairly high angles, the peaks for the substrate are split (having doublets), due to contribution of the $K\alpha_1$ and $K\alpha_2$ radiation. The less intense film peaks are not split. The lattice parameter for the substrate is found to be $a_s=0.3789\pm0.0002$ nm. This agrees well with the expected value $a=0.378\,96$ nm for single-crystal $LaAlO_3$.[6] The out-of-plane lattice parameter for the film is equal to $a_f=0.3838\pm0.0002$ 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 (χ') and the imaginary (χ'') components of the ac susceptibility are shown in Fig. 2(a). In Fig. 2(b), 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 dependencies the Curie temperature, T_C, can be obtained. The value of $T_C\approx276$ 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.[7] 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 magnetoresistance (MR) are shown in Figs. 3 and 4.

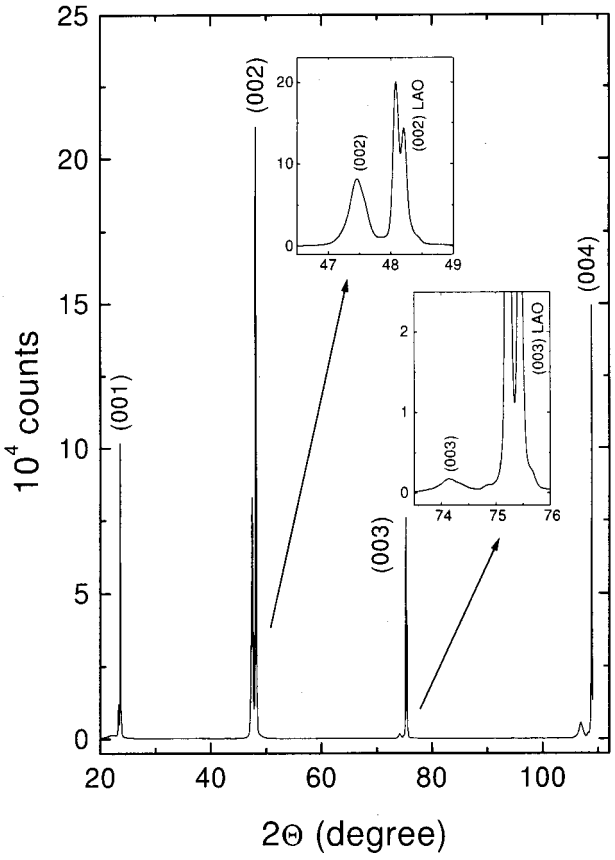

FIG. 1. XRD Θ–2Θ curve of the $La_{0.67}Ca_{0.33}MnO_3$ film on a $LaAlO_3$ substrate. The indexes (001), (002), (003) and (004) (of a pseudo-cubic unit cell) apply to the regions where reflections with these indexes are located for both for the film and the substrate. The regions around the (002) and (003) reflections are magnified in insets.

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 inset to Fig. 3). In general, the observed $\rho(T)$ behavior (as well as the $\chi'(T)$ curve) reflects the high-quality of the film studied. The temperature, $T_p=277.5$ K, where resistance peaks, is very close to T_c, as expected for high quality films.[7] The ratio of resistances at T_p and 4.2 K, $R_p/R_{4.2}$, is extremely high (about 48.6). This large variation of resistance with temperature is attributed mainly to the strengthening of the magnetic order with decreasing temperature. The resistivity at $T=4.2$ K is about 0.9 $\mu\Omega$ m which is one of the lowest values reported for $La_{1-x}Ca_xMnO_3$ ($x\approx1/3$) films (e.g., compared with those in Ref. 8). As a measure of the MR $\delta_H=[R(H)-R(0)]/R(0)$ is plotted in Fig. 4. The MR has a sharp maximum (with an absolute value of 0.65 at $H=5$ T) at $T_m=275.6$ K, that is actually at $T=T_c$. Nearly identical and high values of T_c, T_p, and T_m found in this study provide evidence of the high quality of this highly oriented film.

B. Magneto-optical and optical properties

The spectral dependence of TKE for the film studied [Fig. 5(a)] is consistent with previous data for doped manganites with similar doping level.[9,10] There is a large ''negative

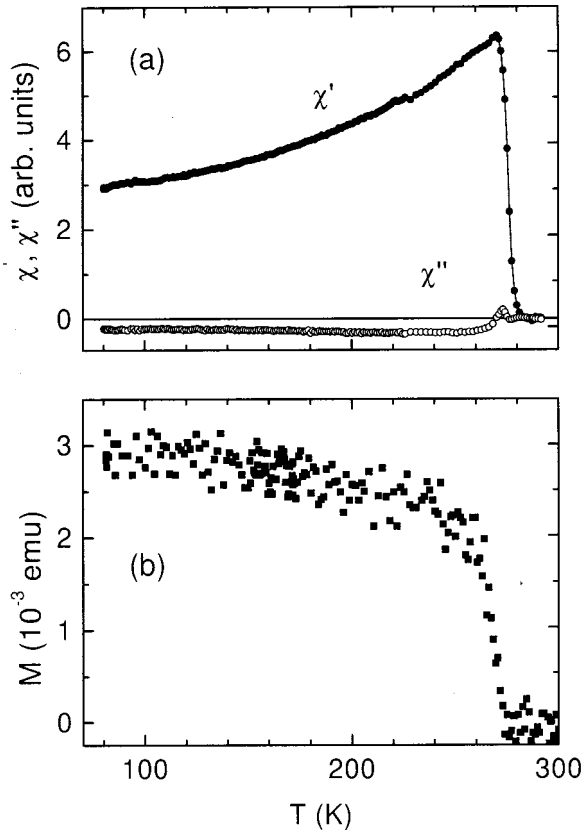

FIG. 2. Temperature dependencies of the ac susceptibility (a) and the magnetization (b). The real (χ') and imaginary (χ'') parts of ac susceptibility were recorded in ac magnetic field $H_{ac}=0.2$ mT at frequency 125 Hz for field direction parallel to the film plane. $M(T)$ dependence was obtained at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

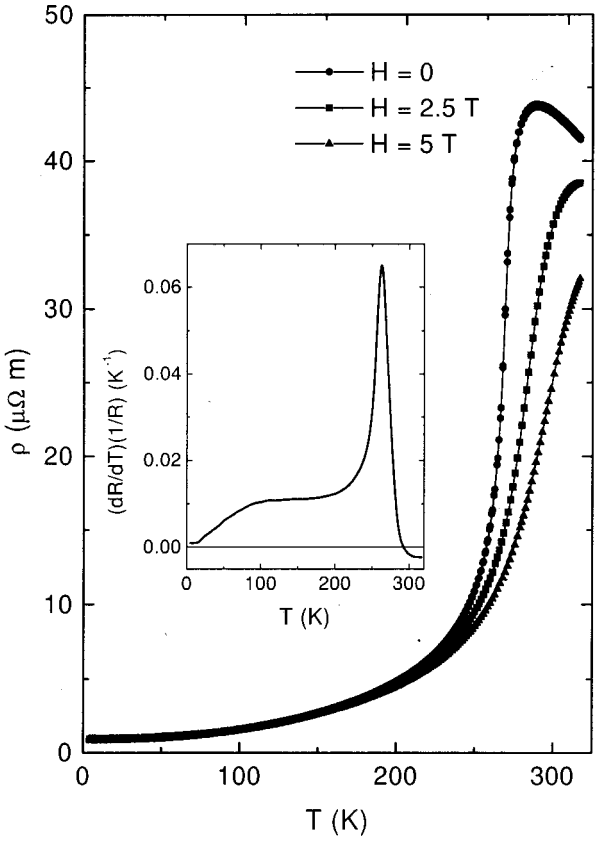

FIG. 3. Temperature dependence of the resistivity of the investigated film in zero-magnetic field and in fields $H=2.5$ T and $H=5$ T. Field H was perpendicular to the film plane. The inset shows the temperature dependence of the TCR at $H=0$.

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 -23×10^{-3}. The temperature dependence of TKE [Fig. 5(b)] was measured at two incident photon energies (1.8 and 2.8 eV), corresponding to the peak positions in TKE spectra [Fig. 5(a)]. These temperature dependencies 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. 2(b)]. 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. 5(a)]; 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,[11] in the spectral range under study, there are an allowed electric–dipole transition in the octahedral complex $(MnO_6)^{9-}$ at $E=3.5$ eV and spin-resolved $d-d$ transition in Mn^{3+} and Mn^{4+} at lower energies. That is, a large MO 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 $T=295$ K is presented in Fig. 6. It can be seen that an increase in wavelength, λ, leads to a decrease in absorption, that can be associated with the influence of ''tails'' of interband 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 $\lambda=10$ μm ($E=0.12$ eV) for manganites and associated with Mn^{4+} ions.[3,4,12] 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 $\lambda=6.4$ μm (Fig. 7).

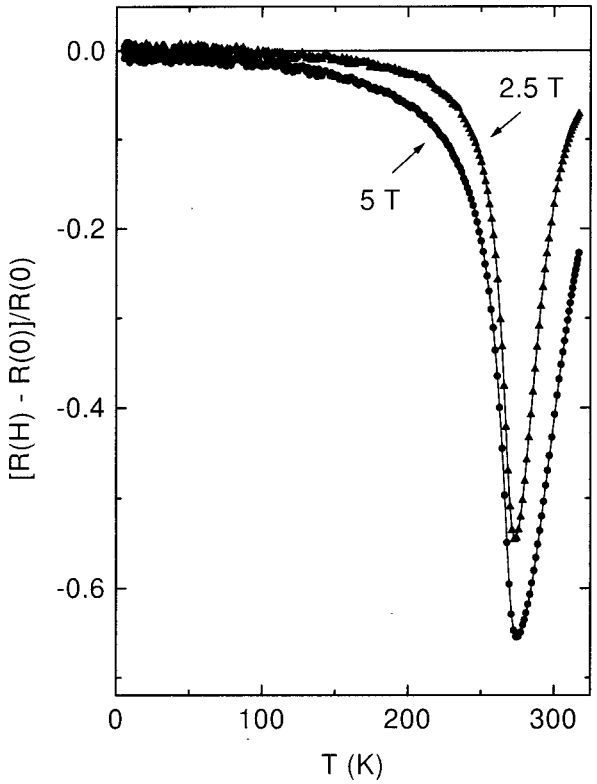

FIG. 4. Temperature dependence of the MR $[R(H)-R(0]/R(0)$ at $H=2.5$ T and $H=5$ T. Field H was perpendicular to the film plane.

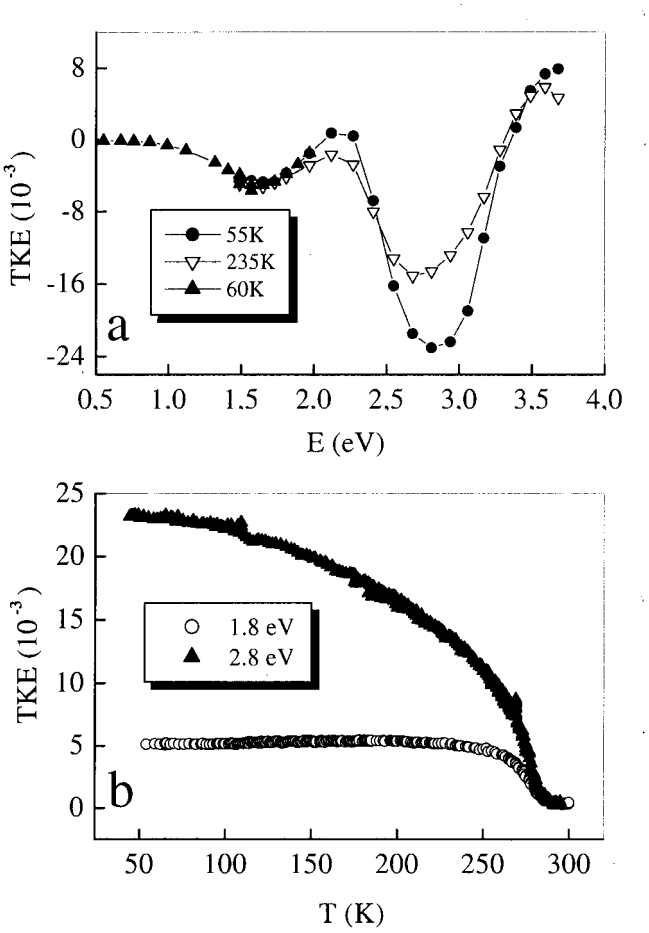

FIG. 5. Spectral dependencies of TKE at different temperatures (a) and temperature dependencies of TKE at different photon energies (b). All dependencies were recorded at light incidence angle $\phi=68°$.

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 thousand-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 [magnetotransmittance (MT)], $\Delta I_H/I_0 = [I_H - I_0]/I_0$, peaks at 28% in a field of 0.8 T at $T=265$ K (see inset in Fig. 7). The MT 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,[3,4] this effect was observed at significantly lower temperatures ($T<200$ 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 quasifree) charge carriers. In spite of extensive experimental and theoretical efforts, a clear understanding of the metal–insulator transition in doped manganites and the colossal magnetoresistance (CMR) associated with it is not yet available. Several possible explanations can be found in review papers.[1,2] 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.[13] However, it is hard to expect a sufficiently high homogeneity in doped manganites.[2] One of the certain things is that a clear correlation exists between transport properties and magnetization in the mixed-valence manganites.[1,2] 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.[14] Actually, the TCR of the film studied is fairly high in the temperature range close to room temperature (see inset 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 thousand-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 $t=(1-R_1)(1-R_2)(1-R_{12})\exp(-Kd)$, where d is film thickness, R_{12}, R_2, and R_1 are reflection coefficients at the boundaries of film substrate, substrate vacuum, film vacuum, respectively. 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

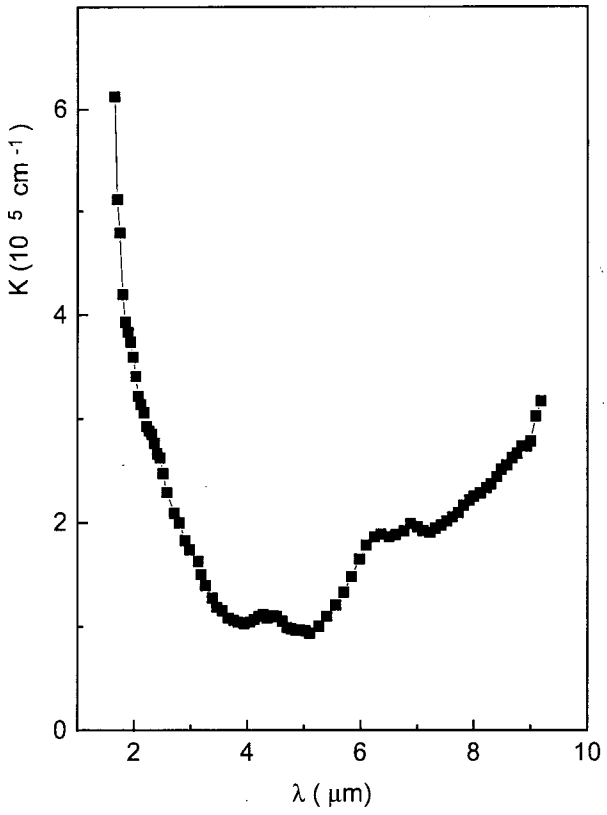

FIG. 6. Optical absorption spectrum of $La_{0.67}Ca_{0.33}MnO_3$ film at $T=295$ K.

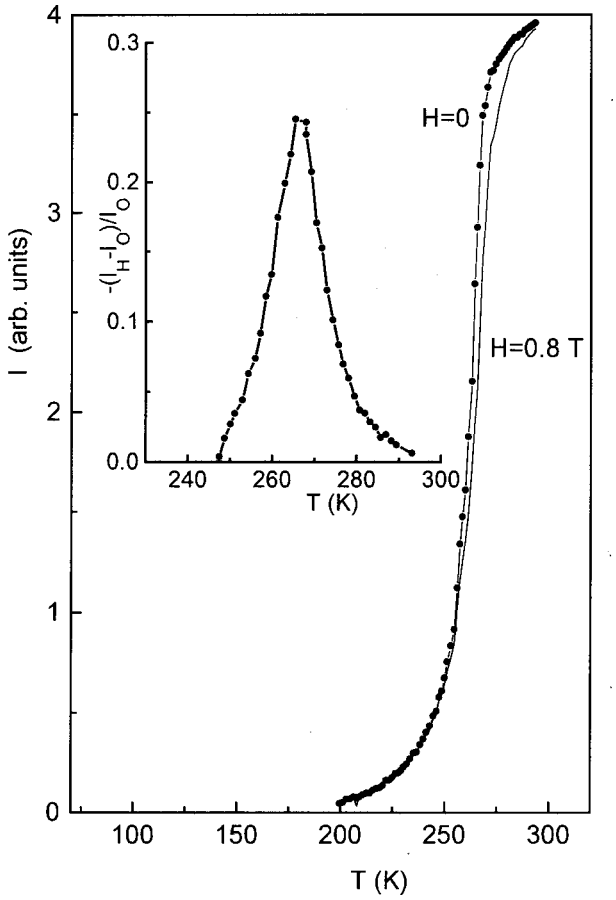

FIG. 7. Temperature dependencies of the intensity of light transmitted through $La_{0.67}Ca_{0.33}MnO_3$ film in zero-magnetic field at field $H=0.8$ T for wavelength $\lambda=6.4$ μm. The inset shows the temperature dependence of MT at $H=0.8$ T for the same wavelength.

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 thousand-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, δ, at $T<200$ K is responsible for the nontransparency of the film in the ferromagnetic state. This can be estimated with the expression $\delta=(2\rho/\mu\mu_0\omega)^{1/2}$ under the assumption that the magnetic permeability is equal to unity to obtain $\delta\approx70$ nm at $T=4.2$ K, and $\delta\approx486$ nm at $T=T_p$ for light with $\lambda=6.4$ μm. That is, the skin depth is far larger than the film thickness ($d\approx150$ 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, $\mathrm{MT}=[I_H-I_0]/I_0$, is certain to be a direct analogue of $\mathrm{MR}=([R(H)-R(0)]/R(0))$. 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 MT and the strong temperature dependence of MT near T_C that has been reported here can be used for development of a number of infrared (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 λ up to 14 μm. 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 ($T\approx270$ K) not far from room temperature, giant temperature changes in light transmittance and large MT has been observed. These effects can be used for IR optoelectronics devices.

ACKNOWLEDGMENTS

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