Study on the stability of charge-ordered state and rectifying properties of heteroepitaxial structure for manganites

T. Qian · T. F. Zhou · X. G. Li

Abstract We report the study on the stability of charge-ordered (CO) state and rectifying properties of heteroepitaxial structure for manganites $R_{1-x}Ca_xMnO_3$ (R = La, Pr, and Sm) by measuring magnetoresistance, magnetization, specific heat, $I-V$ characteristics, and X-ray diffraction. For the $La_{1-x}Ca_xMnO_3$ system, near the Ca^{2+} concentration of $x=0.75$ the CO state is mostly stabilized and insensitive to external magnetic fields, which is supported by the charge transport, magnetic, and specific heat properties. By analyzing powder X-ray diffraction patterns, we found that the Jahn–Teller (JT) distortion in the CO state is the largest at $x=0.75$, which confirms the close relationship between the JT lattice distortion and the stability of the CO state for $La_{1-x}Ca_xMnO_3$. The stability of the CO state is also related to the A-site average ionic radius, $\langle r_A \rangle$. With decreasing the radius of the doped rare-earth elements (La, Pr, and Sm), the most stable CO state for the each doped system shifts gradually toward lower Ca^{2+} concentration. In addition, we have fabricated simple p–n junctions using a heteroepitaxial structure of $La_{1-x}Ca_xMnO_3$/Nb-doped $SrTiO_3$. These junctions show good rectifying properties for temperature from 85 to 305 K. The photovoltage as a function of light wavelength at room temperature has also been studied and the maximum photovoltage can reach 180 mV. The good rectifying behaviors and strong photovoltaic effect make these simple p–n junctions promising for applications.

Keywords Manganites · Charge ordering · Jahn–Teller distortion · Heterojunction

T. Qian · T. F. Zhou · X. G. Li (✉)
Hefei National Laboratory for Physical Sciences at Microscale,
University of Science and Technology of China, Anhui 230026
Hefei, China
e-mail: lixg@ustc.edu.cn

T. Qian · T. F. Zhou · X. G. Li
International Center for Materials Physics,
Academia Sinica, Shenyang 110015, China

1 Introduction

Doped manganites have been a focus of intensive studies because they show rich physics, including colossal magnetoresistance effect, charge ordering (CO) and phase separation, as well as application potential, such as magnetic reading heads and p-n junctions [1, 2]. On cooling to the transition temperature T_{CO}, e_g electrons with their accompanying Jahn–Teller (JT) distortion freeze in a static ordering followed by a long-range antiferromagnetic spin ordering at the Neel temperature $T_N \leq T_{CO}$. There is a close interplay among spin, lattice, charge, and orbital degrees of freedom. In some doping range, magnetic field H can destroy the real-space ordering of e_g electrons and cause an insulator-metal transition below T_{CO} because of the very strong spin-charge coupling [3]. Tokunaga et al. found that the stability of the CO state for $Pr_{1-x}Ca_xMnO_3$ with $0.4 \leq x \leq 0.5$ under external fields is dependent on the Ca^{2+} concentration x [4]. However, for Ca^{2+} concentration higher than 0.5, the stability of the CO state has not been systematically investigated. In this paper, we present a systematic study on the stability of the CO state at higher Ca^{2+} concentration for the $R_{1-x}Ca_xMnO_3$ (R = La, Pr, and Sm) series. We found that the stability of the CO state is related to the magnitude of the JT distortion, and the most stable CO state for each doped system shifts gradually toward lower Ca^{2+} concentration when the radius of the doped rare-earth elements decreases.

In addition, to utilize manganites for electronic devices, perovskite-oxide, such as (La, Ba)MnO$_3$/Sr(Ti,Nb)O$_3$ [2], and (La, Ca)MnO$_3$/SrTiO$_3$/(La, Ce)MnO$_3$ [5], have also been extensively studied in *p-n* and *p-i-n* junctions. Compared to the conventional semiconductor *p-n* junctions, the high sensitivity of electronic and magnetic properties of manganites to external magnetic field, electric field, or light assigns them a magnetically or electronically tunable rectifying characteristic [6–8]. In this paper, we present a study on the heterojunction composed of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) (*x*=1/16, 3/16, 5/16) films and SrTiO$_3$ crystals doped by 0.5 wt.% Nb (SNTO). Our focus is the relation of the rectifying and photovoltaic properties to the Ca^{2+} concentration *x* in La$_{1-x}$Ca$_x$MnO$_3$ films. A strong Ca^{2+} concentration dependence of the photovoltaic effect was observed.

2 Experiment

The polycrystalline La$_{1-x}$Ca$_x$MnO$_3$ samples were synthesized through a coprecipitation method. The polycrystalline Pr$_{1-x}$Ca$_x$MnO$_3$ and Sm$_{1-x}$Ca$_x$MnO$_3$ samples were synthesized by a standard solid-state ceramic technique. LCMO films (150 nm thick) on SNTO single-crystal substrates were grown using dc magnetron sputtering technique. The films were deposited at 720 °C and in situ annealed for 30 min in flowing oxygen at the same temperature, then slowly cooled to room temperature. The resistivity was measured using a standard four-probe technique in the temperatures range from 4.2 to 300 K under magnetic fields up to 14 T. The powder X-ray diffraction (XRD) patterns were recorded by a MacScience MAXP18AHF diffractometer using Cu Kα radiation. Specific heat was measured using a Quantum Design physical property measurement system magnetometer from 50 to 300 K. Magnetization was measured using a commercial superconducting quantum interference device magnetometer from 10 to 300 K. *I–V* characteristics were measured from 85 to 300 K using the Agilent E5270A *I–V* Parameter Measurement System. Photovoltage was measured using Keithly 2182 Nano-voltmeter and the light source was provided by He–Ne laser beam.

3 Results and discussions

Figure 1 shows the temperature dependence of the resistivity ρ and d$\ln\rho$/dT^{-1} under an external field *H* from 0 up to 14 T for La$_{1-x}$Ca$_x$MnO$_3$. T_{CO} is determined from the peak temperature of the d$\ln\rho$/dT^{-1}~T curves. For *x*=0.5 the resistivity below T_{CO} is obviously reduced with increasing field, and T_{CO} shifts dramatically to a lower temperature.

As *x* increases from 0.5 to 0.55, the magnetic field effect on the resistivity and T_{CO} becomes less. At *x*=0.75 the CO state are almost independent of external magnetic fields up to 14 T. For *x*=0.87, the resistivity becomes field dependent again. These results suggest that the stability of the CO state changes with Ca^{2+} doping level. Based on the resistivity data shown in Fig. 1, we analyze the magneto-resistance $[MR = (\rho_0 - \rho_H)/\rho_H]$ effect under a field of 14 T at 75 K for different doping levels, as shown in Fig. 2. The change of T_{CO} by the field of 14 T $[\Delta T_{CO} = T_{CO}(0\text{ T}) - T_{CO}(14\text{ T})]$ is also plotted against *x* in the inset of Fig. 2. It is seen that the MR effect decreases rapidly from the order of 10^5 to nearly zero upon increasing *x* from 0.5 to 0.75, while it increases slightly upon further increasing *x* from 0.75 to 0.87. The *x* dependence of ΔT_{CO} shows a behavior very similar to that of MR. These magnetic field effects on MR and ΔT_{CO} demonstrate that the CO state becomes increasingly stable as *x* increases from 0.5 to 0.75, and appears to be the most stable at *x*=0.75.

We may naturally think that these magnetic-field effects on MR and ΔT_{CO} are related to the intrinsic strength of ferromagnetism of the system. To clarify this point, we measured the temperature dependence of the magnetization at *H*=0.1 and 5 T for La$_{1-x}$Ca$_x$MnO$_3$. As shown in the inset
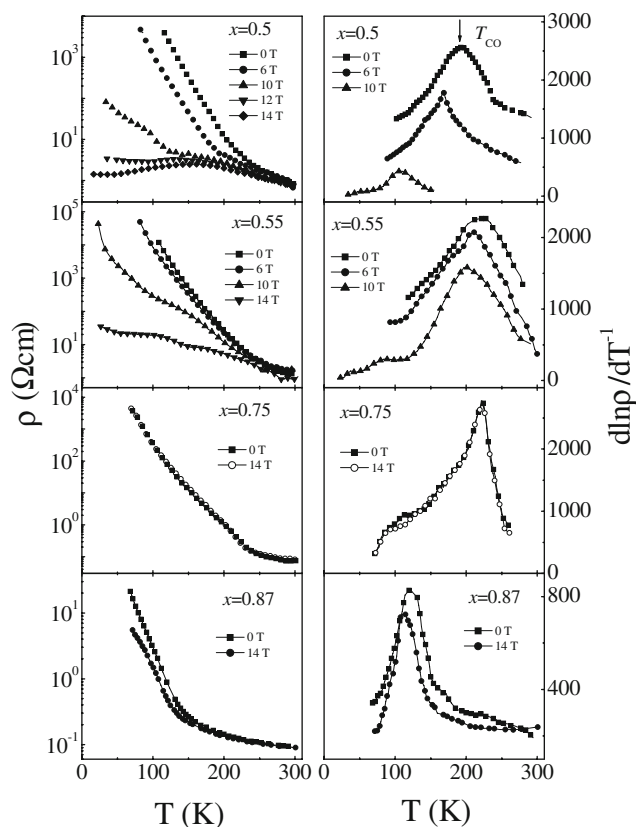

Fig. 1 The temperature dependence of ρ and d$\ln\rho$/dT^{-1} under zero and external fields *H* up to 14 T for La$_{1-x}$Ca$_x$MnO$_3$
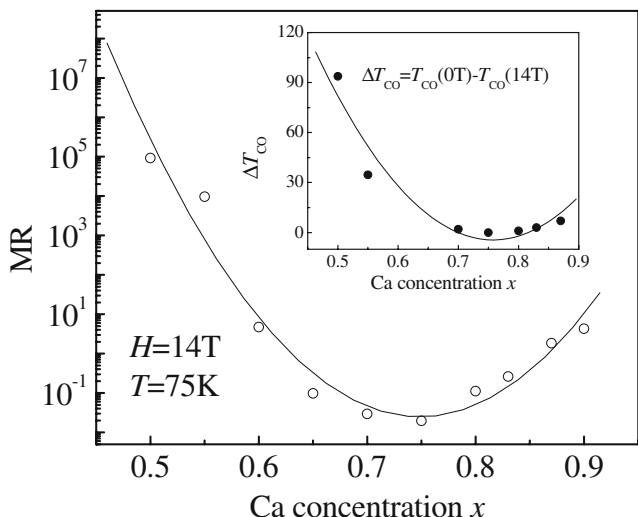
Fig. 2 The MR effect at $T=75$ K and $H=14$ T as a function of doping level x for $La_{1-x}Ca_xMnO_3$. Inset is the x-dependence of the magnetic field (14 T) induced change of the ΔT_{CO}

of Fig. 3, the magnetization shows a peak at T_{CO}, and decreases prominently with the development of charge and orbital ordering. It is interesting to find that the magnetization at T_{CO} (i.e., $M_{T_{CO}}$) is the largest for $x=0.5$, it decreases rapidly upon increasing x from 0.5 to 0.75, and reaches a minimum at $x \approx 0.75$. When x increases from 0.75 to 0.90, the $M_{T_{CO}}$ increases slightly. By comparing the x dependence of MR and ΔT_{CO} with that of $M_{T_{CO}}$, it is straightforward to conclude that the stability of the CO state is intrinsically related to the strength of ferromagnetism of the system.

Now, let us analyze the stability of the CO state from a thermodynamic point of view. Noted that the CO transition in manganites was believed to be a first-order transition, measurements of specific heat across the CO transition should show phase transition latent ΔQ [9]. After subtracting the lattice contribution fitted by using the Einstein model, we
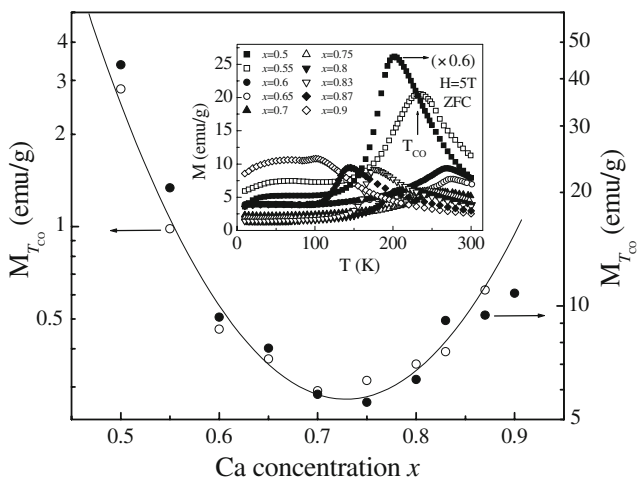

Fig. 3 The magnetization at T_{CO} ($M_{T_{CO}}$) measured at $H=0.1$ and 5 T as a function of doping level x. Inset is the temperature dependence of the magnetization for $La_{1-x}Ca_xMnO_3$

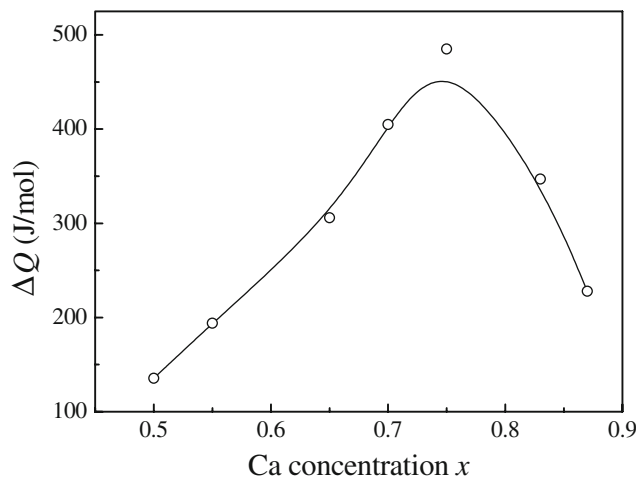**Fig. 4** ΔQ around T_{CO} as a function of x for $La_{1-x}Ca_xMnO_3$

obtained ΔQ around T_{CO}. Figure 4 shows the variation of ΔQ with Ca^{2+} concentration x. With increasing x, ΔQ first increases from 135 J/mol for $x=0.50$ to 485 J/mol for $x=0.75$, and then almost linearly decreases to 228 J/mol for $x=0.87$. The important thing is that the variation tendency of ΔQ with x agrees well with the stability trend of the CO state. Actually, as the compound is transformed from the charge disordered state to the CO state, there is an energy gain due to the formation of the cooperative JT distortion, which induces the decrease of the internal energy in the system and consequently generates ΔQ at T_{CO}. Thus, the larger the ΔQ is, the lower the relative internal energy of the CO state is, and hence the more stable the CO state is.

Since the energy gain originates from formation of the cooperative JT distortion, the magnitude of ΔQ is related to the magnitude of the JT lattice distortion. The JT distortion can be estimated by defining a JT parameter, $\sigma_{JT} = \sqrt{\frac{1}{3}\sum_{i=1}^{3}\left[(Mn-O)_i - \langle Mn-O\rangle\right]^2}$, where $(Mn-O)_i$ and $\langle Mn-O\rangle$ represent the individual and average Mn–O bond lengths in the MnO_6 octahedra, respectively. By analyzing powder X-ray
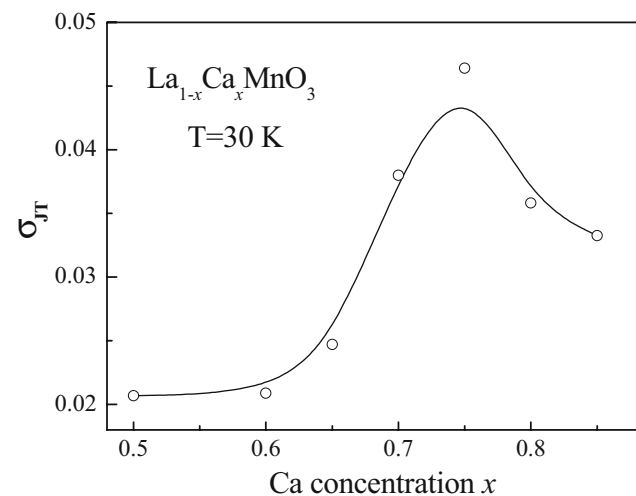

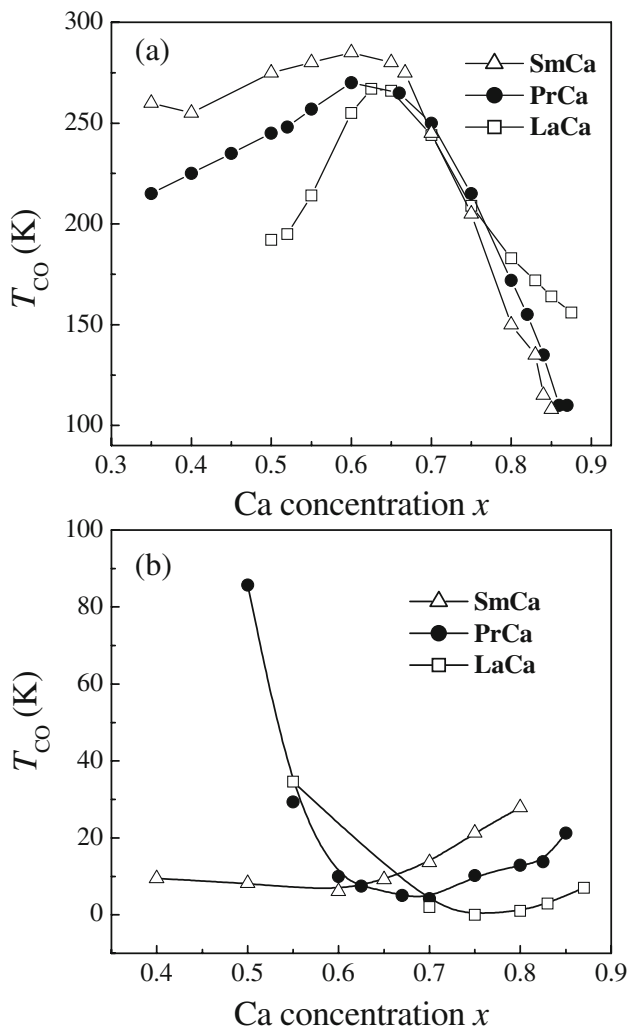**Fig. 5** σ_{JT} at 30 K as a function of x for $La_{1-x}Ca_xMnO_3$

Fig. 6 T_{CO} at zero field (**a**) and ΔT_{CO} under 14 T (**b**) as a function of x for the $R_{1-x}Ca_xMnO_3$ (R=La, Pr, and Sm) series, respectively

become less stable. The abnormal phenomenon persists to not be explained. Furthermore, with decreasing the radius of the doped rare-earth elements, the most stable CO state composition for each doped system shifts gradually toward lower Ca^{2+} concentration, while T_{CO} at zero field reaches a maximum around $x=0.60$ for the three series of compounds. These results suggest that the stability of the CO state is also related to $\langle r_A \rangle$.

Below, we will discuss the rectifying and photovoltaic properties of the LCMO/SNTO junctions. As seen in Fig. 7, X-ray diffraction patterns of the films exhibit only three sets of (00l) reflections. The inset of Fig. 7(b) plots the rocking curve of the LCMO film with $x=3/16$, whose full width of half maximum is 0.1°, signifying the good epitaxy. Figure 8 shows typical temperature dependent I–V curves of the LCMO/SNTO junctions measured by tuning bias voltage. The I–V curves show a good rectifying behavior in a wide temperature range from 85 to 305 K for the two $La_{1-x}Ca_xMnO_3$/SNTO junctions with $x=5/16$ and 3/16. Though the reverse leakage current in $La_{15/16}Ca_{1/16}MnO_3$/SNTO is

diffraction patterns using the Rietveld refinements, we obtained the Mn–O bond lengths of MnO_6 octahedra. Figure 5 shows the variation of σ_{JT} at 30 K as a function of x. It increases rapidly with increasing x from 0.5 to 0.75, and then decreases slightly upon further increasing x from 0.75 to 0.87. The x dependence of σ_{JT} sufficiently confirms the close relationship between the JT lattice distortion and the stability of the CO state for $La_{1-x}Ca_xMnO_3$.

In addition, we investigated the stability of the CO state for the $Pr_{1-x}Ca_xMnO_3$ and $Sm_{1-x}Ca_xMnO_3$ series. Figure 6(a) and (b) show the temperature of T_{CO} at zero field and ΔT_{CO} under 14 T for the $R_{1-x}Ca_xMnO_3$ (R = La, Pr, and Sm) series, respectively. At low Ca^{2+} doping level x, with decreasing the A site average ion radius $<r_A>$, T_{CO} increases, ΔT_{CO} decreases, and the CO state becomes more stable, which is associated with the reduction of the energy band width as well as the double exchange interactions. However at higher Ca^{2+} concentration, with the decrease of $<r_A>$, T_{CO} decreases, ΔT_{CO} increases, and the CO state

Fig. 7 XRD spectra of the $La_{1-x}Ca_xMnO_3$/0.5 wt % Nb-doped $SrTiO_3$ (SNTO) films. The *inset* shows the rocking curve of the film with $x=3/16$, whose full width at half maximum (FWHM) is 0.1°

large, the I–V curves still exhibit an asymmetry for the forward and reverse biases. The depletion layer may be very thin in $La_{15/16}Ca_{1/16}MnO_3$/SNTO, compared to that of the other two junctions.

The photovoltaic effect of the LCMO/SNTO junctions was studied at room temperature. The voltage across the junctions was measured as the LCMO films were perpendicularly illuminated. Figure 9 exemplifies the response of photovoltage (V_{OC}) to light illumination measured at 298 K (light wavelength $\lambda=633$ nm, light intensity $P=6$ mw) for the $La_{1-x}Ca_xMnO_3$/SNTO junction. An obvious photovoltaic effect was observed, and the photovoltage shows a quick switch between ~0 and a specific value, i.e., ~14.5, ~9.4, and ~0.7 mV for $x=5/16$, 3/16 and 1/16, respectively, corresponding to the "off" and "on" situations. It is known that the manganite is a semiconductor with a narrow band gap of ~0.1 eV [10, 11]. Therefore, photo carriers can be created in these junctions by light (photon energy ≈ 1.96 eV)
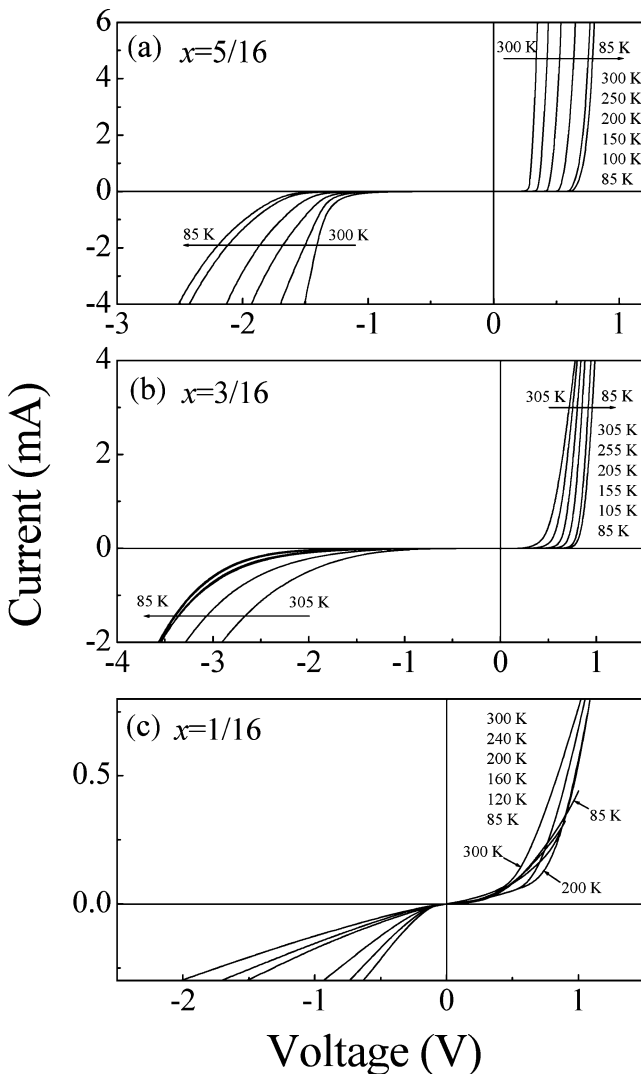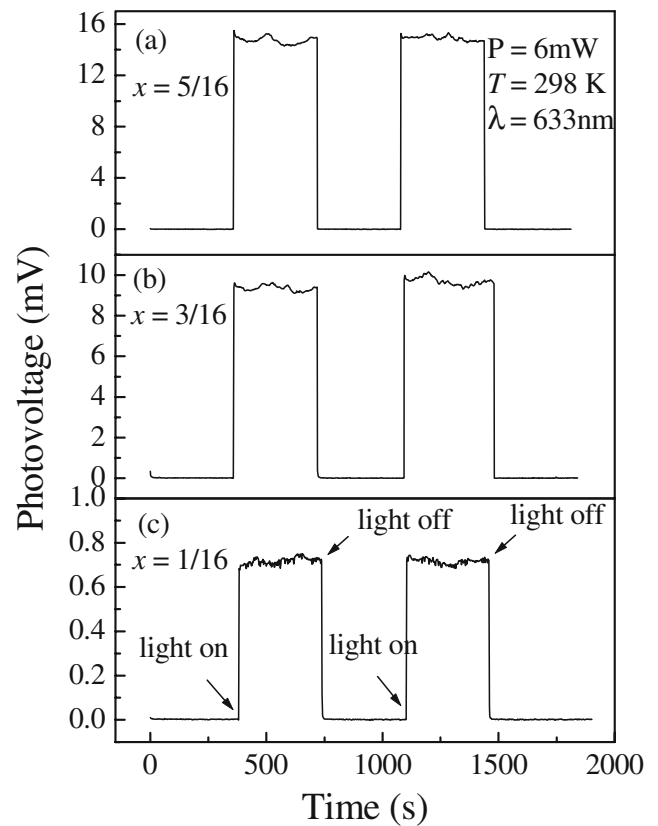

Fig. 9 Response of photovoltage to light illumination measured at 298 K under the light power of 6 mW ($\lambda=633$ nm) in the $La_{1-x}Ca_xMnO_3$/SNTO junctions

illumination through exciting electrons across the band gap. To counteract the current thus produced, a voltage has to be established between the two electrodes of the junction, which is the origin of the photovoltage.

4 Conclusion

We have studied the stability of the CO state for the $R_{1-x}Ca_xMnO_3$ ($R =$ La, Pr, and Sm) series and the rectifying characteristics and photovoltaic effect of the LCMO/SNTO heterojunctions. We found that the stability of the CO state is closely related to the magnitude of the JT distortion, and the composition having the most stable CO state for the each doped system shifts gradually toward lower Ca^{2+} concentration with decreasing the radius of the doped rare-earth elements. These junctions show good rectifying properties in a wide temperature range from 85 to 305 K and a strong photovoltaic effect at room temperature. We believe that this result will motivate further study of the exact electronic structure of both electron and hole doped manganites and may open up an alternative approach towards spintronics.

Fig. 8 I–V characteristics of $La_{1-x}Ca_xMnO_3$/SNTO p–n junction at various temperatures

References

1. Y. Tokura (ed.), *Colossal Magnetoresistive Oxides* (Gordon and Breach, Tokyo, 1999)
2. H. Tanaka, J. Zhang, T. Kawai, Phys. Rev. Lett. **88**, 027204 (2002)
3. Y. Okimoto, Y. Tomioka, Y. Onose, Y. Otsuka, Y. Tokura, Phys. Rev., B **57**, 9377 (1998)
4. M. Tokunaga, N. Miura, Y. Tomioka, Y. Tokura, Phys. Rev., B **57**, 5259 (1998)
5. C. Mitra, P. Raychaudhuri, K. Dörr, K.-H. Müller, L. Schultz, P.M. Oppeneer, S. Wirth, Phys. Rev. Lett. **90**, 017202 (2003)
6. Y.M. Xiong, T. Chen, G.Y. Wang, X.H. Chen, X. Chen, C.L. Chen, Phys. Rev., B **70**, 094407 (2004)
7. J.R. Sun, S.Y. Zhang, B.G. Shen, H.K. Wong, Appl. Phys. Lett. **86**, 053503 (2005)
8. K. Hatsuda, T. Kimura, Y. Tokura, Appl. Phys. Lett. **83**, 3329 (2003)
9. A.K. Raychaudhuri, A. Guha, I. Das, R. Rawat, C.N.R. Rao, Phys. Rev., B **64**, 165111 (2001)
10. J.M.D. Coey, M. Viret, L. Ranno K. Ounadjela, Phys. Rev. Lett. **75**, 3910 (1995)
11. S. Satpathy, Z.S. Popović and Filip R. Vukajlović, Phys. Rev. Lett. **76**, 960 (1996)