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Irreversible photoinduced insulator-metal transition in the Na-doped manganite $Pr_{0.75}Na_{0.25}MnO_3$

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Persistent photoconductivity has been observed in a perovskite manganite doped with an alkali metal element, $Pr_{0.75}Na_{0.25}MnO_3$. Considering the shallow penetration depth ($\sim 0.1\ \mu m$) of visible light, the increase of the conductance is estimated to be of the order of 10^4 to 10^5, which implies an irreversible photoinduced insulator-metal transition. Analysis of the dc- and ac-susceptibility data shows that the system is in a glassy state below 45 K. The system is therefore viewed as being in a highly nonuniform and metastable state, in which ferromagnetic metallic clusters exist in insulating matrix. The photoexcitation helps the clusters to dislodge from a local energy minimum and to seek more stable configuration. The percolative conduction can well explain the observed large increase of the conductivity. We argue that metastability is due to the large charge mismatch between the monovalent Na^+ ion and Pr^{3+} or the incommensurability of the Mn valency from 3.5+.

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I. INTRODUCTION

Phase control by a photon such as photoinduced insulator-metal transition (PIMT) has recently attracted much attention. The photon triggers a collective change of the electronic state. A material that has a mixed valence with localized electrons, and strong electron-lattice coupling can be a good candidate for the PIMT. Photons delocalize the electrons and the excited electrons cause a lattice relaxation, resulting in a collapse of charge gap. Perovskite manganites with general formula $R_{1-x}A_xMnO_3$, where R is a rare-earth ion and A is a monovalent alkaline ion or a divalent alkaline-earth ion, are among the candidates, because they have mixed valent Mn^{3+} and Mn^{4+}, and strong electron-lattice coupling due to the Jahn-Teller effect.

$Pr_{0.7}Ca_{0.3}MnO_3$ is a charge ordered (CO) insulator below 220 K with Mn^{3+} and Mn^{4+} in a checkerboard array due to the Coulomb repulsion and the Jahn-Teller interaction. A first-order phase transition to a ferromagnetic metallic (FM) phase occurs under a magnetic field giving rise to the colossal magnetoresistance (CMR).[1] The transition is accompanied by a relaxation of Jahn-Teller distortions and the metallic state is sustained below 60 K after the removal of the magnetic field.

In a single crystal $Pr_{0.7}Ca_{0.3}MnO_3$, insulator-metal transition by IR/visible light was reported by Miyano *et al.*[2,3] The photoinduced metallic state is not stable and goes back to insulating state when applied electric field is turned off. Therefore, it can be regarded as an avalanche effect or a dielectric breakdown triggered by light illumination.

On the other hand, irreversible insulator-metal transition was observed under x-ray illumination below 40 K in the same compound.[4] It is later argued that ferromagnetic clusters appear below 120 K and the x-ray irradiation leads to the cluster coalescence and phase segregation of the FM state.[5] Transport is thus governed by the percolation.[6]

Persistent photoconductivity (PPC) by visible light was first observed in oxygen deficient $La_{0.7}Ca_xBa_{1-x}MnO_3$ thin film by Cauro *et al.*[7] The mechanism is suggested as follows. First, a photon creates an electron-hole pair. The electron is trapped in an oxygen vacancy while the hole cannot recombine with the electron due to the lattice distortion. Thus the number of the hole carriers increases and the system, initially in the low-doped insulating region in the electronic phase diagram, moves into the high-doped metallic state.[8]

Persistent photoconductivity via yet another route has been recently demonstrated in Cr-doped $Pr_{0.5}Ca_{0.5}MnO_3$ thin films.[9] The Cr acts as a random field that disrupts otherwise stable CO state. As a result, FM cluster appears as the CO state grows. The light illumination connects the clusters resulting in the PPC through the percolative transport. The effect is, however, an increase of conductivity by a modest factor of 2 and no sign of volumetric increase of the FM state is suggested.

$Pr_{1-x}Na_xMnO_3$ is a manganite doped with monovalent alkaline metal Na and a CO insulator in the range $0.2 \leqslant x \leqslant 0.25$.[10] Relatively low magnetic field (~ 1.5 T) induces an insulator-metal transition. This is even lower than the well-studied CMR material, $Pr_{0.7}Ca_{0.3}MnO_3$.[1] Therefore, one can expect that the energy barrier between antiferromagnetic (AF) CO and FM states is small and hope for a significant decrease of resistance by light illumination.

In this paper, we will show that $Pr_{1-x}Na_xMnO_3$ is in cluster glass (CG) state below 45 K based on the resistance and dc/ac magnetization measurements. Furthermore, we have

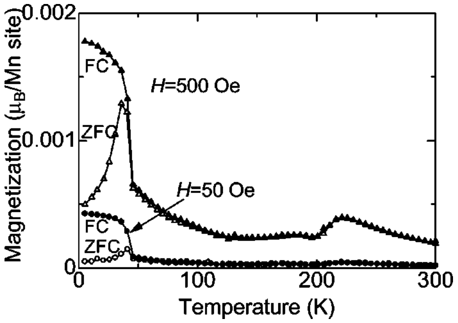

FIG. 1. Temperature dependence of dc magnetization in zero-field- cooled (ZFC) and field-cooled (FC) runs under 50 Oe and 500 Oe.

observed insulator-metal transition by photon in the energy range 0.1–2.3 eV, and ascribe it to an increase of FM cluster in the CO matrix.

II. EXPERIMENTAL

Polycrystalline sample was prepared using a solid state reaction with a detailed description published elsewhere.[11] The sample is oxygen-deficient–actual-valency Mn$^{3.39+}$ by chemical analysis. dc magnetization and ac susceptibility were measured with a SQUID magnetometer (Quantum Design MPMS) in the temperature range of 5–300 K. In the dc measurement, the sample was cooled under either magnetic field (FC) or zero magnetic field (ZFC), and the magnetization was measured during the subsequent warming. The ac susceptibility was measured at 0.1, 1, 10, and 100 Hz as a function of temperature. The resistance was measured by two-wire method with a gap of 50 μm in a constant current mode. The samples were placed inside a He flow type cryostat in which the temperature is controlled within 1 K. We used three types of light sources for illuminating the sample. A second-harmonic light with photon energy of 2.33 eV ($\lambda=532$ nm) pumped with a cw Nd:YVO$_4$ laser light was focused with a cylindrical lens on the gap of the electrodes. A laser light of an optical parametric amplifier (OPA) in the photon energy range of 0.25 eV ($\lambda=5$ μm)$\sim$1.55 eV ($\lambda=800$ nm), pumped with a mode locked Ti:sapphire laser light with a pulse width of 200 fs and at a repetition rate of 1 kHz, was focused in the same way as above. A CO$_2$ laser with photon energy of 0.12 eV ($\lambda=10.6$ μm) was illuminated to the sample without focusing. Since these three measurements were performed under different conditions, one cannot make a quantitative comparison among them.

III. RESULTS AND DISCUSSIONS

We show in Fig. 1 temperature dependence of dc magnetization in ZFC and FC runs under 50 and 500 Oe. The cusps at $T_{\rm CO}=220$ K and $T_N=170$ K are the charge ordering transition temperature and the Néel temperature, respectively. The difference between ZFC and FC appearing below $T_{\rm irr}=45$ K suggests the spin glass (SG) state.

For further investigation into the glassy state, we performed ac susceptibility measurements. Figure 2 shows the temperature dependence of in-phase component $[\chi'(T)]$ of ac-susceptibility in an ac field of 5 G for the frequencies 0.1, 1, 10, and 100 Hz. $\chi'_{\rm ac}$ presents cusps around $T_f=43$ K (see inset), which is close to $T_{\rm irr}$. The cusps shift toward a higher temperature with increasing frequency, which is typical of a glassy state. However, the frequency dependence of the shift of the cusp in $\chi'_{\rm ac}$, i.e., $p=\delta T_f/(T_f\delta\log_{10}f)\sim10^{-4}$, is much smaller than the typical values for canonical spin glass systems in which p ranges from 0.0045 to 0.28.[12] Therefore, the result suggests the system is CG rather than SG.

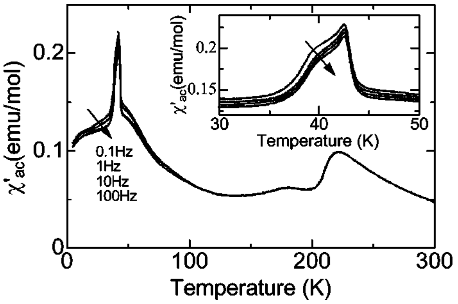

FIG. 2. Temperature dependence of in-phase component $[\chi'_{\rm ac}(T)]$ of ac susceptibility in an ac field of 5 G for the frequencies of 0.1, 1, 10, and 100 Hz, respectively. The inset shows a magnification of the cusp region.

Magnetic measurements under various conditions are complied to construct a magnetic phase diagram of Pr$_{0.75}$Na$_{0.25}$MnO$_3$ shown in Fig. 3. The critical magnetic field

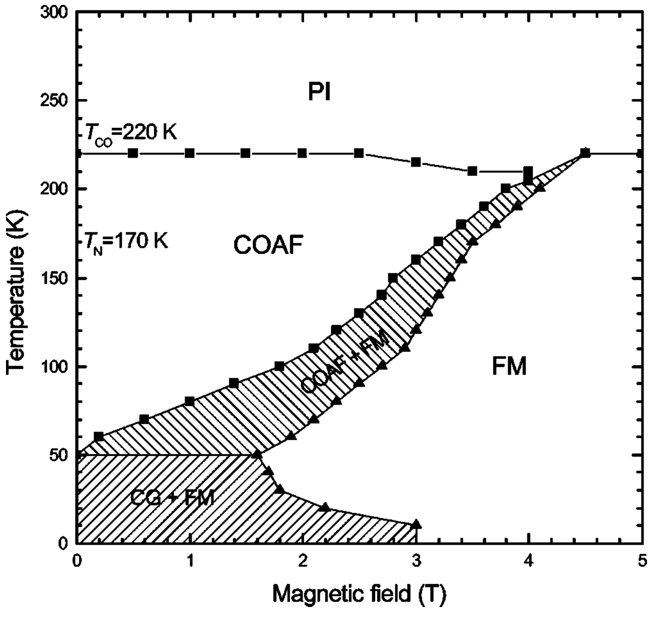

FIG. 3. Magnetic phase diagram of Pr$_{0.75}$Na$_{0.25}$MnO$_3$. The critical magnetic field was determined by M-H loops at each temperature. $T_{\rm CO}$ under each magnetic field was estimated with a temperature dependence of the magnetization. The PI, COAF, FM, and CG denote the paramagnetic insulating, charge ordered antiferromagnetic, ferromagnetic metallic, and cluster glass states, respectively. The $T_{\rm CO}$ denotes the charge ordering transition temperature. Shaded portions above and below 50 K are hysteresis regions between COAF and FM, and between CG and FM, respectively.

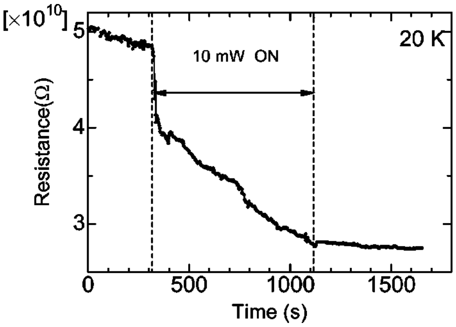

FIG. 4. Resistance as a function of time at 20 K. The sample was irradiated with a cw laser ($h\nu = 2.33$ eV) at the power density of 10 mW/0.01 cm^2.

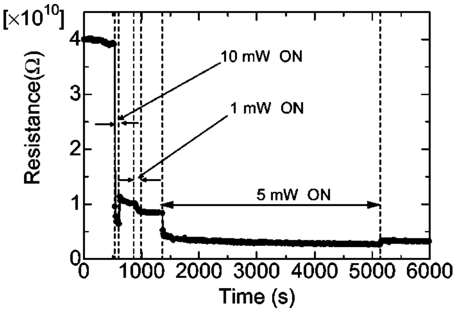

FIG. 6. Resistance as a function of time at 20 K. The sample was irradiated with a pulse laser ($h\nu = 1.55$ eV,200 fs,1 kHz) at the average power density of 10, 1, and 5 mW/0.01 cm^2, respectively.

was determined by M-H loops at each temperature. T_{CO} under each magnetic field was estimated with a temperature dependence of the magnetization. A striking feature is that AFCO-FM transition is induced by relatively low magnetic field (~1.5 T) at 50 K. Below 50 K, the FM state is metastable even without magnetic field, suggesting that FM clusters exist in the CO insulating matrix.

Figure 4 shows the transport response to the light illumination at 2.33 eV at 20 K and Fig. 5 at 60 K. The initial resistance was about 5×10^{10} Ω at 20 K and 1.1×10^7 Ω at 60 K. Just after the light illumination starts, the resistance decreases abruptly. While the resistance at 60 K recovered to the initial value when light is turned off, the resistance at 20 K remains low, i.e., persistent photoconductivity. It lasts as long as the sample is kept below 50 K.

To investigate both pulse width dependence and photon energy dependence, we have utilized a tunable pulse laser (200 fs pulse width, 1 kHz repetition rate) in photon energy range of 0.25 eV ($\lambda = 5$ μm)~1.55 eV (800 nm). Typical results are shown in Figs. 6 and 7. These results obtained at 20 K indicate that even very short pulses can induce the PPC in the photon energy range from 0.25 eV although the excitation with 0.25 eV is less efficient. A comparison between Figs. 4 and 6 shows that the effect depends on the integrated photon fluence and that there is no significant nonlinear process involved. It is worth noting that judged from the penetration depth (~0.1 μm) of the light used, the increase of the conductance in Fig. 6 implies the conductivity increase of the order of 10^4 to 10^5 in the photoexcited portion of the sample.

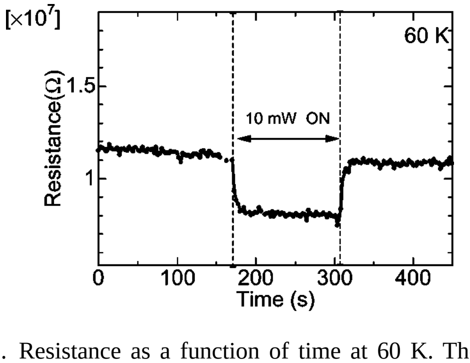

FIG. 5. Resistance as a function of time at 60 K. The sample was irradiated with a cw laser ($h\nu = 2.33$ eV) at the power density of 10 mW/0.01 cm^2.

The photon energy dependence of PPC was further investigated. We used CO_2 laser with 0.12 eV photon energy. As shown in Fig. 8, no PPC was observed at 20 K. The decrease in resistance during the light illumination is probably due to the heating effect.

In a perovskite manganite $R_{0.5}A_{0.5}MnO_3$, in which A site cation radius is small or the mismatch of the cation radii is large, the system has strong randomness. Randomness promotes a glassy state by bringing frustration into the competition between the double exchange ferromagnetic interaction and the superexchange antiferromagnetic interaction. The randomness also induces phase separation.[13] In the case of $Pr_{0.7}Ca_{0.3}MnO_3$, the system is spin glass state due to the incommensurability of Mn valency from 3.5+. The average valency of Mn in $Pr_{0.75}Na_{0.25}MnO_3$ is +3.39, i.e., the same as in $Pr_{0.61}Ca_{0.39}MnO_3$. Therefore, we ascribe the CG state in $Pr_{0.75}Na_{0.25}MnO_3$ below 45 K to the randomness of the large charge mismatch between Pr^{3+} and Na^{+} or the incommensurability of Mn valency from 3.5+.

Although in the case of $Pr_{0.61}Ca_{0.39}MnO_3$, the CO state is stable and robust against the magnetic field, the cation charge mismatch or incommensurability in $Pr_{0.75}Na_{0.25}MnO_3$ appears to be large enough to disrupt the CO state and to bring the critical field down to 1.5 T. The instability of the CO state is such that, once it is destroyed by the screening by the photocarriers, at least part of it does not recover. Hence, the

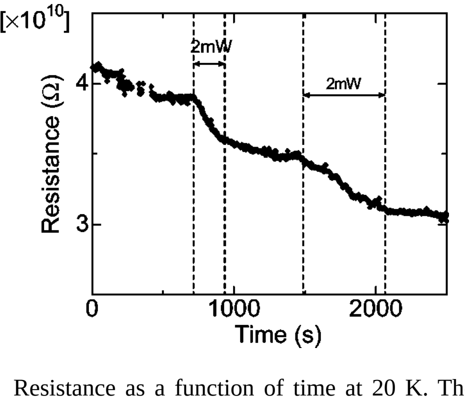

FIG. 7. Resistance as a function of time at 20 K. The sample was irradiated with a pulse laser ($h\nu = 0.25$ mW,200 fs,1 kHz) at the average power density of 2 mW/0.01 cm^2.

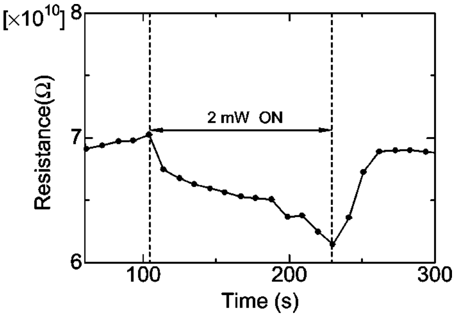

FIG. 8. Resistance as a function of time at 20 K. The sample was irradiated with a cw laser ($h\nu = 0.12$ eV) at the power density of 2 mW/0.1 cm^2.

metastable FM clusters grow, leading to PPC with percolative conduction. Note that the large conductivity increase of the order of 10^4 to 10^5 can only be explained in terms of net growth of the FM state rather than rearrangement of existing FM clusters.[9]

In the case of $Pr_{0.69}Ca_{0.31}MnO_3$, in which detailed optical measurements are available,[14] the CO gap is 0.2 eV. Because the mechanism for the gap formation should be the same in $Pr_{0.75}Na_{0.25}MnO_3$, the CO gap must be of a similar magnitude as well. The fact that the PPC was observed not at 0.12 eV but at 0.25 eV is therefore quite reasonable because a single particle excitation beyond the CO gap muse be a prerequisite for the destruction of the charge order.

Although the observed PPC with the cw laser is similar to that in $La_{0.7}Ca_{0.3}MnO_{3-\delta}$, we doubt that our PPC is due to the oxygen deficiency. $Pr_{0.75}Na_{0.25}MnO_3$ is a CO insulator and no metallic state can appear with increasing hole concentration x contrary to $La_{0.7}Ca_{0.3}MnO_{3-\delta}$. It should be noted that PPC occurs with pulse laser in $Pr_{0.75}Na_{0.25}MnO_3$ while it does not in oxygen deficient material such as $YBa_2Cu_3O_x$.[15]

IV. CONCLUSIONS

$Pr_{0.75}Na_{0.25}MnO_3$ is a charge ordered insulator which shows colossal magnetoresistance under relatively low magnetic field (1.5 T). Below 45 K, the system is in a highly nonuniform and metastable state, in which ferromagnetic metallic clusters exist in insulating matrix. Light illumination makes the charge ordered gap collapse, and the clusters expand. The persistent photoconductivity was observed due to the percolation conduction.

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