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Photo-induced Modulation of Ferroelectric Polarization in Multiferroic $TbMnO_3$

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***Abstract*—$TbMnO_3$ is a multiferroic material with a complex magnetic structure at low temperature, giving rise to spin ordering induced ferroelectricity. We show that this material exhibits a photo-induced transient current below the ferroelectric transition temperature. The result is interpreted in terms of a photo-induced polarization modulation generating the transient pyroelectric current detected by its associated transient voltage. The experiments demonstrate a relatively simple technique to study the ferroelectric polarization modulation in multiferroic materials..**

Keywords—multiferroics, photo-induced transient voltage, polarization modulation

I. Introduction

The ability to control different states of ferroelectric materials by optical means has important applications in device technology such as optically addressed ferroelectric memories [1]–[3] and optically driven mechanical actuators [4]. Among the most widely studied materials in this connection is the lead zirconate titanate (PZT). More recently, efforts have also been dedicated to develop new functional materials, often based on complex oxides [5], [6] exploiting their intricate interplay between the charge, lattice, and spin degrees of freedom in these materials. One of the strong driving forces behind this research is the need for new types of electronic devices and for lead-free non-toxic ferroelectric devices to be used in for instance biomedical applications.

This paper reports the results of a study of photo-induced ferroelectricity modulation in one of the complex oxides, namely the multiferroic material TbMnO3. The interest in this compound derives from its complex magnetic structure which in the low temperature phase is known to display a magnetically driven spontaneous ferroelectric polarization [7]. Possessing a highly distorted orthorhombic crystal structure, TbMnO3 exhibits frustrated magnetic interactions arising from the competition between ferromagnetic (FM) coupling of nearest neighbor and antiferromagnetic (AFM) coupling of next nearest neighbor manganese spins [8]. These competing magnetic interactions lead to the formation of a sinusoidal spin structure below 41K, and a spiral structure below 26K. The latter phase is the one which is responsible for the appearance of a spontaneous ferroelectric polarization.

One of the intriguing phenomena observed in normal ferroelectrics is the photo-excitation induced transient current [9]–[12]; a phenomenon which is sensitive to the polarization state of the material [10]. Several interpretations have been proposed to understand the origin of the induced transient current, including transient pyroelectric current [9], photovoltaic [10], [11], and photo-strictive [12] effects. Here we demonstrate that light irradiation can also induce a transient pyroelectric current in the ferroelectric phase of a TbMnO3 even though the static electric polarization is very small compared to that in conventional ferroelectric materials. We conclude that for TbMnO3 the transient current is induced by a thermal modulation of the ferroelectric polarization. Subsubsection text here.

II. Material Characterization and Experiments

The TbMnO3 single crystal used in this study was grown using a traveling solvent floating zone method utilizing a four mirror furnace (Crystal System Corp., FZT-10000-H-VI-VP). The crystal structure was characterized by X-ray powder diffraction using a Bruker D8 diffractometer for room temperature measurements and a Huber G670 diffractometer for experiments at low temperatures. The diffraction experiments confirm a single crystalline phase with orthorhombic unit cell having Pbnm space group [13]. The lattice parameters at room temperature are a = 5.29969(9)Å, b = 5.84236(9) Åand c = 7.40147(12)Å.

The magnetization of our sample was measured using a Quantum Design MPMS-7 SQUID magnetometer in an applied magnetic field of 0.5T. To show that our sample is indeed multiferroic, we performed a pyroelectric current experiment. For this we used a Keithley 387 voltage source to pole the sample in a field of 150 V/mm while cooling it below the ferroelectric phase transition at 26 K. After removing the poling voltage, we measured the pyroelectric current using a Keithley 6517A electrometer while heating up the sample. The electric polarization was then determined by integrating the detected pyroelectric current.

Having been assured of the multiferroic nature of the sample, we investigated the ferroelectricity modulation by measuring the transient voltage following laser illumination of the sample. The electronic circuit and sample orientation are schematically depicted in Fig. 1. For this experiment, two gold pads of 1 mm^2 were deposited on the *a-c* plane of the sample with 2 mm spacing in the c direction. Platinum wires were used to connect these gold electrodes to the terminals of a chip carrier. The sample was mounted on the cold finger

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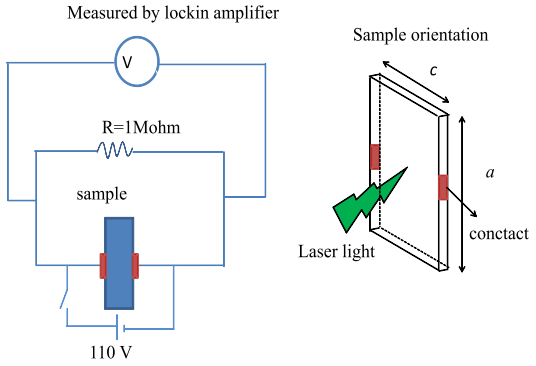

Fig. 1. The experimental setup and sample orientation for photo-induced transient voltage experiment

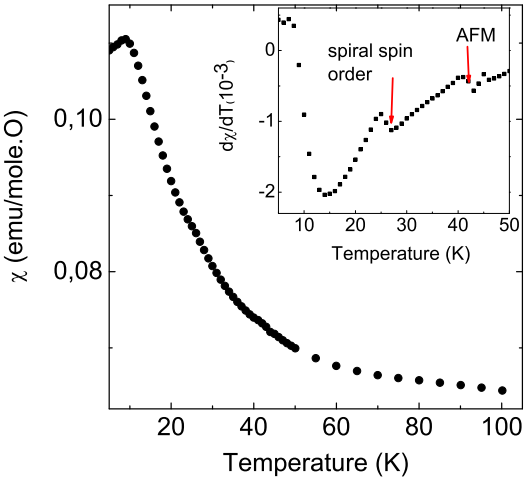

Fig. 2. The magnetic susceptibility measured along the *c*-axis. The inset shows the derivative of the susceptibility displaying the AFM and spiral spin order transisition

of a He flow cryostat. A 110 V external voltage from a Keithley 236 was used to pole the sample during cooling and was disconnected during measurement of the induced transient voltage along the *c* axis (Vc). The photo-induced voltage was measured by illuminating the sample in the *ac* plane with a 532 nm continuous wave laser modulated by a 100 Hz chopper and recording the resulting amplitude of the transient voltage across the sample using a SR-830 lock-in amplifier synchronized to the chopper frequency from 10K up to 35K. In order to get insight into thermal effects on transient voltage, a separate transient voltage measurement was performed using a heat pulse generated by Philips PM 5712 pulse generator with 1 kHz frequency and output energy of 1 μJ/pulse. The transient signal was measured with the same set up as for photo-induced transient voltage measurement.

III. Results

The magnetic susceptibility (χ) observed along the *c* axis direction is shown in Fig. 2. The magnetic susceptibility is dominated by the response of the Tb^{3+} sublattice, which shows the typical paramagnetic 1/T dependence and antiferromagnetic ordering below 7 K. The inset of Fig. 2 shows the temperature derivative of the susceptibility to highlight the changes occurring at the temperatures where the Mn sublattice orders. These phase transitions are clearly marked by abrupt changes at 41K and 26K, associated with the occurrence of the sinusoidal AFM and the spiral spin structures, respectively.

The spiral spin transition coincides with the appearance of spontaneous polarization along the *c* axis, as indicated in Fig. 3, evidencing the multiferroicity of the sample. It is shown that the polarization sets in at 26 K and reaches a maximum of about 600 $\mu C/cm^2$, consistent with earlier reports [7]. This spontaneous polarization is about 1000 times smaller than the polarization observed in PZT [14]. The enhancement observed below 7K, a phenomenon not observed in conventional ferroelectric materials, coincides with the formation of AFM ordering in the Tb sublattice. Supposedly, it is due to the magnetic coupling between the Tb and Mn spins that leads to the observed enhancement of the electric polarization as proposed previously [15], [16].

Having presented the results of those initial characterization experiments, we now turn to the photo-induced pyroelectric experiment. Fig. 4 shows some typical photo-induced transient voltage curves obtained using the configuration depicted in Fig. 1 for a number of photo-excitation power densities. The curves show a sudden rise of the signal below a certain temperature in the vicinity of the ferroelectric transition temperature. Upon lowering the temperature the voltage rapidly reaches a peak value and thereafter reduces again to a more or less temperature independent level at lower temperatures. The amplitude of the transient voltage is seen to increase with increasing laser power density. The fact that the onset of the initial transient signal is about 2 K below that of ferroelectric transition is due to the reduced thermal contact of the sample mounted in a chip carrier with the cold finger of the cryostat. Apart from that, the onset temperature is also observed to depend on power density. We attribute this latter shift to a temperature rise of the sample due to laser heating (about 3 K at 21 W/cm^2).

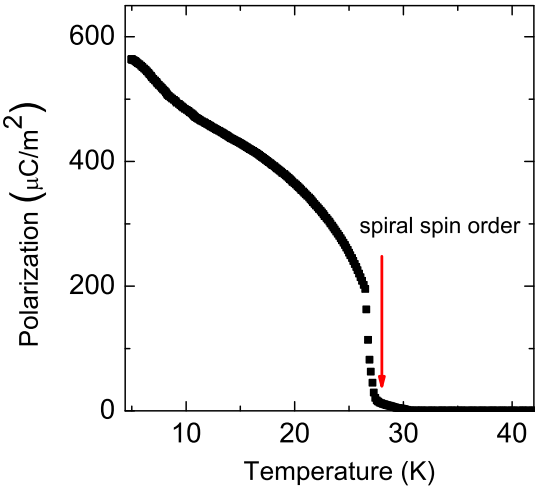

Fig. 3. The temperature dependent electric polarization measured along the *c*-axis.

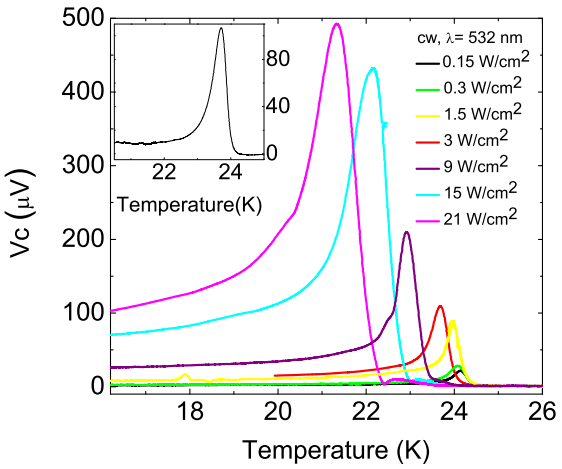

Fig. 4. The temperature dependent transient voltage induced by 532 nm laser light of power density varying from 0.15 up to 21 W/cm^2. The inset shows a typical curve of the transient voltage induced by heat pulse.

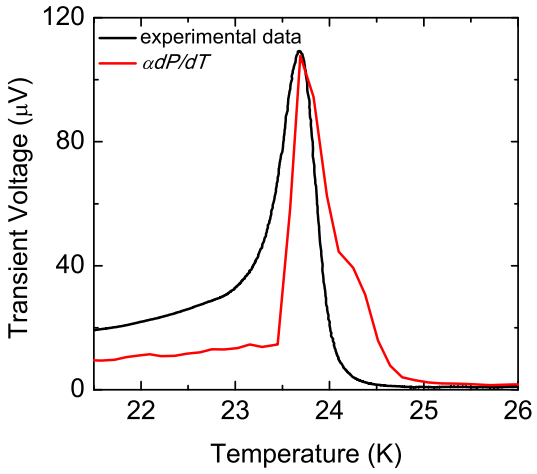

Fig. 5. Comparison between the observed transient voltage (black line) at a laser power density of 3 W/cm^2 with the derivative of the curve of Fig. 3, *dP/dT* (red line). The temperature scale of *dP/dT* has been shifted to match with the onset of transient voltage

The inset of Fig. 4 shows the similarity between temperature dependent photo-induced transient voltage and a typical result obtained using the heat pulse method. This similarity indicates that the observed transient voltage has its origin in the pyroelectric current produced most likely by thermally modulating ferroelectric polarization.

IV. Discussion

The observed pyroelectric current (*I*) is induced by the time variation of the ferroelectric polarization (*P*) [17]:

$$I = A\frac{dP}{dt} = A\frac{dP}{dT}\frac{dT}{dt} \tag{1}$$

where *A* is the electrode area. In static experiments, one keeps the rate of change of temperature constant over a wide temperature range. Hence the electric polarization can be approximated as the integral of current over temperature (*T*), or alternatively over time (*t*):

$$P = \int \frac{I}{A}\left[\frac{dT}{dt}\right]^{-1} dT = \int \frac{I}{A} dt \tag{2}$$

This formula is used to obtain the electric polarization as presented in Fig. 3.

As discussed above, we interpret the appearance of the observed transient voltage as due to a modulation of the temperature, and hence of the polarization, induced by the modulated laser irradiation. To find the connection between the transient voltage and the temperature modulation we consider a simplified situation where the temperature variation is modeled by a sinusoidal modulation at the frequency ω of the optical chopper:

$$T(t) = T_i + \Delta T_{av} + \Delta T_m sin(\omega t) \tag{3}$$

where T_i and T_{av} are the temperature without laser illumination, and the laser induced average temperature rise, respectively. The third term represents the temperature modulation due to the chopped laser which induces the polarization modulation. Substituting Eq. 3 into Eq. 1 yields the pyroelectric current modulation

$$I(T) = A\Delta T_m \omega cos(\omega t)\frac{dP}{dT} \tag{4}$$

Therefore, assuming small modulations such that *dP/dT* can be taken as constant, the root mean square (rms) transient voltage measured by the lock-in amplifier can be expressed as

$$V_{rms} = RI_{rms} = \frac{RA\Delta T_m \omega cos(\omega t)}{\sqrt{2}}\frac{dP}{dT} \tag{5}$$

where *R* is the total resistance in the electronic circuit and *dP/dT* is the derivative of the curve in Fig. 3.

Though the approximations made above are not always fully justified, in particular the assumption of constant *dP/dT* at high laser powers, the simplified model does show a fairly good agreement between the temperature dependence of the measured transient voltage and derivative of Fig. 3 (scaled by a constant α), as shown in Fig. 5.

V. Conclusion

We have shown that the ferroelectric nature of the multiferroic complex oxide $TbMnO_3$ can be studied by means of laser induced pyroelectric current modulation experiments. Even though the electric polarization in this system is very small in comparison to those of conventional ferroelectric systems, the polarization modulation is readily observed in our experiment and is interpreted in terms of a temperature modulation of the ferroelectric polarization on the basis of rms response. It would be interesting to extend this method into the time domain in order to elucidate the dynamical properties of the polarization modulation in multiferroic oxides and their potential in fast switching applications.

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REFERENCES

[1] J.F. Scott and C.A. P. De Araujo, *Ferroelectric Memory* , Science, vol. 246, pp. 1400-1403, Dec 1989.

[2] S. Takhoor, *High speed, nondestructive readout from thinfilm ferroelectric memory*, Appl. Phys. Lett., vol 60, pp. 3319-3321, Jun 1992

[3] S. Takhoor, E. Olson, and R. H. Nixon, *Optically Adressed Ferroelectric Memory and Its Applications*, Integrated Ferroelectrics vol 4. pp.257-269, Aug 2006

[4] T. Ikehara, M. Tanaka, S. Shimada, and H. Matshuda, *Optically Driven Actuator Using Photo-Induced Phase Transition Polymer*, Sensor and Acutuator, vol. 22, pp. 239-234, Nov 2001.

[5] G. Catalan and J.F. Scott, *Physics and Applications of Bismute Ferrite*, Advanced Materials, vol. 21, pp. 2563-2485, May 2009

[6] W. Prellier, M.P. Shingh, and P. Murugavel, *The Single-Phase Multiferroic Oxide*, J. Phys. Condens. Matt., vol.17, pp. R803, July 2005.

[7] T. Kimura, T. Goto, H. Shintani , K. Ishizaka, T. Arima and Y. Tokura, *Magnetic Control of Ferroelectric Polarization*, Nature, vol. 426, pp. 55, Nov 2003.

[8] T. Kimura, S. Ishihara, H. Shintani, T. Arima T, K.T. Takahashi, K. Ishizaka, and Y. Tokura , 2003, *Distorted Perovskite with e_g^1 Configuration as a Frustrated Spin System*, Phys. Rev. B, vol. 68, pp. 060403

[9] J. Lee, S. Esayan, J. Prohaska, and A. Safari, *Reversible pyroelectric and photogalvanic current in epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films*, Appl. Phys. Lett. Vol. 64, pp. 294, 1994.

[10] A. Kholkin, O. Boiarkine, and N. Setter, *Transient photocurrents in lead zirconate titanate thin films*, Appl. Phys. Lett, vol. 72, pp. 130, 1998.

[11] Kui Yao, Bee Keen Gan, Meima Chen, and Santiranjan Shannigrahi, *Large photo-induced voltage in a ferroelectric thin film with in-planepolarization*, App. Phys. Lett. 87, 212906, 2005.

[12] A. L. Kholkin, S. O. Iakovlev, and J. L. Baptista, *Direct effect of illumination on ferroelectric properties of lead zirconate titanite thin films*, Appl. Phys. Lett., vol. 79, pp. 2055, 2001.

[13] N. Mufti, A.A. Nugroho, G.R. Blake, and T.T.M. Palstra, *Relaxor ferroelectric behavior in Ca-doped $TbMnO_3$*, Phys. Rev. B ., vol 78, pp. 024109, 2008

[14] H. Nakaki, H. Uchida, S. Koda, S. Okamoto, H. Funakubo, *Enhancement of spontaneous polarization in lead zirconate titanate thin films by Dy^{3+} substitution*, App. Phys. Lett., vol. 87, pp. 182906, 2005

[15] T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, *Ferroelectricity and Giant Magnetocapacitance in Perovskite Rare-Earth Manganites*, Phys. Rev. Lett., vol. 92, pp. 257201, June 2004

[16] O. Prokhnenko, R. Feyerherm, E. Dudzik, S. Landsgesell, N. Aliouane, L.C. Chapon, and D.N. Argyriou, "Enhanced Ferroelectric Polarization by Induced Dy Spin Order in Multiferroic DyMnO3" Phys. Rev. Lett., vol. 98, pp. 057206, Feb 2007.

[17] H.J.Sajosh, *The Influence of Temperature Gradient on The Dynamic Pyroelectric Current in Monoaxial Ferroelectric Having a Second Order Phase Transformation*, Infrared Physics, vol. 28, pp.263-269, 1988.