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The origin of thermally stimulated depolarization currents in multiferroic CuCrO$_2$

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We have measured the thermally stimulated depolarization currents (TSDC) of multiferroic CuCrO$_2$. We observe a sharp peak near the antiferromagnetic ordering temperature $T_N \sim 24\,K$, below which the material becomes ferroelectric. In addition, we observe three other peaks above T_N at $\sim$50, 120, and 150 K, when the poling is done at a higher temperature than T_N. These peaks are not related to exotic kinds of ferroelectricity. Using the poling field dependence of TSDC, the origins of the first two peaks are ascribed to the relaxation of defect dipoles and to space charge relaxation due to the release of trapped charges, respectively. Upon polishing, the peaks observed at 120 and 150 K disappear, suggesting a surface defect origin. Moreover, using temperature and frequency dependent dielectric measurements, we find Maxwell–Wagner type dielectric relaxation. In connection with the mechanism of one of the TSDC peaks, we suggest a Schottky barrier formation to explain the dielectric relaxation. © 2015 AIP Publishing LLC.
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The pyroelectric effect is of increasing significance for characterizing ferroelectrics (FE). This effect is being used when the measurements of polarization-electric field (P-E) hysteresis loop are not effective. This can be caused by the small electric polarization obtained in improper ferroelectric materials such as multiferroics.[1] In general, the pyroelectric effect occurs for pyro- or ferroelectric materials when the inversion symmetry is restored on heating the material through the polar ordering temperature.[2] However, the effect can also be detected in non-polar materials, such as in dielectric materials exposed to an external electric field, in secondary pyroelectrics[3] and even in non-piezoelectric materials that produce the flexoelectric effect.[4]

Current electrical polarization measurement methods involve either the direct measurement of polarization at constant temperature (P-E loops) or the measurement of the pyroelectric current (PC) with continuous temperature ramping. Although the PC measurement appears to be straightforward, the results can be easily misinterpreted, especially in the range where no phase transitions are observed using other measurement techniques. For instance, the PC measurement of GdMnO$_3$ performed by Zhang *et al*.[1] shows a deviation of $+7\,K$ from the transition reported by Noda *et al*. at 13 K.[5] An additional peak which does not correspond to a ferroelectric phase transition was also observed in the high temperature range. Current peaks that do not originate from ferroelectric phase transitions are commonly observed in different systems such as polymers, insulators, and semiconductors.[3,4] Here, they are called Thermal Stimulated Depolarization Currents (TSDC).[6,7] Various other reports interpret a current peak as a PC, without considering the

possibility of a TSDC.[8] Basically, the experimental procedures of a PC measurement and a TSDC measurement are similar. However, the technique measures a PC for polar materials in which the depolarization current originates from the disappearance of the spontaneous polarization resulting in a current peak. On the other hand, in non-polar materials, current peaks are observed due to the relaxation of poled defect dipoles due to the randomizing effect of increased temperatures. Therefore, a TSDC measurement is used for dielectrics to obtain information about defect dipoles, trap charges, and mobile ions.[9,10] Although the TSDC technique has been widely used to characterize defect properties and dielectric relaxation in many different systems, its use in characterization of defects and relaxation in multiferroic materials has only been recently demonstrated for multiferroic perovskites as well as related Y$_3$Fe$_5$O$_{12}$.[1,11–13] In this letter, we report on the observation and characterization of three distinct TSDC peaks in a multiferroic material. In comparison to other TSDC peaks reported on multiferroics so far, all of which having a bulk defect dipole origin, we observe additional peaks originating from different and surface related mechanisms. We show that the characteristics of the surface related peaks are different from those of the dipolar defect originated one.

In this study, we performed PC and TSDC measurements on polycrystalline delafossite CuCrO$_2$. The magnetism originates from Cr^{3+} forming the triangular lattice planes. CuCrO$_2$ is a multiferroic with two magnetic phase transitions at $T_N \sim 23.6\,K$ and 24.2 K.[14,15] However, Poienar and Hardy only verified one transition at $\sim$24 K.[16] It is confirmed that there is a strong coupling between the small lattice distortion and the magnetic ordering with an incommensurate proper screw spiral spin order resulting in ferroelectric polarization.[17] Since no other phase transition has been found in

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$CuCrO_2$, it is a good candidate for distinguishing possible TSDC peaks from the single PC peak related to ferroelectric phase transition induced by magnetic ordering. The origin of these TSDC peaks will be investigated from the poling field dependence of the TSDC. The activation energies will be evaluated from these current peaks.

Polycrystalline $CuCrO_2$ material was synthesized using CuO (99.99%) and Cr_2O_3 (99.99%) as starting oxides. A stoichiometric mixture of these oxides was heated to 1200 °C for 12 h to obtain $CuCrO_2$ in powder form. The powder was pressed into pellets and sintered at 1200 °C for 12 h. The process was repeated several times until $CuCrO_2$ was confirmed single phase by the refinement of the Powder X-ray Diffraction (PXRD) pattern. Silver electrodes were painted on the pellet with a surface area of 8.5 mm^2 and a thickness of 0.5 mm. The contacts at the two surfaces of the pellet were connected to the sample holder using 0.05 mm Pt wires. A poling electric field was applied to the sample at different temperatures, followed by cooling at a rate of 5 K/min to align the electric dipoles. Finally, the field is removed at 5 K and the stabilization of the polarization P was reached after shorting the circuit in 2 h to remove surface charges. The current was then recorded during heating using a Keithley 6517A electrometer. Dielectric properties were measured using an Agilent LCR Meter between 20 Hz and 1 MHz. Dc resistivity was measured using the Van der Pauw technique between 100 and 300 K. Physical Properties Measurement System (PPMS) was used to control the temperature of the measurement.

The PXRD pattern of polycrystalline $CuCrO_2$ (not shown) confirms that the material was the single phase delafossite structure. The space group $R\bar{3}m$ is in the hexagonal setting. The refined lattice parameters $a = 2.97528(5)$ Å $c = 17.1072(32)$ Å at room temperature are consistent with other studies.[15,16,18]

In Figure 1, we show the temperature dependence of the PC, which was measured with a heating rate of 5 K/min and after poling at 35 K at different electric fields. The PC is revers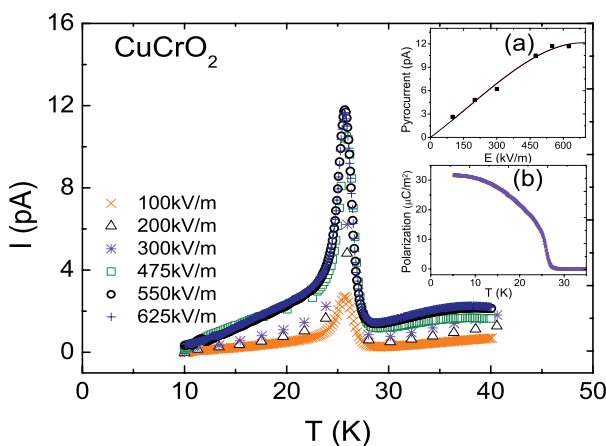ed when applying a reversed poling field. This confirms ferroelectric order by its reversible nature. We observe that a higher poling field results in a larger PC peak. In the inset (a), the dependence of the PC peak on the poling field is shown. The peak current saturates at ∼12 pA with a poling field of ∼500 kV/m. Hence, applying a higher external field to obtain a larger PC peak is unnecessary for determining the spontaneous polarization. Inset (b) presents the temperature dependence of polarization obtained by integrating the PC over time, recorded with a heating rate of 5 K/min after applying a poling field of +300 kV/m. The magnitude of the polarization is comparable to that reported in another study.[18]

The PC peaks are observed at ∼25.7 K in Figure 1 and do not exactly correspond to the phase transition temperature ∼24 K. Different heating rates of 1, 2, 5, and 10 K/min. were used while measuring the peak position to test the effect of heating rate. We observed that the PC peaks shift to higher temperatures for larger heating rates. The peak temperature has a linear dependence on the heating rate (not shown). This thermal lag depends on the specific heat and the thermal conductivity of the material, the dimensions of the sample and the measurement setup. A ramping rate of 1–2 K/min is the maximum to determine a reliable transition temperature.

In Figure 2, we present current curves obtained from poling at different temperatures measured with a heating rate of 5 K/min. It is clear that the temperature of the PC peak due to the phase transition ∼24 K is not affected by the temperature at which the poling is performed. However, the PC does not go to zero when the temperature exceeds T_N. Instead, two additional peaks above T_N can be clearly observed at ∼50 K (peak A) and ∼120 K (peak B) when poling is done at 35 K or 80 K. If the poling temperature is as high as 125 K, one more peak appears at ∼150 K (peak C). These additional current peaks above T_N have the same sign as the poling field. They are absent when the poling is done at temperatures lower than T_N. Poling below T_N reduces the ferroelectric PC as we observe in Figure 2. Nevertheless, an anomaly can be clearly seen at 15–20 K as a result of poling at 15 K. The black line demonstrates that no peak was observed when no external electric field was applied. It is clear that the temperature at which the poling electric field is applied plays a crucial role. Other studies have not reported observation of peaks other than that at $T_N \sim 24$ K, probably because they have not
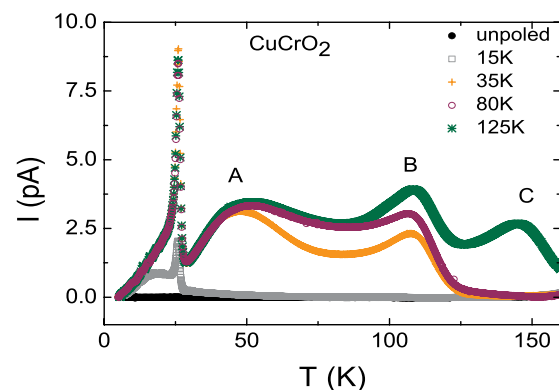
FIG. 1. Temperature dependence of the pyrocurrent of $CuCrO_2$ at different poling fields and a heating rate of 5 K/min. The inset shows (a) the poling field dependence of the magnitude of the PC peak associated with the phase transition and (b) the polarization calculated from a measurement using a poling field of 300 kV/m.

FIG. 2. TSDC versus temperature at different polarization temperatures at a heating rate of 5 K/min and a poling field of +400 kV/m.
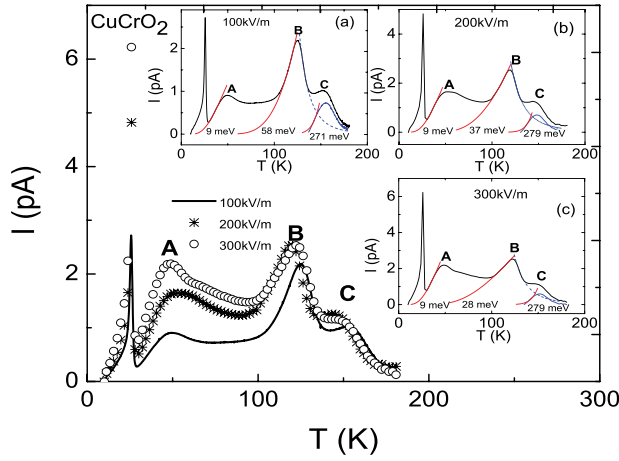
FIG. 3. Temperature dependence of TSDC at a heating rate of 5 K/min and peak fit for the sample poled at 125 K with an electric field of 100 kV/m (a), 200 kV/m (b), and 300 kV/m (c).

FIG. 4. Poling field dependence of the TSDC peaks A–C and of T_m^2 of peak B at a heating rate of 5 K/min and a poling temperature of 125 K.

started poling from such high temperatures.[18] Since these additional peaks are unrelated to the ferroelectric transition, they are called hereafter as the TSDC peaks.

A poling temperature of 125 K gives rise to three TSDC peaks. We investigated the poling field dependence of the peak current at this temperature at a heating rate of 5 K/min, shown in Figure 3 for three external fields 100, 200, and 300 kV/m. Peaks A, B, and C overlap. We notice that the TSDC peak is much broader than the sharp PC peak. We note that also other reported TSDC studies on polymers and inorganic crystals show broad TSDC peaks.[1,10,19,20] The broad TSDC peak in $CuCrO_2$ system might result from peak overlap due to closely spaced energy levels of relevant defect states. A peak cleaning process can be used to resolve the overlapping peaks.[20] We use the initial rise method[21] to fit the left side of the peaks with the relation $I = A \exp(-E_a/kT)$ to extract the activation energies E_a as demonstrated in the insets (a)–(c) of Figure 3. Since peak C is overlapped, it is resolved by subtracting from the original data the fitted data of peak B on the right side. The resulting peak is then fitted on the left side. The activation energy of peak A is fixed at 9 meV for three poling fields. For peak B, increasing poling fields give rise to a decrease of E_a from 58 to 28 meV. Activation energies of peak C show comparable values from 271 to 279 meV for three poling fields.

By plotting the maximum peak currents of each TSDC peak versus poling fields as shown in Figure 4, we observe a field dependence that can be used to assign the origin of the peaks. Peak A exhibits a linear relation of the maximum TSDC with the poling field. In addition, the temperature of the maximum of the peak, T_m, of peak A (observed in Figure 3) does not change for different poling fields. These characteristics are consistent with the reorientation of dipolar defects. These defects can be mathematically described by the below equation[7]

$$J(T) = \frac{P_e}{\tau_0} \exp\left(-\frac{E_a}{kT}\right) \exp\left[-\frac{1}{\beta\tau_0} \times \int_{T_0}^{T} \exp\left(-\frac{E_a}{kT'}\right) dT'\right],$$
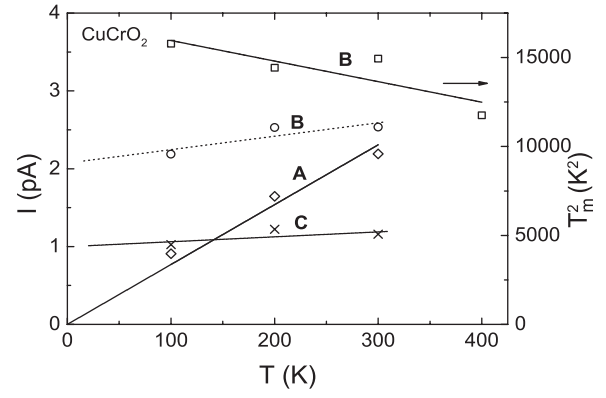
(1)

where $J(T)$ is the current density, τ_0 is the dipole relaxation time at infinite temperature, E_a is the activation energy of dipoles, k is the Boltzmann's constant, β is the heating rate, and P_e is the equilibrium polarization. P_e depends linearly on the poling field E_p given by $P_e = N\mu^2\alpha E_p/kT_p$,[7] where N is the dipole concentration, μ is electrical dipole moment for one dipole, α is a geometrical factor, and T_p is the poling temperature. By differentiating Eq. (1), we obtain the relation $T_m^2 = (E_a/k)\beta\tau_0 \exp(E_a/kT_m)$, which shows that T_m is independent of T_p and E_p, but is a function of β. Hence, T_m is a constant for a given heating rate, as we observe for peak A.

Thus, the data shows that peak A is consistent with the reorientation of defect dipoles. Similar TSDC peaks of dipole reorientation origin have been observed.[10,22] For example, Fe-doped $SrTiO_3$ ceramics show a TSDC peak with a linear dependence on E_p, also ascribed to dipolar relaxation. It has been suggested that defect dipole pair consists of a Fe^{3+} ion substituting the Ti^{4+} site and the compensating oxygen vacancies.[10] Dipolar defects in our case must be formed intrinsically because doping was not introduced during the synthesis. There are possible p-type conduction mechanisms with Cu^+/Cu^{2+} or Cr^{3+}/Cr^{4+} hole mobility.[23] According to first principles theoretical calculations by Scanlon and Watson[23] and Zhi-Jie et al.,[24] the prominent intrinsic defect in $CuCrO_2$ system is a Cu^+ vacancy which is compensated by the formation of Cu^{2+}, introducing holes. Based on these calculations, we suggest that the defect dipole pair in our case consists of a negatively charged Cu^+ vacancy and a hole localized at the Cu^{2+} site. In multiferroics $DyMnO_3$ and $TbMnO_3$, TSDC peaks around 90 K[11] and 110 K,[12] respectively, have been reported. These peaks have been assigned to hole carriers that redistribute and form dipoles upon the application of poling field,[11] which suggests a similar mechanism to that of our peak A. In these orthorhombic manganites, holes form due to the introduction of Mn^{4+} ions substituting Mn^{3+} in order to compensate the excess oxygen present due to growth conditions.[11,12] Activation energy of peak A calculated from the initial rise method is lower than the values reported in the literature for peaks originating from defect dipole reorientation. This can be accounted for in part by the observation of the peak at a much lower temperature than typical measurement temperatures in the literature. In TSDC measurements, liquid helium

temperatures are probed only recently for multiferroics due to their low ordering temperatures and TSDC peaks originating from defects are reported close to the ferroelectric ordering temperatures as mentioned above.

Figures 3 and 4 show that Peak B does not exhibit a linear dependence of the maximum peak current with the poling field. The maximum current does not change noticeably with the poling field. Therefore, peak B appears unrelated to dipole reorientation. We observe that peak B shifts to lower temperatures with increasing poling fields. A linear relation of the poling field with T_m^2 of the TSDC peaks has been observed for trapped charges.[25] Here, T_m shifts to lower temperatures with increasing field. We plot the poling field dependence of T_m^2 for peak B also in Figure 4. This shows a linear relation as reported.[10] Therefore, peak B is consistent with a relaxation of space charge polarization due to the release of trapped charges. These trapped states must be caused also by intrinsic defects in the bulk and/or at the interfaces between the semiconducting sample and the electrodes. Space charge polarization arises due to the formation of depletion layers at the Schottky barriers between the sample and the electrodes at the surface. These Schottky barriers can also give rise to Maxwell–Wagner type dielectric relaxation behaviour. We investigated the temperature dependence of the capacitance and dielectric loss measured at different frequencies. A step-like increase in the capacitance and a corresponding peak in the dielectric loss are observed (not shown). The step and the peak shifts to higher temperatures with increasing frequency, consistent with Maxwell–Wagner type relaxation resulting from the formation of Schottky barriers at the sample-contact interfaces at the surface.

The origin of peak C is more difficult to assign since the peak current does not clearly increase with the poling field nor varies T_m^2 linearly with the poling field. A possible origin can be the migration of ionic charge carriers (forming ionic space charge) to the electrodes under the poling field E_p at the poling temperature. Current peaks originating from the depolarization of the ionic space charge are reported to show no linear dependence on Ep and complex peak shapes.[26] On the other hand, there are also reports where a sin*h* function type dependence of the current on E_p is suggested.[20]

The activation energy derived from the thermally activated relaxation in the capacitance measurements is 270 meV (not shown), which is comparable with that calculated from the dc conductivity in the range of 250–300 K (275 meV) and more interestingly with that calculated for peak C. For ionic materials, it was reported that the activation energy for the release of an ionic space charge at a specific temperature will be the same as the activation energy for ionic conduction at the same temperature.[27] Therefore, despite the different temperature interval of observation, based on the very similar activation energies extracted for peak C and from dc conductivity between 250 and 300 K, we suggest an ionic space charge depolarization as the origin of peak C.

We performed a repeat TSDC measurement on a well-polished sample. Aside from the ferroelectric peak, peak A is clearly observed. However, peaks B and C are absent. We conclude that peaks B and C originate from depolarization processes at the surface and can be avoided by careful treatment of the surface layer. The disappearance of peaks B and

C upon polishing is consistent with the space charge related origin of both peaks, involving the electrodes. The observation of two surface related TSDC peaks in a multiferroic demonstrates the importance of controlling the surface properties.

$CuCrO_2$ shows in addition to the PC peak at the ferroelectric transition, TSDC peaks when the material is poled at temperatures above T_N. The ferroelectric transition is well-defined with a clear sharp peak at $\sim$24 K. When the sample is poled at 125 K, three TSDC peaks are observed at $\sim$50, 120, and 150 K. We observe that the PC peak is narrow and sharp and conforms to the first order derivative of a second order phase transition. The TSDC peaks are absent if the sample is poled below the magnetic transition temperature. By studying the poling field dependence of the current, the origins of the TSDC peaks can be assigned to different mechanisms. The peak near 50 K is consistent with the defect dipole relaxation because the TSDC increases linearly with the increase of poling fields with a fixed T_m. The second peak near 120 K is assigned to space charge relaxation due to the release of trapped charges. This assignment is based on the observation that the TSDC peak at T_m shifts quadratically with the poling field to low temperature. Finally, the third peak around 150 K is assigned to ionic space charge depolarization. The space charge related origins of the peaks around 120 and 150 K are consistent with the observation of Maxwell–Wagner type dielectric relaxation originating from a Schottky barrier formation at the interface between the electrodes and the sample. The two TSDC peaks at $\sim$120 and 150 K are absent for well-polished sample. This indicates a surface defect originating from different types of trapped charge carriers. Thus, we demonstrate that the TSDC technique is remarkably sensitive to the presence of small amount of defects and trapped states even when they exist only on the surface. The observation of TSDC peaks implies the presence of internal electric fields which will interfere with the external field applied during a PC measurement in a multiferroic. Therefore, characterization of both bulk and surface states is important.

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