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To cite this article: Haruka Taniguchi *et al* 2018 *J. Phys.: Conf. Ser.* **969** 012094

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Dielectric anomaly and magnetoelectric effect accompanying a charge ordering in the electron-doped manganite $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$

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Abstract. We report on the dielectric and magnetic properties of the A-site substituted perovskite compounds $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3), to examine the magnetoelectric effect of electron-doped manganites. The dielectric constant of these compounds shows a broad peak around the magnetic transition temperature, which is probably associated with a charge ordering transition. Application of magnetic field suppresses the broad maximum of the dielectric constant, indicating the presence of the strong magnetoelectric effect. The observed dielectric anomaly and magnetoelectric effect have been discussed on the basis of the combined charge ordering model.

1. Introduction

Multiferroicity includes interesting physics and is expected to be applied to useful devices. One famous origin of the multiferroicity is inverse Dzyaloshinskii-Moriya (DM) interaction [1, 2], as widely observed in cycloid magnetic ordering systems, for example, TbMnO_3 [3], $\text{Ni}_3\text{V}_2\text{O}_8$ [4], LiCu_2O_2 [5], and LiCuVO_4 [6]. The multiferroicity of the inverse DM type is discovered also in MnWO_4 with an elliptical cycloid ordering [7, 8, 9] and CoCr_2O_4 with a transverse cone ordering [10]. The ferroelectricity in the low-temperature incommensurate ordering phase of YMn_2O_5 is categorized into the inverse DM type as well [11, 12]. Another origin of the multiferroicity is d - p hybridization [13], as reported in the magnets with a proper screw ordering such as CuFeO_2 [14] and CuCrO_2 [15]. Moreover, the multiferroicity of the d - p hybridization type is realized also in other magnetic orderings, for example, in CuB_2O_4 [16] and $\text{Ba}_2\text{CoGe}_2\text{O}_7$ [17]. The third origin of the multiferroicity is magnetic exchange striction, as observed in YMnO_3 [18], HoMnO_3 [18, 19], GdFeO_3 [20]. The ferroelectricity in the commensurate ordering phase of YMn_2O_5 is categorized into the magnetic exchange striction type as well [11, 12].

The effectiveness of some charge orderings (COs) is pointed out as the fourth origin of the multiferroicity. Importantly, the COs do not need atomic displacement in order to induce ferroelectricity. An example is the simultaneous presence of the site-centered CO and the bond-centered CO [21, 22, 23, 24, 25]. Here, the site-centered CO means the checkerboard pattern which is observed in manganites containing Mn^{3+} and Mn^{4+} with a ratio of 1:1. On the other hand, the bond-centered CO means Zener polaron which is proposed by A. Daoud-Aladine *et al.* [26]. The high-resolution transmission electron spectroscopy of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ revealed the existence of Zener polaron [27, 28]. Notably, the linear



combination of the site-centered CO and the bond-centered CO breaks inversion symmetry and has a macroscopic electric polarization. A broad peak in the temperature dependence of the dielectric constant and the shift of the peak by a magnetic field are reported in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.3, 0.33$ and 0.4) [29, 30, 31, 32] and $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.4, 0.45$ and 0.5) [33]. These findings strongly indicate a spontaneous electric polarization and a magneto-electric coupling in hole-doped CO manganite systems. Moreover, the existence of ferroelectricity is directly proved by the remanent polarization measurement in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ [34].

In this study, in order to shed light on electron-doped systems as a new candidate for the multiferroics of the combined CO type, we have investigated the temperature dependence of the dielectric constant of polycrystalline $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ in magnetic field. On $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Sb}_y\text{O}_3$ system, previous studies exist for $y \leq 0.1$. From the X-ray photoelectron spectroscopy, it is confirmed that the valence of Sb is 5+ [35]. The substitution of Sb^{5+} ion for Mn^{4+} site causes one-electron doping with the chemical formula $\text{Ca}^{2+}\text{Mn}_{1-2x}^{4+}\text{Mn}_x^{3+}\text{Sb}_x^{5+}\text{O}_3^{2-}$ accompanied by a monotonic increase of unit-cell volume as a function of x . The further doping of Sb ion breaks conduction paths along the Mn-O-Mn network, resulting in a carrier localization. In the magnetization and ac susceptibility measurements, a canted antiferromagnetic (AFM) ordering is detected below about 100 K [36, 37, 35, 38]. Moreover, by analogy with $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ of the two electron doping [39, 40], CO is expected in a certain range of y . In this study, aiming for the combined CO, we deviate the y value from 1/3 at which the site-centered CO is expected. We have observed a CO-like anomaly in the magnetization, and discovered a broad FE-like peak in the dielectric constant at almost the same temperature. Moreover, our investigations reveal a magnetoelectric effect on the dielectric anomaly. These results are consistent with the scenario that $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ is a multiferroics of the combined CO type.

2. Experimental

Polycrystalline samples of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3) were prepared by a solid-state reaction method. The stoichiometric mixtures of CaCO_3 , SrCO_3 , Mn_3O_4 and Sb_2O_3 powders were calcined in air at 1000°C for 48 h. The products were ground and pressed into disk-like pellets. The pellets were sintered at 1350°C for 48 h. We performed X-ray diffraction measurements with an Ultima IV diffractometer (Rigaku) using Cu $K\alpha$ radiation.

As the main topic of this study, we measured the temperature dependence of the dielectric constant under DC magnetic field using the parallel mode of a LCR meter (Agilent, E4980A). Samples were cut into a parallel plate with $3.2 \times 6.0 \text{ mm}^2$ area and 0.7 mm thickness, and Au wires for electric lead were connected by Ag paint (Dupont, 4929N). In order to improve electric conductivity, sample surfaces were polished to be flat using $9 \mu\text{m}$ diamond slurry, and Ag paint was heated at 110°C for 30 min. After field cooling, measurements were performed with AC voltage of 1 V and 10 kHz. In order to detect a CO, we also measured magnetization with a commercial SQUID (Quantum Design, MPMS) under 0.01 mT after field cooling.

3. Results and Discussion

Figure 1(a) presents X-ray diffraction spectrum of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3). We have confirmed that all the samples are described as a $Pnma$ orthorhombic structure and consist of a single phase. As shown in Fig. 1(b), (200) and (002) peaks are clearly split for $x = 0$ and 0.1 , whereas they form one combined peak for $x = 0.2$ and 0.3 . This substitution effect indicates that Sr ions with a larger radius than Ca ions reduce lattice distortion, and the value of the lattice parameter c approaches that of a . Obtained lattice parameters and unit cell volume are plotted in Fig. 1(c). Quantitatively, the difference between a and c at $x = 0.3$ is as about half as that at $x = 0$. We have also observed that the values of a , b and c are enhanced by Sr substitution.

In Fig. 2, we show the temperature dependence of the dielectric constant ϵ'_r of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3) under a magnetic field (0 T, 10 mT and 1 T). First of all, the ϵ'_r values of all the

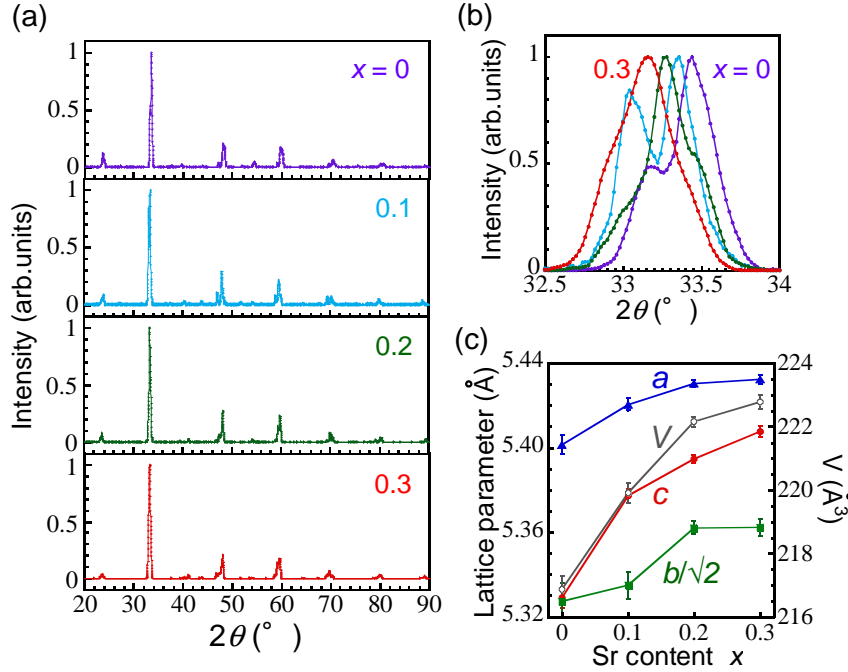


Figure 1. (a) X-ray diffraction spectrum of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3). (b) Enlarged view of the (200) and (002) diffractions. (c) Lattice parameters and unit cell volume of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ with error bars.

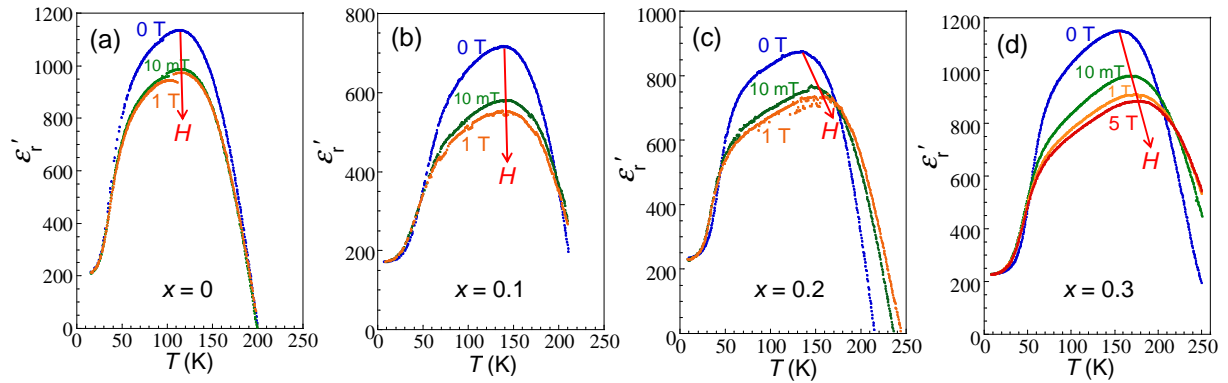


Figure 2. Temperature dependence of the dielectric constant of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3) under AC voltage of 1 V and 10 kHz after field cooling. In every sample, a broad peak is suppressed by an applied magnetic field.

samples exhibit common broad peaks at intermediate temperatures and then rapidly decrease at low temperatures near 50 K. These trends are not changed under the application of magnetic fields. The peak structure which suggests that the response of dipole moments to an applied AC voltage becomes slow below the peak temperature T_{peak} can be interpreted as the result of a FE ordering, because an electric polarization is directly proved in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ [34] in which a similar dielectric peak is observed [29, 30, 32]. Moreover, we have revealed a magnetoelectric effect: the peak of $\epsilon'_T(T)$ is shifted by magnetic field. The peak height $\epsilon'_T(T_{\text{peak}})$ is suppressed in all the samples, and T_{peak} is remarkably enhanced above x of 0.2. The suppression of the peak height suggests that the direction of the electric polarization cannot completely follow the plus-minus switching of the AC voltage under magnetic field. The enhancement of T_{peak} indicates that magnetic field supports the FE ordering. Therefore, these results can be understood by the scenario that a spontaneous electric polarization along a certain direction is stabilized by magnetic field.

Focusing on the Sr substitution effect, we plotted $\epsilon'_r(T)$ curves of every sample together in Fig. 3(a). Here, we define ferroelectric temperature T_{FE} as the temperature at which $\epsilon'_r(T)$ under 10 mT exhibits a peak. As indicated by arrows, we have clarified that T_{FE} is enhanced by Sr substitution.

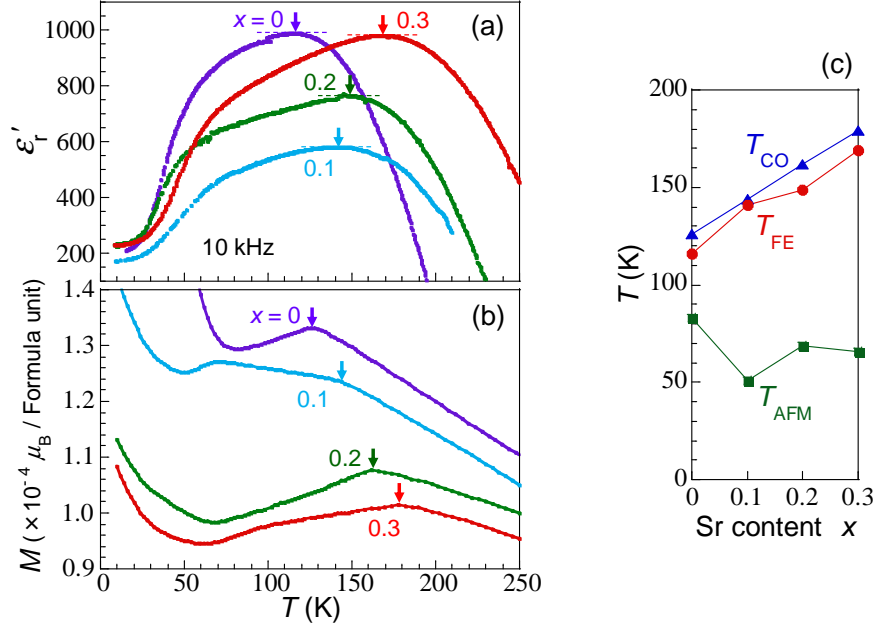


Figure 3. Comparison between dielectric anomalies and magnetic anomalies of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3). (a) Dielectric constant measured under AC voltage of 1 V and 10 kHz after field cooling of 10 mT. Arrows indicate a ferroelectric-like peak for each sample. (b) Magnetization measured under 10 mT after field cooling. Arrows indicate a charge-ordering-like peak/kink for each sample. (c) Phase diagram of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$. Red circles present ferroelectric temperature T_{FE} defined as the temperature at which dielectric constant exhibits a peak, blue triangles present charge ordering temperature T_{CO} defined as the temperature at which magnetization exhibits a small peak/kink, and green rectangles present antiferromagnetic onset temperature T_{AFM} defined as the temperature at which magnetization starts rapid increase toward lower temperature.

In order to clarify the origin of the dielectric anomaly and magnetoelectric effect in $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3), we investigated the magnetic properties. As shown in Fig. 3(b), the temperature dependence of the magnetization M exhibits a remarkable increase below about 50 K, which is understood as an AFM transition by analogy with the AFM transition in $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Sb}_y\text{O}_3$ of $y \leq 0.1$ [36, 37, 35, 38]. Above 50 K, we observed a small peak or kink. The anomaly is expected to be caused by a CO, because similar anomalies are observed in the magnetization of $\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ [39] in which a CO is proved by the neutron diffraction [40]. The CO-like anomaly appears at two temperatures for $x = 0.1$ and 0.3 : at 69 and 144 K for $x = 0.1$, and at 89 and 179 K for $x = 0.3$. In this study, we focus on the anomaly at the higher temperature, because its temperature shown by arrows in Fig. 3(b) exhibits a systematic x dependence. On the anomaly at the lower temperature, we consider specific heat measurement as a future work in order to obtain detailed information. Thus, we define CO temperature T_{CO} as the temperature at which the the slope of $M(T)$ below 250 K changes. We also define AFM onset temperature T_{AFM} as the temperature at which the negative dM/dT from 0 K changes to positive one. The three characteristic temperatures T_{FE} , T_{CO} , and T_{AFM} are summarized in Fig. 3(c).

Importantly, we have found that T_{FE} and T_{CO} exhibit a similar value and are enhanced together by Sr substitution. These results strongly indicate that the FE-like anomaly of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3) is induced by the CO. Moreover, the AFM temperature roughly corresponds to the temperature at which $\epsilon'_r(T)$ exhibits the shoulder structure. This result suggests that a part of the CO region transfers to an AFM phase and the FE volume is suppressed. We note that the maximum value of ϵ'_r at $x = 0$ is larger than those at $x = 0.1$ and 0.2 . These differences between the parent and lightly Sr substituted samples are related to the volume fraction of the original CO phase, which contributes to the formation of a ferroelectric state. The CO phase has a fragile nature against lattice disorder and is easily diminished in the Sr substituted samples. (For the $x = 0.3$ sample, the peak value is comparable to that of the parent sample. The lattice distortion is relaxed in the heavily Sr substituted sample because the value of the lattice parameter c approaches that of a . We expect that the lattice relaxation prevents a decrease of the CO volume fraction, giving the comparable peak value with the parent sample.) As described in the introduction, the CO which causes the FE-like anomaly in $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ is expected to be the linearly combined state of the site-centered CO and the bond-centered CO. Since the inversion center of the site-centered CO is different from that of the bond-centered one, the combined CO lacks inversion symmetry and induces a spontaneous electric polarization [21, 22].

Moreover, a magnetoelectric effect is expected in the combined CO for the following reason. The site-centered CO and the bond-centered CO are accompanied by the CE magnetic ordering ($\Phi = 0$) and the \perp magnetic ordering ($\Phi = \pi/2$), respectively [21, 22]. Since these two magnetic orderings are connected by a continuous rotation, the combined CO is expected to have a corresponding magnetic ordering ($0 < \Phi < \pi/2$). Therefore, a magneto-electric coupling is predicted under the combined CO. The observed suppression of the dielectric constant by magnetic field is consistent with this scenario. We would like to emphasize that this study has experimentally suggested the multiferroicity by the combined CO for the first time in electron-doped systems.

As a future issue, we are interested in the effect of Sb concentration y of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Sb}_y\text{O}_3$. Further discussion will be enabled by revealing the y range in which the dielectric anomaly with the magnetoelectric effect is realized and the y value at which T_{FE} exhibits a maximum value. We are also trying a detailed investigation using single crystals in order to reveal anisotropy and perform quantitative discussion.

4. Summary

Our investigations reveal that the temperature dependence of the dielectric constant of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3) exhibits a broad peak, which can be understood as a FE transition. Importantly, the peak temperature coincides well with the temperature of the CO-like anomaly in magnetization. Moreover, we have shown that the dielectric constant is suppressed by a magnetic field. These tendencies, which were commonly observed in $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ($x = 0, 0.1, 0.2$ and 0.3), are consistent with the scenario that the combined state of the site-centered CO and the bond-centered CO is realized in this system and induces a macroscopic electric polarization, which is stabilized by a magnetic field. This magnetoelectric effect suggests that the carrier doping which is deviated from the composition of the site-centered CO is a hopeful way to induce the multiferroicity via the combined CO state.

Acknowledgments

This work is supported by Iwate University and JSPS KAKENHI Grant Number JP17K14101.

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