

Pressure Effect on the Dielectric Anomaly in the Antiferromagnetic Manganite $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$

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Pressure plays a critical role in tuning the interactions and controlling the electronic state. In this study, the physical pressure effects on the dielectric constant, magnetization, and local activation energy were investigated for $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ of which dielectric constant is substantially changed by a magnetic field. The dielectric peak temperature T_ε which suggests a dipole ordering exhibited a decreasing trend, whereas the magnetization peak temperature T_M which indicates an antiferromagnetic transition and the local maximum temperature of the local activation energy T_ρ which suggests a charge ordering were slightly enhanced by pressure. The observed negative correlation of T_ε with T_M and T_ρ under physical pressure is surprising because T_ε exhibits a positive correlation with T_M and T_ρ under the isovalent Sr substitution for Ca which induces a chemical pressure. The enhancement of the antiferromagnetism and the accompanying charge ordering by physical pressure could be attributed to the increasing superexchange interaction due to the suppression of the Mn-O bond length. Although the mechanism of the pressure dependence of T_ε is not resolved at present, it might suggest the existence of two competing interactions similarly to the displacive type ferroelectrics.

KEYWORDS: manganite, pressure, electric polarization, antiferromagnetism, charge ordering

1. Introduction

In general, pressure plays a critical role in controlling the electronic state. For example, extensive research on conventional ferroelectrics has shown that the pressure P effect on the ferroelectric transition temperature T_{FE} is classified by the origin of the electric polarization: the sign of dT_{FE}/dP is negative for displacive type ferroelectrics induced by a zone-center-type phonon mode, positive for displacive type ferroelectrics induced by a zone-boundary-type phonon mode, positive for order-disorder type ferroelectrics, and negative for hydrogen-bond type ferroelectrics [1–3]. Regarding magneto-electrics, significant pressure effects on the dielectric properties were reported in TbMnO_3 [4]: at approximately 5 GPa the direction of the electric polarization rotates from the c axis to the a axis and its size becomes 15 times larger, accompanying the magnetic phase transition from the cycloid magnetic phase to the E-type antiferromagnetic phase.

In 2004, Efremov *et al.* proposed a new type of magneto-electrics of which origin is a charge ordering [5]. In 2018, we reported that $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ of which crystal structure is a perovskite as shown in Fig. 1 (d) is a possible candidate of this charge-ordering type magneto-electrics [6, 7]. In $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$, both the local activation energy $E_{\text{local}} = d(\ln\rho)/d(1/T)$ (ρ : electric resistivity, T : temperature) and the magnetization exhibits a local maximum at approximately 130 K. Since the valency of Sb is proved to be 5+ by the x-ray photoelectron spectroscopy and the deviation of the oxygen content from 3 is evaluated to be between -0.02 and $+0.01$ by the electron probe micro analyzer,

Mn^{3+} of $(3d)^4$ and Mn^{4+} of $(3d)^3$ coexist in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$. The local maximum in $E_{\text{local}}(T)$ observed also in a single crystalline sample which is free from grain boundary effects seems to originate from a charge ordering between Mn^{3+} and Mn^{4+} similarly to $(\text{Ca},\text{Sr})(\text{Mn},\text{Mo})\text{O}_3$ [8]. The maximum in $M(T)$ indicates an antiferromagnetic transition, which is consistent with the negative Weiss temperature estimated from the Curie-Weiss fit. Although the magnetic structure of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ is not resolved yet, a candidate is the C-type antiferromagnetism which is realized in $(\text{Ca},\text{Ce})\text{MnO}_3$ with the ratio of Mn^{3+} to Mn^{4+} same as $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ [9]. Interestingly, at a temperature similar to the charge ordering temperature T_ρ , the real part of the dielectric constant exhibits a broad peak which is substantially sensitive to a magnetic field. We performed the Maxwell-Wagner fit which describes the system with four components of bulk capacitance, bulk resistance, surface capacitance and surface resistance, and revealed that the peak is caused by the bulk capacitance component [10]. The relaxation time and the activation energy estimated from the Arrhenius plot based on the frequency dependence of the dielectric peak temperature T_ε suggests that dipoles consisting of polarons are ordered and form an electric polarization below T_ε . We also performed the isovalent Sr^{2+} substitution for Ca^{2+} in which a negative chemical pressure is expected because of the difference of the ionic radius between Sr^{2+} and Ca^{2+} , and revealed that T_ε is enhanced similarly to T_ρ and the Neel temperature T_M . The observed positive correlation between T_ε and T_ρ is consistent with the scenario of the charge-ordering type magneto-electrics. However, it should be noted that the elementary substitution inevitably includes the disorder effect as well as the pressure effect.

In this study, in order to clarify the pure pressure effect in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$, we measured the dielectric constant, magnetization, and resistivity under physical pressures up to 2.0, 1.0, and 1.5 GPa, respectively. T_ε exhibited a decreasing trend, whereas T_ρ and T_M were slightly enhanced by the pressure. The negative correlation of T_ε with T_ρ and T_M under the physical pressure which was newly revealed in this study is contrast to the positive correlation under the Sr substitution and cannot be interpreted based on the simple model supposing the charge-ordering type magneto-electrics. The observed enhancement effects on the antiferromagnetism and the accompanying charge ordering by the positive physical pressure as well as the negative chemical pressure can be consistently understood by considering the Mn-O-Mn bond angles and the Mn-O bond length which are two important factors affecting the strength of the superexchange interaction.

2. Experimental

Polycrystalline samples were synthesized by the following sol-gel method. Stoichiometric CaCO_3 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and Sb were dissolved in nitric acid. Citric acid was added to form chelate complexes and ethylene glycol was added to cause ester polymerization. The obtained sol was heated at approximately 80 °C to evaporate excess water. The remaining gel was dried at 600 °C for 6 hours. The obtained powder was pressed into a pellet and calcined in air twice, at 1000 °C for 48 hours and at 1350 °C for 48 hours. By the Rietveld analysis utilizing the RIETAN-FP program [11], the powder x-ray diffraction pattern was described by a $Pnma$ orthorhombic structure ($a = 5.387 \text{ \AA}$, $b = 7.548 \text{ \AA}$, $c = 5.344 \text{ \AA}$), as same as our previous samples synthesized by a solid state reaction [10]. All the samples in this work (S1-3) were cut from the same pellet. S1 with the dimensions of $4.20 \text{ mm}^2 \times 1.00 \text{ mm}$ was used for the dielectric constant measurement. S2 of 11.9 mg was used for the magnetization measurement. For S3 with the dimensions of $2.60 \times 1.85 \times 0.60 \text{ mm}^3$ of which resistivity and dielectric constant were measured, annealing in O_2 gas flow at 1000 °C for 24 hours was performed before the dielectric constant measurement in order to release possible remaining lattice distortion obtained by the preceding resistivity measurement under pressure.

For detecting the dielectric constant and the resistivity under pressure, we designed a piston-cylinder type pressure cell made of Ni-Cr-Al and Cu-Be and a self-made probe which can be installed in a commercial PPMS (Quantum Design). The dielectric constant was measured by the parallel mode

of an LCR meter (Agilent, E4980A) with an AC electric field of 1 V and the resistivity was measured by the resistivity mode of the PPMS. The magnetization was measured by the background subtraction mode of a commercial MPMS (Quantum Design) under 1 T after field cooling with a piston-cylinder type pressure cell made of Cu-Be. In all the measurements, we utilized the mixture of fluorinert FC-70 and FC-77 with the ratio of 1:1 as the pressure medium, which is common for measuring dielectric constant [3, 12–14] as well as resistivity [15, 16] and magnetization [17].

3. Results and Discussion

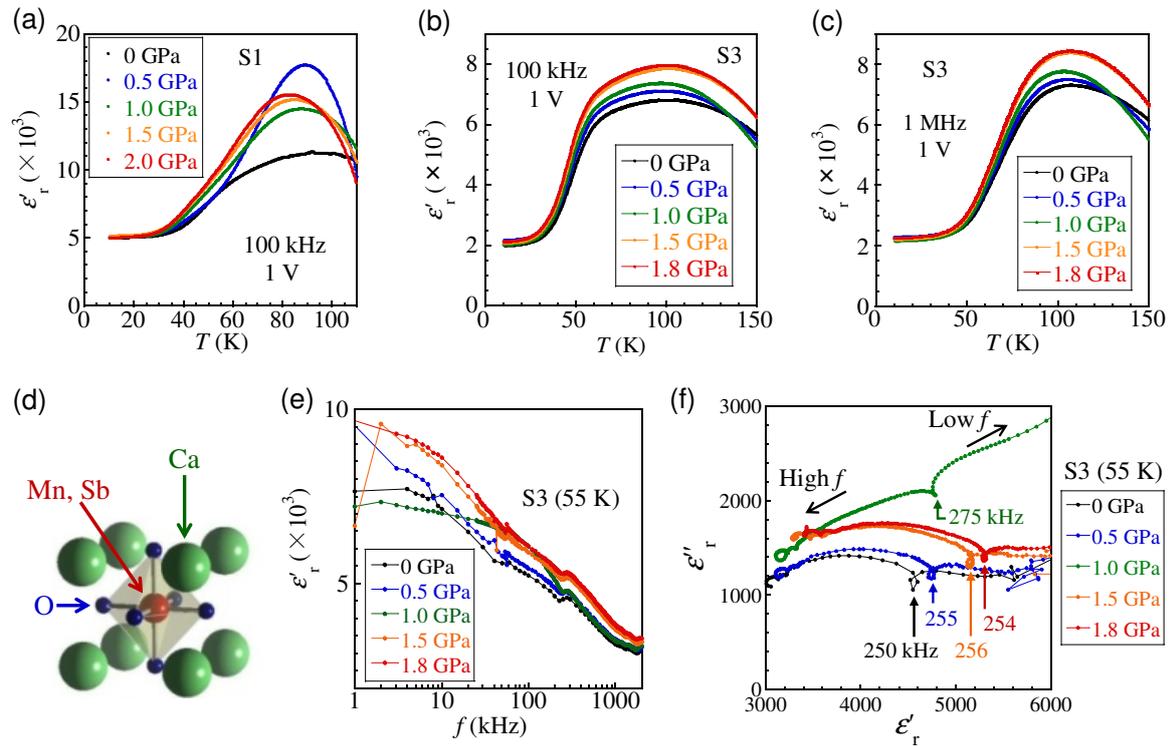


Fig. 1. The temperature dependence of the real part of the dielectric constant of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ under several pressures for (a) the sample S1 with an electric field of 100 kHz, (b) the sample S3 with an electric field of 100 kHz, and (c) the sample S3 with an electric field of 1 MHz. (d) The crystal structure of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$. (e) The frequency dependence of the real part of the dielectric constant and (f) the Cole-Cole plot for the sample S3 at 55 K under several pressures.

Figure 1 (a-c) presents the temperature dependence of the real part of the dielectric constant ϵ'_r of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ under several pressures. Among these measurements with different samples (S1 and S3) and different conditions (100 kHz and 1 MHz), the broad dielectric peak was sustained under high pressures. As discussed in detail in our previous paper [10], the dielectric peak is induced by the bulk capacitance component: First, if the dielectric peak is induced by the bulk resistance component, the sign of the apparent "magneto-capacitance effect" should be positive [18, 19], which is opposite to the observed magneto-capacitance effect. Second, the calculated dielectric constant using the Maxwell-Wagner model and the measured resistivity value excludes the possibility of the surface resistance component. The calculation does not reproduce the observed peak, and the difference of the calculated dielectric constant between 0 T and 1 T is within the error margin in contrast to the observed significant magneto-capacitance effect. Third, the possibility of the surface capacitance component is also excluded, because the dielectric peak was not affected by the thickness ratio of the

sample (bulk) to the Ag paste terminal (surface) and also observed in single crystalline samples which are free from the grain boundary. Therefore, the dielectric peak suggests a glassy electric polarization. The peak temperature T_ε of S1 was monotonically suppressed up to 2.0 GPa. T_ε of S3 also exhibited a decreasing trend, but was enhanced between 1.0 and 1.5 GPa. The reason for this T_ε enhancement is not clear, but could be attributed to the decline of the pressure homogeneity by the solidification of fluorinert at 1.0 GPa.

Comparing the panel (b) with (c), the $\varepsilon'_r(T)$ curve at 100 kHz exhibited a 2-step decrease below T_ε , whereas $\varepsilon'_r(T)$ at 1 MHz exhibited a 1-step decrease. The steep decrease below approximately 60 K for the $\varepsilon'_r(T)$ curve at 100 kHz can be interpreted as the surface effect as we previously showed by the Maxwell-Wagner fit [10]. The surface contribution as well as the bulk contribution was also observed in the frequency f dependence of ε'_r (Fig. 1 (d)) and the Cole-Cole plot (Fig. 1 (e)) at 55 K at which $\varepsilon'_r(T)$ of 100 kHz exhibited the steep decrease. The ε'_r decrease with increasing f temporarily stopped at approximately 250 kHz. Corresponding to the anomaly observed in $\varepsilon'_r(f)$, the Cole-Cole plot exhibited two semicircles. This behavior is typical of the materials with multi-component dielectric responses: the bulk contribution is dominant above the critical frequency f_c at which one semicircle ends and another starts, whereas the surface contribution is not negligible below f_c . In $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$, the f_c value was almost unchanged by the pressure: f_c was 250, 255, 275, 256, and 254 kHz at 0, 0.5, 1.0, 1.5, and 1.8 GPa, respectively.

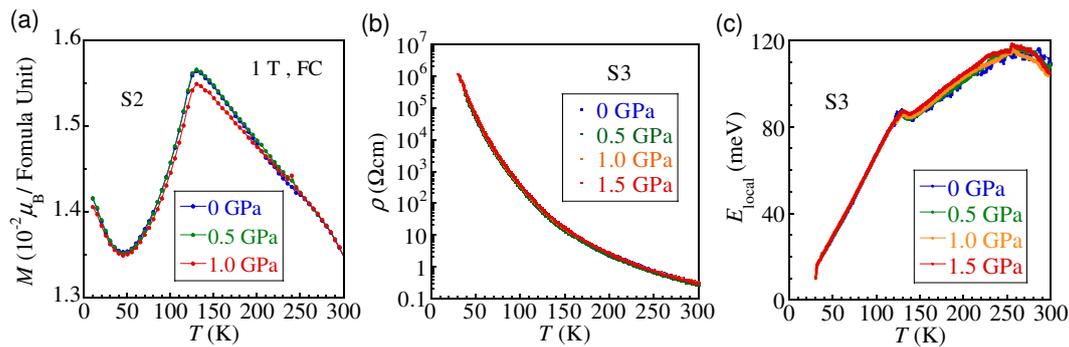


Fig. 2. (a) The temperature dependence of the magnetization of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ under several pressures for the sample S2 under 1 T after field cooling. The temperature dependence of (b) the resistivity ρ and (c) the local activation energy $E_{\text{local}} = d(\ln\rho)/d(1/T)$ of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ under several pressures for the sample S3.

Figure 2 presents the temperature dependence of the magnetization M , the resistivity ρ and the local activation energy E_{local} under several pressures. The $M(T)$ curves and the $E_{\text{local}}(T)$ curves were not significantly affected by the pressure. The peak at approximately 135 K in $M(T)$ indicates the antiferromagnetic transition, and the local maximum at approximately 130 K in $E_{\text{local}}(T)$ suggests the charge ordering.

The pressure dependence of the dielectric peak temperature T_ε , the magnetization peak temperature T_M , and the local maximum temperature of the local activation energy T_ρ revealed by the present study is summarized in Fig. 3. For comparison, the chemical pressure effect by the isovalent Sr substitution for Ca [10] is also plotted. The chemical pressure values were estimated using the unit cell volume of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ [10] and the bulk modulus of CaMnO_3 [20] under the approximation that the bulk modulus of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ is comparable to that of CaMnO_3 . Surprisingly, in contrast to the Sr substitution in which T_ε , T_M , and T_ρ exhibited a similar trend, the physical pressure effects on T_M and T_ρ were qualitatively different to that on T_ε : T_M and T_ρ were slightly enhanced under the physical pressure, whereas T_ε was suppressed. The enhancement of the Neel temperature by the physical pressure has been reported in many other manganites AMnO_3 ($A = \text{Ca}, \text{Sr}, \text{La}, \text{Pr}, \text{and Sm}$) [21].

We consider that the origin of the T_M enhancement by the positive physical pressure is different

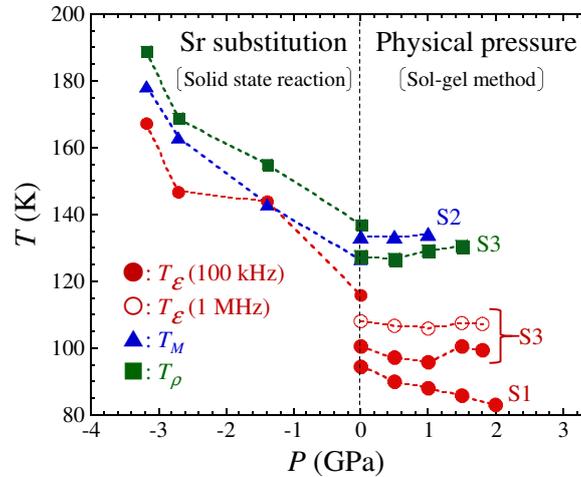


Fig. 3. The pressure dependence of the dielectric peak temperature T_ϵ , the magnetization peak temperature T_M , and the local maximum temperature of the local activation energy T_ρ of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$. For comparison, the chemical pressure effect under the isovalent Sr substitution for Ca [10] is also plotted. The chemical pressure values were estimated using the unit cell volume of $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ [10] and the bulk modulus of CaMnO_3 [20] under the approximation that the bulk modulus of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ is comparable to that of CaMnO_3 . Open circles, filled circles, triangles, and squares denote T_ϵ at 1 MHz, T_ϵ at 100 kHz, T_M , and T_ρ , respectively.

from that by the negative chemical pressure. The antiferromagnetism in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ should be induced by the superexchange interaction resulting from the overlap of the d orbitals of Mn and the p orbitals of O. Both the Mn-O-Mn bond angle and the Mn-O bond length are important factors to determine the orbital overlap. Under the physical pressure, the Mn-O bond length should be decreased, enhancing the superexchange interaction. In contrast, the Mn-O-Mn angle substantially approaches 180 degrees by the Sr substitution in CaMnO_3 [22]. For the Sr substitution in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$, the observed drastic T_M enhancement suggests that the change of the Mn-O-Mn angle is similar to that in Sr-substituted CaMnO_3 and enhances the superexchange interaction exceeding the increasing effect of the Mn-O bond length.

The charge ordering phase in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ under the ambient pressure emerged almost simultaneously with the antiferromagnetic phase, similarly to that in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [23]. It seems that this relation was sustained also under the physical pressure and the Sr substitution and T_ρ was enhanced accompanying the T_M enhancement which was induced by the increased superexchange interaction.

With respect to the dielectric peak, the sign of dT_ϵ/dP of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ was negative both under the physical pressure and under the chemical pressure. The negative correlation of T_ϵ with T_ρ under the physical pressure indicates the difficulty to explain the electric polarization by the simple charge ordering model. Further study is required to clarify the mechanism of the dipole ordering in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$. As a possible scenario, the situation might be somewhat similar to the displacive type ferroelectrics induced by a zone-center phonon mode which exhibit a negative dT_{FE}/dP : a shorter range interaction which prevents the electric polarization exists in addition to the interaction which promotes the electric polarization [1].

4. Summary

We investigated the physical pressure effects on the dipole ordering, antiferromagnetism, and charge ordering of $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$ by measuring the dielectric constant, magnetization, and electric resistivity. The dielectric peak temperature T_ϵ exhibited a decreasing trend in both the samples,

although T_ε was temporarily enhanced between 1.0 and 1.5 GPa in one sample, which could be attributed to the solidification of the pressure medium. In contrast to the T_ε suppression, the magnetization peak temperature T_M and the local maximum temperature of the local activation energy T_ρ were slightly enhanced. The observed T_M enhancement by the physical pressure suggests that the superexchange interaction was enhanced by the decrease of the Mn-O bond length, whereas the T_M enhancement by the isovalent Sr substitution which induces a negative pressure could be explained by the Mn-O-Mn bond angle approaching 180 degrees. The observed negative correlation of T_ε with T_ρ indicates that the simple charge ordering model is insufficient to fully understand the electric polarization in $\text{CaMn}_{0.85}\text{Sb}_{0.15}\text{O}_3$.

5. Acknowledgment

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