# Electron-Doping Effect on the Magnetic-Field-Sensitive Dielectric Anomaly in $CaMn_{1-x}Sb_xO_3$

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**We measured the temperature dependence of the dielectric constant of the electron-doped manganite $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The real part exhibits a broad peak and the imaginary part exhibits a shoulder structure at a lower temperature in all the samples, suggesting a gradual growth of clusters which has a dipole ordering. We newly revealed that the temperatures of these dielectric anomalies are enhanced by more than 90 K by the Sb substitution from $x = 0.1$ to $x = 0.2$. The result indicates that the carrier concentration should be a decisive parameter for the dipole ordering in $CaMn_{1-x}Sb_xO_3$. Moreover, a magnetocapacitive effect is observed in all the samples.**

*Index Terms*—**Dielectric constant, relaxor ferroelectrics.**

## I. Introduction

MANGANITES exhibit a wide variety of electronic phases because of electron interactions [for example, the competition between ferromagnetic double exchange interaction and antiferromagnetic (AFM) superexchange interaction]. Carrier doping is one of the powerful tools to control the electronic states. For example, an electron-doped system $CaMn_{1-x}Mo_xO_3$ changes the ground state from a G-type AFM ordering to a charge/orbital-ordered C-type AFM ordering [1], [2]. In another electron-doped system $Ca_{1-x}La_xMnO_3$, dielectric properties are reported [3], [4]. Moreover, in hole-doped systems such as $Pr_{1-x}Ca_xMnO_3$ and $Y_{1-x}Ca_xMnO_3$ [5]–[9], the temperature dependence of the real part of the dielectric constant exhibits a peak which is sensitive to a magnetic field around the charge-ordering (CO) temperature.

Aiming to discover new phenomena in manganites, our group has investigated an electron-doped system $CaMn_{1-x}Sb_xO_3$ for $x \leq 0.1$ [10]–[13]. The result of X-ray photoelectron spectroscopy indicates that the valence of Sb is 5+ [12]. Thus, the substitution of $Sb^{5+}$ ion for $Mn^{4+}$ site causes one-electron doping with the chemical formula $Ca^{2+}Mn^{4+}_{1-2x}Mn^{3+}_xSb^{5+}_xO^{2-}_3$ accompanied by a monotonic increase of unit-cell volume as a function of $x$. The magnetization and ac susceptibility measurements suggest a canted AFM ordering below about 100 K [10]–[13], although the long-range order might be suppressed by the substitutional disorder. Interestingly, a magnetization reversal is observed after a field cooling for $0.02 \leq x \leq 0.08$ [10], [11]. We consider that the local lattice distortion of $MnO_6$ octahedra induced by the Sb substitution changes the orbital state of the $e_g$ electron of $Mn^{3+}$ and reverses the local easy axis of the magnetization. For $x = 0.05$, the physical and chemical pressure effect is also studied [12], [13].

Just recently, we investigated the dielectric properties of $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15], because manganites provide interesting dielectric materials, such as multiferroics and relaxors. A broad and large peak is found in the temperature dependence of the dielectric constant. Surprisingly, the peak is sensitive to a magnetic field. One candidate for this magnetic-field effect is the magnetoelectric effect in multiferroics. Many multiferroics have been really discovered in manganites, such as $YMnO_3$, $TbMnO_3$, and $MnWO_4$ [16]–[22]. Inhomogeneous systems, such as a relaxor $Pb(Fe_{1/2}Nb_{1/2})O_3$, can be a multiferroic material as well [23]. In relaxors, the polar nanoregions embedded in a nonpolar matrix cause a large relative dielectric constant of about $10^4$ [24], whereas the homogeneous multiferroics, such as $TbMnO_3$, usually exhibit $\epsilon'$ of about 10.

In this paper, in order to reveal the carrier-concentration effect on the dielectric properties of the $CaMn_{1-x}Sb_xO_3$ system, we have newly synthesized polycrystalline $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2) and measured the dielectric constant. In all the samples, we observed a relaxor-like broad peak in the temperature dependence of the real part, which is followed by an anomaly of the imaginary part. Notably, the characteristic temperatures of the dielectric anomalies are remarkably enhanced by more than 90 K with increasing the carrier concentration. This drastic change of the anomaly temperatures indicates that the carrier concentration is a crucial parameter for the dielectric properties in the $CaMn_{1-x}Sb_xO_3$ system. Moreover, all the samples exhibit a magnetocapacitive effect: the peak of the real part is suppressed by a magnetic field of 1 T.

## II. Experiment

The polycrystalline samples of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2) were prepared by a solid-state reaction method [14]. The stoichiometric mixtures of $CaCO_3$,

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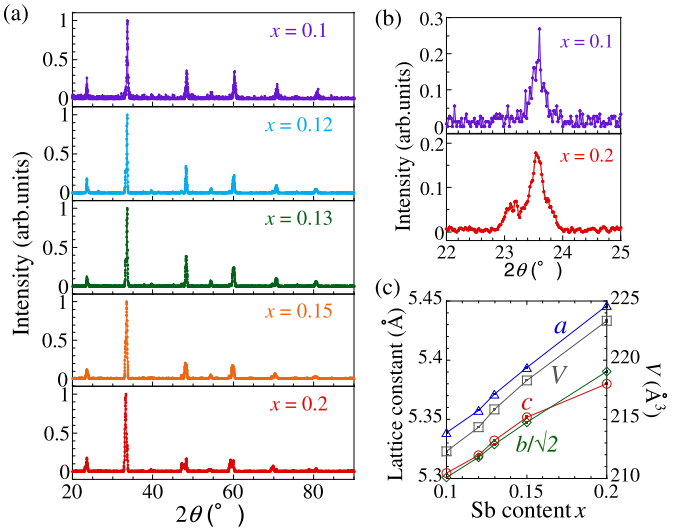


Fig. 1. (a) X-ray diffraction spectrum of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). (b) Enlarged view around the (101) peak for $x = 0.1$ and 0.2. (c) Lattice constants and unit cell volume of $CaMn_{1-x}Sb_xO_3$ with error bars.

$SrCO_3$, $Mn_3O_4$, 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 the X-ray diffraction measurements at room temperature with an Ultima IV diffractometer (Rigaku) using Cu K$\alpha$ radiation.

We measured the temperature dependence of the dielectric constant under the dc magnetic field using the parallel mode of an $LCR$ meter (Agilent, E4980A) [14]. The samples were cut into a parallel plate with a $3.2 \times 6.0$ mm$^2$ area and a 0.7 mm thickness, and the Au wires for electric lead were connected by Ag paint (Dupont, 4929N). In order to improve electric conductivity, the sample surfaces were polished to be flat using 9 $\mu$m diamond slurry, and the Ag paint was heated at 110 °C for 30 min. We performed measurements with an ac voltage of 1 V/mm and 10, 50, or 100 kHz under 0, 0.01, or 1 T (field cooling), obtained capacitance $C$ and dielectric loss tan$\delta$, and estimated the real and imaginary parts of the dielectric constant, $\epsilon'$ and $\epsilon''$.

## III. Results

Fig. 1(a) presents the X-ray diffraction spectrum of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The samples of $x \leq 0.15$ present a $Pnma$ orthorhombic structure, whereas the sample of $x = 0.2$ is described by a $P2_1/m$ monoclinic structure. As shown in Fig. 1(b), a new peak appears at 23.1° in addition to the peak at 23.5° for $x = 0.2$. The peak at 23.1° is expected to result from the (10–1) reflection, whereas the (101) and (020) reflections are combined into one peak at 23.5°. Therefore, the appearance of a peak at 23.1° indicates a structural transition from $Pnma$ to $P2_1/m$. This result is consistent with the previous study on $x = 0.1$ and 0.2 [25]. The obtained lattice parameters and unit cell volume are plotted in Fig. 1(c). The values of $a$, $b$, and $c$ exhibit an almost linear increase with increasing the Sb content $x$. This substitution effect on the lattice is reasonable: the Sb substitution decreases the number of smaller $Mn^{4+}$ ions whose ionic radius is 0.530 Å, whereas it increases the number of larger $Sb^{5+}$ and $Mn^{3+}$ ions whose ionic radius is 0.60 and 0.645 Å, respectively [26].

In Fig. 2(a) and (b), we compare the temperature dependence of the dielectric constant among $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2), which is measured under a magnetic field of 0 T and an ac voltage of 1 V/mm and 100 kHz. We have revealed that all the samples exhibit a broad peak in the real part $\epsilon'$ and a shoulder structure in the imaginary part $\epsilon''$. Interestingly, both of these dielectric anomalies are shifted to a higher temperature by increasing the Sb content. The values of $\epsilon'$ and $\epsilon''$ in Fig. 2 are normalized to be 1 at the peak temperature of $\epsilon'$. The raw value of the real part of the relative dielectric constant $\epsilon_r$ is $10^3$–$10^4$ at the peak, whereas the raw value of the imaginary part of $\epsilon_r$ drastically changes on cooling from $10^4$–$10^5$ to 1–$10^2$. Except for the shoulder structure, the temperature dependence of $\epsilon''$ seems to be roughly described by a power law. The electrical resistivity $\rho$ of $CaMn_{1-x}Sb_xO_3$ is smaller than that of the typical insulators by several orders of magnitude, although its temperature dependence is described by the band-gap model $\rho \propto \rho_0 \exp(\Delta/k_BT)$. Therefore, the dielectric loss of $CaMn_{1-x}Sb_xO_3$ is expected to exhibit an extremely large value at higher temperatures and to be suppressed remarkably on cooling; the large values of $\epsilon''$ at higher temperatures and its quasi-power-law temperature dependence would be originated from the conduction current. Comparably large $\epsilon''$ is really observed in a low resistivity system $Pr_{1-x}Ca_xMnO_3$ [27]. Therefore, we consider that the shoulder structure in $\epsilon''(T)$ is a peak appeared on a quasi-power-law background.

We estimate the characteristic temperatures of the dielectric anomalies as follows and plot them in Fig. 2(c). The temperature at which $\epsilon'$ exhibits a maximum value is defined as the peak temperature of the real part $T_p$. In order to determine the shoulder temperature of $\epsilon''$, we plot $d\epsilon''/dT(T)$. As shown in the inset of Fig. 2(b), the curve exhibits one minimum and one maximum. Since the minimum of $d\epsilon''/dT(T)$ is expected to correspond to the middle of the shoulder in $\epsilon''(T)$, we define the temperature of this minimum as the shoulder temperature of the imaginary part $T_s$.

In this paper, we have newly clarified that both $T_p$ and $T_s$ are almost linearly enhanced by more than 90 K from $x = 0.1$ to 0.2. Notably, the drastically enhanced $T_s$ in the Sb substitution in $CaMn_{1-x}Sb_xO_3$ is contrast to the almost unchanged $T_s$ in the Sr substitution in $Ca_{1-y}Sr_yMn_{0.85}Sb_{0.15}O_3$ [15].

We have also investigated the effect of the magnetic field on the dielectric constant of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, and 0.2), because we found a magnetocapacitive effect in $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15]. A magnetocapacitive effect was observed in all the samples. A magnetic field of 1 T suppresses the peak value of the real part by 3%–15%. As an example, the result for $CaMn_{0.88}Sb_{0.12}O_3$ is shown in Fig. 3(a). Since we have confirmed that the magnetoresistance effect of $CaMn_{0.85}Sb_{0.15}O_3$ below 4 T is within error margin [15], we consider that these magnetocapacitive effects in $CaMn_{1-x}Sb_xO_3$ are really related to the capacitive carriers.

For $x = 0.1$, 0.15, and 0.2, we have studied the frequency dependence of the dielectric constant and found a common tendency. As the result of $x = 0.1$ is shown in Fig. 3(b),

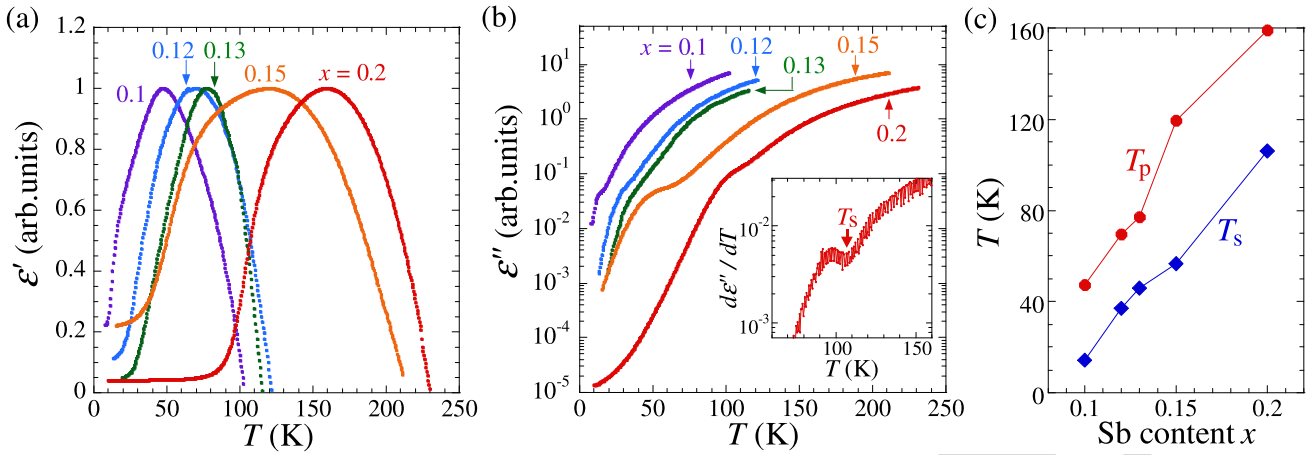


Fig. 2. Temperature dependence of the dielectric constant of $CaMn_{1-x}Sb_xO_3$ ($x$ = 0.1, 0.12, 0.13, 0.15, and 0.2) (an ac voltage of 1 V/mm and 100 kHz, 0 T). (a) Real part $\epsilon'$. (b) Imaginary part $\epsilon''$. The inset of (b) is the temperature dependence of $d\epsilon''/dT$ for $x$ = 0.2. The arrow indicates the minimum of which temperature is defined as the shoulder temperature $T_s$. (c) Sb content dependence of the characteristic temperatures of the dielectric anomalies in $CaMn_{1-x}Sb_xO_3$, which are determined from the measurements of (a) and (b). $T_p$ (circle) is the peak temperature of the real part, whereas $T_s$ (diamond) is the shoulder temperature of the imaginary part.

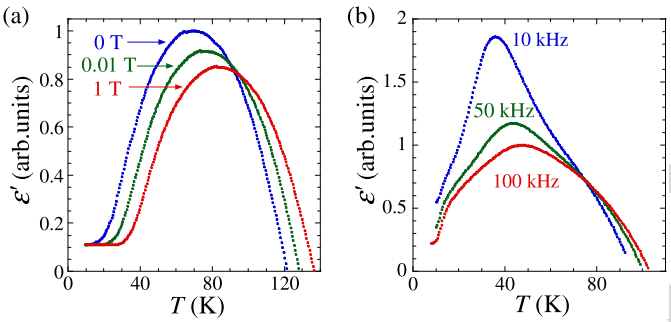


Fig. 3. (a) Magnetocapacitive effect in the real part of the dielectric constant $\epsilon'$ of $CaMn_{0.88}Sb_{0.12}O_3$ (an ac voltage of 1 V/mm and 100 kHz). (b) Frequency dependence of $\epsilon'$ of $CaMn_{0.9}Sb_{0.1}O_3$ (0 T, 1 V/mm).

the peak of $\epsilon'(T)$ is suppressed and shifted to a higher temperature with an increasing frequency.

## IV. Discussion

As discussed for $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15], the peak structure of $\epsilon'(T)$ in $CaMn_{1-x}Sb_xO_3$ ($0.1 \le x \le 0.2$) suggests that it becomes difficult for the dipole moments to follow the plus-minus switching of an applied ac voltage below $T_p$. This behavior can be interpreted as the result of a spontaneous dipole ordering. The large value and the broad peak of $\epsilon'$ as well as its frequency dependence suggest that $CaMn_{1-x}Sb_xO_3$ is a relaxor in which the polar nanoregions exist in a non-polar matrix [24]. The inevitable disorder induced by substitution is consistent with the relaxor scenario. Since the shoulder structure of $\epsilon''(T)$ is understood as a peak appeared on a quasi-power-law background, the shoulder is expected to indicate a dielectric energy dissipation. These results in $CaMn_{1-x}Sb_xO_3$ ($0.1 \le x \le 0.2$) suggest that local dipole-ordering clusters which start to form at $T_p$ expand remarkably around $T_s$ for an energy dissipation to be detectable in $\epsilon''$. Since some relaxors exhibit ferroelectricity much below the peak temperature of $\epsilon'(T)$, it is expected to be reasonable for dipole-ordering clusters to grow gradually on cooling.

The suppression of the peak height of $\epsilon'$ by a magnetic field suggests that the response of dipole moments to an applied ac voltage is interfered by the magnetic field. In other words, a spontaneous dipole ordering along a certain direction is stabilized by a magnetic field.

In order to discuss the origin of the dielectric anomalies and the magnetocapacitive effect in $CaMn_{1-x}Sb_xO_3$, the $x - T$ phase diagram would be important. Focusing on the dielectric properties, we have newly revealed that $T_p$ and $T_s$ are almost linearly enhanced from $x$ = 0.1 to 0.2. On other properties such as the magnetic phase, we can speculate based on the phase diagram of the similar carrier-doped manganites. Comparing the one-electron-doped system $CaMn_{1-x}Sb_xO_3$ with a two-electron-doped system $AeMn_{1-z}Mo_zO_3$ ($Ae$: Alkaline earth metal), from the viewpoint of the average valence $\alpha$ of Mn ions, $CaMn_{0.85}Sb_{0.15}O_3$ with $\alpha = +3.82$ and $CaMn_{0.8}Sb_{0.2}O_3$ with $\alpha = +3.75$ correspond to $AeMn_{0.917}Mo_{0.083}O_3$ and $AeMn_{0.889}Mo_{0.111}O_3$, respectively. Considering that the structural phase transition from $Pnma$ to $P2_1/m$ at the room temperature occurs between $CaMn_{0.85}Sb_{0.15}O_3$ and $CaMn_{0.8}Sb_{0.2}O_3$, the phase diagram of $CaMn_{1-x}Sb_xO_3$ is expected to be similar to that of $Ca_{0.75}Sr_{0.25}Mn_{1-z}Mo_zO_3$ in which the same structural transition occurs between $z$ = 0.083 and 0.111 [2]. In the phase diagram of $Ca_{0.75}Sr_{0.25}Mn_{1-z}Mo_zO_3$, the ground state for $0.052 \le z \le 0.111$, which corresponds to $0.1 \le x \le 0.2$ in $CaMn_{1-x}Sb_xO_3$, is the C-type AFM phase with charge/orbital ordering, whose ordering temperature is linearly enhanced by more than 130 K in this range. In $CaMn_{0.85}Sb_{0.15}O_3$, we really observed a magnetic anomaly that suggests a CO near $T_p$ [14], [15].

Therefore, the dielectric peak in $CaMn_{1-x}Sb_xO_3$, which indicates the formation of a dipole ordering, is expected to have a positive correlation with a charge/orbital ordering. As for the magnetocapacitive effect, since charge/orbital orderings in $CaMnO_3$ series stabilize a certain magnetic ordering [28], we consider that the dipole ordering related to a charge/orbital ordering is affected by a magnetic field through a magnetic ordering. This magnetic-field-sensitive dielectric peak, which seems to be related to a charge/orbital ordering, is similar to that in the hole-doped system $Pr_{1-x}Ca_xMnO_3$ and

$Y_{1-x}Ca_xMnO_3$ [5]–[9], but it is the first example among electron-doped $CaMnO_3$ systems.

Concerning the dielectric anomaly in the imaginary part which indicates the active development of electrically polarized regions, $T_s$ is notably sensitive to the one-electron-doping Sb substitution in $CaMn_{1-x}Sb_xO_3$, whereas it is not affected by the isovalent Sr substituion in $Ca_{1-y}Sr_yMn_{0.85}Sb_{0.15}O_3$ [15]. From these contrast results, we emphasize that the carrier concentration is a crucial parameter for the expansion of polar nanoregions in the $Ca_{1-y}Sr_yMn_{1-x}Sb_xO_3$ system.

As a next issue, it would be important to clarify whether macroscopic electric polarization exists at low temperatures. In order to check our scenario on the mechanism of the dipole anomalies and the magnetocapacitive effect in the $Ca_{1-y}Sr_yMn_{1-x}Sb_xO_3$ system, the magnetic ground state and the possibility of a charge/orbital ordering should be studied.

## V. Conclusion

We measured the dielectric constant of the electron-doped manganite $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The temperature dependence of the real part exhibits a broad and large peak of which value is suppressed and of which temperature is enhanced by increasing frequency, whereas the imaginary part shows a shoulder anomaly on a quasi-power-law temperature dependence. These results suggest that $CaMn_{1-x}Sb_xO_3$ is a relaxor: clusters with a short-range dipole ordering appear at the peak temperature and grow gradually, especially actively at the shoulder temperature.

Importantly, we have revealed that the shoulder temperature is remarkably enhanced with the increasing Sb content $x$. This result indicates that the growth of the clusters is strongly affected by the carrier concentration. Moreover, the dielectric peak is sensitive to a magnetic field in all the samples. By analogy with other $CaMnO_3$ systems, a charge/orbital ordering and an accompanying magnetic ordering might play an important role for the dielectric ordering in $CaMn_{1-x}Sb_xO_3$.

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**We measured the temperature dependence of the dielectric constant of the electron-doped manganite $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The real part exhibits a broad peak and the imaginary part exhibits a shoulder structure at a lower temperature in all the samples, suggesting a gradual growth of clusters which has a dipole ordering. We newly revealed that the temperatures of these dielectric anomalies are enhanced by more than 90 K by the Sb substitution from $x = 0.1$ to $x = 0.2$. The result indicates that the carrier concentration should be a decisive parameter for the dipole ordering in $CaMn_{1-x}Sb_xO_3$. Moreover, a magnetocapacitive effect is observed in all the samples.**

*Index Terms*—**Dielectric constant, relaxor ferroelectrics.**

## I. Introduction

MANGANITES exhibit a wide variety of electronic phases because of electron interactions [for example, the competition between ferromagnetic double exchange interaction and antiferromagnetic (AFM) superexchange interaction]. Carrier doping is one of the powerful tools to control the electronic states. For example, an electron-doped system $CaMn_{1-x}Mo_xO_3$ changes the ground state from a G-type AFM ordering to a charge/orbital-ordered C-type AFM ordering [1], [2]. In another electron-doped system $Ca_{1-x}La_xMnO_3$, dielectric properties are reported [3], [4]. Moreover, in hole-doped systems such as $Pr_{1-x}Ca_xMnO_3$ and $Y_{1-x}Ca_xMnO_3$ [5]–[9], the temperature dependence of the real part of the dielectric constant exhibits a peak which is sensitive to a magnetic field around the charge-ordering (CO) temperature.

Aiming to discover new phenomena in manganites, our group has investigated an electron-doped system $CaMn_{1-x}Sb_xO_3$ for $x \leq 0.1$ [10]–[13]. The result of X-ray photoelectron spectroscopy indicates that the valence of Sb is 5+ [12]. Thus, the substitution of $Sb^{5+}$ ion for $Mn^{4+}$ site causes one-electron doping with the chemical formula $Ca^{2+}Mn^{4+}_{1-2x}Mn^{3+}_xSb^{5+}_xO^{2-}_3$ accompanied by a monotonic increase of unit-cell volume as a function of $x$. The magnetization and ac susceptibility measurements suggest a canted AFM ordering below about 100 K [10]–[13], although the long-range order might be suppressed by the substitutional disorder. Interestingly, a magnetization reversal is observed after a field cooling for $0.02 \leq x \leq 0.08$ [10], [11]. We consider that the local lattice distortion of $MnO_6$ octahedra induced by the Sb substitution changes the orbital state of the $e_g$ electron of $Mn^{3+}$ and reverses the local easy axis of the magnetization. For $x = 0.05$, the physical and chemical pressure effect is also studied [12], [13].

Just recently, we investigated the dielectric properties of $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15], because manganites provide interesting dielectric materials, such as multiferroics and relaxors. A broad and large peak is found in the temperature dependence of the dielectric constant. Surprisingly, the peak is sensitive to a magnetic field. One candidate for this magnetic-field effect is the magnetoelectric effect in multiferroics. Many multiferroics have been really discovered in manganites, such as $YMnO_3$, $TbMnO_3$, and $MnWO_4$ [16]–[22]. Inhomogeneous systems, such as a relaxor $Pb(Fe_{1/2}Nb_{1/2})O_3$, can be a multiferroic material as well [23]. In relaxors, the polar nanoregions embedded in a nonpolar matrix cause a large relative dielectric constant of about $10^4$ [24], whereas the homogeneous multiferroics, such as $TbMnO_3$, usually exhibit $\epsilon'$ of about 10.

In this paper, in order to reveal the carrier-concentration effect on the dielectric properties of the $CaMn_{1-x}Sb_xO_3$ system, we have newly synthesized polycrystalline $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2) and measured the dielectric constant. In all the samples, we observed a relaxor-like broad peak in the temperature dependence of the real part, which is followed by an anomaly of the imaginary part. Notably, the characteristic temperatures of the dielectric anomalies are remarkably enhanced by more than 90 K with increasing the carrier concentration. This drastic change of the anomaly temperatures indicates that the carrier concentration is a crucial parameter for the dielectric properties in the $CaMn_{1-x}Sb_xO_3$ system. Moreover, all the samples exhibit a magnetocapacitive effect: the peak of the real part is suppressed by a magnetic field of 1 T.

## II. Experiment

The polycrystalline samples of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2) were prepared by a solid-state reaction method [14]. The stoichiometric mixtures of $CaCO_3$,

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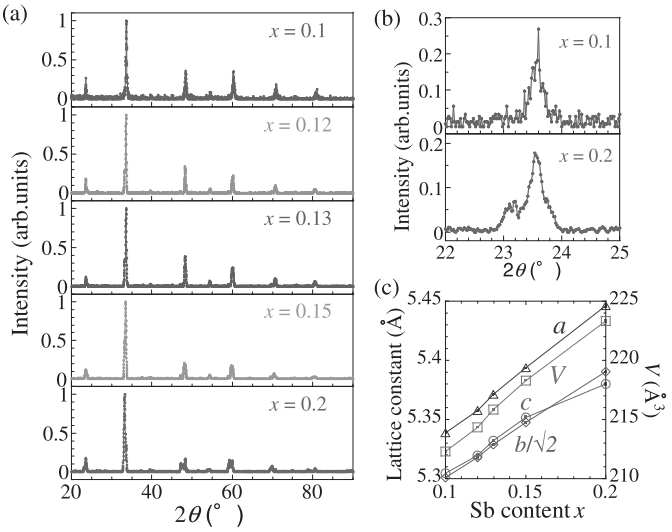


Fig. 1. (a) X-ray diffraction spectrum of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). (b) Enlarged view around the (101) peak for $x = 0.1$ and 0.2. (c) Lattice constants and unit cell volume of $CaMn_{1-x}Sb_xO_3$ with error bars.

$SrCO_3$, $Mn_3O_4$, 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 the X-ray diffraction measurements at room temperature with an Ultima IV diffractometer (Rigaku) using Cu K$\alpha$ radiation.

We measured the temperature dependence of the dielectric constant under the dc magnetic field using the parallel mode of an $LCR$ meter (Agilent, E4980A) [14]. The samples were cut into a parallel plate with a $3.2 \times 6.0$ mm$^2$ area and a 0.7 mm thickness, and the Au wires for electric lead were connected by Ag paint (Dupont, 4929N). In order to improve electric conductivity, the sample surfaces were polished to be flat using 9 $\mu$m diamond slurry, and the Ag paint was heated at 110 °C for 30 min. We performed measurements with an ac voltage of 1 V/mm and 10, 50, or 100 kHz under 0, 0.01, or 1 T (field cooling), obtained capacitance $C$ and dielectric loss tan$\delta$, and estimated the real and imaginary parts of the dielectric constant, $\epsilon'$ and $\epsilon''$.

## III. Results

Fig. 1(a) presents the X-ray diffraction spectrum of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The samples of $x \leq 0.15$ present a $Pnma$ orthorhombic structure, whereas the sample of $x = 0.2$ is described by a $P2_1/m$ monoclinic structure. As shown in Fig. 1(b), a new peak appears at 23.1° in addition to the peak at 23.5° for $x = 0.2$. The peak at 23.1° is expected to result from the (10–1) reflection, whereas the (101) and (020) reflections are combined into one peak at 23.5°. Therefore, the appearance of a peak at 23.1° indicates a structural transition from $Pnma$ to $P2_1/m$. This result is consistent with the previous study on $x = 0.1$ and 0.2 [25]. The obtained lattice parameters and unit cell volume are plotted in Fig. 1(c). The values of $a$, $b$, and $c$ exhibit an almost linear increase with increasing the Sb content $x$. This substitution effect on the lattice is reasonable: the Sb substitution decreases the number of smaller $Mn^{4+}$ ions whose ionic radius is 0.530 Å, whereas it increases the number of larger $Sb^{5+}$ and $Mn^{3+}$ ions whose ionic radius is 0.60 and 0.645 Å, respectively [26].

In Fig. 2(a) and (b), we compare the temperature dependence of the dielectric constant among $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2), which is measured under a magnetic field of 0 T and an ac voltage of 1 V/mm and 100 kHz. We have revealed that all the samples exhibit a broad peak in the real part $\epsilon'$ and a shoulder structure in the imaginary part $\epsilon''$. Interestingly, both of these dielectric anomalies are shifted to a higher temperature by increasing the Sb content. The values of $\epsilon'$ and $\epsilon''$ in Fig. 2 are normalized to be 1 at the peak temperature of $\epsilon'$. The raw value of the real part of the relative dielectric constant $\epsilon_r$ is $10^3$–$10^4$ at the peak, whereas the raw value of the imaginary part of $\epsilon_r$ drastically changes on cooling from $10^4$–$10^5$ to 1–$10^2$. Except for the shoulder structure, the temperature dependence of $\epsilon''$ seems to be roughly described by a power law. The electrical resistivity $\rho$ of $CaMn_{1-x}Sb_xO_3$ is smaller than that of the typical insulators by several orders of magnitude, although its temperature dependence is described by the band-gap model $\rho \propto \rho_0 \exp(\Delta / k_B T)$. Therefore, the dielectric loss of $CaMn_{1-x}Sb_xO_3$ is expected to exhibit an extremely large value at higher temperatures and to be suppressed remarkably on cooling; the large values of $\epsilon''$ at higher temperatures and its quasi-power-law temperature dependence would be originated from the conduction current. Comparably large $\epsilon''$ is really observed in a low resistivity system $Pr_{1-x}Ca_xMnO_3$ [27]. Therefore, we consider that the shoulder structure in $\epsilon''(T)$ is a peak appeared on a quasi-power-law background.

We estimate the characteristic temperatures of the dielectric anomalies as follows and plot them in Fig. 2(c). The temperature at which $\epsilon'$ exhibits a maximum value is defined as the peak temperature of the real part $T_p$. In order to determine the shoulder temperature of $\epsilon''$, we plot $d\epsilon''/dT(T)$. As shown in the inset of Fig. 2(b), the curve exhibits one minimum and one maximum. Since the minimum of $d\epsilon''/dT(T)$ is expected to correspond to the middle of the shoulder in $\epsilon''(T)$, we define the temperature of this minimum as the shoulder temperature of the imaginary part $T_s$.

In this paper, we have newly clarified that both $T_p$ and $T_s$ are almost linearly enhanced by more than 90 K from $x = 0.1$ to 0.2. Notably, the drastically enhanced $T_s$ in the Sb substitution in $CaMn_{1-x}Sb_xO_3$ is contrast to the almost unchanged $T_s$ in the Sr substitution in $Ca_{1-y}Sr_yMn_{0.85}Sb_{0.15}O_3$ [15].

We have also investigated the effect of the magnetic field on the dielectric constant of $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, and 0.2), because we found a magnetocapacitive effect in $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15]. A magnetocapacitive effect was observed in all the samples. A magnetic field of 1 T suppresses the peak value of the real part by 3%–15%. As an example, the result for $CaMn_{0.88}Sb_{0.12}O_3$ is shown in Fig. 3(a). Since we have confirmed that the magnetoresistance effect of $CaMn_{0.85}Sb_{0.15}O_3$ below 4 T is within error margin [15], we consider that these magnetocapacitive effects in $CaMn_{1-x}Sb_xO_3$ are really related to the capacitive carriers.

For $x = 0.1$, 0.15, and 0.2, we have studied the frequency dependence of the dielectric constant and found a common tendency. As the result of $x = 0.1$ is shown in Fig. 3(b),

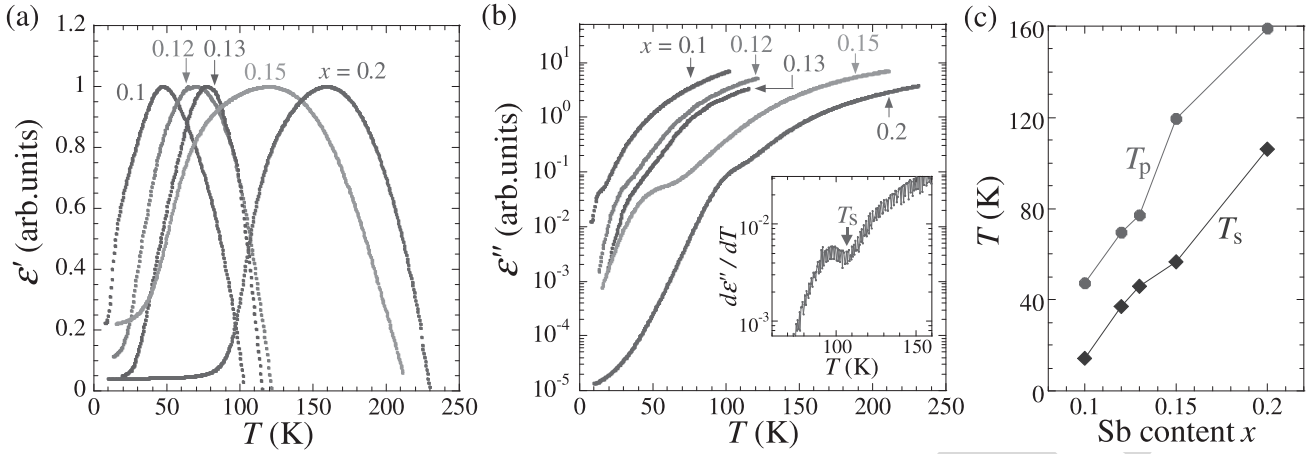


Fig. 2. Temperature dependence of the dielectric constant of $CaMn_{1-x}Sb_xO_3$ ($x$ = 0.1, 0.12, 0.13, 0.15, and 0.2) (an ac voltage of 1 V/mm and 100 kHz, 0 T). (a) Real part $\epsilon'$. (b) Imaginary part $\epsilon''$. The inset of (b) is the temperature dependence of $d\epsilon''/dT$ for $x = 0.2$. The arrow indicates the minimum of which temperature is defined as the shoulder temperature $T_s$. (c) Sb content dependence of the characteristic temperatures of the dielectric anomalies in $CaMn_{1-x}Sb_xO_3$, which are determined from the measurements of (a) and (b). $T_p$ (circle) is the peak temperature of the real part, whereas $T_s$ (diamond) is the shoulder temperature of the imaginary part.

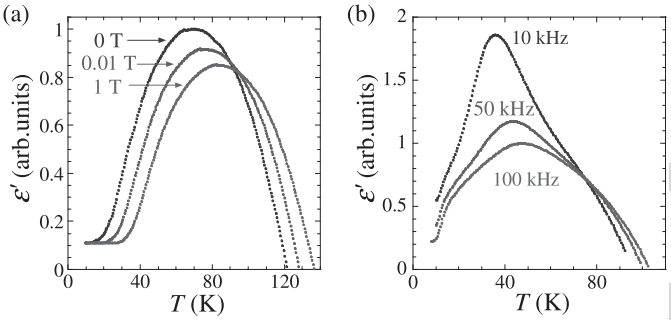


Fig. 3. (a) Magnetocapacitive effect in the real part of the dielectric constant $\epsilon'$ of $CaMn_{0.88}Sb_{0.12}O_3$ (an ac voltage of 1 V/mm and 100 kHz). (b) Frequency dependence of $\epsilon'$ of $CaMn_{0.9}Sb_{0.1}O_3$ (0 T, 1 V/mm).

the peak of $\epsilon'(T)$ is suppressed and shifted to a higher temperature with an increasing frequency.

## IV. Discussion

As discussed for $CaMn_{0.85}Sb_{0.15}O_3$ [14], [15], the peak structure of $\epsilon'(T)$ in $CaMn_{1-x}Sb_xO_3$ ($0.1 \leq x \leq 0.2$) suggests that it becomes difficult for the dipole moments to follow the plus-minus switching of an applied ac voltage below $T_p$. This behavior can be interpreted as the result of a spontaneous dipole ordering. The large value and the broad peak of $\epsilon'$ as well as its frequency dependence suggest that $CaMn_{1-x}Sb_xO_3$ is a relaxor in which the polar nanoregions exist in a non-polar matrix [24]. The inevitable disorder induced by substitution is consistent with the relaxor scenario. Since the shoulder structure of $\epsilon''(T)$ is understood as a peak appeared on a quasi-power-law background, the shoulder is expected to indicate a dielectric energy dissipation. These results in $CaMn_{1-x}Sb_xO_3$ ($0.1 \leq x \leq 0.2$) suggest that local dipole-ordering clusters which start to form at $T_p$ expand remarkably around $T_s$ for an energy dissipation to be detectable in $\epsilon''$. Since some relaxors exhibit ferroelectricity much below the peak temperature of $\epsilon'(T)$, it is expected to be reasonable for dipole-ordering clusters to grow gradually on cooling.

The suppression of the peak height of $\epsilon'$ by a magnetic field suggests that the response of dipole moments to an applied ac voltage is interfered by the magnetic field. In other words, a spontaneous dipole ordering along a certain direction is stabilized by a magnetic field.

In order to discuss the origin of the dielectric anomalies and the magnetocapacitive effect in $CaMn_{1-x}Sb_xO_3$, the $x - T$ phase diagram would be important. Focusing on the dielectric properties, we have newly revealed that $T_p$ and $T_s$ are almost linearly enhanced from $x$ = 0.1 to 0.2. On other properties such as the magnetic phase, we can speculate based on the phase diagram of the similar carrier-doped manganites. Comparing the one-electron-doped system $CaMn_{1-x}Sb_xO_3$ with a two-electron-doped system $AeMn_{1-z}Mo_zO_3$ (*Ae*: Alkaline earth metal), from the viewpoint of the average valence $\alpha$ of Mn ions, $CaMn_{0.85}Sb_{0.15}O_3$ with $\alpha = +3.82$ and $CaMn_{0.8}Sb_{0.2}O_3$ with $\alpha = +3.75$ correspond to $AeMn_{0.917}Mo_{0.083}O_3$ and $AeMn_{0.889}Mo_{0.111}O_3$, respectively. Considering that the structural phase transition from *Pnma* to $P2_1/m$ at the room temperature occurs between $CaMn_{0.85}Sb_{0.15}O_3$ and $CaMn_{0.8}Sb_{0.2}O_3$, the phase diagram of $CaMn_{1-x}Sb_xO_3$ is expected to be similar to that of $Ca_{0.75}Sr_{0.25}Mn_{1-z}Mo_zO_3$ in which the same structural transition occurs between $z$ = 0.083 and 0.111 [2]. In the phase diagram of $Ca_{0.75}Sr_{0.25}Mn_{1-z}Mo_zO_3$, the ground state for $0.052 \leq z \leq 0.111$, which corresponds to $0.1 \leq x \leq 0.2$ in $CaMn_{1-x}Sb_xO_3$, is the C-type AFM phase with charge/orbital ordering, whose ordering temperature is linearly enhanced by more than 130 K in this range. In $CaMn_{0.85}Sb_{0.15}O_3$, we really observed a magnetic anomaly that suggests a CO near $T_p$ [14], [15].

Therefore, the dielectric peak in $CaMn_{1-x}Sb_xO_3$, which indicates the formation of a dipole ordering, is expected to have a positive correlation with a charge/orbital ordering. As for the magnetocapacitive effect, since charge/orbital orderings in $CaMnO_3$ series stabilize a certain magnetic ordering [28], we consider that the dipole ordering related to a charge/orbital ordering is affected by a magnetic field through a magnetic ordering. This magnetic-field-sensitive dielectric peak, which seems to be related to a charge/orbital ordering, is similar to that in the hole-doped system $Pr_{1-x}Ca_xMnO_3$ and

$Y_{1-x}Ca_xMnO_3$ [5]–[9], but it is the first example among electron-doped $CaMnO_3$ systems.

Concerning the dielectric anomaly in the imaginary part which indicates the active development of electrically polarized regions, $T_s$ is notably sensitive to the one-electron-doping Sb substitution in $CaMn_{1-x}Sb_xO_3$, whereas it is not affected by the isovalent Sr substituion in $Ca_{1-y}Sr_yMn_{0.85}Sb_{0.15}O_3$ [15]. From these contrast results, we emphasize that the carrier concentration is a crucial parameter for the expansion of polar nanoregions in the $Ca_{1-y}Sr_yMn_{1-x}Sb_xO_3$ system.

As a next issue, it would be important to clarify whether macroscopic electric polarization exists at low temperatures. In order to check our scenario on the mechanism of the dipole anomalies and the magnetocapacitive effect in the $Ca_{1-y}Sr_yMn_{1-x}Sb_xO_3$ system, the magnetic ground state and the possibility of a charge/orbital ordering should be studied.

## V. Conclusion

We measured the dielectric constant of the electron-doped manganite $CaMn_{1-x}Sb_xO_3$ ($x = 0.1$, 0.12, 0.13, 0.15, and 0.2). The temperature dependence of the real part exhibits a broad and large peak of which value is suppressed and of which temperature is enhanced by increasing frequency, whereas the imaginary part shows a shoulder anomaly on a quasi-power-law temperature dependence. These results suggest that $CaMn_{1-x}Sb_xO_3$ is a relaxor: clusters with a short-range dipole ordering appear at the peak temperature and grow gradually, especially actively at the shoulder temperature.

Importantly, we have revealed that the shoulder temperature is remarkably enhanced with the increasing Sb content $x$. This result indicates that the growth of the clusters is strongly affected by the carrier concentration. Moreover, the dielectric peak is sensitive to a magnetic field in all the samples. By analogy with other $CaMnO_3$ systems, a charge/orbital ordering and an accompanying magnetic ordering might play an important role for the dielectric ordering in $CaMn_{1-x}Sb_xO_3$.

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