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*Published in:*
Applied Physics Letters

*DOI:*
10.1063/1.3551540

*Published: 01/01/2011*

*Please cite the original version:*
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Citation: Appl. Phys. Lett. 98, 072903 (2011); doi: 10.1063/1.3551540
View online: http://dx.doi.org/10.1063/1.3551540
View Table of Contents: http://aip.scitation.org/toc/apl/98/7
Published by the American Institute of Physics
Magnetodielectric response of square-coordinated MnO\(_2\) unit in cubic BiMn\(_7\)O\(_{12}\)

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(Received 1 November 2010; accepted 22 December 2010; published online 14 February 2011)

The magnetodielectric (MD) effect for BiMn\(_7\)O\(_{12}\) with the cubic \(A^\prime A''^3 B_2 O_{12}\)-type \(A\)-site-ordered perovskite structure has been investigated. A clear negative MD response around and beyond \(T_N\) has been observed and attributed to antiferromagnetic spin fluctuations. With further decreasing temperature (\(T < T_N\)) a switching to a complex positive MD effect is found confirming additional contribution coming from the magnetic ordering. The present study underlines the importance of square-coordinated Mn\(_{14}\)O\(_2\) units for generating MD coupling in an \(A^\prime A''^3 B_2 O_{12}\)-type structure; the magnitude of the MD effect then strongly depends on the precise chemical composition. © 2011 American Institute of Physics. [doi:10.1063/1.3551540]

Materials that show drastic responses to various external stimuli attract considerable attention due to their high technological potentials, or multifunctionality, as well as scientific interest. Strongly coupled multiple degrees of freedom of electron, e.g., spin, charge, and orbital, in the strongly correlated electron systems are expected to lead to unprecedented device applications, e.g., colossal magnetoresistance and spin-driven ferroelectricity in perovskite manganites.\(^{1-3}\) The so-called magnetodielectric (MD) effect observed in some exotic magnetic insulators/semiconductors is a phenomenon resultant from strongly coupled dielectric/magnetic interactions which provide additional tunability of dielectric constant by means of controlling the external magnetic field.\(^3\) In general the intrinsic MD coupling in a magnetic insulator is large only about the magnetic ordering temperature, while that is subtle in the paramagnetic phase including the geometrically frustrated magnetic state. For practical application larger MD coupling and high controllability by magnetic fields are highly desired. Thus it is necessary to gain deeper understanding and materials design concept of the MD phenomena. In the present study we investigated the MD effect in the \(A\)-site-ordered manganese perovskite (BiMn\(_3\))(\(A\)Mn\(_{14}\))\(_3 B_2 O_{12}\) or BiMn\(_7\)O\(_{12}\), where Bi\(^{3+}\) with the \(6s^2\) lone-electron-pair and Mn\(^{3+}\) show very unusual ordered arrangement at the \(A\)-site of the simple \(ABO_3\) perovskite [see Fig. 1(a); visualized with the software VESTA (Ref. 5)].

Depending on the excess oxygen content, or in other words cation deficiency, BiMn\(_7\)O\(_{12}\) takes monoclinic LaMn\(_7\)O\(_{12}\)-type and cubic CaCu\(_3\)Ti\(_4\)O\(_{12}\)-type structures, both of which consist of the same Mn\(_{14}\)O\(_2\) unit.\(^6,8\) Intriguing MD effect was discovered depending on temperature range or magnetic state in monoclinic BiMn\(_7\)O\(_{12}\) of single-valent Jahn–Teller (JT) system,\(^6\) whereas the relaxation of the JT distortion for the Mn\(_{14}\)O\(_6\) octahedra and the corresponding lack of Mn\(_{14}\) magnetic ordering were found in the more strongly oxygenated phase of cubic BiMn\(_7\)O\(_{12}\).\(^7\) It has been reported that not only spin fluctuations induced by antiferromagnetic (AFM) ordering and the shift of the magnetic transition temperature caused by external magnetic fields but also magnetic-field-induced spin realignment may contribute to the MD response in monoclinic BiMn\(_7\)O\(_{12}\).\(^6\) Thus it is interesting to investigate the MD effect in oxygen-rich cubic BiMn\(_7\)O\(_{12}\) and compare with that in the monoclinic one to gain deeper understanding of the coupled magnetic dielectric properties.

Cubic BiMn\(_7\)O\(_{12}\) was prepared through high-pressure synthesis as reported previously.\(^7\) Electron diffraction (ED) coupled with energy dispersive spectroscopy (EDS) has been carried out to check the lattice. As illustrated by [100] and

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which is evidenced in the clear drop in slope around the AFM ordering temperature for cubic BiMn$_7$O$_{12}$, as shown in Fig. 3(b). These findings are compatible with the magnetic susceptibility data, indicating that the AFM transition in cubic BiMn$_7$O$_{12}$ is very sensitive to $H$. Accordingly $\varepsilon'$ is also strongly affected by $H$.

To explore the effect of $H$ on $\varepsilon'$ in cubic BiMn$_7$O$_{12}$ we measured the MD ratio $\varepsilon' = [\varepsilon'(\mu_0 H) - \varepsilon'(\mu_0 H = 0)] / \varepsilon'(\mu_0 H = 0)$ as a function of $H$ at several temperatures, as shown in Fig. 4. It is found that the sign and shape of the MD versus $H$ curve depend on temperature. A symmetric negative MD effect with smooth $H$-dependence is observed around $T_N$ being compatible with the expectation for AFM compounds, whereas a positive MD response is as well seen below $T_N$. These observations are very similar to the case of monoclinic BiMn$_7$O$_{12}$. A closer look to the MD data collected from 25 to 5 K clearly reveals the existence of a shoulder at a characteristic magnetic field ($H_{\text{flop}} \approx 5$ T at 20 K). This $H_{\text{flop}}$ value increases with decreasing temperature. The origin of this feature is not clear, and further experiments are required to clarify the feature. In addition, the MD measurements show a negative MD effect just above $T_N$ in the paramagnetic region (see 35 and 50 K data in Fig. 4), which may be due to short-range AFM spin fluctuations. The MD response above $T_N$ does not vary too much with increasing temperature.

The magnitude of the MD ratio is found to be smaller in cubic BiMn$_7$O$_{12}$ compared to that in monoclinic BiMn$_7$O$_{12}$, which is consistent with the tiny change in $\varepsilon'$ around $T_N$ presented in Fig. 2(b). The negative-to-positive MD switching below $T_N$ clearly suggests the different origin of the MD effect observed around and well below $T_N$, besides the high-sensitivity of $T_N$ to $H$. These findings are common in cubic and monoclinic BiMn$_7$O$_{12}$, and we may thus conclude that the intriguing MD effects in cubic and monoclinic BiMn$_7$O$_{12}$ are presumably of the same origin.

Important structural features of cubic and monoclinic BiMn$_7$O$_{12}$ are that (1) the square-coordinated Mn$_A$-O$_2$ unit exists in both the forms, and (2) the monoclinic phase exhibits distorted or JT-active Mn$_B$-O$_6$ octahedra, whereas regular octahedral coordination is seen for the cubic phase. The rigidity of the lattice is related to how strongly multiple degrees of freedom of electrons are coupled. Hence, from a viewpoint of crystal structure and magnetic behavior, the observed complex MD effects may be caused by the peculiarly ordered square-coordinated Mn$_A$-O$_2$ unit, which induces coupled magnetic and dielectric interactions. The difference in magnitude could be understood by considering the degree of Bi 6$s^2$ lone-pair-induced orbital hybridization, which reflects the strength of the chemical bonding and may thus cause different structural features. Another possible explanation might be the difference in the rigidity of the lattice through the Mn$_{A'}$-O-Mn$_{B'}$-O-Mn$_{A''}$ magnetic exchange pathway. Namely, the stronger connection between Mn$_{A'}$ and Mn$_B$ via common O is expected in monoclinic BiMn$_7$O$_{12}$ with JT-active Mn$_B$-O$_6$ octahedra than in the JT-inactive cubic form. Supерexchange interaction through the $A''-O-B-O-A''$ path in addition to the direct exchange interaction between the $A'$ cations is known to play a significant role in the sign and magnitude of the magnetic coupling in $A''B_2O_{12}$. Therefore the Mn$_{A}$-O-Mn$_{B}$-O-Mn$_{A''}$ path in monoclinic BiMn$_7$O$_{12}$ would play a role not only in global magnetic interactions but also in the MD coupling.

It is worth to mention that similar coupled magnetic-dielectric interactions below $T_N$ have been observed in iso-

![Image](https://example.com/image.jpg)  
FIG. 2. (Color online) (a) Magnetic susceptibility depending on temperature for cubic and monoclinic BiMn$_7$O$_{12}$ measured under 0.05 T. (b) Dependence on temperature of real part of relative dielectric constant ($\varepsilon'$: at 100 kHz) under 0 T for cubic and monoclinic BiMn$_7$O$_{12}$. The inset shows $\varepsilon'/T$ for cubic BiMn$_7$O$_{12}$ as a function of temperature. The data for monoclinic BiMn$_7$O$_{12}$ were taken from Ref. 6, for comparison.

[111] ED patterns shown in Figs. 1(b) and 1(c), an hexagonal network is observed along the [111] zone axis, while the [100] ED pattern leads to a cell parameter close to 7.5 Å in agreement with the expected cubic ($2a_0 \times 2a_0 \times 2a_0$) lattice. Corresponding EDS data reveal a homogeneous average cation composition close to the nominal one. A thin layer of indium was deposited on the opposite parallel surfaces of the polished bulk sample for capacitance measurements. Capacitance and dielectric loss were measured from 8 K to room temperature (rate: 2 K/min) using an Agilent 4248A RLC bridge allied with physical property measurement system (Quantum Design) at different frequencies (1–100 kHz) to ensure that the results are not frequency-dependent and the loss angle is always below 0.2% (not shown here).

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi$ and the dielectric constant $\varepsilon'$ for cubic and monoclinic BiMn$_7$O$_{12}$. We found clear dielectric anomalies associated with the magnetic phase transition(s) for both cubic and monoclinic phases. For cubic BiMn$_7$O$_{12}$ there is a clear drop in slope around the AFM ordering temperature $T_N$, which is evidenced in the $\varepsilon'/T$ versus $T$ plot [see the inset of Fig. 2(b)]. In cubic BiMn$_7$O$_{12}$ the decrease in $\varepsilon'$ below $T_N$ indicates the coupling between the polarization and the magnetization, which is related to the AFM ordering, while the smaller change in $\varepsilon'$ around $T_N$ suggests a weaker MD coupling.

The effect of external magnetic field $H$ on dielectric property for cubic BiMn$_7$O$_{12}$ is presented in Fig. 3. The inflection temperature, where $\varepsilon'$ decreases sharply, shifts to the lower temperature side with increasing $H$, as clearly evidenced in the dielectric loss [see Fig. 3(b)]. These findings are compatible with the magnetic susceptibility data, indicating that the AFM transition in cubic BiMn$_7$O$_{12}$ is very sensitive to $H$. Accordingly $\varepsilon'$ is also strongly affected by $H$.

[10] 35 and 50 K data in Fig. 4, which may be due to short-range AFM spin fluctuations. The MD response above $T_N$ does not vary too much with increasing temperature.

The magnitude of the MD ratio is found to be smaller in cubic BiMn$_7$O$_{12}$ compared to that in monoclinic BiMn$_7$O$_{12}$, which is consistent with the tiny change in $\varepsilon'$ around $T_N$ presented in Fig. 2(b). The negative-to-positive MD switching below $T_N$ clearly suggests the different origin of the MD effect observed around and well below $T_N$, besides the high-sensitivity of $T_N$ to $H$. These findings are common in cubic and monoclinic BiMn$_7$O$_{12}$, and we may thus conclude that the intriguing MD effects in cubic and monoclinic BiMn$_7$O$_{12}$ are presumably of the same origin.

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It is worth to mention that similar coupled magnetic-dielectric interactions below $T_N$ have been observed in iso-
A magnetic ordering temperature. The picture of strongly coupled magnetic-dielectric interactions below the ordering temperature in monoclinic and cubic BiMn$_7$O$_{12}$ and in CaCu$_3$Ti$_4$O$_{12}$ confirm that the $A''$O$_2$ unit in the $A'\!A''\!A''\!B_4$O$_{12}$-type compounds is important for the generation of the MD response. In other words, the unusually ordered arrangement of the $A''$O$_2$ units favors coupled magnetic-dielectric interactions below the $A''$-site magnetic ordering temperature. The picture of strongly connected crystal and magnetic structures can be valid not only in CaCu$_3$Ti$_4$O$_{12}$, but also in many other $A'\!A''\!A''\!B_4$O$_{12}$-type compounds. The $A'\!A''\!A''\!B_4$O$_{12}$-type structure is known to be robust against chemical substitution blocked by the $A''$-site -O-B-O-$A''$ path, the $A'\!A''\!A''\!B_4$O$_{12}$-type system appears to be a very promising family to generate MD devices.

N. Imamura thanks CNRS for postdoctoral fellowships.