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Magnetodielectric effect in EuZrO$_3$

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Following recent report on antiferromagnetic ordering in EuZrO$_3$ we performed dielectric measurements of this material as a function of temperature and magnetic field. Dielectric constant of dense EuZrO$_3$ ceramics is 30.1 at 300 K. It gradually decreases upon cooling without any quantum paraelectric behavior; however, below $T_N=4.1$ K it shows a pronounced drop that qualitatively resembles that observed in EuTiO$_3$. We report that dielectric constant of EuZrO$_3$ is magnetic field dependent. The magnitude of the magnetodielectric effect in both EuTiO$_3$ and EuZrO$_3$ is discussed in the light of the recently proposed coupling of the Eu–O–Eu superexchange interactions with electrons involved in partially covalent Ti(Zr)–O bond. © 2010 American Institute of Physics. [doi:10.1063/1.3456730]

Recent interest in magnetoelectric materials has brought to light several compounds containing divalent europium. For example, EuTiO$_3$, a G-type antiferromagnet below Néel temperature, $T_N=5.5$ K, demonstrates a strong magnetocapacitance effect. In view of very low electrical conductivity of EuTiO$_3$ at $T\lesssim 60$ K, observed magnetocapacitance is attributed solely to the magnetic field dependence of dielectric constant, $\varepsilon(H)$. Most recently, electric field induced magnetoelectric coupling in EuTiO$_3$ has been reported by Shvartsman et al.

Although theoretical support for magnetoelectric coupling in EuTiO$_3$ is abundant, a direct proof of magnetic dependence of the optical phonon mode(s) has yet to be found. Recent analysis of the infrared active phonon modes in EuTiO$_3$ indicates that, similar to SrTiO$_3$, the (soft) phonon mode that contributes the largest dielectric weight to the phonon spectrum and presumably is responsible for the magnetoelectric effect, is Slater-type mode. Remarkably, this mode does not involve magnetically active (Eu$^{2+}$) ions. as opposed to the Last-type mode where Eu$^{2+}$ ions vibrate against the TiO$_6$ octahedra. According to Cohen$^2$, the properties of the Slater-type mode in the AB$_3$O$_{12}$ perovskites with A= Sr, Ba, and Pb and B=Ti are largely dependent on the overlap between the O 2$p$ and B 3$d$ orbitals, i.e., on the degree of covalency of the B–O bond. Recently, Goian et al.$^3$ have suggested that the magnetoelectric effect in EuTiO$_3$ can be understood in terms of the impact of Eu–O–Eu superexchange on the electron density involved in (partially) covalent Ti–O bond. One way to examine this hypothesis is to find another Eu$^{2+}$B$^{4+}$O$_4$ perovskite with similar magnetic structure but different degree of covalency of the B–O bond.

Here we report on synthesis, crystal structure, and physical properties of EuZrO$_3$ perovskite with a special emphasis on its magnetodielectric effect. Until recently, EuZrO$_3$ was considered paramagnetic with a cubic (space group $Pm\bar{3}m$) perovskite structure. Recently Viallet et al.$^8$ and Zong et al.$^9$ have revised the crystal structure of EuZrO$_3$ and found that it crystallizes in orthorhombic (space group Pbnm) symmetry similar to that of SrZrO$_3$. Most importantly, Zong et al.$^9$ found that EuZrO$_3$ develops an antiferromagnetic (AFM) ordering below $T_N=4.1$ K. Although direct confirmation of the type of the AFM structure in EuZrO$_3$ has yet to be provided by neutron diffraction, the indirect evidence indicates that EuZrO$_3$ and EuTiO$_3$ are magnetically very similar. In particular, analysis of the sign and magnitude of the magnetic exchange constants, $J_i$, between nearest, $J_1$, and next-nearest, $J_2$, Eu$^{2+}$ ions in EuZrO$_3$ (Ref. 9) favors the G-type AFM structure, similar to that found in EuTiO$_3$. On the other hand, one may expect the valence electronic structure of these two perovskites to be quite different. Namely, in contrast to partially covalent Ti–O bond in EuTiO$_3$, the Zr–O bond in EuZrO$_3$ is more ionic, similar to the case of SrZrO$_3$. This makes EuZrO$_3$ an important reference material for understanding of the magnetodielectric effect in Eu$^{2+}$-based perovskites.

EuZrO$_3$ was prepared from Eu$_2$O$_3$ and ZrO$_2$ (both 99.9% pure, sourced from Kanto Chemicals, Japan). The stoichiometric mixture of Eu$_2$O$_3$ and ZrO$_2$ was treated at 1300 °C for 20 h in pure hydrogen at a flow rate of 80 cm$^3$/min, with intermediate regrounding until a yellow, single phase EuZrO$_3$ product was obtained. Phase purity was confirmed by powder x-ray diffraction (Rigaku Ultima III x-ray diffractometer, $\lambda=0.154\,\text{06 }\text{nm radiation}$. Lattice parameters were obtained from Rietveld refinement of the x-ray data using RIETAN 2000. Magnetic susceptibility in the 2–100 K range was measured using superconducting quantum interference device (Quantum Design, MPMS, USA). EuZrO$_3$ ceramic with 98% density was obtained by spark plasma sintering (SPS) (Dr. Sinter, SPS-1050, Japan) at 1450 °C under 130 MPa uniaxial pressure and base vacuum pressure of $2 \times 10^{-2}$ Pa. To release the residual lattice strain after SPS, the samples were annealed at 1300 °C in $H_2$ gas for 20 h. For dielectric measurements, Au electrodes were spattered
on the EuZrO$_3$ disks of 7 mm diameter and 1 mm thickness. Dielectric properties were measured with Agilent E4980 Precision LCR Meter in the temperature interval of 2.5–300 K and magnetic field of 0–80 kOe utilizing a home-made dielectric measurements probe coupled with the Physical Property Measurement System (QP, USA).

Powder x-ray analysis (Fig. 1) has confirmed orthorhombic (space group $Pbnm$) symmetry of EuZrO$_3$ with lattice constants $a=5.8019(4)$, $b=5.8236(5)$, and $c=8.2051(9)$ Å. The x-ray pattern was refined to the reliability factor $R_p = 11.2\%$ in close agreement with Ref. 8. According to the lattice parameters, the absolute density of EuZrO$_3$ is 6.976 g cm$^{-3}$.

Temperature dependence of magnetic susceptibility, $\chi$, measured at $H=50$ Oe and shown in Fig. 2 indicates an AFM phase transition at $T_N \approx 4.1$ K. Linear fit of the $\chi^{-1}(T)$ dependence yields a Weiss temperature $\theta_W = +0.1$ K. According to Ref. 9, positive $\theta_W$ is a rare case that indicates coexistence of both ferromagnetic and AFM interactions in EuZrO$_3$. Remarkably, positive $\theta_W \approx +3.3$ K has also been found in EuTiO$_3$, thus supporting similar G-type AFM magnetic structure.

Since EuZrO$_3$ and SrZrO$_3$ are structurally identical with the difference in the lattice constants of $\approx 0.04\%$, one may expect similar dielectric properties. Indeed, room temperature $\varepsilon'$ of EuZrO$_3$ determined in this work and that of SrZrO$_3$ reported in Ref. 13 are 30.1 and 30.4, respectively. Dielectric constant of EuZrO$_3$ is weakly temperature dependent [Fig. 3(a)] with $d\varepsilon'/dT = 6.8 \times 10^{-3}$ K$^{-1}$. The $\varepsilon'$ gradually decreases from 30.1 at 300 K to 28.45 at 5 K with no indication of the quantum paraelectric behavior. This supports our original assumption of the predominantly ionic Zr–O bond which does not favor formation of the low-energy (soft) phonon mode in EuZrO$_3$. Above 175 K, $\varepsilon'$ shows low-frequency dispersion which, we believe, is attributed to the finite electronic conductivity also evidenced from the large tan $\delta$ values [Fig. 3(b)]. From the linear tan $\delta$ vs. $\omega^{-1}$ dependence (not shown) we conclude that above 175 K the imaginary part of the dielectric constant is dominated by the electronic conductivity, $\sigma'$, according to

$$\varepsilon'' = \varepsilon' + i\frac{\sigma'}{\varepsilon_0\omega},$$

where $\varepsilon_0$ is the electric constant and $\omega$ is the angular frequency, $\omega = 2\pi f$.

The low-temperature behavior of $\varepsilon'$ is shown in Fig. 4(a) as a function of applied magnetic field. Dielectric constant of EuZrO$_3$ at $H=0$ demonstrates an anomalous drop below $T \approx 4$ K, the temperature corresponding to the AFM phase transition. Pronounced change in the $\varepsilon'(T)$ dependence is found upon application of magnetic field. Low-$T$ dielectric constant increases with magnetic field and saturates at $\varepsilon' = 28.48$ for $H \geq 30$ kOe. Qualitatively, magnetodielectric effect in EuZrO$_3$ is similar to that reported for EuTiO$_3$. On the quantitative scale, the magnitude of the magnetodielectric effects in EuZrO$_3$ and EuTiO$_3$ is quite different. Katsufuji et al.$^1$ proposed a simple equation to describe the magnetodielectric effect as follows:

$$\varepsilon'(H) = \varepsilon'(H=0)(1 + \alpha \langle S_i \cdot S_j \rangle),$$

where $\varepsilon'(H=0)$ is dielectric constant at zero magnetic field, $\langle S_i \cdot S_j \rangle$ is the spin pair correlation between nearest neighbor Eu$^{2+}$, and $\alpha$ is the coupling constant between spin correlation and dielectric constant. In order to estimate $\langle S_i \cdot S_j \rangle$ in EuZrO$_3$, we have performed a mean-field calculation based on a Heisenberg model under an assumption that the 4f spins of Eu$^{2+}$($S=7/2$) are located on a simple cubic lattice with a G-type AFM ordering.$^9$ The Heisenberg Hamiltonian of the spin system, with restriction to the nearest-neighbor and next-nearest-neighbor interactions, is given by

FIG. 1. Room temperature x-ray diffraction pattern of EuZrO$_3$ (+). Calculated diffraction pattern from Rietveld refinement of EuZrO$_3$ (solid line). The vertical bars indicate the positions of expected Bragg peaks. The difference between observed and calculated data is shown at the bottom of the plot.

FIG. 2. Temperature dependence of zero field cooled molar magnetic susceptibility, $\chi$, and $\chi^{-1}$ of EuZrO$_3$. The AFM transition at $T_N = 4.1$ K is detected from the $\chi(T)$ anomaly. Linear fit of the $\chi^{-1}(T)$ dependence yields a positive Weiss temperature, $\theta_W = +0.1$ K.

FIG. 3. Temperature dependence of (a) dielectric constant, $\varepsilon'$ and (b) dielectric loss, $\tan \delta$, of EuZrO$_3$ at selected frequencies $f = 0.1$, 0.3, 0.7, 1.7, 4.4, 11.3, 29.2, 75.3, 194, and 500 kHz.
where $S_i$ is the operator of the $4f$ spin localized at the site $i$. The sums of the first and the second terms run over the nearest-neighbor $(i,j)$, and the next-nearest-neighbor pairs $(i,j)$, respectively. In our calculation, we used $J_1/k_B=-0.032$ K and $J_2/k_B=0.017$ K which yield $T_N=4.1$ K and $\theta_B=0.1$ K, where $k_B$ is the Boltzmann constant. Figure 4(b) shows temperature dependence of $\langle S_i \cdot S_j \rangle$ calculated from the product of $\langle S \rangle$ on the two sublattices under different $H$.

From the data given in Figs. 4(a) and 4(b) and using Eq. (2), one finds for EuZrO$_3$ the magnetodielectric coupling constant $\alpha=1.1 \times 10^{-4}$, which is a factor of 27 lower than that of EuTiO$_3$ (i.e., $\alpha=2.74 \times 10^{-3}$).

In conclusion, at low $T$, EuZrO$_3$ shows magnetodielectric effect whose features are qualitatively similar to that reported for EuTiO$_3$, albeit the former perovskite is not a quantum paraelectric. That said, the magnitude of the magnetodielectric coupling in EuZrO$_3$ is much smaller than that of EuTiO$_3$. In accord with the hypothesis of Goian et al., we attribute this difference to stronger covalency of the Ti–O bond in EuTiO$_3$ which favors formation of the soft phonon mode which, in turn, facilitates coupling with the low-energy magnetic excitations.

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