

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.^{1,2} In view of very low electrical conductivity of EuTiO_3 at $T \leq 60$ K, observed magnetocapacitance is attributed solely to the magnetic field dependence of dielectric constant, $\epsilon(H)$. Most recently, electric field induced magnetoelectric coupling in EuTiO_3 has been reported by Shvartsman *et al.*³

Although theoretical support for magnetoelectric coupling in EuTiO_3 is abundant,⁴ 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.⁵ 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,⁶ the properties of the Slater-type mode in the ABO_3 perovskites with A=Sr, Ba, and Pb and B=Ti are largely dependent on the overlap between the O 2p and B 3d orbitals, i.e., on the degree of covalency of the B–O bond. Recently, Goian *et al.*,⁵ 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 bonding. One way to examine this hypothesis is to find another $\text{Eu}^{2+}\text{B}^{4+}\text{O}_3$ 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.⁷ 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 $T_N \approx 4.1$ 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 .^{10,11} 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_2O_3 and ZrO_2 (both 99.9% pure, sourced from Kanto Chemicals, Japan). The stoichiometric mixture of Eu_2O_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 regrinding 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, $\lambda=0.15406$ 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 2×10^{-2} Pa.¹² 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 sputtered

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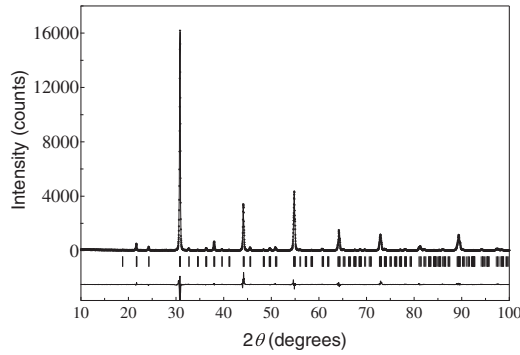


FIG. 1. Room temperature x-ray diffraction pattern of EuZrO_3 (+). Calculated diffraction pattern from Rietveld refinement of EuZrO_3 (solid line). The vertical bars indicate the positions of expected Bragg peaks. The difference between observed and calculated data is shown at the bottom of the plot.

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 (QD, 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, χ , 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 $\theta_W \approx +0.1$ K. According to Ref. 9, positive θ_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 $\approx 0.04\%$,¹³ one may expect similar dielectric properties. Indeed, room tempera-

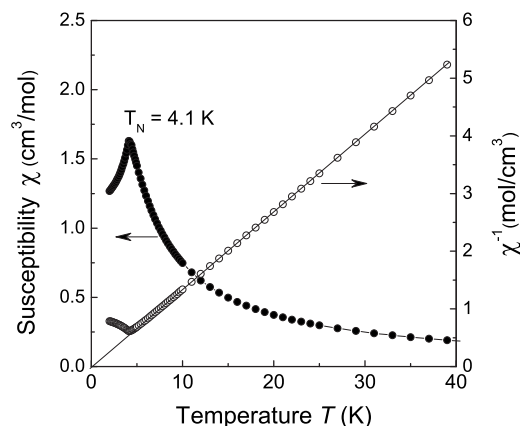


FIG. 2. Temperature dependence of zero field cooled molar magnetic susceptibility, χ , and χ^{-1} of EuZrO_3 . The AFM transition at $T_N \approx 4.1$ K is detected from the $\chi(T)$ anomaly. Linear fit of the $\chi^{-1}(T)$ dependence yields a positive Weiss temperature, $\theta_W \approx +0.1$ K.

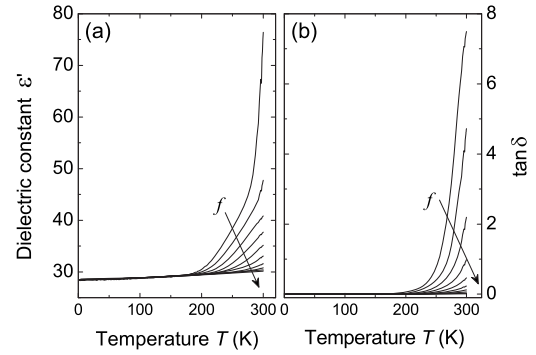


FIG. 3. Temperature dependence of (a) dielectric constant, ϵ' and (b) dielectric loss, $\tan \delta$, of EuZrO_3 at selected frequencies $f=0.1, 0.3, 0.7, 1.7, 4.4, 11.3, 29.2, 75.3, 194,$ and 500 kHz.

ture ϵ' 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 $d\epsilon'/dT \approx 6.8 \times 10^{-3} \text{ K}^{-1}$. The ϵ' 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, ϵ' 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. ω^{-1} dependence (not shown) we conclude that above 175 K the imaginary part of the dielectric constant is dominated by the electronic conductivity, σ' , according to

$$\epsilon^* = \epsilon' + i \frac{\sigma'}{\epsilon_0 \omega}, \quad (1)$$

where ϵ_0 is the electric constant and ω is the angular frequency, $\omega = 2\pi f$.

The low-temperature behavior of ϵ' 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 $\epsilon'(T)$ dependence is found upon application of magnetic field. Low- T dielectric constant increases with magnetic field and saturates at $\epsilon' \approx 28.48$ 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:

$$\epsilon'(H) = \epsilon'(H=0)(1 + \alpha \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle), \quad (2)$$

where $\epsilon'(H=0)$ is dielectric constant at zero magnetic field, $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is the spin pair correlation between nearest neighbor Eu^{2+} , and α is the coupling constant between spin correlation and dielectric constant. In order to estimate $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ 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

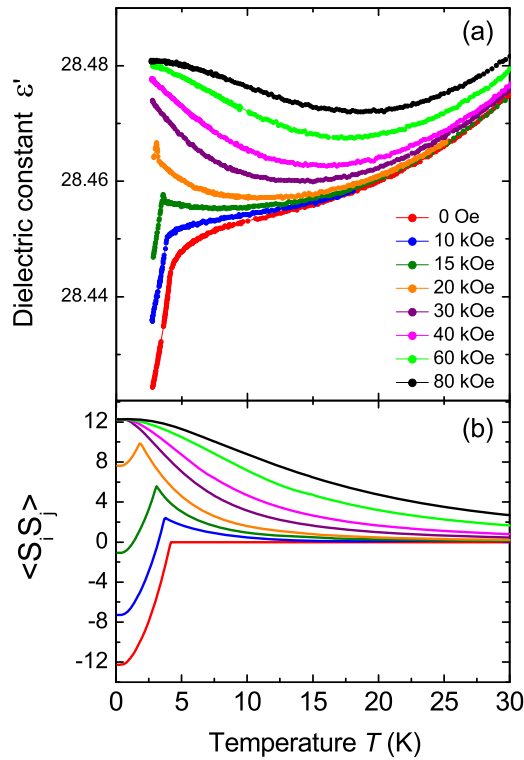


FIG. 4. (Color online) (a) Low-temperature behavior of dielectric constant of EuZrO₃ measured at 200 kHz in magnetic field of 0, 10, 15, 20, 30, 40, 60, and 80 kOe. (b) Spin correlation function for cubic EuZrO₃ calculated using a mean-field approximation.

$$H = -2J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - 2J_2 \sum_{\{i,j\}} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (3)$$

where \mathbf{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 $\langle i,j \rangle$, 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 $\theta_W = 0.1$ K, where k_B is the Boltzmann constant. Figure 4(b) shows temperature dependence of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ calcu-

lated 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 EuZrO₃ the magnetodielectric coupling constant $\alpha \approx 1.1 \times 10^{-4}$, which is a factor of 27 lower than that of EuTiO₃ (i.e., $\alpha \approx 2.74 \times 10^{-3}$).¹

In conclusion, at low T , EuZrO₃ shows magnetodielectric effect whose features are qualitatively similar to that reported for EuTiO₃, albeit the former perovskite is not a quantum paraelectric. That said, the magnitude of the magnetodielectric coupling in EuZrO₃ is much smaller than that of EuTiO₃. In accord with the hypothesis of Goian *et al.*,⁵ we attribute this difference to stronger covalency of the Ti–O bond in EuTiO₃ which favors formation of the soft phonon mode which, in turn, facilitates coupling with the low-energy magnetic excitations.

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