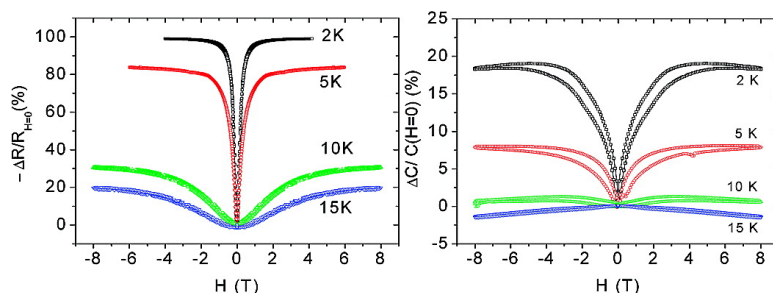


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Large Coupled Magnetoresponses in EuNbO_2N

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Materials in which magnetism is coupled to large changes in electronic conductivity (magnetoresistance effect)^{1,2} or electrical polarization (magnetocapacitance)^{3,4} are of fundamental interest and practical importance for new memory and sensor technologies. These responses are found separately in many materials based on magnetic transition metals notably manganese oxides; insulating BiMnO_3 ,⁵ YMnO_3 ,⁶ and TbMnO_3 ⁷ are multiferroics showing magnetocapacitive effects, whereas colossal magnetoresistances are observed in doped manganites such as $(\text{La,Pr,Ca})\text{MnO}_3$.² Coupled colossal magneto-resistive and capacitive effects have recently been observed in chromium chalcogenide spinels such as HgCr_2S_4 .⁸ To discover similar coupled effects, we have synthesized the perovskite oxynitrides EuMO_2N ($M = \text{Nb, Ta}$) which are found to have different defect chemistries. EuNbO_2N shows colossal (>99%) magnetoresistances at low temperatures and an apparent giant (20%) magnetocapacitance. However, the latter response is shown to result from microstructural effects predicted by a recent model,^{9,10} rather than an intrinsic multiferroism.

Most of the multiferroic materials explored in recent years combine magnetism from transition metal ion spins (notably Mn and Cr) with electrical polarization from a “lone pair” cation, for example, Bi^{3+} in BiMnO_3 ,⁵ or some other loss of inversion symmetry such as cycloidal magnetic order in TbMnO_3 .⁷ An alternative strategy is to combine magnetic lanthanides which have large spins with d^0 transition metal cations whose “off-center” instabilities can generate large ferroelectric polarizations, for instance, in BaTiO_3 and LiNbO_3 . Eu^{2+} compounds are particularly attractive as ferromagnetic order of the $S = 7/2$ spins is often observed. EuTiO_3 has been proposed as a suitable material for multiferroic devices in strained thin films,¹¹ as measurements on bulk samples have revealed a significant magnetocapacitance at low temperatures.¹² We have explored a chemical strategy for enhancing the dielectric properties through the substitution of a higher valent transition metal ion ($M = \text{Nb, Ta}$) with a charge-compensating substitution of nitride for oxide. Ferroelectric cation displacements are favored as $M\text{--N}$ bonds are more covalent than Ti--O , and any $\text{O}^{2-}/\text{N}^{3-}$ anion ordering will help to align the displacements of neighboring ions.

EuMO_2N perovskites are conveniently synthesized by the ammonolysis of EuMO_4 precursors at 950 °C (see Supporting Information). This reduces Eu^{3+} to Eu^{2+} and substitutes nitride for oxide giving single phase products. EuNbO_2N is a new phase and the Ta analogue corresponds to the phase “ $\text{EuTa}(\text{O,N})_3$ ” reported previously.¹³ These appear to be cubic perovskites, but splittings of synchrotron X-ray diffraction peaks reveal slight tetragonal lattice distortions ($a = 4.03215(2)$, $c = 4.04411(3)$ Å

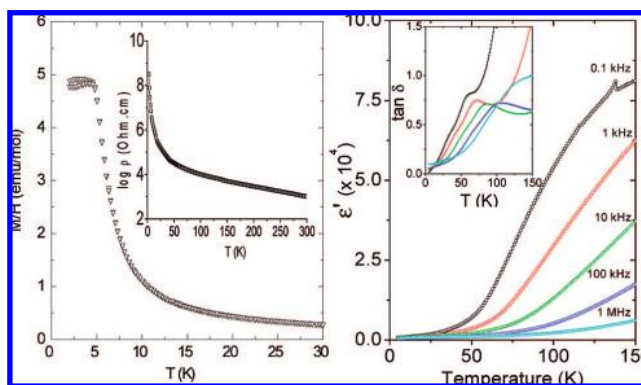


Figure 1. Temperature dependent physical measurements for EuNbO_2N : (left) magnetization/field in a 0.0025 T field, showing the ferromagnetic transition at 5.2 K, with electrical resistivity inset; (right) the dielectric constant and loss (inset) at different frequencies.

for EuNbO_2N ; $a = 4.02054(2)$, $c = 4.03079(4)$ Å for EuTaO_2N ; $c > a$ is consistent with some anion ordering, although O/N site occupancies cannot be determined directly from X-ray data. The tetragonal elongation could also arise from tilting of the Nb/Ta(O,N)₆ octahedra, evidenced as a further superstructure by electron diffraction. There is no X-ray evidence for an acentric distortion (see Supporting Information).

Chemical analysis reveals an important difference between the defect chemistries of EuNbO_2N and EuTaO_2N arising from the different M^{4+}/M^{5+} transition metal redox potentials. The Ta materials tend to be nitrogen rich so the formal metal valence distribution is $(\text{Eu}^{2+}_{1-x}\text{Eu}^{3+}_x)\text{Ta}^{5+}\text{O}_{2-x}\text{N}_{1+x}$ with $x = 0\text{--}0.20$ ($x = 0.05$ in the sample used for physical measurements below). The high activation barrier for $\text{Eu}^{2+}/\text{Eu}^{3+}$ hole hopping is consistent with the strongly insulating behavior. However, the relative ease of niobium reduction leads to nitrogen-deficient materials under the same reaction conditions; $\text{Eu}^{2+}(\text{Nb}^{5+}_{1-y}\text{Nb}^{4+}_y)\text{O}_{2+y}\text{N}_{1-y}$ with $y = 0\text{--}0.14$ ($y = 0.04$ in the sample used for physical measurements) with a more facile electron hopping between the Nb states.

EuNbO_2N and EuTaO_2N are both insulating paramagnets with effective moments (from Curie–Weiss fits to 50–300 K data) of 7.95 and 7.85 μ_B , close to the ideal value of 7.94 μ_B for Eu^{2+} , and Weiss temperatures of 2.0 and 0.7 K, respectively. They order ferromagnetically at $T_C = 5.2$ and 5.1 K (Figure 1), with saturated moments of 5.5 and 6.3 μ_B at 2 K. However, their magnetoresponses are very different. EuTaO_2N is highly insulating, with resistivities too large to be measured at low temperatures ($\rho > 10^9 \Omega\cdot\text{cm}$ below 165 K). The low temperature dielectric constant $\epsilon' = 37$ has a small frequency dependence, and shows a very small magnetocapacitance ($\text{MC}(H,T) = [\epsilon'(H,T) - \epsilon'(0,T)]/\epsilon'(0,T)$), rising from $\text{MC}_{H=8T} = 0.07\%$ at 25 K to 0.25% at 5 K. The resistivity of the ceramic

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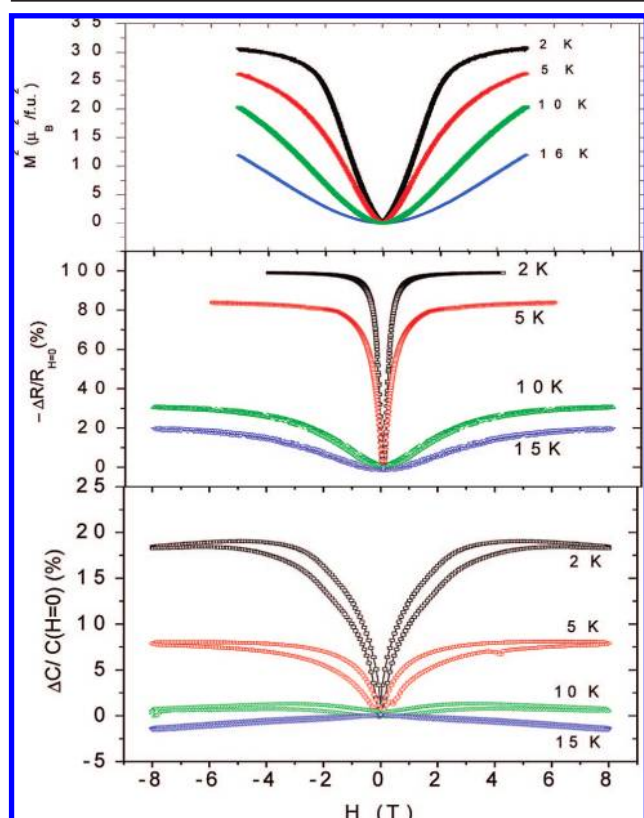


Figure 2. Magnetic field dependence of (a) the magnetization (plotted as M^2), (b) the magnetoresistance, and (c) the magnetocapacitance (measured at 100 kHz frequency) for EuNbO₂N.

sample of EuNbO₂N increases from $10^3 \Omega \cdot \text{cm}$ at room temperature to $>10^9 \Omega \cdot \text{cm}$ at 2 K and a large increase in the dielectric constant that shifts to high temperature with increasing frequency is observed above 40 K, accompanied by a peak in the loss (Figure 1). At low temperatures, large magneto-capacitances and resistances are observed (Figure 2). Giant negative magnetoresistances ($\text{MR}(H,T) = [\rho(H,T) - \rho(0,T)]/\rho(0,T)$) are observed above T_C , increasing to colossal values ($-\text{MR} > 99\%$; from $\rho \approx 10^9 \Omega \cdot \text{cm}$ at $H = 0$ to $\rho \approx 10^7 \Omega \cdot \text{cm}$ at $H = 4$ T) below the transition with a sharp low-field response. The magnetocapacitance switches from small negative values above the Curie transition to a giant positive MC = 20% at 4 T and 2 K.

The magnetotransport properties of EuNbO₂N arise from the coupling of the carrier spins to those of the localized $S = 7/2$ Eu²⁺. This is analogous to the double exchange mechanism observed in manganites, although the carriers and core spins in EuNbO₂N are associated with different cations. The electron hopping probability is proportional to $\cos^2 \phi$, where ϕ is the misalignment angle between neighboring spins, and hence to M^2 . The tunnelling magnetoresistance between grains or magnetic domains also has an M^2 dependence. Figure 2 shows that $-\text{MR}$ follows M^2 behavior above T_C due to tunnelling behavior, with an additional sharp contribution below the Curie transition.

The coupling of an apparent giant magnetocapacitance to the CMR in EuNbO₂N is a notable result. Large magneto-resistive and capacitive effects have recently been discovered in sulfide spinels such as CdCr₂S₄¹⁴ and HgCr₂S₄.⁸ A mechanism based on

intrinsic multiferroic relaxor behavior has been developed,¹⁵ but an alternative explanation is that the magnetocapacitance is a microstructural effect due to Maxwell–Wagner polarization,^{9,10} an interfacial polarization arising from charge depleted grain boundaries. The increase of bulk conductivity relative to that of grain boundaries when a magnetic field is applied produces an additional polarization without an intrinsic multiferroic coupling. This is the likely origin of the MC in EuNbO₂N. The large increase in the dielectric constant that shifts to high temperature with increasing frequency above 40 K accompanied by a peak in the loss (Figure 1) is a typical Maxwell–Wagner behavior. The strong link between the magneto-responses (Figure 2), the switch from negative to positive MC on cooling through the Curie transition, and the field variations of MC are as predicted for a change of the dominant magnetoresistance mechanism from tunnelling above T_C to an intrinsic double-exchange-type mechanism in the ferromagnetic region within the microstructural model.⁹

In summary, these results demonstrate an excellent potential for large magneto-responses in materials like EuNbO₂N, combining the large Eu²⁺ spin and the off-center instability of Nb⁵⁺ enhanced by bonding to nitride. The slight anion nonstoichiometry of our initially studied EuNbO_{2+y}N_{1-y} materials dopes electron carriers into the Nb:d-band, giving rise to CMR but obscuring any intrinsic multiferroism. The apparent giant MC arises from microstructural inhomogeneities in the doping, validating the proposed model and showing that ac magnetocapacitance measurements must be interpreted with care. Precise control of the stoichiometry and microstructure for EuNbO₂N and related materials will be needed to explore further the possibilities for intrinsic multiferroic couplings and other magnetoresponses.

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Supporting Information Available: Details of the synthesis, analysis, structural characterisations, and property measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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