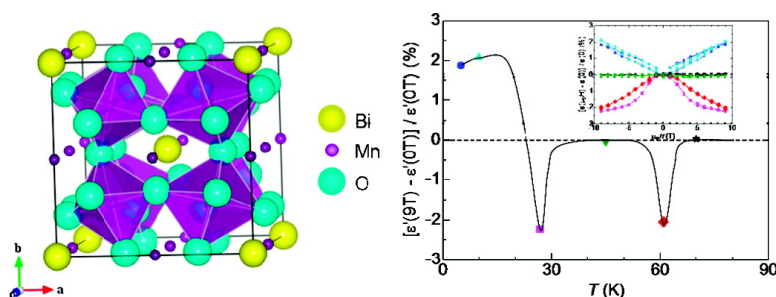


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J. Am. Chem. Soc., **2008**, 130 (45), 14948-14949 • DOI: 10.1021/ja806487d • Publication Date (Web): 17 October 2008

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Positive and Negative Magnetodielectric Effects in A-Site Ordered (BiMn₃)Mn₄O₁₂ Perovskite

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Materials with mutually coupled magnetic and (di)electric properties are the very focus of current interest as they are expected to provide us with novel phenomena of highly scientific and technological impact.^{1,2} The so-called magnetodielectric or magnetocapacitance (MC) effect, seen for some exotic magnetic insulators/semiconductors, such as multiferroic BiMnO₃³ and magnetoresistive La₂NiMnO₆,⁴ is expected to lead to unprecedented device applications, in which the magnitude of dielectric constant may be controlled by the magnetic field. The challenge is to expand the yet limited number of MC compounds to gain a deeper understanding of the magneto(di)electric phenomena and also to open up ways to put them to practical use.

Here we present a novel bismuth manganese perovskite oxide, BiMn₇O₁₂ or (BiMn₃)Mn₄O₁₂, that exhibits either a positive or a negative dielectric constant response of appreciable magnitude in an external magnetic field depending on the temperature range/type of magnetic ordering. The BiMn₇O₁₂ sample was prepared in an essentially single-phase form through a high-pressure synthesis route at 5 GPa and 1100 °C with only minute amounts of BiMnO₃ and Bi₂O₂CO₃ as impurity phases. The new compound BiMn₇O₁₂ is isostructural with the reported (LaMn₃)Mn₄O₁₂,⁵ possessing (at room temperature) a strongly distorted monoclinic perovskite structure with space group *I2/m* and lattice parameters *a* = 7.548(3) Å, *b* = 7.393(3) Å, *c* = 7.556(3) Å, β = 91.229(2)°, based on X-ray powder diffraction data. Rietveld refinement confirmed that the Bi³⁺ and Mn³⁺ ions are ordered in a 1:3 ratio at the perovskite A-site, *i.e.* (BiMn₃)Mn₄O₁₂ (see Figure 1). Resistivity showed an insulating/semiconducting-type dependence on temperature, being ~10⁴ Ω cm at room temperature.

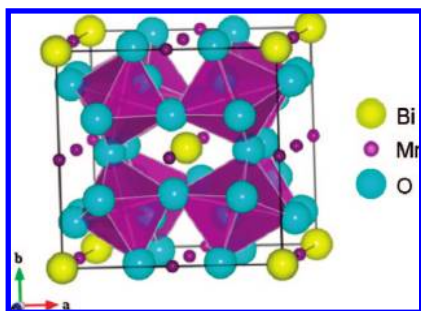


Figure 1. Room-temperature crystal structure of (BiMn₃)Mn₄O₁₂.

Figure 2a shows the dependence of magnetization on temperature for (BiMn₃)Mn₄O₁₂ under various magnetic fields. Parallel to the case of (LaMn₃)Mn₄O₁₂,⁶ two magnetic transitions are observed

with decreasing temperature: an FM-like transition appears at *T*₂ ≈ 59 K and an AFM-like transition at *T*₁ ≈ 28 K.

Taking analogy to the (LaMn₃)Mn₄O₁₂ phase, we tentatively assign the lower-temperature AFM-type transition and the higher-temperature FM-type transition to Mn³⁺-ion spin ordering at the A- and B-cation site, respectively. [For (LaMn₃)Mn₄O₁₂ both transitions at 20 and 76 K are of the AFM type.⁶] A Curie–Weiss fit to the paramagnetic susceptibility data resulted in a Weiss temperature of –259 K and a paramagnetic moment of 4.96 μ_B per one Mn³⁺ ion which is close to the theoretical value of 4.9 μ_B. An FM hysteresis can be clearly observed at temperatures below *T*₂ [see the inset of Figure 2a]. The resultant spontaneous magnetization (~1 μ_B/formula unit with seven Mn³⁺ ions) is rather small indicating an AFM coupling between the Mn³⁺ ions at the B site. Therefore we attribute the FM feature to spin canting as has been done for many BiMO₃ perovskites,^{7–9} except for the orbital-ordered BiMnO₃ ferromagnet.¹⁰ Below *T*₁ a large difference is seen between the ZFC and FC curves when a small magnetic field is applied, indicating a frustrated AFM state.

A somewhat unusual feature of the present material (BiMn₃)Mn₄O₁₂ is that the weak-FM regime in terms of temper-

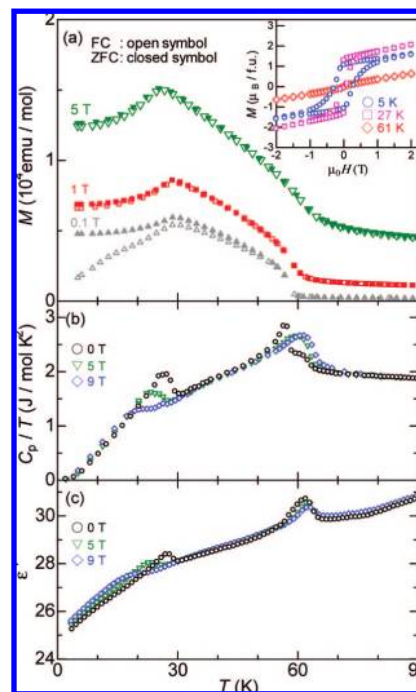


Figure 2. Dependence on temperature (*T*) of (a) magnetization (*M*), (b) specific heat (expressed as *C_p/T*), and (c) real part of relative dielectric constant (*ε'*; at 100 kHz) for (BiMn₃)Mn₄O₁₂ under various magnetic fields (*H*). The inset in (a) shows *M/H* curves at selected temperatures.

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ature, i.e., the regime from T_1 to T_2 , expands with increasing applied magnetic field [see Figure 2a], which is also revealed through the specific heat data presented in Figure 2b. Further seen from Figure 2b is that with increasing strength of the magnetic field the specific-heat anomaly near T_1 becomes less clearly defined, indicating a strong magnetic-field dependence of the transition. On the other hand, an additional small specific-heat anomaly is detected just above T_2 , which then upon increasing the applied magnetic field merges with that induced by the magnetic transition, hence pointing to the possibility of some yet unknown phase transition. Careful investigation at low temperatures is required for the deeper understanding of the transition.

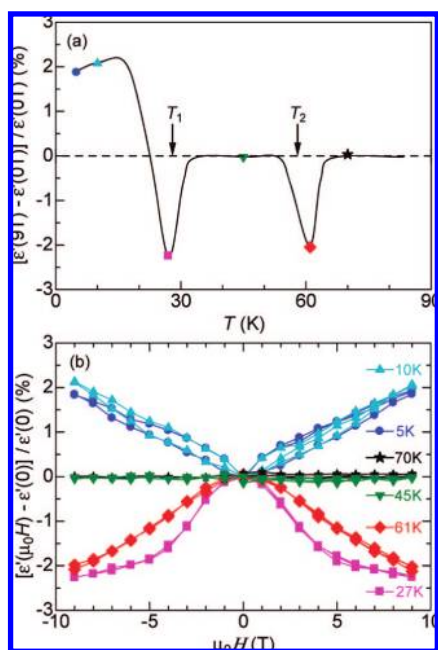


Figure 3. Dependence of the MC ratio $\equiv (\epsilon'(\mu_0H) - \epsilon'(0))/\epsilon'(0)$ of $(\text{BiMn}_3)\text{Mn}_4\text{O}_{12}$ on (a) temperature (T) and (b) magnetic field (H).

Dependence of the dielectric constant ϵ' on temperature is displayed in Figure 2c. Clear anomalies are observed at both the magnetic transition temperatures, T_1 and T_2 ; the change in the magnitude of ϵ' is on the order of a few percent. The dependence of the MC ratio $\equiv (\epsilon'(\mu_0H) - \epsilon'(0))/\epsilon'(0)$ on temperature is summarized in Figure 3a. In Figure 3b shown is the dependence of the MC ratio on applied magnetic field at representative temperatures. Interestingly either a negative or a positive MC response is observed depending on the magnetic state. A clear negative MC effect is revealed in the vicinity of the FM-like transition temperature T_2 (Figure 3b; see the 61-K data). This resembles the cases of the multiferroic perovskites BiMnO_3 and $\text{Bi}_2(\text{NiMn})\text{O}_6$, but the effect is much larger in magnitude for the present $(\text{BiMn}_3)\text{Mn}_4\text{O}_{12}$ (i.e., 2.0% at 9 T) in comparison to those for BiMnO_3 (0.6%)³ and $\text{Bi}_2(\text{NiMn})\text{O}_6$ (0.7%)¹¹ at their magnetic transition temperatures of 100 and 140 K, respectively. The smooth H -dependence of MC for small H values observed near T_2 is consistent with the behavior expected for AFM compounds,¹² in agreement with the anticipated AFM coupling between the B -site Mn^{3+} ions. A notable negative MC effect is also seen near the AFM-like magnetic transition temperature T_1 (Figure 3b; see the 27-K data). The dependence of MC on magnetic field around T_1

is, however, peculiar compared to that near T_2 . Near T_1 the magnitude of MC is drastically increased by a magnetic field of a few tesla. This may be caused by not only the magnetic ordering itself but also the shift of the magnetic transition temperature. Another possible explanation is some competitive interaction of AFM ordering and magnetic-field-induced rerotation of the Mn^{3+} spins at the A site (cf. the spin reorientation of Ho^{3+} in the HoMnO_3 perovskite¹³). Then finally below T_1 a positive MC effect is observed (Figure 3b; see the 5-K and 10-K data). Here the decay of MC below T_1 is clearly smaller than those near the magnetic transition points, indicating that the positive MC ratio observed below T_1 is not just due to spin fluctuation induced by the magnetic ordering at T_1 but caused by magnetic-field-induced spin realignment of the A -site Mn^{3+} ions. The fact that the magnitude of the positive MC in this region increases upon approaching T_1 is in line with our assumption that the AFM ordering and the Mn^{3+} -spin rotation induced by applied magnetic field at the A site compete with each other.

In conclusion, we have synthesized a novel A -site ordered perovskite oxide, $(\text{BiMn}_3)\text{Mn}_4\text{O}_{12}$, with indeed uncommon magnetodielectric properties. The compound exhibits an FM-like transition at 59 K and an AFM-like transition at 28 K, and a relatively large negative MC effect of ca. 2% near both the magnetic transition temperatures. Moreover seen for the compound is a positive MC effect at temperatures below the lower magnetic transition temperature of 28 K. We believe that the strongly distorted MnO_6 network due to Jahn–Teller Mn^{3+} ions and Bi^{3+} ions with the $6s^2$ lone pair at the A -cation site and the presence of magnetic Mn^{3+} ions at both A - and B -cation sites are the important crystal-chemical factors behind the observed magnetic and electrical interactions in $(\text{BiMn}_3)\text{Mn}_4\text{O}_{12}$.

Acknowledgment. This work was partly supported by Tekes (No. 1726/31/07) and Academy of Finland (Nos. 114517 and 116254).

Supporting Information Available: Details of sample synthesis and experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA806487D