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$InMnO_3$: A biferroic

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$InMnO_3$ which has a hexagonal structure similar to that of $YMnO_3$ is found to show a canted antiferromagnetic behavior below 50 K (T_N) and a ferroelectric (FE) transition at 500 K accompanied by hysteresis. We have determined the structure, polarization, and energetics of the FE and paraelectric (PE) phases of $InMnO_3$ using first-principles density functional theory calculations based on pseudopotentials and a plane-wave basis, and find the polarization of the PE phase to be a half-integer quantum. The difference in polarization of the FE and PE phases calculated along a simple path is different from the absolute value of polarization of the FE phase. A weak piezoelectric response is exhibited by $InMnO_3$ to uniaxial strain. © *2006 American Institute of Physics*.
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Multifunctional materials, specially biferroics, have attracted considerable attention in the last few years because of their potential applications.[1–5] One of the well-known biferroics is $BiFeO_3$ which is antiferromagnetic ($T_N = 670$ K) and ferroelectric ($T_{CE} = 1110$ K).[6] Another material in this category is $YMnO_3$ which is antiferromagnetic ($T_N = 80$ K) and ferroelectric ($T_{CE} = 914$ K).[7] It has been recently found that the $BiMnO_3$ is ferromagnetic ($T_C = 105$ K) and ferroelectric ($T_{CE} = 450$ K).[8,9] $InMnO_3$, which has a structure similar to that of $YMnO_3$, is expected to be ferroelectric,[10,11] but this has not been experimentally verified. We have investigated the magnetic and dielectric properties of $InMnO_3$ and find it to be weakly ferroelectric with a T_{CE} of ~500 K, exhibiting canted antiferromagnetism below 50 K. We have examined the characteristics of $InMnO_3$ in detail by carrying out first-principles calculations.

X-ray diffraction studies show that $InMnO_3$ has a hexagonal structure[12,13] with the $P6_3cm$ space group ($a = 5.8813$ Å, $c = 11.413$ Å) similar to that of $YMnO_3$. In Fig. 1, we show the temperature variation of magnetization of polycrystalline pellets of $InMnO_3$ under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The high-temperature inverse susceptibility data could be fitted to a Curie-Weiss behavior, with a Weiss temperature of −85 K. At low temperatures, the magnetization increases markedly around 50 K and the material behaves like a canted antiferromagnetic (AFM) system. We observe magnetic hysteresis at low temperatures (see inset of Fig. 1). Magnetic properties of $InMnO_3$ are comparable to those of $YCrO_3$.[14]

We have investigated the dielectric properties of pressed pellets as well as polycrystalline thin films of $InMnO_3$, having deposited the thin films on ⟨111⟩ oriented $Pt/TiO_2/SiO_2/Si$ substrates using a KrF excimer laser of 248 nm (Lambda Physik) at 650 C in an oxygen ambient of 100 mTorr with a pulse energy of 140 mJ/pulse. The dielectric constant (ε) data in Fig. 2(a) reveal the occurrence of a transition over the 460–490 K range with a T_{max} of 470 K at 10 kHz, the T_{max} being frequency dependent. The Curie-Weiss plot of $1/\varepsilon$ vs T gives a T_{CE} of 500 K which is frequency independent as expected of a ferroelectric material.[15] The dielectric constant shows a large dispersion below T_{CE}, but is frequency independent above T_{CE}, a behavior observed commonly in relaxor ferroelectrics.[16] A broad transition in normal ferroelectrics is attributed due to the presence of fine grains, a relaxorlike behavior may arise from the presence of charged oxygen vacancies, and the short range polar regions can give rise to a relaxorlike behavior in a normal

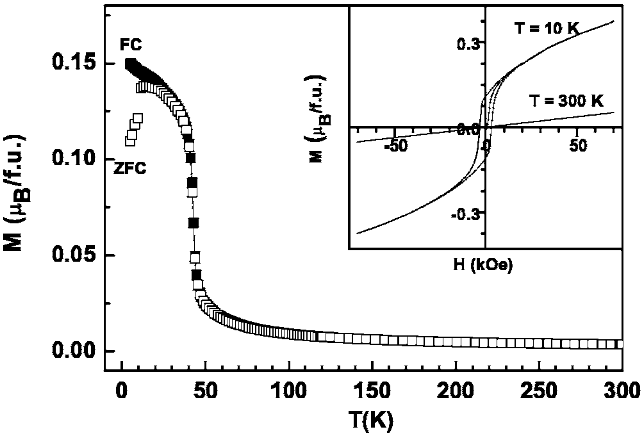

FIG. 1. Temperature variation of magnetization of $InMnO_3$ (pellet) under field-cooled (FC) and zero-field-cooled (ZFC) conditions ($H = 100$ Oe). Inset shows magnetic hysteresis curves at two different temperatures.

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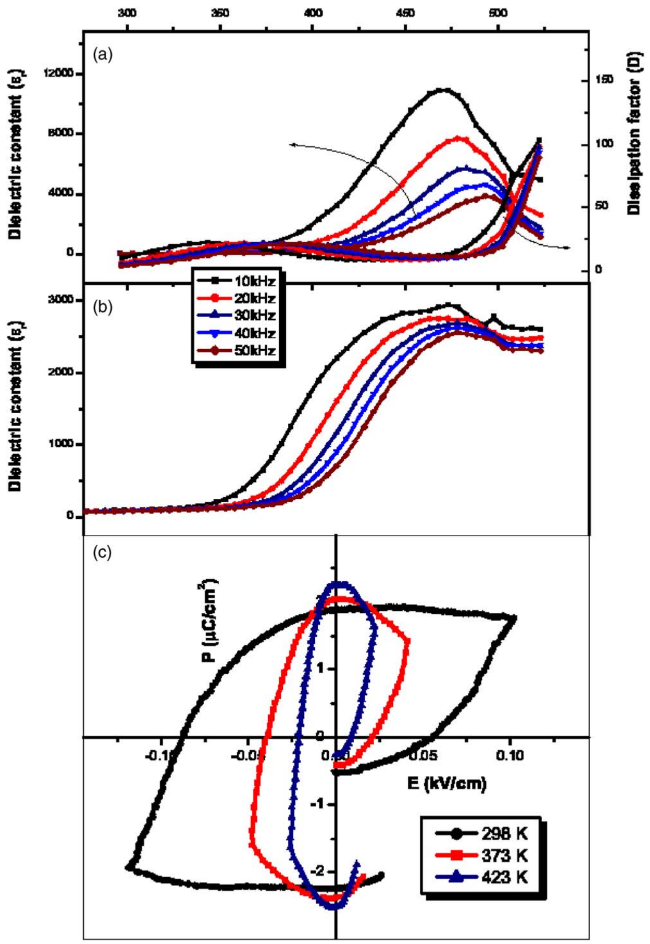

FIG. 2. (Color online) Temperature variation of dielectric constant of $InMnO_3$ at different frequencies: (a) pellet and (b) thin film. In (c), we show hysteresis loops at different temperatures.

ferroelectric.[17] This can also cause frequency dependence of the dielectric constant. The room-temperature dielectric constant of $InMnO_3$ is around 71.1 at 5 kHz. The dissipation factors are 14.724 and 0.898 (5 kHz) at room temperature in the bulk and the thin film samples, respectively. The high-temperature loss shows a monotonous rise due to the increase in the dc leakage current.

Studies of the $InMnO_3$ thin films show a dielectric phase transition around 465 K at 10 kHz as can be seen from Fig. 2(b). The dielectric phase transition found both in the pellets and the thin films also lends evidence to the presence of a ferroelectric phase in $InMnO_3$. It is noteworthy that the transition temperature found by us is close to the predicted value.[11] The difference between the dielectric properties of the films compared to the pellets can be due to artifacts such as the electrodes used, but more so because of grain contribution in the bulk samples.

Polarization-electric field (P-E) measurements show the presence of hysteresis at 300 K similar to leaky dielectrics [see Fig. 2(c)]. The maximum polarization observed was 2 $\mu C/cm^2$ at 300 K. We therefore surmise $InMnO_3$ exhibits weak ferroelectric behavior from T_{CE} down to low temperatures through the magnetic transition at 50 K.

The origin of ferroelectricity in $YMnO_3$ has been shown to be mainly structural, involving electrostatic interactions.[10] In the light of the group theoretical analysis of Fennie and Rabe,[18] the mechanism of ferroelectricity in $InMnO_3$ is expected to be somewhat similar. It could be an improper ferroelectric with the primary instability associated with a zone-boundary phonon mode, which induces a linear field on the ferroelectric mode. Polarization properties in biferroics are often subtle[19] and depend on the structural paths.[20] Secondly, the piezoelectric response of improper ferroelectrics could involve factors different from those in conventional ferroelectrics. To this end, we use first-principles calculations to characterize polarization of $InMnO_3$ along a switching path and its piezoelectric response to uniaxial strain.

Our calculations are based on density functional theory within a local spin density approximation (LSDA), as implemented in the PWSCF package[21] with ultrasoft pseudopotentials[22] and a plane-wave basis. We include effects of correlations beyond LSDA through a LSDA+U approximation with Hubbard parameters $U=8$ eV and $J=0.88$ eV as calculated in Ref. 23 and used in calculations on $YMnO_3$.[18] An energy cutoff of 30 Ry (180 Ry) on the plane-wave basis was used in representing the Kohn-Sham wave functions (electron density). As $InMnO_3$ undergoes a cell-tripling phase transition, we use a unit cell with 30 atoms in our calculations to describe its paraelectric (PE) and ferroelectric (FE) phases on the same footing. Brillouin zone integrations are sampled with a $3\times3\times2$ uniform mesh of k points. In all our calculations, we have used experimental lattice parameters of the crystal unit cell and determined the lowest energy structure using Hellman-Feynman forces.

Calculations were carried out using two types of AFM orderings: (a) A type in which spins on Mn atoms in the (0001) planes are parallel, and those in the adjacent planes are antiparallel, and (b) frustrated AFM ordering, wherein the Mn atoms on the triangular lattice in an ab plane are magnetically ordered (+, −, +) whereas those on the neighboring ab plane are ordered as (−, +, −). In (a), we find that the band gap closes along the (001) axis and it is not possible to estimate the polarization, whereas a gap of 0.14 eV opens up in the ferroelectric phase in (b). In the present work, we use frustrated AFM ordering, considering that the results for $YMnO_3$ were insensitive to different magnetic orderings.[18] Structural parameters of the ferroelectric phase determined in our calculations agree well with experiment.[12,13] Although we did not optimize the lattice constants, calculated stresses are about 70 kbar, which would lead to an underestimation of lattice constants by a couple of percent, typical of LDA calculations.

The PE phase of $InMnO_3$ has only one free structural parameter. We have calculated energetics associated with off centering of cations to probe the chemical factors responsible for ferroelectricity. Our estimates for the harmonic spring constants associated with In and Mn off centering are 17.1 and 30.1 $eV/Å^2$ per f.u., respectively. It is clear that cation off centering alone cannot yield ferroelectricity in $InMnO_3$ and the stiff energy well seen by Mn would prohibit off centering in the FE phase. This is consistent with the structure of the FE phase of $InMnO_3$ and is similar to the behavior of $YMnO_3$.[10] We considered a simple path that connects the paraelectric structure ($s=0$) to the ferroelectric one ($s=1$), where s parametrized the path. Evolution of the structural parameters along this path is given by linear functions such as $(As+B)$. Energy along this path exhibits a double well behavior and can be fitted well to an even quartic polynomial. The FE phase is 0.162 eV lower in energy than the PE phase (for 30 atoms cell), indicating a shallower energy well in $InMnO_3$ in comparison to that in $YMnO_3$.[10,18]

We have computed the polarization using the geometric phase formalism[24] along the path. Similar to $BiFeO_3$,[19] we find a half-integer quantum polarization ($P=26.8\ \mu C/cm^2$) for the PE phase of $InMnO_3$. It arises from the ionic contribution (just the same as in $BiFeO_3$) and remains unchanged for different choices of ionic charges including that of nominal charges. We believe that the same holds true for $YMnO_3$. The absolute value of polarization for FE $InMnO_3$ is 19 $\mu C/cm^2$, which differs from that of the PE phase only by 7.8 $\mu C/cm^2$. Our estimate of P is larger than the measured value reported here, possibly due to extrinsic factors. Since there are metallic states in the neighborhood of the PE phase of $InMnO_3$, its polarization properties are expected to be interesting.

We have examined the piezoelectric response e_{33} of $InMnO_3$ to uniaxial strain ε_{zz}. For $\varepsilon_{zz}=\pm 0.01$, we optimized its structure and computed polarization of the strained unit cells. We find rather small changes in polarization yielding a piezoelectric constant (e_{33}) of 15 $\mu C/cm^2$. This is a relatively weak response, in comparison with perovskite oxides and is within the error of our calculations. The measured dielectric constant of $InMnO_3$ in the present work is also relatively small. To understand the cause for such a weak response, we have examined the structural distortions (in response to strain) with respect to the ferroelectric phase. They comprise mainly of the displacements of oxygens at $2a$ and $4b$ sites. Secondly, four of them displace parallelly along the c axis and the other two displace in the opposite direction. This displacement pattern corresponds to a combination of strong component of the zone-boundary phonon mode K_3 and a weak component of the zone-center polar mode Γ_2^-, yielding a small polarization due to the cancellation of dipoles from the different atoms. Our finding is not surprising in terms of the Landau theorylike free energy[18] of $InMnO_3$. As the K_3 mode is the primary order parameter, it is expected to be softer in the FE phase than the Γ_2^- (a secondary order parameter) mode and to respond more strongly to strain and other external fields. The oxygen atoms responding strongly to strain are the neighbors of indium along the z direction. The bonds formed by indium and oxygen seem to be relevant to the structural response of $InMnO_3$ to strain, similar to that in ZnO. In $InMnO_3$, the broad transition can arise because the primary order parameter of the structural transition is the K_3 phonon and the FE order parameter is induced by it through $Q_{FE}Q_{K_3}{}^3$ coupling.

In conclusion, our experimental studies on $InMnO_3$ show it to be biferroic, with a canted AFM transition around 50 K and a FE transition at 500 K. The biferroic properties of $InMnO_3$ are somewhat comparable to those reported recently in the case of $YCrO_3$.[25] Our first-principles calculations on $InMnO_3$ highlight subtle aspects of its polarization properties and those of the isostructural improper biferroic, $YMnO_3$. It may be noted that the primary order parameter in Landau theory for $YMnO_3$ is the K_3 mode and the secondary parameter is the polar Γ_2^- mode. At the transition, the K_3 mode freezes in and induces ferroelectric polarization through a third order coupling. As a result, polarization (which is proportional to displacements of Γ_2^- mode) varies very slowly with cube of K_3 mode displacements. Until the magnitude of primary order parameter becomes sizeable, polarization remains small in a broad range of temperatures near the transition. As a result, dielectric response (which basically relates to fluctuations in polarization) exhibits a broad peak. Secondly, within the Landau theory, it follows that only mode K_3 (and not the ferroelectric mode Γ_2^-) softens. Because both the dielectric and piezoelectric responses are inversely proportional to the square of polar phonon frequency, this results in relatively weak dielectric and piezoelectric responses.[26] As $YMnO_3$ and $InMnO_3$ are isostructural, our arguments apply to both of them. Thus, the geometric (mode K_3) origin of ferroelectricity in these materials appears to provide a means to design multiferroics,[10] but it also dominates their response to strain and gives rise to relatively small piezoelectric and dielectric constants.

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