Substantial magnetoelectric coupling in nanocrystalline-Fe$_2$TeO$_6$ at room temperature

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Abstract

There is a confocal attention of the multifunctional material science and condensed matter physics research community to the room temperature (RT) magnetoelectric multiferroics through past several decades for its novel physical and chemical properties. Materials with substantial coupling at RT are still an unsaturated problem in the field of condensed matter physics. Apart from searching new magnetoelectrics, enhancement of the coupling as well as physical properties by manipulating the size dependency of these properties also very popular. Here, we report the presence of substantial magnetoelectric coupling in Nanocrystalline Fe$_2$TeO$_6$ (FTO) at room temperature synthesized by sol-gel process. The nano aspect of FTO is confirmed from transmission electron microscopy, where the particles of sizes 10 – 40 nm are seen. Magnetic measurement on nano-FTO confirms the antiferromagnetic nature of particles having Néel temperature $T_N = 167$ K, which is much lower than that of bulk (210 K). PE loop measurement at room temperature gives the remanent polarization ($P_r$) value of 0.098 μC/cm$^2$, confirming ferroelectricity in FTO. A nonmonotonous increase in the remanent polarization is noticed when an external magnetic field is applied on the sample. This is a clear indication of prevailing substantial magnetoelectric (ME) coupling in the sample at room temperature. Quantification of magnetoelectricity is done by directly measuring the ME voltage (V) in the presence of varying dc magnetic field (H) and the ME coefficients are obtained using a quadratic relation in H. Presence of ferroelectricity and magnetoelectricity above the Néel temperature is very unusual phenomenon in this material. The presence of short range magnetic ordering which prevails even upto RT, much higher that of long range magnetic ordering temperature is suspected to be responsible for this.

Keywords: Ferroelectricity, Magnetoelectric coupling, Polarization, Antiferromagnetism.
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Outlines

- Magnetoelectric coupling and its applications
- Motivation
- \( \text{Fe}_2\text{TeO}_6 \) and its novel properties
- Synthesis and structural property of \( \text{Fe}_2\text{TeO}_6 \)
- Magnetic properties
- Magnetoelectric properties
- Conclusions
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Introduction

Multiferroic materials exhibit novel magnetoelectric properties such as control of electric state by applying magnetic field (or strain) and vice versa.

Type-I

- Magnetism and FE exist independently
- Different sources
- Weak coupling
- Different group of electrons

*6s² lone pair of Bi or Pb* (Seshadri & Hill Chem. Mat. 2001)

\[
\begin{align*}
\text{Pb}(A,B)O_3 &\ (A=\text{Fe, Mn, Co}; \ B=\text{W, Nb}) \quad [T_C(\text{FE})\sim300\sim400K \ T_N(\text{M})\sim100\sim200K] \\
\text{BiFeO}_3 &\quad [T_C(\text{FE})\sim1123K \ T_N(\text{M})\sim650K] \\
\text{BiMnO}_3 &\quad [T_C(\text{FE})\sim773K \ T_C(\text{M})\sim110K]
\end{align*}
\]


Hexagonal \(R\text{MnO}_3\) \((R=\text{Y, Ho, Er, Tm, Yb, Lu, Sc})\) [\(T_C(\text{FE})\sim900K \ T_N(\text{M})\sim80\sim120K\)]


\[
\begin{align*}
\text{LuFe}_2\text{O}_4 \\
(\text{Pr},\text{Ca})_3\text{Mn}_2\text{O}_7
\end{align*}
\]

Type- II

- FE due to certain type of magnetic ordering
- Only in the magnetic state

*Spiral magnetic ordering* (Katsura et al. PRL 2005, Mostovoy PRL 2006)

- TbMnO$_3$, $[T_C(FE)\sim 27K \ T_N(M)\sim 41K]$
- Ni$_3$V$_2$O$_8$ $[T_C(FE)\sim 9K \ T_N(M)\sim 13K]$
- MnWO$_4$ $[T_C(FE)\sim 9K \ T_N(M)\sim 13K]$

*Exchange striction [collinear spin order]* (Chapon et al. PRL 2006, Sergenko et al. PRL 2006)

- RMn$_2$O$_5$ ($R=$Tb, Dy, Y, Ho, Er, Tm, Yb) $[T_C(FE)\sim 37K \ T_N(M)\sim 39K]$
- Ca$_3$CoMnO$_6$
- DyFeO$_3$

P. Nayaka et al., Ceramics International (2018).
Deepak Swain et al., Nanotechnology (2017)
P. Nayak et al., Ceramics International (2017).

S. R. Mohapatra et al., Ceramics International (2016)
Applications

- Sensor industry: Magnetic field Sensors  
  [Physics Today, 26 April (1995)]

- Data storage, and recording  

- Quantum electromagnet  
  [Science 312, 1481 (2006)]

- Microelectronics  

- Solar cells  
  [Science 324, 64 (2009), Appl. Phys. Lett. 95, 62909 (2009)]

- Detectors (SONAR)

- Transducers

- Filter probes and filters

- Spintronics applications
Motivation

✓ Search of room temperature ME material with large coupling is still on.

✓ Enhancement of the coupling as well as the physical properties by manipulating the size dependency needs to be explored.

✓ Previous investigation on Fe$_2$TeO$_6$ is reported to show AFM transition temperature below 210 K.

✓ The microscopic origin of coupling is not well explored.

✓ ME coupling at nano scale in Fe$_2$TeO$_6$. 
Sample preparation (Bulk)

TeO$_2$ + Fe$_2$O$_3$ $\xrightarrow{700 \, ^\circ\text{C}}$ 24 hrs $\rightarrow$ Fe$_2$TeO$_6$
Structural properties of Fe$_2$TeO$_6$

- **Calcined at 750°C**
- **2 Hour grinding and pelletized**
- **Sintered at 750°C**

Fe$_2$O$_3$ + TeO$_2$

Fe$_2$Te$_{(1-x)}$Nb$_x$O$_6$

- **χ$^2$**: 6.04
- **R$_{wp}$**: 7.57
- **R$_{exp}$**: 3.08
- **a in Å**: 4.60457(2)
- **c in Å**: 9.08859(8)
- **V in Å$^3$**: 192.697(2)

Fe-O$_1$ (Å): 1.966616(10)
Fe-O$_2$ in Å: 1.981794(6)

O$_1$-Fe-O$_1$ (degree): 80.3692(5)
O$_1$-Fe-O$_2$ (degree): 89.7089(6)
Fe-O$_1$-Fe (degree): 99.6308(13)
Fe-O$_2$-Fe (degree): 128.9936(7)
FTO possess two anomalies at 201 K and 233 K associated with short range and long range magnetic ordering, respectively.
**Bulk Fe₂TeO₆ (ME measurement)**

- Nonlinear ME voltage response at RT
- $V' = h_0 (\alpha + \beta H + \gamma H^2)$
- With coupling coefficient: $\alpha/d \sim 0.32 \text{ mV cm}^{-1} \text{ Oe}^{-1}$; $\beta/d \sim -0.07 \text{ mV cm}^{-1} \text{ Oe}^{-2}$ and $\gamma/d \sim -1.54 \ 0.07 \text{ mV cm}^{-1} \text{ Oe}^{-3}$
Bulk Fe$_2$TeO$_6$ (PE measurement under magnetic field)

- Exhibit ferroelectricity with remanent polarization 4.5 nC/cm$^2$ at RT
Bullet points:

- FTO is having collinear magnetic structure at 4.2 K.
- Collinear magnetic moments of the Fe3+ are arranged AFM along the crystal c axis.
Bulk $\text{Fe}_2\text{TeO}_6$ (Raman Spectra)

wavelength 532 nm

temperature 80–400 K
Temperature dependence of frequency for the modes P2, P6, P7, and P10

Deviation in phonon frequency from anharmonic behavior as a function of squared normalized magnetization.
NANO Fe$_2$TeO$_6$

The XPS spectra reveal the presence of Fe$^{3+}$ and Te$^{6+}$ ions.

ZFC and FC data shows the transition at 167 K.

$m$ is the proximity effect constant which can be considered as 1 for NP.

$D_0$ depends on dimensionality and nearest neighbor spacing.

The XPS spectra reveal the presence of Fe$^{3+}$ and Te$^{6+}$ ions.

NANO Fe$_2$TeO$_6$

![Graphs and data plots related to NANO Fe$_2$TeO$_6$.]
Conclusion

- The magnetic property of the synthesized nanomaterial is significantly different from the bulk material. AFM transition decreases from 210 K to 185 K in the nano form.

- The value of magnetic moment enhances by 20% in the nano form with respect to bulk Fe$_2$TeO$_6$.

- The nanocrystalline Fe$_2$TeO$_6$ shows a substantial RT magneto-electric coupling.

- The origin of the coupling may be the presence of short range magnetic ordering, spin frustration, as well as magnetostructural distortion on the application of the magnetic field.

- This report opens up a new avenue, where nano-form of a material may be utilized to enhance the magnetoelectricity above the ordering temperatures so that RT magnetoelectricity may be realized.
References


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Thank you for your kind attention...