



Room-temperature multiferroic behavior in layer-structured Aurivillius phase ceramics

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Zheng Li, Vladimir Koval , Amit Mahajan, Zhipeng Gao, Carlo Vecchini, Mark Stewart, Markys G. Cain , Kun Tao, Chenglong Jia , Giuseppe Viola, and Haixue Yan 



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Zheng Li,¹ Vladimir Koval,² Amit Mahajan,³ Zhipeng Gao,⁴ Carlo Vecchini,⁵ Mark Stewart,⁵ Markys G. Cain,⁶ Kun Tao,⁷ Chenglong Jia,^{7,a)} Giuseppe Viola,³ and Haixue Yan^{3,b)}

AFFILIATIONS

¹Guangdong Provincial Key Laboratory of Applied Superconductivity, Institute of Superconducting Ceramics, Guangdong Academy of Sciences, Guangzhou 510650, China
²Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China
³Department of Physics, University of Turin, I.N.F.N. Laboratori Nazionali del Sud, I-66100 Chieti, Italy
⁴National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565, Japan
⁵National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
⁶Department of Physics, University of Maryland, College Park, Maryland 20742, USA
⁷Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

a)Email: jiacl@sz.tsinghua.edu.cn

b)Author to whom correspondence should be addressed: yanhx@sustech.edu.cn

ABSTRACT

Room-temperature multiferroic behavior is observed in layer-structured Aurivillius phase ceramics $B_{5.25}La_{0.75}FeC_{3}O_{18}$. The $B_{5.25}La_{0.75}FeC_{3}O_{18}$ exhibits a ferroelectric (FE) phase transition at $T_C \approx 300$ K and a magnetic (M) phase transition at $T_M \approx 350$ K. The FE phase is characterized by a polar structure with $P_{\text{spont}} \approx 0.02$ C/m². The M phase is characterized by a magnetic structure with $M_{\text{spont}} \approx 0.05$ T. The coexistence of FE and M phases at room temperature is confirmed by *in situ* X-ray diffraction and neutron diffraction measurements. The observed multiferroic behavior is attributed to the presence of $B_{5.25}La_{0.75}FeC_{3}O_{18}$ in the Aurivillius phase structure.

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Multiferroic (MF) materials, which exhibit both ferroelectric (FE) and magnetic (M) properties, have attracted significant attention due to their potential applications in spintronics and quantum computing. Layer-structured Aurivillius phase ceramics, $B_n A_{n-1} C_3 O_{18}$ ($n = 1-6$), are a class of MF materials. Among them, $B_5 A_{4.5} C_3 O_{18}$ ($A = \text{La, Pr, Sm, Eu, Gd}$) is a promising candidate for room-temperature MF behavior. However, the room-temperature MF behavior in $B_5 A_{4.5} C_3 O_{18}$ has been controversial. Some studies reported room-temperature MF behavior in $B_5 A_{4.5} C_3 O_{18}$, while others reported no MF behavior. In this work, we report room-temperature MF behavior in $B_{5.25}La_{0.75}FeC_{3}O_{18}$. The $B_{5.25}La_{0.75}FeC_{3}O_{18}$ exhibits a ferroelectric phase transition at $T_C \approx 300$ K and a magnetic phase transition at $T_M \approx 350$ K. The FE phase is characterized by a polar structure with $P_{\text{spont}} \approx 0.02$ C/m². The M phase is characterized by a magnetic structure with $M_{\text{spont}} \approx 0.05$ T. The coexistence of FE and M phases at room temperature is confirmed by *in situ* X-ray diffraction and neutron diffraction measurements. The observed multiferroic behavior is attributed to the presence of $B_{5.25}La_{0.75}FeC_{3}O_{18}$ in the Aurivillius phase structure.

$B_{5.25}La_{0.75}F_{1-x}C_xO_{18}$ (BLFC) (P_r) (P_r) .
 F, A $a b$ P_r C D $14,17$
 BLFC A $a b$ P_r C D 18
in situ I H I K
 N AL D O K
 F A BLFC
 BLFC P_r A BLFC
 F 1 (D) BLFC
 $B2cb$ A
 $A2_1a$ A $19,20$
 $B2cb$ $a = 5.4530(2) \text{ \AA}$, $b = 5.4427(1) \text{ \AA}$, $c = 50.670(2) \text{ \AA}$
 $A2_1am$ $a = 5.4651(6) \text{ \AA}$, $b = 5.3943(6) \text{ \AA}$, $c = 41.487(2) \text{ \AA}$
 F P_r $(//$

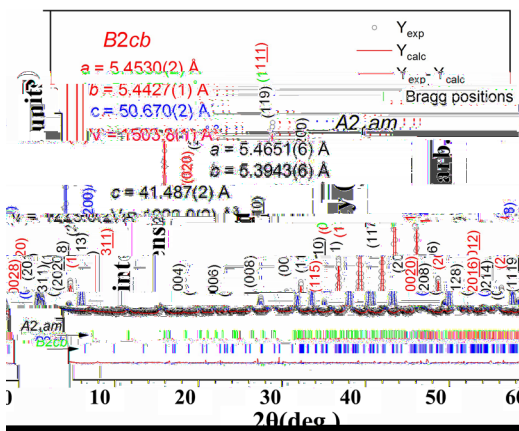


FIG. 1. XRD patterns of B2cb and A2₁am phases.

BLFC A N D'
 $= 4$ $= 5$ $(a-b)$ M
 BLFC F 1 EM $(a-b)$ M
 P_r $(F$ 1 EM $(a-b)$ M
 F 1 EM $(a-b)$ M
 1.4 $(F$ 2
 $1)$ $(F$ 2
 $F, C, O,$ $(F$ 2
 $C_2F O_4$ $(F$ 2
 A $B_{5F 0.5C 0.5}O_{15}$ 16
 F $2(a)$ $(50, 70 100,$
 P_r $(50, 70 100,$
 $300,$ $500 \text{ H})$ $(50, 70 100,$
 1060 K $FE T$ $BLFC$ H $(50, 70 100,$
 $BLFC$ $BLFC$ B_6 $3F_2O_{18}$
 $(a 973 \text{ K})$ F $2()$ $P-E$ $I-E$
 $BLFC$ $P-E$ $I-E$
 P_r $I-E$ $21,22$
 $BLFC$ $10 \mu C/$ $2.$
 F $2()$ (FC) (FC) $BLFC$ $BLFC$
 (FC) $200 O$ $BLFC$ $BLFC$

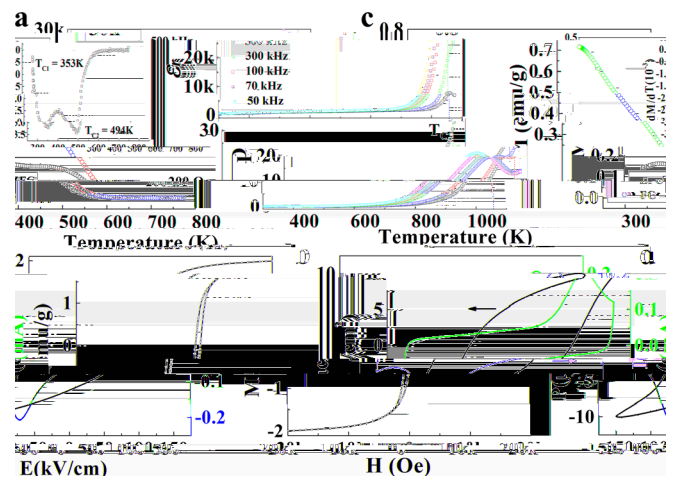


FIG. 2. (a) Temperature dependence of dielectric loss tangent ($\tan \delta$) for BLFC at frequencies of 300 kHz, 100 kHz, 70 kHz, and 50 kHz. $T_g = 353 \text{ K}$ and $T_g = 494 \text{ K}$ are indicated. (b) Temperature dependence of dielectric constant (ϵ') and loss tangent ($\tan \delta$) for BLFC. (c) Temperature dependence of dielectric constant (ϵ') and loss tangent ($\tan \delta$) for BLFC. (d) Temperature dependence of dielectric constant (ϵ') and loss tangent ($\tan \delta$) for BLFC. (e) Temperature dependence of dielectric constant (ϵ') and loss tangent ($\tan \delta$) for BLFC. (f) Temperature dependence of dielectric constant (ϵ') and loss tangent ($\tan \delta$) for BLFC.

~ 494 K (M/),
 $B_6FC_3O_{18}$ (526 K).²³
 BLFC
 $F^{3+} O F^{3+}, C^{3+} O C^{3+}, F^{3+} O C^{3+}$ (.
 ED
 FC ~ 353 K
 $C_2F_2O_4$ (460 K) 16.25 %
 $(M) C_2F_2O_4$ 0.22 0.32 /,
 16.235 / 25 , 1.4 %
 $C_2F_2O_4$ 0.22 0.32 /,
 $M = 1.85$ / , $F_2()$ I BLFC
 $M H$
 $2(F_2)$ 425 K 1.58 / , 0.27 / , ED
 BLFC
 F_3 $F^{3+} O C^{3+}$
 (DF) $ab initio$
 $(A P)$ H
 $F = 2$ $C = 3$ F C ,
 (GGA) I
 BLFC
 $F_3(a)$, F^{3+} C^{3+} (3.1 $2.1 \mu_B/a$,)
 O $0.1 \mu_B/a$)
 $F O_6$ $C O_6$
 F/C $F_3()$
 F O / $F_3()$
 F^{3+} C^{3+}
 $()$ $()$ $()$
 $()$ $()$
 $E_{FM} - E_{AFM}$
 $= -144.1$
 H (FM)
 43.5 (~ 504.6 K), FM
 1 FC/FC $F_2()$
 $a b$
 010
 F_4
 BLFC I
 $399 O$
 F
 $5()$ A PFM BLFC F

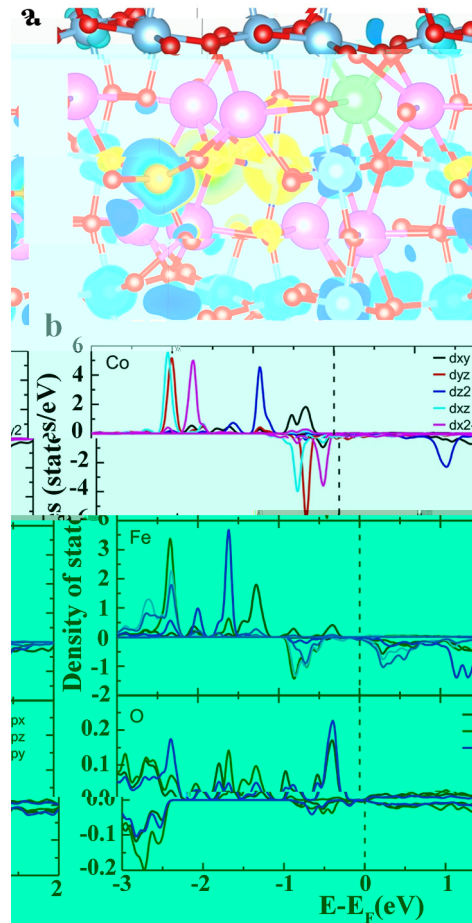


FIG. 3. (a) Crystal structure of BLFC showing Co, Fe, and O atoms. (b) Density of states (DOS) for Co, Fe, and O atoms, showing contributions from d_{xy} , d_{yz} , d_{z^2} , d_{xz} , and $d_{x^2-y^2}$ orbitals. The x-axis is $E - E_F$ (eV) from -3 to 1, and the y-axis is Density of states (states/eV) from -2 to 6.

N
 I F_4
 A $(0 1 20)$
 $2 < H < 5$,
 $M H$ $F_2()$ $3.F$,
 F_5
 BLFC P $F M$
 $399 O$
 PFM BLFC F
 $5()$ A PFM BLFC F

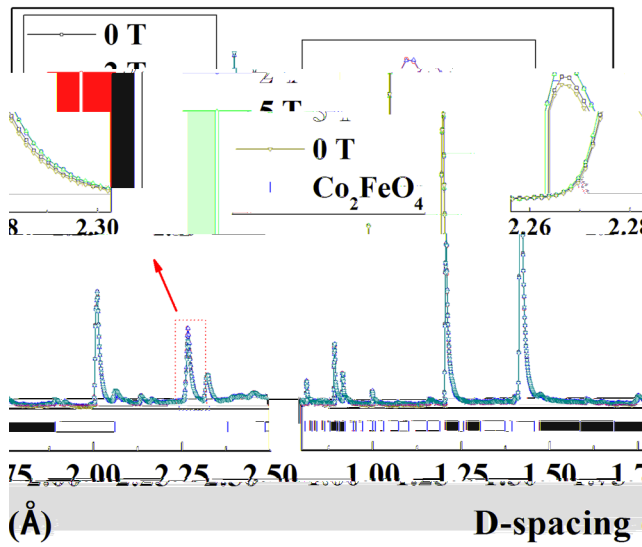


FIG. 4. XRD patterns of Co_2FeO_4 at 0 T and 2 T. The inset shows the schematic of the sample and the magnetic field setup.

Figure 4 shows the XRD patterns of Co_2FeO_4 at 0 T and 2 T. The patterns show a peak at $d = 2.26$ Å, which is indexed to the (100) plane. The intensity of this peak increases with the magnetic field, indicating a change in the crystal structure or orientation of the domains. The inset shows the schematic of the sample and the magnetic field setup.

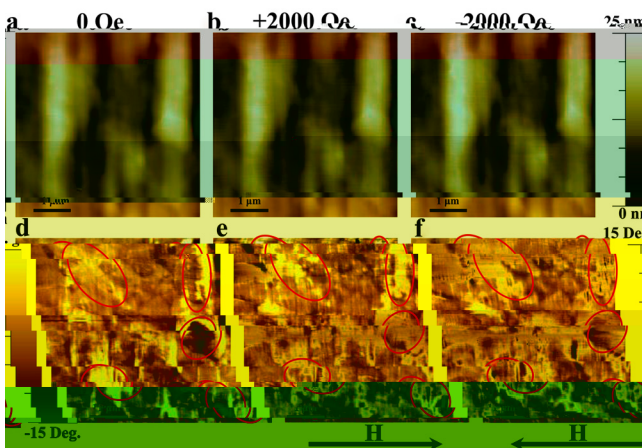


FIG. 5. MFM images of Co_2FeO_4 at 0 Oe, +2000 Oe, and -2000 Oe. The top row shows MFM images and the bottom row shows topographic images. Scale bars are 1 μm and 25 nm.

The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis.

The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis. The magnetic field H is applied along the c -axis.

DATA AVAILABILITY

The data supporting this article have been included as part of the online version of this article.

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