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Cite as: Appl. Phys. Lett. **117**, 052903 (2020); <https://doi.org/10.1063/5.0017781>

Submitted: 09 June 2020 . Accepted: 25 July 2020 . Published Online: 07 August 2020

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Published Online: 7 August 2020 · Corrected: 11 August 2020



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## ABSTRACT

Multiferroic Aurivillius phase ceramics with the general formula  $B_{5-2x}L_{0.75}F_{0.75}C_{3-2x}O_{18}$  ( $B = \text{Bi, Pb, Sr, Ba, Ca}; L = \text{La, Ce, Pr, Nd}; C = \text{Fe, Mn, Ni, Co}$ ) were synthesized via a solid-state reaction. The structure of these ceramics was investigated by *in situ* x-ray diffraction and neutron diffraction. The structure is based on the layered Aurivillius structure, where the  $\text{A}^{2+}$  sites are occupied by  $\text{B}^{3+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^{2-}$ , and  $\text{C}^{3+}$  ions. The  $\text{A}^{2+}$  sites are occupied by  $\text{B}^{3+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^{2-}$ , and  $\text{C}^{3+}$  ions. The  $\text{A}^{2+}$  sites are occupied by  $\text{B}^{3+}$ ,  $\text{O}^{2-}$ ,  $\text{F}^{2-}$ , and  $\text{C}^{3+}$  ions.

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$B_{5.25}F_{0.75}C_{18}O_{18}$   
 $(BLFC)_{1-x}A_x$   
 $a = 5.4530(2) \text{ \AA}$ ,  $b = 5.4427(1) \text{ \AA}$ ,  
 $c = 50.670(2) \text{ \AA}$ ,  $c = 41.487(2) \text{ \AA}$   
 $b = 5.3943(6) \text{ \AA}$ ,  $c = 41.487(2) \text{ \AA}$

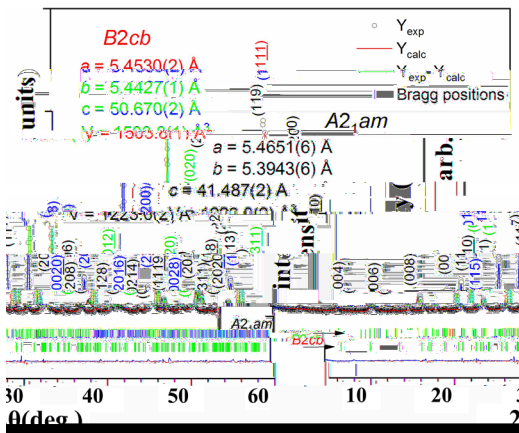


FIG. 1. XRD pattern of BLFC showing Bragg positions and lattice parameters for B2cb and A2,am phases.

$B_{5.25}F_{0.75}C_{18}O_{18}$   
 $(BLFC)_{1-x}A_x$   
 $a = 5.4530(2) \text{ \AA}$ ,  $b = 5.4427(1) \text{ \AA}$ ,  
 $c = 50.670(2) \text{ \AA}$ ,  $c = 41.487(2) \text{ \AA}$   
 $b = 5.3943(6) \text{ \AA}$ ,  $c = 41.487(2) \text{ \AA}$

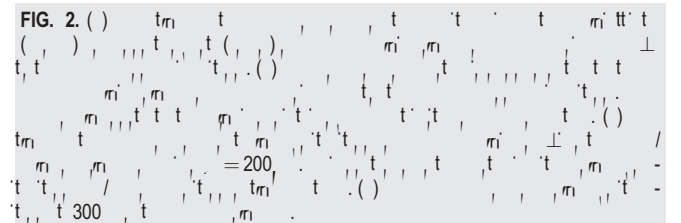
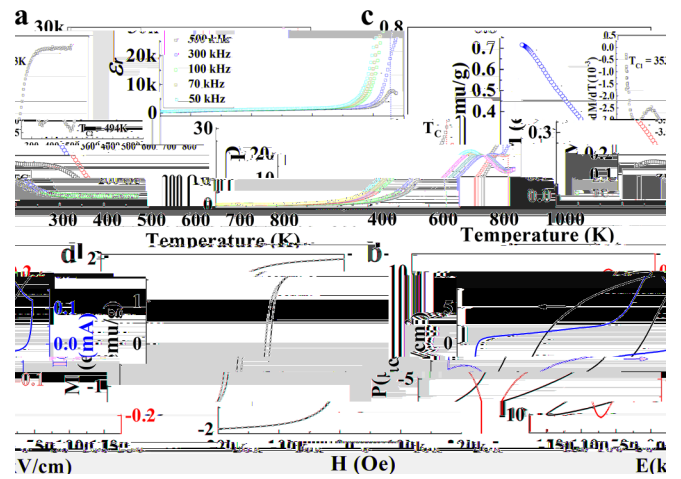


FIG. 2. Temperature dependence of dielectric constant, loss tangent, and P-E loop for BLFC.

$\sim 494$  K  
 $M/\mu_B$ ,  
 $B_6F_2C_{18}O_{18}$  (526 K).<sup>23</sup>  
 BLFC  
 $F^{3+} O F^{3+}, C^{3+} O C^{3+}, F^{3+} O C^{3+}$  ( ).<sup>24</sup>  
 ED  
 $\sim 353$  K  
 $FC$   
 $C_2F_4O_4$  (460 K)  
 $(M) C_2F_4O_4$  16,25  
 $16.235 /$  ,  
 $C_2F_4O_4$  0.22 0.32 / , 1.4 .%  
 $M = 1.85 /$  ,  $F = 2$  . I  
 $M H$   
 $\sim 425$  K 1.58 / .  
 $0.27 /$  ,  
 ED  
 $BLFC$   
 $F^{3+} O C^{3+}$   
 (DF) *ab initio*  
 $(A)$   $H$   
 $\mu_F = 2$   $\mu_C = 3$   $F$   $C$  ,  
 (GGA)+ $\mu$  . I  
 $BLFC$   
 $F = 3$  ,  $F^{3+} C^{3+}$  (3.1 2.1  $\mu_B$  / , ) ,  
 $0.1 \mu_B /$  ) .  
 $F O_6 C O_6$   
 $F / C$   
 $F$   $O$  /  $F = 3$  .  
 $F^{3+} C^{3+}$   
 $(\dots)$   $(\dots)$   
 $E_{FM} - E_{AFM}$   
 $= -144.1$  .  
 $H$  ,  
 $43.5$  ( , 504.6 K), (FM)  
 $FC/FC$  .  $F = 2$  .  
 $a b$   
 $0.70$   
 $BLFC$  . I  
 $F = 4$   
 $BLFC$  . I  
 $FM$   
 $BLFC$  ,  
 $5$  . A  
 $FM$   
 $BLFC$  ,  
 $399 O$  .  
 $F$  .  
 $F$  -

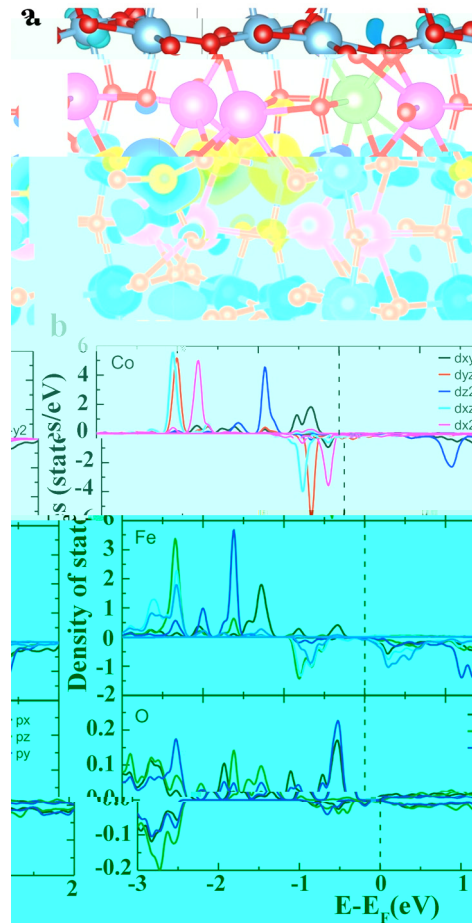


FIG. 3. (a) Crystal structure of BLFC. (b) Density of states (DOS) for Co, Fe, and O atoms. The DOS is plotted in states/eV versus energy  $E - E_F$  (eV). The O DOS is further decomposed into px, py, and pz orbitals. The legend indicates the contributions of different orbitals: dxy (black), dyz (red), dz2 (blue), dxz (green), and dx2 (magenta).

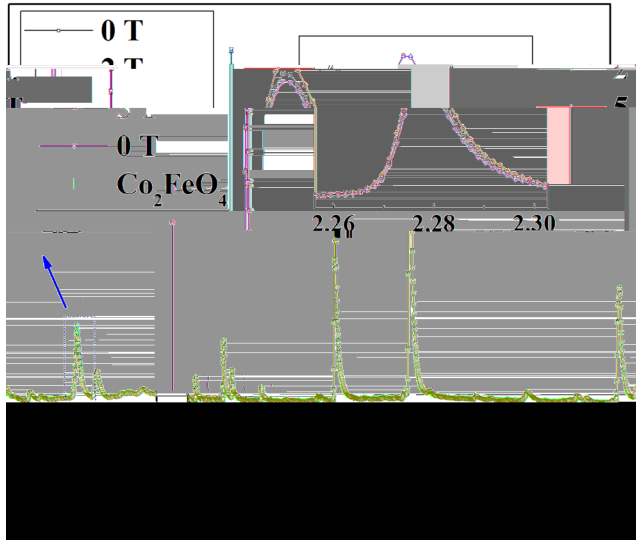


FIG. 4. XRD patterns of  $\text{Co}_2\text{FeO}_4$  at 0 T (left) and 2000 Oe (right). The red line represents the fit to the experimental data (black line). The green line shows the difference between the fit and the experimental data. The peaks are labeled at 2.26, 2.28, and 2.30.

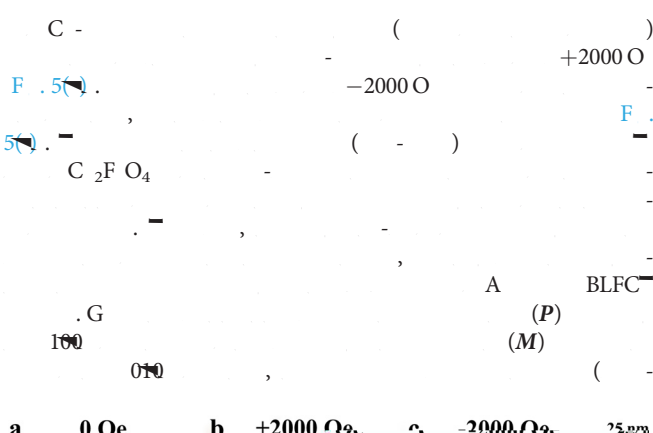


FIG. 5. EPR spectra of  $\text{Co}_2\text{FeO}_4$  at 0 Oe (left), +2000 Oe (middle), and -2000 Oe (right). The x-axis is magnetic field in Oe, and the y-axis is derivative of absorption.

$T = P \times M$   
 $\text{BLFC}^-$   
 $\text{BLFC}^-$   
 $\text{F}^{3+} \text{O} \text{F}^{3+}$   
 $\text{C}^{3+} \text{O} \text{C}^{3+}, \text{F}^{3+} \text{O} \text{C}^{3+}$   
 $\text{C} / \text{F}$   
 $\text{EM}^-$  (ED)  
 $\text{BLFC}^-$   
 $\text{D} \cdot \text{M}$ ,  $\text{D} \cdot \text{K}$ ,  $\text{D}$ .  
 $\text{D}$  I H I I N, AL,  
 $\text{D}$ , O, K.  
 $\text{A}$  E D F,  
 $\text{G}$  A A (G N. 2/  
 $0038/20$ ), C (G N. K2015-0602006), N FC (G  
 $\text{N}$ . 11474138 11834005). A  
 $\text{E}$  M (EM)  
 $\text{IND54 N}$  EM  
 $\text{EM}$  E AME E

DATA AVAILABILITY

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