Study of the properties of Co-substituted $Ba_2Mg_2Fe_{12}O_{22}$ hexaferrites

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Outline

- Introduction - multiferroic materials and magneto-electric effect
- Y-type hexaferrite
- Synthesis of $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$
- Structural properties
- Magnetic properties
- Summary

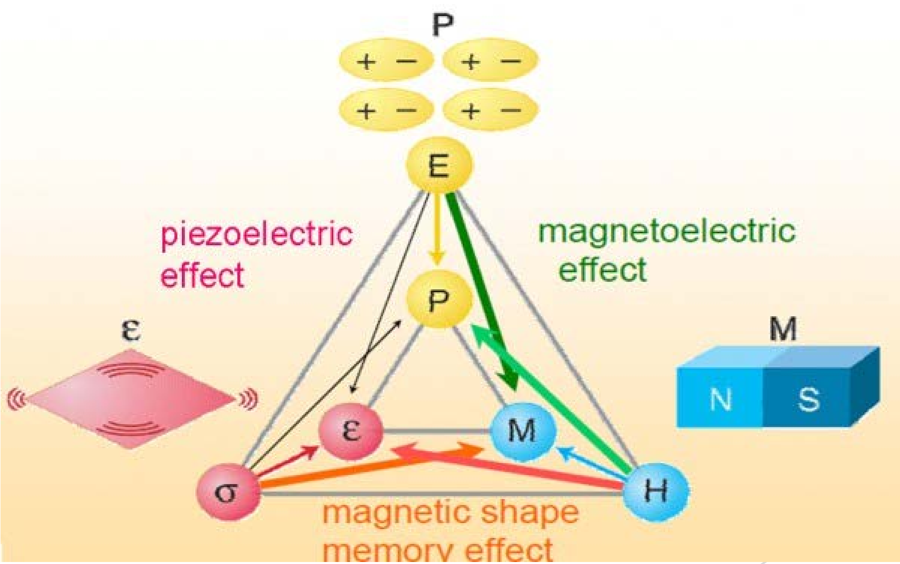
Multiferroic materials

The term multiferroic was coined by H Schmid to denote matter in which at least two of the three types of ordering are simultaneously present: ferromagnets (antiferromagnets), ferro-electrics, and ferroelastics.

H. Schmid, Ferroelectrics 162, 317 (1994).

Ferroelectric

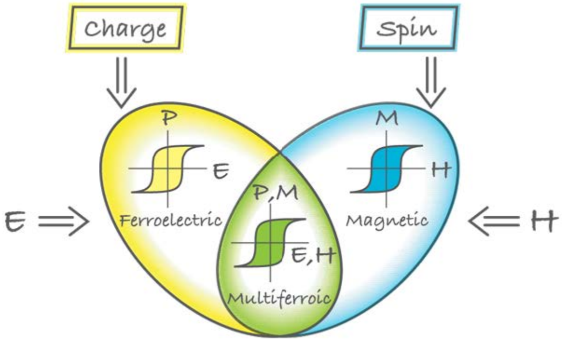
Ferroelastic

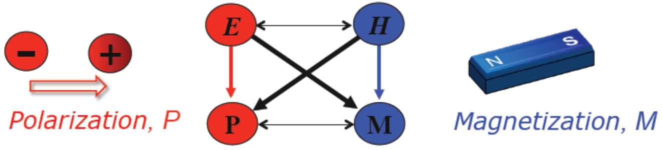


Ferromagnetic

Spaldin et al., Science, 309, 391 (2005)

Magneto-electric multifeffoics





Single-phase multiferroics

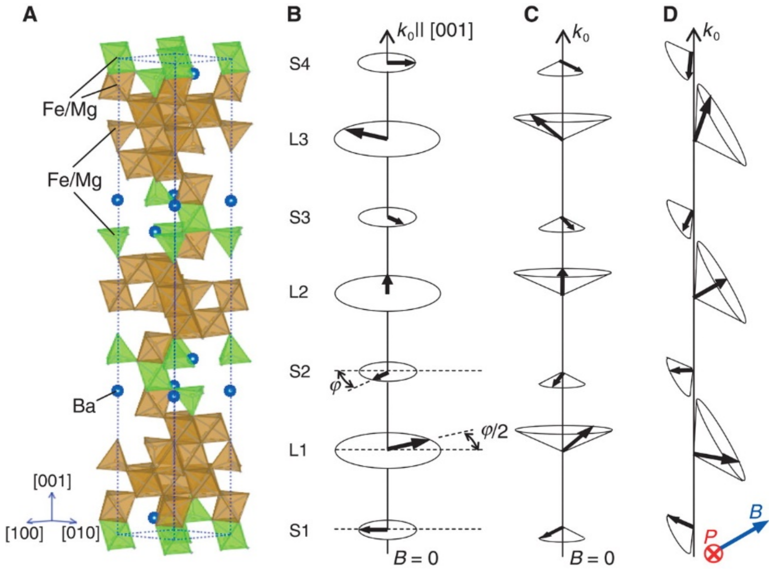
- ***Perovskite type: ABO_3, $A_2B`B``O_6$ (e. g., $BiFeO_3$, $TbMnO_3$)***
- ***Hexagonal structure: hexaferrites, manganates $RMnO_3$ with R = Sc, Y, Ho-Lu***
- ***Boracites: $M_3B_7O_{13}X$ with M = Cr, Mn, Fe ...; X = Cl, Br, I***
- ***Orthorhombic $BaMF_4$ compounds M = Mg, Mn, Fe, Co, Ni, Zn***

D. Khomskii, Physics 2, 20 (2009); C. J. Fennie, Ascona 2012

Magneto-electric effect in multiferroics

Type	Molecular formula	Hexaferrite blocks	Magnetoelectric effect
M	$BaFe_{12}O_{19}$	RSR*S*	$BaFe_{12-x-\delta}Sc_xMg_\delta O_{19}$
W	$BaMe_2Fe_{16}O_{27}$	RS_2R*S*_2	
X	$Ba_2Me_2Fe_{28}O_{46}$	$(RSR*S*_2)_3$	
Y	$Ba_2Me_2Fe_{12}O_{22}$	$(TS)_3$	$Ba_2Mg_2Fe_{12}O_{22}$, $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$, $Ba_{0.5}Sr_{1.5}Zn_2Fe_{11-x}Al_xO_{22}$
Z	$Ba_3Me_2Fe_{24}O_{41}$	RSTSR*S*T*S*	$Sr_3Co_2Fe_{24}O_{41}$
U	$Ba_4Me_2Fe_{36}O_{60}$	RSR*S*T*S*	$Sr_4Co_2Fe_{36}O_{60}$

Y-type hexaferrite – a multiferroic material



(A) Schematic crystal structure of $Ba_2Mg_2Fe_{12}O_{22}$.

(B) Helicoidal spins with proper screw (50 < T < 195 K)

(C) Longitudinal conical (T < 50 K)

(D) Slanted conical (T < 195 K and B ~ 30 mT).

Ishiwata et al. Science 319, (2008) 1643
Taniguchi et al. Appl. Phys. Exp. 1 (2008) 031301

Synthesis of $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$ powder material

Sonochemical co-precipitation method

$Co(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$
$Fe(NO_3)_3.9H_2O$, $Ba(NO_3)_2$

↓

homogenization

↓

co-precipitation process
(NaOH)
pH = 11.5

← High-power ultrasound stirring

↓

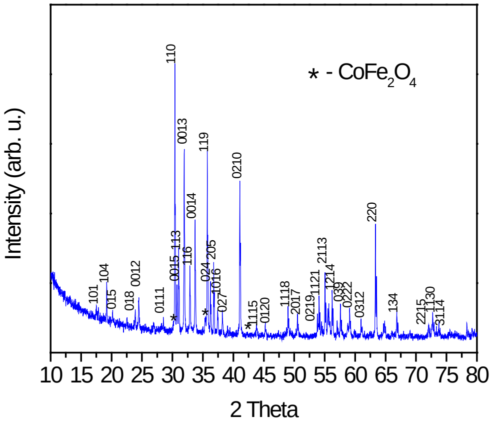
centrifugation, drying and milling

↓

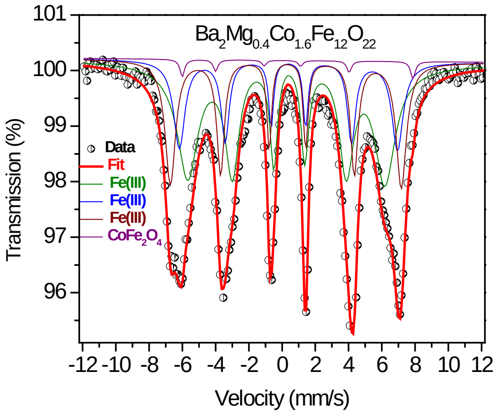
calcination at 700 °C → heat treatment in air at 1170 °C → $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$ powder

Sonics ultrasonic processor (750 W)

Structural properties of $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$ powder



$CoFe_2O_4$ impurity (< 2 %)



Mössbauer spectrum recorded at room temperature of $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$.

$Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$

$a = b = 5.88(5)$ Å
$c = 43.58(4)$ Å

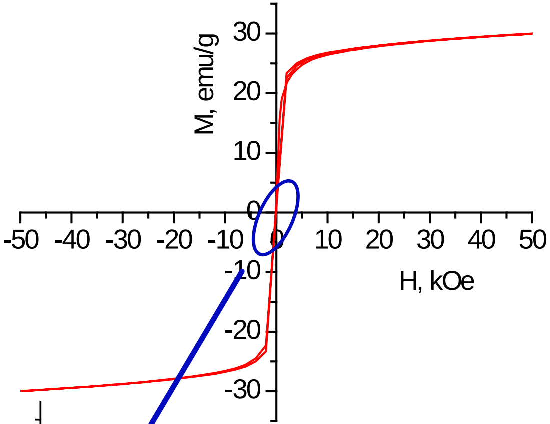
[1]$Ba_2Mg_2Fe_{12}O_{22}$

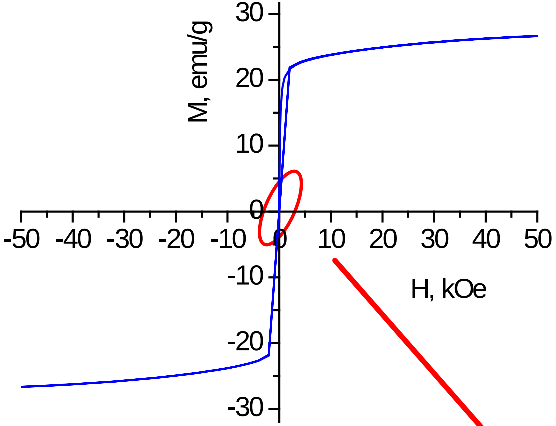
$a = b = 5.8694(1)$ Å
$c = 43.4962(1)$ Å

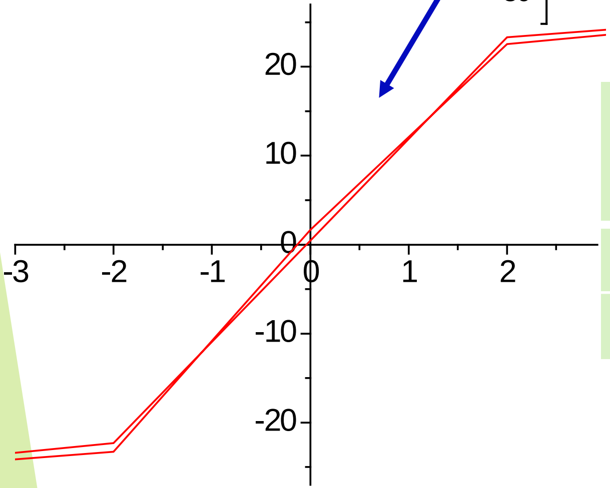
Iron sites	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	B_{hf} (T)	Area (%)
a-Fe(III)	0.34 (1)	-0.18 (1)	0.40 (1)	37.1 (1)	50 (1)
b-Fe(III)	0.38 (2)	0.00	0.28 (2)	40.7 (1)	21 (1)
c-Fe(III)	0.27 (1)	-0.09 (1)	0.28 (1)	43.1 (1)	27 (1)
$CoFe_2O_4$	0.48 (2)	0.92 (2)	0.33 (1)	43.0 (1)	2 (1)

[1]T. Koutzarova et al. *J. Supercond. Novel Magnetism* **2012**, *25*, 2631

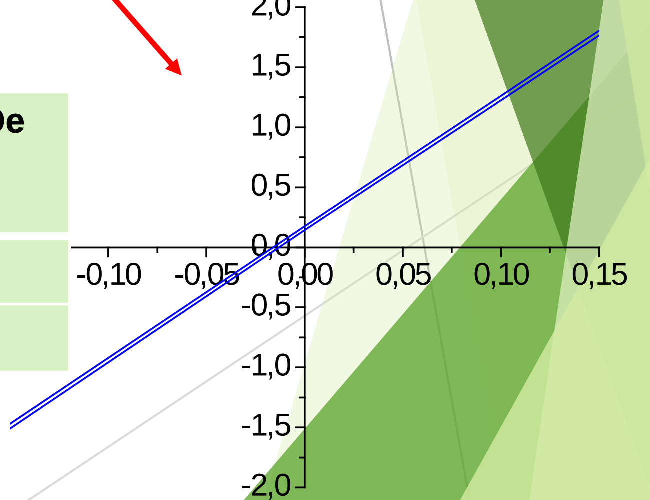
Magnetic properties $Ba_2Mg_{0.4}Co_{1.6}Fe_{12}O_{22}$ powder material



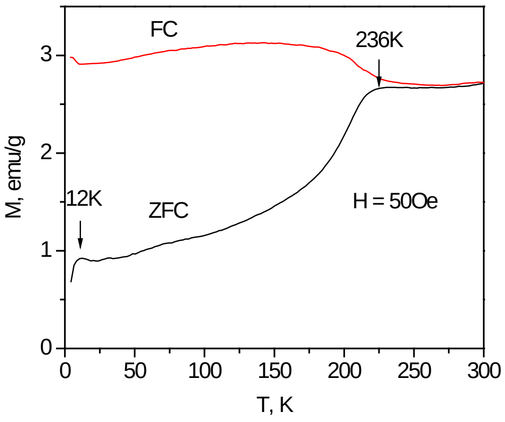


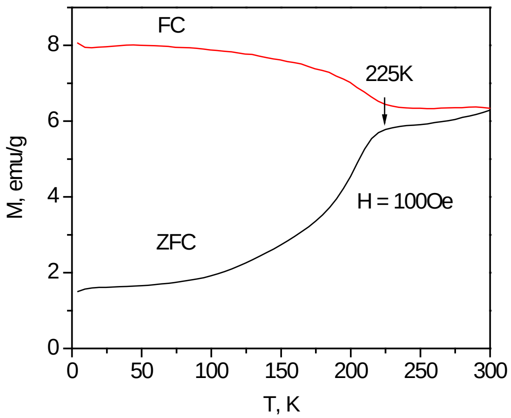


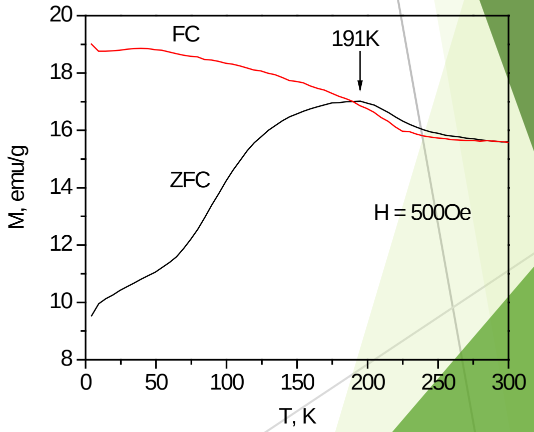
T, K	M (50kOe), emu/g	M_r , emu/g	H_c , Oe
300	26.6	low	2
4.2	30.0	low	48



Temperature dependence of ZFC- and FC-magnetization







magnetic phase transition from
a ferrimagnetic to a helical spin order

236 K (50 Oe)

225 K (100 Oe)

191 K (500 Oe)

Summary

- The substantial cobalt substitution for magnesium in the $Ba_2Mg_2Fe_{12}O_{22}$ basic composition did not lead to a significant change of the unit cell parameters.
- The Co^{2+} substitution in the Y-type $Ba_2Mg_2Fe_{12}O_{22}$ hexaferrite leads to an increase of the magnetic phase transition temperature to the specific helical spin arrangement believed to be a precondition for the multiferroic properties of the undoped material.

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