Structure,Rietveld Refinement Study of $BaCo_xTi_xFe_{12-2x}O_{19}$ ferrite Using Powder XRD Analysis

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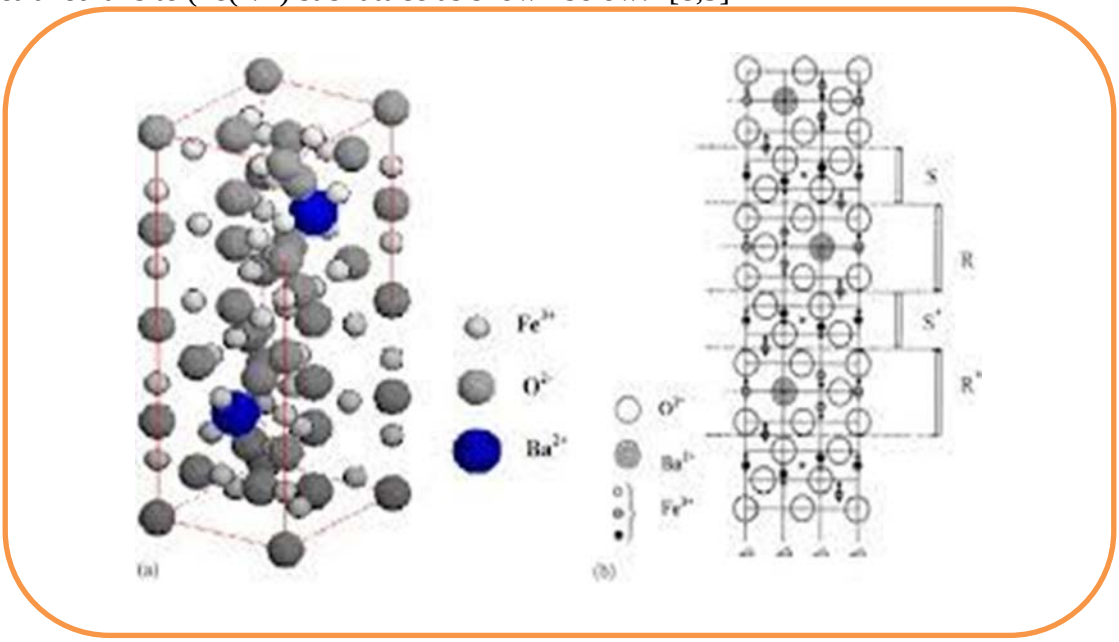
Abstract

$BaCo_xTi_xFe_{12-2x}O_{19}$ (x=0.1, 0.5, 0.7, 0.9, 1.7) were prepared using powder technology technique . X-ray diffraction with diffractometer CuKα radiation analysis and Rietveld refinement of the samples were studied and showed a single phase of hexagonal structure with $SP6_3/mmc$ space group . Lattice parameters, cell volume , crystallite size and x-ray density were determined .The hexagonal structure was represented by using PowderCell program showing the atomic positions of Co ,Ti, and Fe ions.

Keywords: M-type hexaferrite-XRD analysis-Rietveld refinement

Introduction

Barium hexaferrite with a chemical formula $BaCo_xTi_xFe_{12-2x}O_{19}$ is one of the most important compositions for perpendicular magnetic recording due to its large saturation magnetization; and good stability [1] .M-type barium hexa-ferrite has been investigated as a material for microwave absorber devices and also in various applications [2]. Because of the industrial relevance of barium hexa-ferrite ,scientific interest ,they have been extensively studied because of their large intrinsic uniaxial anisotropy and high coercively ,which make them widely used in various applications [3].In order to reduce the anisotropy field which causes poor overwrite modulation[1-5] and satisfy the desired applications many studies were taken out to modify the magnetic properties of barium hexaferrite by the substitution of the Fe^{3+} ion with cations such as (Sn^{4+}, Ni^{2+} ,Co^{2+} ,Co^{3+} Ti^{4+}…..) [1-5] .The structure of M-type barium hexaferrite with the formula $BaCo_xTi_xFe_{12-2x}O19$ has been studied in the present work using powder x-ray diffraction analysis technique and we have investigated the advantages of this technique to study and measure the most important features and properties of our ferrite [4-15] such as the average grain size ,x-ray density ,lattice parameters of the unit cell and the cell volume of samples and the atomic positions sites in the lattice structure[6-15].The structure of the M-type barium ferrite ($BaFe_{12}O_{19}$) with space group $SP6_3/mmc$ is symbolically described (RSR*S*)where R is three layers block (two O_4 containing one BaO_3) with composition $Ba^{2+}Fe_6^{2+}O_{11})^{2-}$ and S is two layers O_4-layer block with compositions ($Fe_6^{3+}O_8)^{2+}$ when the asterisk means that the corresponding block has been turned 180° around the c-axis.In this structure the metallic cations are distributed within three different kinds of octahedral sites (2a , $4f_{VI}$, and 12K sub lattice) ,one tetrahedral site ($4f_{VI}$ sub lattice) and one pseudo tetrahedral site (4e(1/2) sub lattice as shown below:- [8,9]



cations	Sub lattice	coordination	Block	No. of ions/Fu	Spin direction
M1	2a	octahedral	S	1	Up
M2	4e(1/2)	Pseudo-tetrahedral	R	1	Up
M3	$4f_{IV}$	Tetrahedral	S	2	Down
M4	$4f_{IV}$	octahedral	R	2	Down
M5	12K	octahedral	R-S	6	up

In this work we report the intrinsic structure of the classical $BaCo_xTi_xFe_{12-2x}1O19$ doping scheme.

Experimental procedures

The synthesis of polycrystalline $BaCo_xTi_xFe_{12-2x}O_{19}$ samples (x=0.1 0.5 ,0.7 ,0.9 ,1.7)were prepared by powder technology method with different sintering temperatures listed in Tab.1 . X-ray diffraction analysis was carried out using SHIMADZU6000 diffractometer with CuKα radiation. The obtained XRD data was compared with standard pattern of JCPDS-ICDD (International Center for Diffraction Data).Powder diffraction (PXRD) is a technique used to characterize the crystal structure, grain size, volume, x-ray density and lattice parameters and used to identify unknown substances by comparing diffraction data by the (ICDD) [10-15]. First we calculated the lattice parameters using the well-known relation bellow:-[10]
For hexagonal structure a=b≠ c, α=β=90° γ=120°

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2}{a^2} + \frac{hk}{a^2} + \frac{K^2}{a^2}\right)\frac{l^2}{c^2} \quad \text{.....(1)}$$

Volume of hexagonal unit cell:

$$\mathbf{V=\left(\frac{\sqrt{3}}{2}\right) a^2c=0.886\ a^2c\ldots\ldots(\ 2)}$$

x-ray density for hexagonal structure is:-

$$\boldsymbol{\rho_{x\text{-}ray} = Z.M\ /\ V.N_A \ldots\ldots\ldots(3)}$$

M=molecular weight , V=x-ray volume , Z=2 for hexa-unitcell , N_A=Avogadro number
And to calculate the crystallite grain size we used scherrer 's equation from the diffraction peaks broadening.

$$\mathbf{D=0.94.\lambda\ /\ \beta.\cos\theta \ldots\ldots..(4)}$$

Where: - β=FWHM in radiant , D=polycrystalline grain size(nm)
wavelength Λ forCuKα =0.154059 (nm) , θ=Brag angle.
Porosity ratio for the prepared samples was calculated using the relation:-

$$\mathbf{P= 1- (\rho_{bulk}/\rho_{x\text{-}ray}) \quad \ldots\ldots\ldots(5)}$$

Where ρ_{bulk}=mass/volume (gram/Cm^2).
Rietveld analysis:-

Rietveld refinement data of all the prepared hexa-ferrite carried out by using the Fullprof and UnitCell programs and studied very carefully and from Rietveld refinement data we calculated the atomic positions of our samples (x,y,z) and exihibited the structure of our hexagonal M-type barium ferrite doped with Co-Ti using the PowderCell program.

Results and Discussion

Fig.1 shows XRD patterns of Co-Ti doped barium hexa-ferrite ($BaCo_xTi_xFe_{12-2x}O_{19}$) with different concentrations ,comparing with the standard pattern of ($BaFe_{12}O_{19}$) with space group $SP6_3/mmc$ (JCPDS file no. 043-0002)all the XRD patterns have been indexed (hkl) manually and by using equations (1-5) we calculated lattice parameters, x-ray cell volume and x-ray density .Table.1 summarizes the composition dependence of lattice parameters determined by x-ray diffraction analysis . All the patterns showed single phase hexagonal structure with $SP6_3/mmc$ and from these data we may propose that the lattice parameter (c-values) increases due to greater ionic radii of Co-Ti than the ionic radius of iron ions (~0.55 A°) and the average crystallite size decreases with doped barium ferrite (Co- Ti).The Rietveld refinement data is shown in Fig.2 and the refined lattice parameters are summarized in Table.2. Fig.3 shows the hexagonal structure representation and the atomic positions (xyz) by using data information from the refinement file and PowderCell programs. The samples possess a hexagonal structure $SP6_3/mmc$ with two molecules in unit cell (z-z).

Conclusions

$BaCo_xTi_xFe_{12-2x}O_{19}$ (x=0.1, 0.5, 0.7, 0.9, 1.7) were synthesized by powder technology technique. The x-ray diffraction analysis and Rietveld refinement for all the prepared samples revealed existence of single phase identified by JCPDS file no. hexagonal phase with space group $SP6_3/mmc$ in agreement with the data reported in most scientific researches. We also showed that XRD analysis is a very powerful tools in material science and technology researches.

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Table No(1): lattice parameters and average crystallite size with x-ray volume and density of $BaCo_xTi_xFe_{12-2x}O_{19}$ measured by XRD.

sample	x	$BaC0_xTi_xFe_{12-2x}O_{19}$	$T_{sintering}$ °C	a=b A^0	C A^0	C/a	$\rho_{x\text{-}ray_3}$ gm/cm	Dnm	Vol. of the cell $x10^{24}$ Cm^3
B1	0.1	$BaCo_{0.1}\ Ti_{0.1}Fe_{11.8}O_{19}$	1450	5.89	23.21	3.94	5.091	52	697.306
B2	0.5	$BaCo_{0.5}\ Ti_{0.5}Fe_{11}\ O_{19}$	1250	5.9	23.27	3.94	5.24	58.17	701.4848
B3	0.7	$BaCo_{0.7}\ Ti_{0.7}Fe_{10.6}O_{19}$	1350	5.89	23.28	3.952	5.25	52	699.409
B4	0.9	$BaCo_{0.9}\ Ti_{0.9}Fe_{10.2}O_{19}$	1450	5.89	23.3	3.95	5.091	42	720.94682
B5	1.7	$BaCo_{1.7}\ Ti_{1.7}Fe_{8.6}O_{19}$	1450	5.9	23.16	3.92	5.23	42.822	699.1688

Table No(2): lattice parameters of prepared samples after refinements using Fullprof programs

samples	a =b (A°)	C (A°)	ρ (gm/cm^2)	Space group
B1	5.883	23.176	5.092	$P6_3/mmc$
B2	5.886	23.186	5.124	P63/mmc
B3	5.887	23.213	5.25	P63/mmc
B4	5.889	23.231	5.12	P63/mmc
B5	5.891	23.321	5.23	P63/mmc

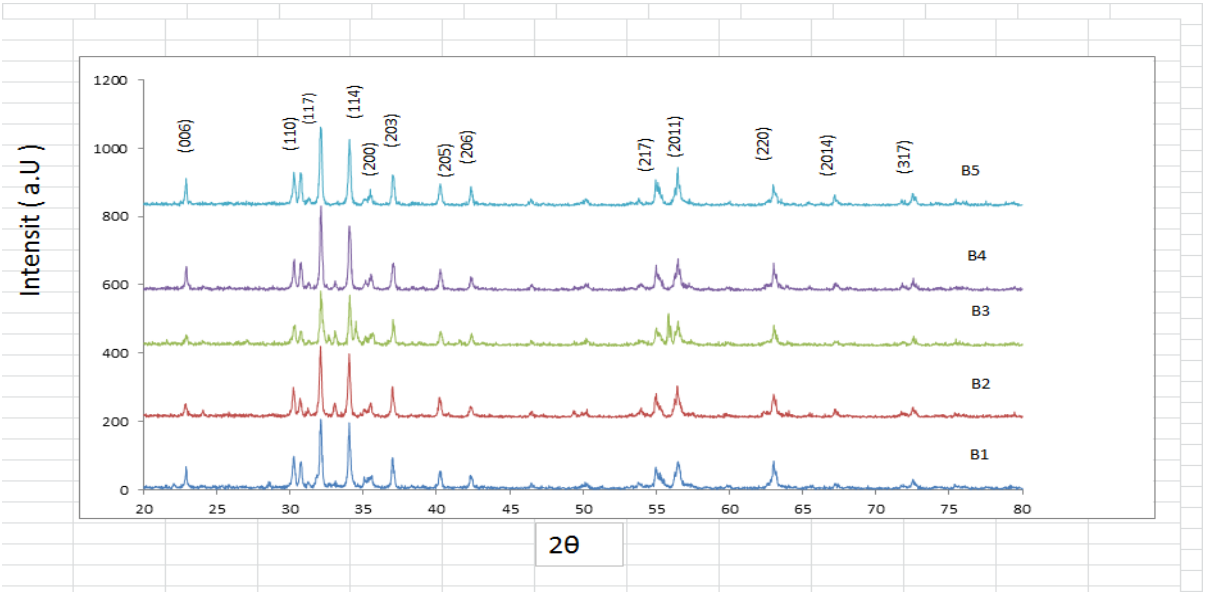

Figure No(1): XRD patterns of $BaC0_xTi_xFe_{12-2x}O_{19}$ with different dopant concentrations

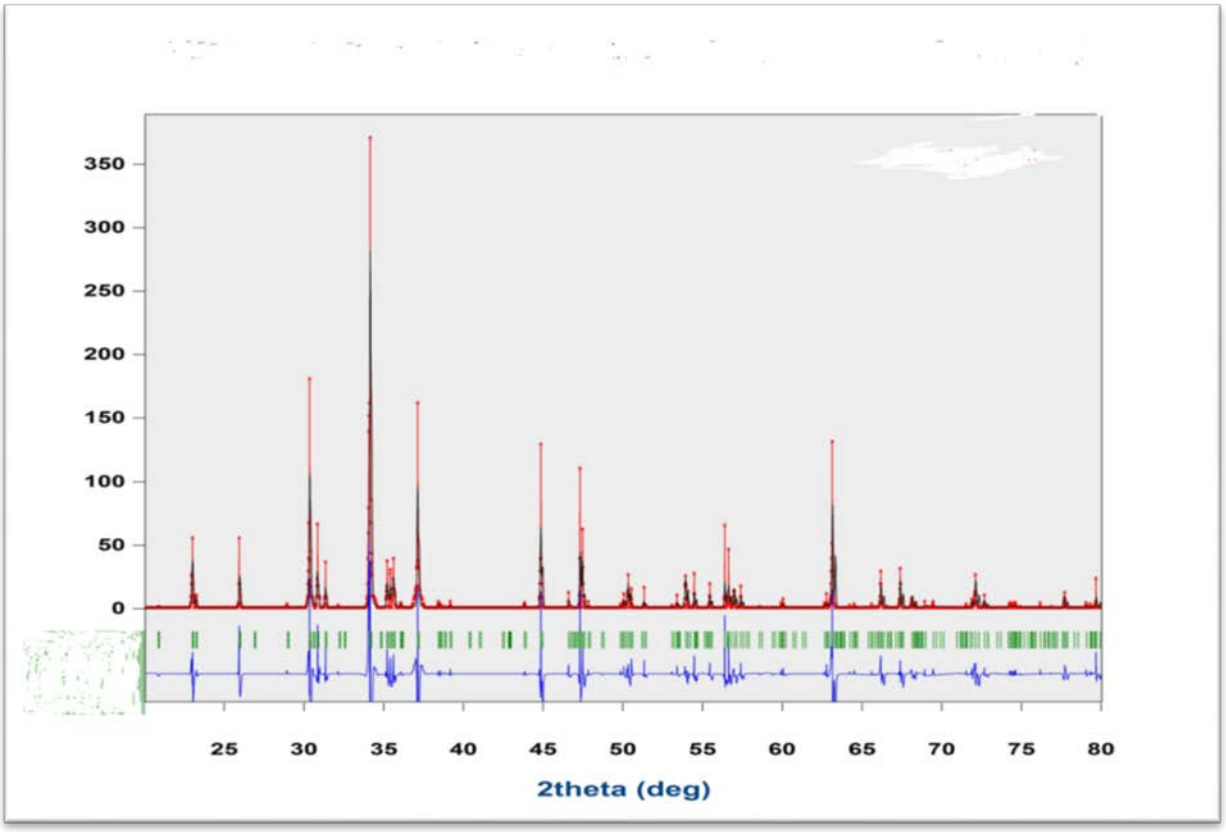

Figure No(2): the Rietveld refinement data of prepared sample B10 by Fullprof program

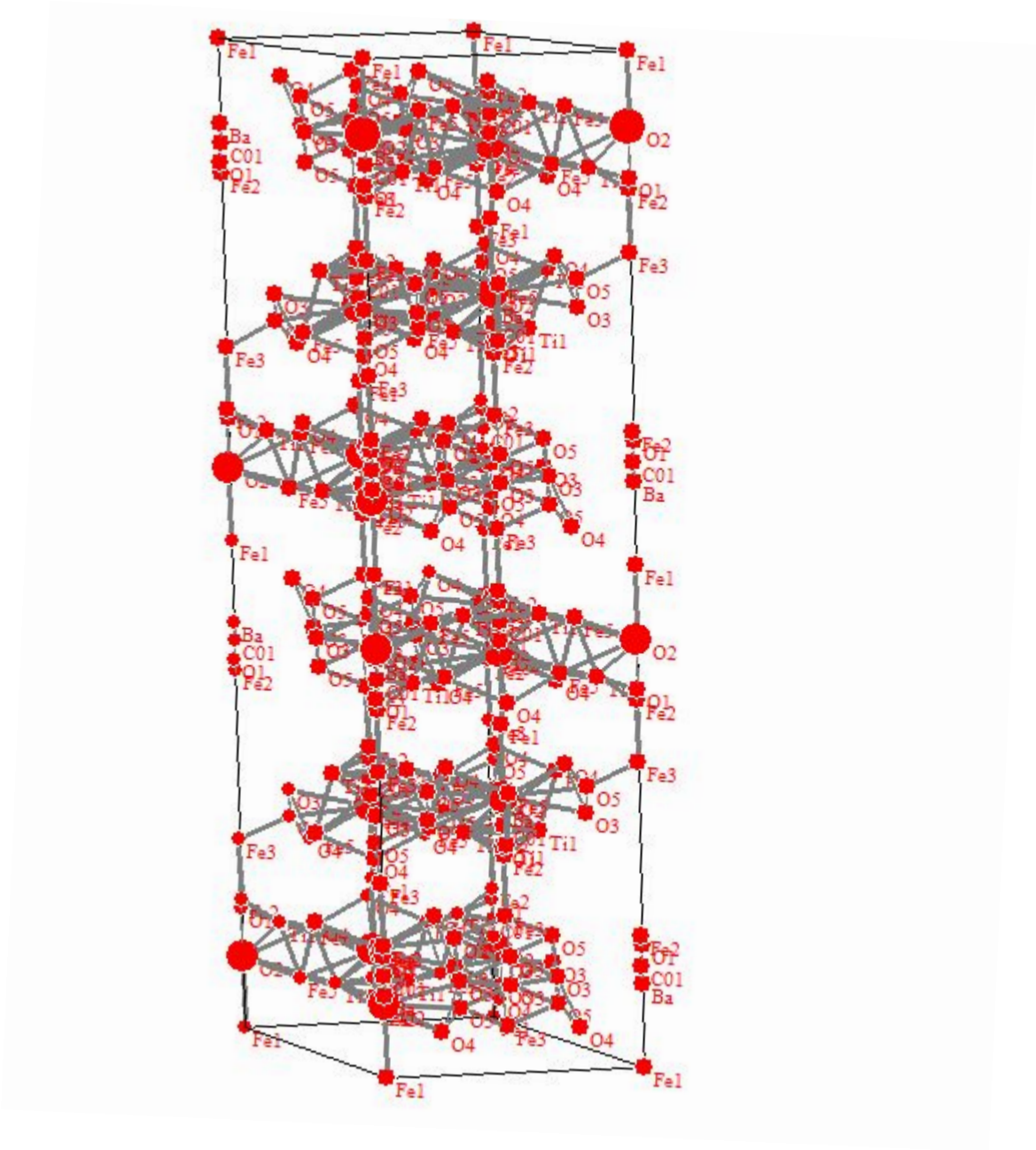

Figure No.(3): structure representation for barium hexa-ferrite doped with Co-Ti by using PowderCell programs

دراسة تركيب وتصفية ريتفيلد للفيرايت السداسي بصيغة $BaCo_xTi_xFe_{12-2x}O_{19}$ باستخدام تحليل حيود الاشعة السينية (PXRD)

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الخلاصة

تم تحضير الفيرايت ذو الصيغة الكيميائية $BaCo_xTi_xFe_{12-2x}O_{19}$ باستخدام تقنية تكنولوجيا المساحيق وبنسب تطعيم مختلفة لكل من الكوبلت والتيتانيوم (x=0.1 0.5 ,0.7 ,0.9 ,1.7) واجريت فحوصات حيود الاشعة السينية وممقارنتها مع ملفات JCPDS التابعة للمركز الدولي لبيانات الحيود (ICDD) واظهرت جميع النماذج طور سداسي واحد وقيست الابعاد البلورية لها (a=b , c, c/a) وكذلك الحجم الحبيبي والكثافة باستخدام تحليل الاشعة السينية لها والمعادلات الخاصة بهذا التحليل ، واعادة القياسات باستخدام تصفية ريتفيلد ودراسة المواقع للذرات في شبيكة الباريوم فيرايت المطعم بالكوبلت والتيتانيوم ورسم الشبيكة باستخدام البرامج الحاسوبية Fullprof و PowderCell.

الكلمات المفتاحية :- حيود الاشعة السينية – تصفية ريتفيلد – باريوم فيرايت السداسي