

# X-ray diffraction and Mössbauer Spectroscopic Study of

*BaCo<sub>0.5x</sub>Zn<sub>0.5x</sub>Ti<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> (M-type hexagonal ferrite)*

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*A series of pure polycrystalline M-type hexagonal ferrite with the formula BaCo<sub>0.5x</sub>Zn<sub>0.5x</sub>Ti<sub>x</sub>Fe<sub>12-2x</sub>O<sub>19</sub> (x = 0.0, 0.4, 0.8, 1.2, 1.6, 2.0) has been synthesized and studied by x-ray diffraction and Mössbauer spectroscopy. With increasing substitution the Mössbauer spectra change from magnetically ordered (x=0) towards magnetically ordered with strong line broadening (X= 0.4 to 1.6) to nonmagnetic (x=2.0), due to decreasing of Curie temperatures. Differential line broadening and relative area of components indicate that for small values of x, substitutions occurs preferentially in 4f<sub>1</sub> and 4f<sub>2</sub> sites indirectly affecting Fe in the 12k site.*

## 1. Introduction:

Barium ferrite (BaM) is well established for use as a permanent magnetic material [1]. BaM exhibits a fairly large magnetocrystalline anisotropy and high Curie temperature, and has in addition a relatively large saturation magnetization, chemical stability and corrosion resistivity [2]. It is also a suitable material for high-density magnetic recording applications [1-3]. BaM has a hexagonal ferrite structure (P6<sub>3</sub>/mmc) which is symbolically described by RSR\*S\* where R is a three-layer block (containing two O<sub>4</sub> and one BaO<sub>3</sub>) with composition (BaFe(III)<sub>6</sub>O<sub>11</sub>)<sup>2-</sup> and S is a two O<sub>4</sub>-layer block with composition (Fe(III)<sub>6</sub>O<sub>8</sub>)<sup>2+</sup>, where the asterisk imply that the corresponding block has been rotated 180° around the hexagonal c-axis. In this structure the metallic cations are distributed among five different sites (sublattice). These sites have different coordinations and are designated: tetrahedral(4f<sub>1</sub> sublattice), bipyramidal (2b sublattice) and three different octahedral (12k, 4f<sub>2</sub>, and 2a sublattices). Opposite spin directions cause a ferrimagnetic structure.

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$\text{Sr}^{2+}$  or  $\text{Pb}^{2+}$  can replace the  $\text{Ba}^{2+}$  ion in the M type hexagonal ferrites partly or completely, without changing the crystal structure. Substitutions of  $\text{Fe}^{3+}$  ion and  $\text{O}^{2-}$  are also possible. In all cases, substitutions must keep electrical neutrality and have nearly similar ionic radii with the original one. For the various magnetic applications of BaM a high saturation, a suitable coercivity, and low temperature coefficients of coercivity and remanence are desired properties. Therefore, much work has been done to modify the magnetic properties through the substitutions of  $\text{Fe}^{3+}$  ions. Substitution of Fe can be accomplished in two ways: Direct substitution by trivalent ions ( $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Mn}^{3+}$ ) or by combined substitution of divalent and tetravalent ions ( $\text{Co}^{2+}+\text{Ti}^{4+}$ ,  $\text{Zn}^{2+}+\text{Ti}^{4+}$ ,  $\text{Zn}^{2+}+\text{Sn}^{4+}$ ). Various combinations of substituents (Co-Ti, Co-Sn, Zn-Ti, Co-Zn-Nd, Co-Ti-Sn, Co-Mo and Zn-Zr) have been studied by Mössbauer spectroscopy [4-14].

The magnetic properties of the substituted hexaferrites are strongly dependent upon the electronic configuration of the substituting cations as well as on their site preference. Substitutions by non-magnetic ions are expected to lower the magnetic ordering temperatures and differences primarily in the charge of the substituents may cause different neighbor effects.

In this work coupled substitution of magnetic ( $\text{Co}^{2+}$ ) and non-magnetic ions ( $\text{Zn}^{2+}-\text{Ti}^{4+}$ ) for  $\text{Fe}^{3+}$  in BaM was investigated using X-ray diffraction and  $^{57}\text{Fe}$  Mössbauer spectroscopy.

## 2. Experimental:

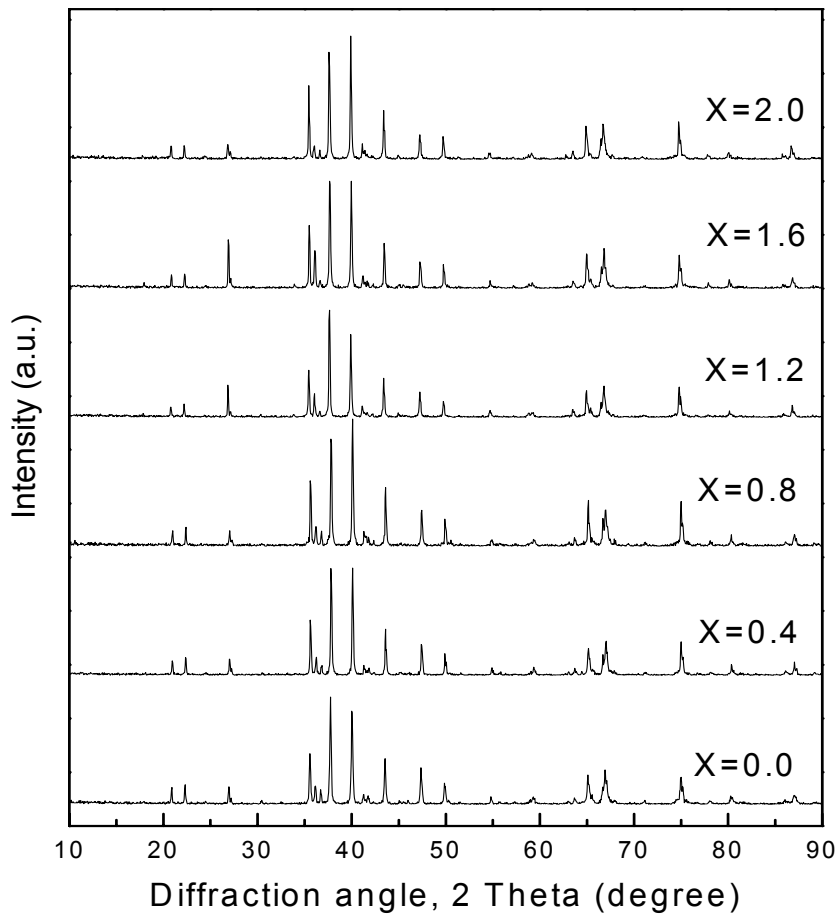
The starting materials used for samples preparation were high purity barium carbonate and cobalt, zinc, titanium and ferric oxides. The compounds were mixed together in appropriate ratios to prepare a series of polycrystalline M-type hexagonal ferrites of composition  $\text{BaCo}_{0.5x}\text{Zn}_{0.5x}\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$  with ( $x = 0.0, 0.4, 0.8, 1.2, 1.6$  and  $2.0$ ) using conventional ceramic technique. The powders were mixed for 5 hr using a grinding machine. The final powders were pressed and pre-sintered for 6 hr at  $950\text{ }^\circ\text{C}$ . After slowly cooling to room temperature, the reaction mixtures were again ground for 5 hr and then pressed into a disc shape. The discs were sintered at  $1150\text{ }^\circ\text{C}$  for 6 hr, and the samples were slowly cooled to room temperatures. The last heating step was repeated.

X-ray diffraction was used to confirm the existence of single-phase M-type hexagonal ferrites. The X-ray diffractograms were recorded with a Siemens D-5000 X-ray diffractometer using  $\text{Co K}_\alpha$  radiation.

The  $^{57}\text{Fe}$  Mössbauer spectra were obtained using a constant acceleration spectrometer with a  $^{57}\text{Co}$  source in Rh matrix. The spectrometers were calibrated using a thin foil of  $\alpha\text{-Fe}$  at room temperature. Spectra were obtained at room temperature and at  $80\text{ K}$ .

### 3. Results and discussion:

The X-ray diffraction patterns of the  $\text{BaCo}_{0.5x}\text{Zn}_{0.5x}\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$  samples are shown in Fig.(1). They demonstrate that all the samples of this series have the magnetoplumbite structure, and no trace of other phases was detected. On the other hand sharp lines are observed for all samples, indicating that the samples consist of large crystallites. Although the lattice constant 'a' does not change significantly with the mole ratio x, the constant 'c' slightly increases monotonically as x increases, as seen in Table (1). This may be attributed to the larger ionic radius of  $\text{Ti}^{4+}$  (0.68 Å),  $\text{Zn}^{2+}$  (0.74 Å) and  $\text{Co}^{2+}$  (0.72 Å) compared to  $\text{Fe}^{3+}$  (0.64 Å). This is in accordance with the fact that all hexagonal classes (M-, Y- and W-type) are characterized by constant lattice parameter 'a' (of order 5.88 Å) but the parameter 'c' is varied [1]. The change in the relative intensities may be ascribed to the occupation of the lattice sites by different ions.



**Fig.(1):** XRD patterns of the  $\text{BaCo}_{0.5x}\text{Zn}_{0.5x}\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$  samples. The mole fraction of substitution is indicated at each trace.

**Table (1):** Lattice constants ( $a$  and  $c$ ) of the  $\text{BaCo}_{0.5x}\text{Zn}_{0.5x}\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$  samples as a function of the mole fraction ( $x$ ).

$x$	$a$ (Å)	$c$ (Å)
0	$5.8688 \pm 0.008$	$23.19848 \pm 0.043$
0.4	$5.87458 \pm 0.019$	$23.23328 \pm 0.082$
0.8	$5.83336 \pm 0.073$	$23.25161 \pm 0.091$
1.2	$5.87992 \pm 0.0148$	$23.28674 \pm 0.063$
1.6	$5.86254 \pm 0.0168$	$23.31093 \pm 0.072$
2	$5.87256 \pm 0.0123$	$23.32603 \pm 0.038$

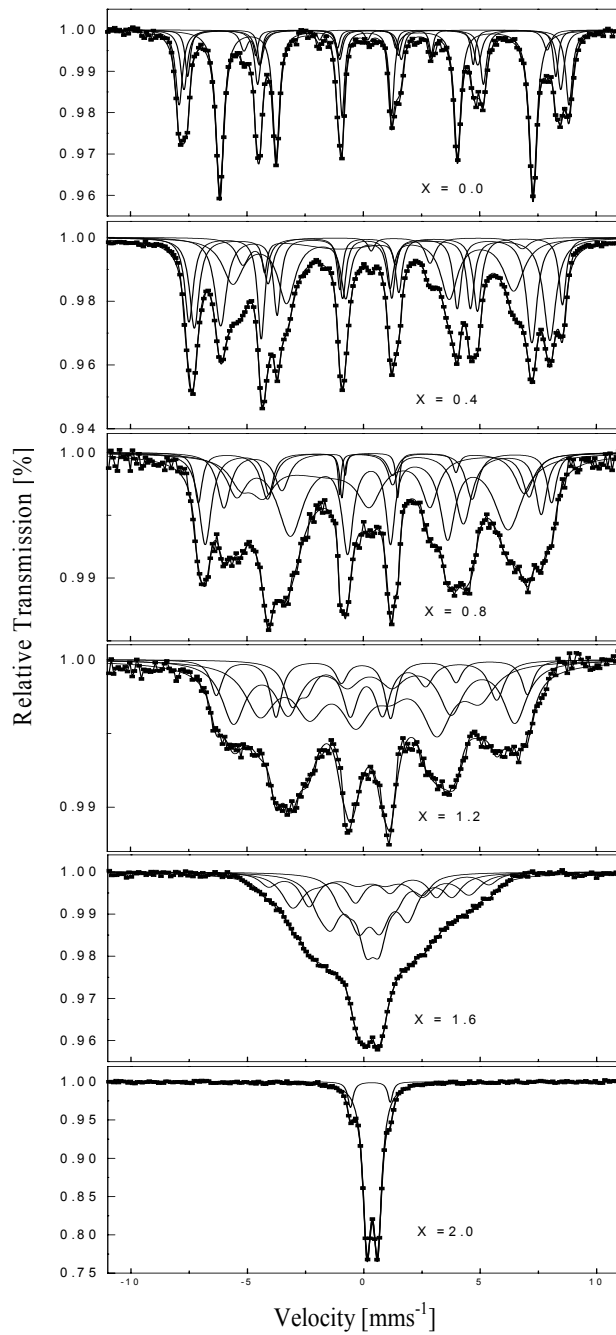
The Mössbauer spectrum of the  $\text{BaFe}_{12}\text{O}_{19}$  end member consists at room temperature of five magnetically split and overlapping components. In Table (2) are given the parameters of a fit using five components. The parameters of the  $4f_2$  and the 2a sites are so similar that most frequently only four components are used, taken these two sites as one component. The hyperfine parameters are in good agreement with previously published values [6,8,15-17]. The substitution of the iron ions by other cations leads to line broadening due to perturbation of the magnetic interaction. In particular, the  $x=0.4$  sample exhibits a strong asymmetry in the component due to the 12k site. Introducing two components for the modified 12k site (into 12k' and 12k'' sites) and treating  $4f_1$  and 2a as one component the derived hyperfine values are reported in Table (2).

**Table (2):** Mössbauer parameters of the spectra measured at room temperature for  $x=0.0$  and  $0.4$ .

$x$ value	Site	Isomer shift $\delta$ ( $\text{mms}^{-1}$ )	Quadrupole shift $\epsilon$ ( $\text{mms}^{-1}$ )	Hyperfine field $B_{\text{hf}}$ (Tesla)	Width of line 1 ( $\text{mms}^{-1}$ )	Relative area (%)
0.0	12k	0.36	0.21	41.7	0.40	49
	$4f_1$	0.25	0.11	49.0	0.27	9
	$4f_2$	0.39	0.07	51.9	0.35	20
	2a	0.31	0.08	50.2	0.36	16
	2b	0.27	1.12	40.4	0.38	6
0.4	12k'	0.35	0.19	41.4	0.57	21
	12k''	0.35	0.15	37.3	1.12	35
	$4f_2$	0.39	0.12	49.8	0.40	13
	$4f_1+2a$	0.29	0.07	47.4	0.55	25
	2b	0.16	0.93	38.6	0.81	6

These results demonstrate strong line broadening and some reduction in the magnetic hyperfine fields. It has previously been reported that Co substitution induces a splitting of the component due the 12k site [13].

Increasing the substitution to 0.8 and 1.2 causes further line broadening and reduction of magnetic hyperfine field. At these substitution levels fitting becomes meaningless (in Fig 2 is indicated fits using five components for x = 0.8 to 1.6, but no assignment can be argued. The results indicate that at high



**Fig.(2):** Mössbauer spectra of the  $\text{BaCo}_{0.5x}\text{Zn}_{0.5x}\text{Ti}_x\text{Fe}_{12-2x}\text{O}_{19}$  samples obtained at room temperature. Mole fractions are indicated in the figure.

substitution level all sites are affected. At highest levels of substitution ( $x= 1.6$  and  $2.0$ ) magnetic order vanish indicating Curie temperatures around and below RT. Magnetic order in these samples is restored by lowering the temperature to 80 K (spectra not shown). The magnetic susceptibility at RT (not shown) is almost constant for  $X= 0$  to  $1.2$ , but decreases sharply for larger values of  $x$ , in agreement with a lowering of the Curie temperatures. Based on the intensity of the 12k sites for  $x= 0.4$  it appears that the substitution for low  $x$  values occur not in the 12 k site itself but rather in the neighboring  $4f_1$  and  $4f_2$  sites. It is plausible that  $4f_1$  host  $Ti^{4+}$  and  $Co^{2+}$  ions whereas  $Zn^{2+}$  maybe preferred in  $4f_2$ , but more detailed analysis of the x-ray data is needed.

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