

Comparing the Structural and Electrical Properties of Barium Hexaferrite after Substituting Co-Sn and Zn -Sn

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Abstract

Barium Hex ferrite ($\text{BaFe}_{12}\text{O}_{19}$) is widely used in recording media and as permanent magnets. The Fe ion is partially substituted by Co-Sn and Zn-Sn to get $\text{BaFe}_{10.4}\text{Co}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ and $\text{BaFe}_{10.4}\text{Zn}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ which are prepared by solid state diffusion method. Several possible site distributions and an electron transfer may occur. The identification of the compounds is done by X-ray diffraction. They are found to have single phase magnetoplumbite structure. Electrical properties are studied and electrical conductivity study shows that Cobalt substituted compound has more electrical conductivity than Zinc substituted compound. The activation energies of both the compounds are also calculated. The activation energy of Cobalt substituted compound is less than that of zinc substituted compound. Also conductivity increases with rise in temperature which shows semiconducting nature of the newly synthesized samples.

Keyword- Magnetoplumbite, $\text{BaFe}_{10.4}\text{Co}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$, $\text{BaFe}_{10.4}\text{Zn}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$, Electrical Conductivity, Activation Energy

I. INTRODUCTION

Ferrites are magnetic materials with Fe_3O_4 as main constituent. Ferrites are divided into two categories as “soft” and “hard” on the basis of their coercivity. The compounds with less coercivity are soft ferrites whereas those with high coercivity are termed as hard ferrites. They differ in many aspects such as structure, chemical composition, electrical and magnetic properties. The cubic tetragonal ferrites have spinel and distorted- spinel structures with general chemical composition as XY_2O_4 . While for hexagonal ferrites several chemical compositions with different unit cells are possible. The ferrites are widely used as permanent magnets and also in recording media. The trivalent Fe ion is partially substituted by another trivalent ion or by combination of divalent and tetravalent ions in equal proportion so that the stoichiometry is maintained.

The present work is done on M-ferrites. These are hard ferrites with low value of lattice constant c and least molecular weight. These M type hexagonal ferrites are characterized as ceramic and magnetically hard substances and thus at times are called as ceramic magnets or hard ferrites or even ferroxdures. Magnetoplumbite are compounds with hexagonal structure [1 - 4] having general chemical formula $\text{XY}_{12}\text{O}_{19}$ where X and Y are usually divalent and trivalent cations.

An attempt has been made in the present work to study the stoichiometric effect of substitution on $\text{BaFe}_{12}\text{O}_{19}$. Here the substitution is effected by replacing trivalent Fe ions by half divalent cobalt or zinc ions along with quadrivalent Sn in equal proportions. Thus there is no charge imbalance in lattice. The present work is done to see the effect of double substitution on structural and electrical properties of the compounds. Thus the compounds $\text{BaFe}_{10.4}\text{Co}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ and $\text{BaFe}_{10.4}\text{Zn}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ are prepared by solid state diffusion method and studied further [5-9].

II. EXPERIMENTAL

In the present work the compounds $\text{BaFe}_{12}\text{O}_{19}$, $\text{BaFe}_{10.4}\text{Co}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ and $\text{BaFe}_{10.4}\text{Zn}^{+2}{}_{.8}\text{Sn}^{+4}{}_{.8}\text{O}_{19}$ are prepared from analar grade or highly pure oxides. The reacting oxides are first heated in oven to remove the traces of moisture. After cooling them to room temperature they were finely ground and mixed in proper molar ratio. After grinding them thoroughly in acetone, they are heated at about 1100°C for about 120 hours. These samples were used for further study.

Using the X-ray diffraction, following study was undertaken.

- 1) Calculation of values of inter planer distances (d) with respective (hkl) planes
- 2) Measurement of the lattice parameters ‘ a ’ and ‘ c ’
- 3) X-ray density for the said compounds

Pellets of samples were prepared using polyvinyl acetate in acetone as binder in a clean stainless steel die of diameter 1.28×10^{-2} m under a pressure of 5000 psi in a hydraulic press. This binder was evaporated by heating the pellets at 260°C . The two surfaces of pellets were silvered. Using digital LCR meter, the resistance of the pellets was measured at various temperatures. A graph was plotted for $\ln \sigma$ versus $1/T$. Further the activation energy for each compound is also calculated.

III. RESULTS AND DISCUSSION

For hexagonal system the inter planar spacing 'd' is related to unit cell dimension by the following relation

$$\frac{1}{d^2_{hkl}} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{1}{c^2} \quad (1)$$

Where d_{hkl} is inter planar spacing, 'a' and 'c' are lattice parameters and hkl are Miller indices of the crystal plane. The possible combinations of h and k are considered and values of a^2 are deduced. Knowing 'a' and using equation (1) the value of 'c' is calculated.

The lattice parameters of $BaFe_{10.4}Co^{+2}.8Sn^{+4}.8O_{19}$ (sample 1) were found to be $a = 5.8228 \times 10^{-10}$ m and $c = 22.0379 \times 10^{-10}$ m and the X-ray density is found to be 5.9774×10^3 kg/m³ whereas lattice parameters of $BaFe_{10.4}Zn^{+2}.8Sn^{+4}.8O_{19}$ (sample 2) are $a = 5.8321 \times 10^{-10}$ m and $c = 22.2938 \times 10^{-10}$ m and the X-ray density is found to be 5.9160×10^3 kg/m³.

The X-ray diffraction results are summarized in the following tables 1 and 2.

The X-ray diffraction (XRD) study shows that hkl values of the substituted compounds match well with the standard results thus the substituted compounds must have taken place of Fe ions [5].

Table 1: X-ray diffraction results of $BaFe_{10.4}Co^{+2}.8Sn^{+4}.8O_{19}$

d(observed) Å	d(calculated) Å	1/d ²	(hkl)
2.92	2.91	0.1169	110
2.79	2.81	0.1282	112
2.7	2.7	0.1368	113
2.63	2.67	0.1444	107
2.52	2.52	0.1573	200
2.41	2.41	0.1714	108
2.26	2.28	0.1953	116
2.2	2.2	0.2055	0010
1.78	1.8	0.3143	214
1.76	1.75	0.3212	209
1.69	1.69	0.3479	0013
1.66	1.65	0.3602	2010
1.62	1.63	0.377	217

Table 2: X-ray diffraction results of $BaFe_{10.4}Zn^{+2}.8Sn^{+4}.8O_{19}$

d(observed) X10 ⁻¹⁰ m	d(calculated) X10 ⁻¹⁰ m	1/d ²	(hkl)
2.92	2.99	0.1164	106
2.89	2.89	0.119	111
2.75	2.71	0.1316	113
2.65	2.69	0.1419	107
2.62	2.58	0.1451	114
2.52	2.52	0.1568	200
2.49	2.46	0.161	202
2.29	2.29	0.1894	116
2.01	2.01	0.2469	118
1.68	1.67	0.3536	301
1.57	1.59	0.4023	0014
1.48	1.48	0.4514	0015
1.46	1.47	0.467	1113
1.39	1.39	0.5126	1114
1.3	1.31	0.5887	316

The electrical conductivity σ was calculated using the relation $\sigma = t/RA$ ($\Omega^{-1} \text{ cm}^{-1}$) where t is thickness, A is area, R is Resistance of sample measured with LCR bridge with change in temperature T(K).The variation of conductivity with variation in temperature are as shown below.

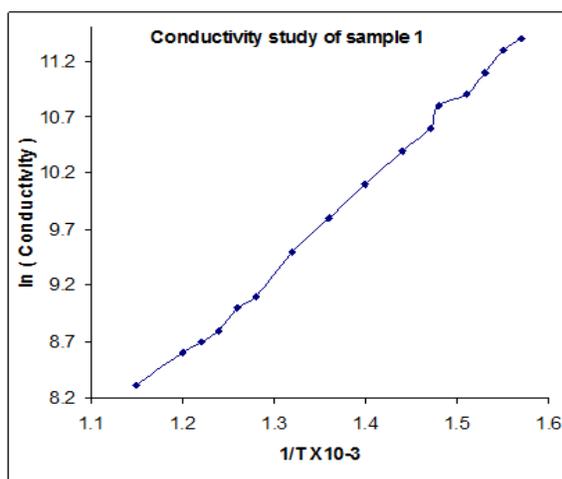


Fig. 1: Conductivity Study of sample 1

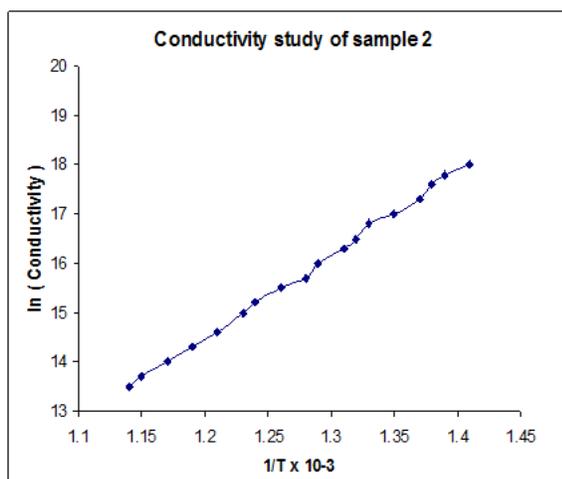


Fig. 2: Conductivity Study of sample 2

(The values on Y axis should be treated with a negative sign)

The activation energies of sample 1 and sample 2 are found to be $0.6137 \text{ eV} = 0.9819 \times 10^{-19} \text{ J}$ and $1.475 \text{ eV} = 2.36 \times 10^{-19} \text{ J}$.

IV. CONCLUSIONS

The observed and calculated interlunar spacing agree very well. The structural results show that both these compounds have single phase magnetoplumbite structure. It is further observed that out of these two different types of captions present in the compound $\text{BaFe}_{10.4}\text{Co}^{+2}_{.8}\text{Sn}^{+4}_{.8}\text{O}_{19}$, Fe^{+3} ions have stronger preference for tetrahedral sites, than the remaining ions. As the number of Fe^{+3} ions per unit cell is 20.8, the tetrahedral sites will get occupied by Fe^{+3} ions completely and remaining Fe^{+3} will preside over the octahedral sites. Thus due to the differences in site preferences of Fe^{+3} , Co^{+2} and Sn^{+4} ions, the large amount of Fe^{+3} ions is deciding and governing the site distribution in the lattice. Thus Fe^{+3} ions occupy tetrahedral ($4f_1$), bipyramidal (2b) and then octahedral (12k,2a) sites 1.6 ions of Co^{+2} and Sn^{+4} each along with remaining Fe^{+3} ions occupy octahedral ($4f_2$) sites while Ba^{+2} is present in 2d position.

In the compound $\text{BaFe}_{10.4}\text{Zn}^{+2}_{.8}\text{Sn}^{+4}_{.8}\text{O}_{19}$ also Fe^{+3} ions are predominant over Zn^{+2} and Sn^{+4} ions for occupying tetrahedral and bipyramidal sites. So Fe^{+3} ions take positions in tetrahedral ($4f_1$) and bipyramidal (2b) sites and 1.6 ions of Zn^{+2} and Sn^{+4} each and remaining Fe^{+3} ions go to the octahedral sites.

In the DC resistivity measurements it was observed that the activation energy of cobalt substituted compound is less than that of zinc substituted compound. This is due to the different electronic configuration of the substituted atoms.

More energy is required to activate the conduction in Zn substituted compound because of high resistivity at room temperature. As compared to this less energy is required for Co substituted compound because of presence of weak bonding in the compound.

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