

Structural and Electrical Properties of Co-Sn substituted $BaFe_{12}O_{19}$

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ABSTRACT:- In Barium hexaferrite $BaFe_{12}O_{19}$ Fe ions were partially substituted by Co-Sn to get $BaFe_{10.4}Co^{+2}_{0.8}Sn^{+4}_{0.8}O_{19}$. The synthesis was carried out by solid state diffusion method. Several possible site distributions and an electron transfer may occur. The identification of the compounds was done by X-ray diffraction. They are found to have single phase magnetoplumbite structure. 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.

Keywords:- Activation energy, Barium hexaferrite, $BaFe_{10.4}Co^{+2}_{0.8}Sn^{+4}_{0.8}O_{19}$, Electrical conductivity, Magnetoplumbite

I. INTRODUCTION

Ferrites are divided into two categories as “soft” and “hard” on the basis of magnetic properties. 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 [1-4]. While for hexagonal ferrites several chemical compositions with different unit cells are possible. In case of cubic ferrites, thorough substitution of Fe^{+3} ion is possible by some suitable ions, the common term spinel rather than ferrites appears to be more appropriate. Similarly, substitution of Pb^{+2} , Ba^{+2} and or Fe^{+3} cations are called magnetoplumbites even in the absence of Plumbum if it crystallises in M-structure [5,6].

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. Magnetoplumbites are compounds with hexagonal structure [1, 7] having general chemical formula $XY_{12}O_{19}$ where X and Y are usually divalent and trivalent cations. The term Magnetoplumbite is derived from $PbFe_{12}O_{19}$ mineral. (plumbum) and now is extended to oxides with general formula $XY_{12}O_{19}$ crystallising in structure of the mineral.

Barium hexaferrite is widely studied magnetoplumbite because of its high retentivity, less corrosiveness, and magnetic nature. Its high magnetic permeability makes it useful in applications like magnetic media, hard disks, storage devices etc. Many researchers studied this parent compound alongwith some substitution. The trivalent Fe ions are partially substituted by another trivalent ions like Al, Mn etc. The trivalent Fe ions can also be partially substituted by combination of divalent and tetravalent ions by maintaining proper stichiometry. With the substitution the changes in the magnetic and electrical properties were observed [8-10]. An attempt has been made in the present work to study the stoichiometric effect of substitution on $BaFe_{12}O_{19}$. Here the substitution is effected by replacing trivalent Fe ions by half divalent cobalt 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 electrical properties of the compounds. Thus the compounds $BaFe_{10.4}Co^{+2}_{0.8}Sn^{+4}_{0.8}O_{19}$ and are prepared by solid state diffusion method [11,12] and studied further.

II. EXPERIMENTAL

In the present work the compounds $BaFe_{12}O_{19}$ and $BaFe_{10.4}Co^{+2}_{0.8}Sn^{+4}_{0.8}O_{19}$ 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 $1100^{\circ}C$ 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 interplaner 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 x 10⁻² m under a pressure of 5000 psi in a hydraulic press .This binder was evaporated by heating the pellets at 260⁰C .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 σ versus 1/T. Further the activation energy for each compound is also calculated.

III. RESULTS AND DISCUSSION

For hexagonal system the interplanar spacing ‘d’ is related to unit cell dimension by the following relation

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

where d_{hkl} is interplanar 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 a² are deduced. Knowing ‘a’ and using equation (1) the value of ‘c’ is calculated. The X-ray diffraction results are summarized in the following table 1.

Table 1: X-ray diffraction results of BaFe_{10.4}Co⁺²_{0.8}Sn⁺⁴_{0.8}O₁₉

| 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 |

D is the interplanar spacing measured in Å

The lattice parameters of BaFe_{10.4}Co⁺²_{0.8}Sn⁺⁴_{0.8}O₁₉ were found to be a = 5.8228 X10⁻¹⁰ m and c = 22.0379 X10⁻¹⁰ m and the X-ray density is found to be 5.9774 x 10³ kg/m³ .

The electrical conductivity σ was calculated using the relation σ = t /RA (Ω⁻¹ 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 .

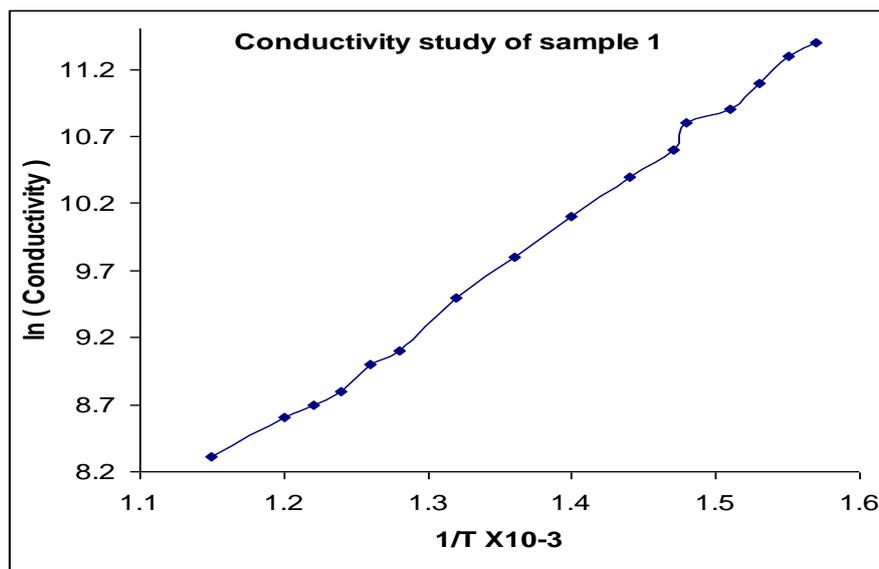


Fig. 1 variation of conductivity with temperature

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

The activation energy of the sample is found to be 0.6137 eV = 0.9819 x 10⁻¹⁹ J.

IV. CONCLUSIONS

The observed and calculated interplanar 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 cations present in the compound BaFe_{10.4}Co⁺²₈Sn⁺⁴₈O₁₉, 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 reside 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 (4f₁), 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 (4f₂) sites while Ba⁺² is present in 2d position.

In the DC resistivity measurements it was observed that the activation energy of cobalt substituted compound is small due to the different electronic configuration of the substituted atoms. Less energy is required for Co substituted compound because of presence of weak bonding in the compound.

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