STRUCTURAL, ELECTRICAL AND MAGNETIC INVESTIGATION OF $Ca_2ZnO_2Fe_{11}AlO_{22}$ FERRITES

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Abstract:
In the present work the samples with chemical composition $Ca_2ZnO_2Fe_{11}AlO_{22}$ has been synthesized and characterized by X-ray diffraction technique. The samples possesses hexagonal crystal structure with the space group R 3 m(166). The value of lattice parameters a and c for the sample is found to be 5.907 Å and 44.013 Å respectively. The dc electrical conductivity and the inverse molar susceptibility measurements have been carried out over the temperature range of 300 K – 800 K. The activation energy of the compound is found to be 0.185 & 0.238 eV respectively. The electrical conductivity of these ferrites is explained on the basis of hopping mechanism. The Tc is found to be 529 K.

Keywords: Synthesis, characterization, Hexagonal ferrites, Curie temperature, conductivity

Introduction:

The interest in the field of hexagonal ferrites is increasing due to their use as permanent magnet[1], microwave device materials and magneto-optic recording media[2].It is possible to synthesize a ferrite of specific properties, by controlling the chemical composition and nature of substituting elements[3]. The widely studied Y-type hexagonal ferrites is Ba2Zn2Fe12O22, which is structurally represented as (TS)(TS)*(TS)**, where S is two oxygen-layered block having chemical composition $Fe6^{+3}O8^{-2}$, while T is four oxygen-layered block having chemical composition $Ba2^{+2}Fe8^{+3}O14^{-2}$ (Fig. 1). The symbol * indicates rotation of corresponding blocks through 120°, about the **c**-axis[4-6]. In the crystal structure, Fe^{+3} ions prefer six crystallographic sites 6cvi*, 6cvi, 6civ, 3bvi, 18hvi, and 3avi. Out of these six positions, 6cvi* and 6civ are tetrahedral, while 6cvi, 3bvi, 18hvi and 3avi are octahedral. Oxygen ions occupy 6c and 18h sites[7]. Co^{+2} ions prefer 3avi, 18hvi and 3bvi sites[8]. The substitution of Ba^{+2} by other divalent cations (i.e. Ca^{+2} in the present case) does not affect the site distribution[9].

The compound $Ca_2ZnO_2Fe_{11}AlO_{22}$ belongs to the new series of hexagonal Y–ferrites[10]. In the compound, the Al^{+3} ion replaces one of the Fe^{+3} ions in the unit cell of crystal structure. The compound is characterized by the X-ray diffraction pattern. The compound shows single phase with hexagonal crystal structure having lattice parameters **a** and **c**, as 5.907 Å and 44.013 Å respectively. The effect of substitution of ions on electrical and magnetic properties of compound is studied.

Experimental Detail:

The ferrite was synthesized by the standard ceramic technique[11] by prolonged heating of reacting oxides in proper stoichiometric proportion. Reacting oxides of AR grades were first sintered[12] in air at 200°C for 4 to 5 hours, for the removal of moisture. Then, they were mixed in pure acetone in an agate mortar continuously for about 5 to 6 hours to achieve homogeneity and uniform grain size. The mixture was then heated in air for about 120 hours in furnace at 1100°C. The formation of ferrite was checked by X–Ray diffraction technique[13], using Philips X-ray diffractometer with Ni filtered copper radiation having wavelength 1.54439 Å have been used.

The magnetic susceptibility measurements were carried out by using Guoy's balance method [14]. The inverse molar susceptibility measurements were carried out over the temperature range of 300 K-800 K.

For the measurement of electrical conductivity, samples in the form of pellets were prepared by mixing 5% of polyvinyl acetate as a binder, under the pressure of 5 ton per cm^2. The pellets were coated with thin layer of conducting silver paste. The electrical conductivity of the samples was measured using two-probe method.

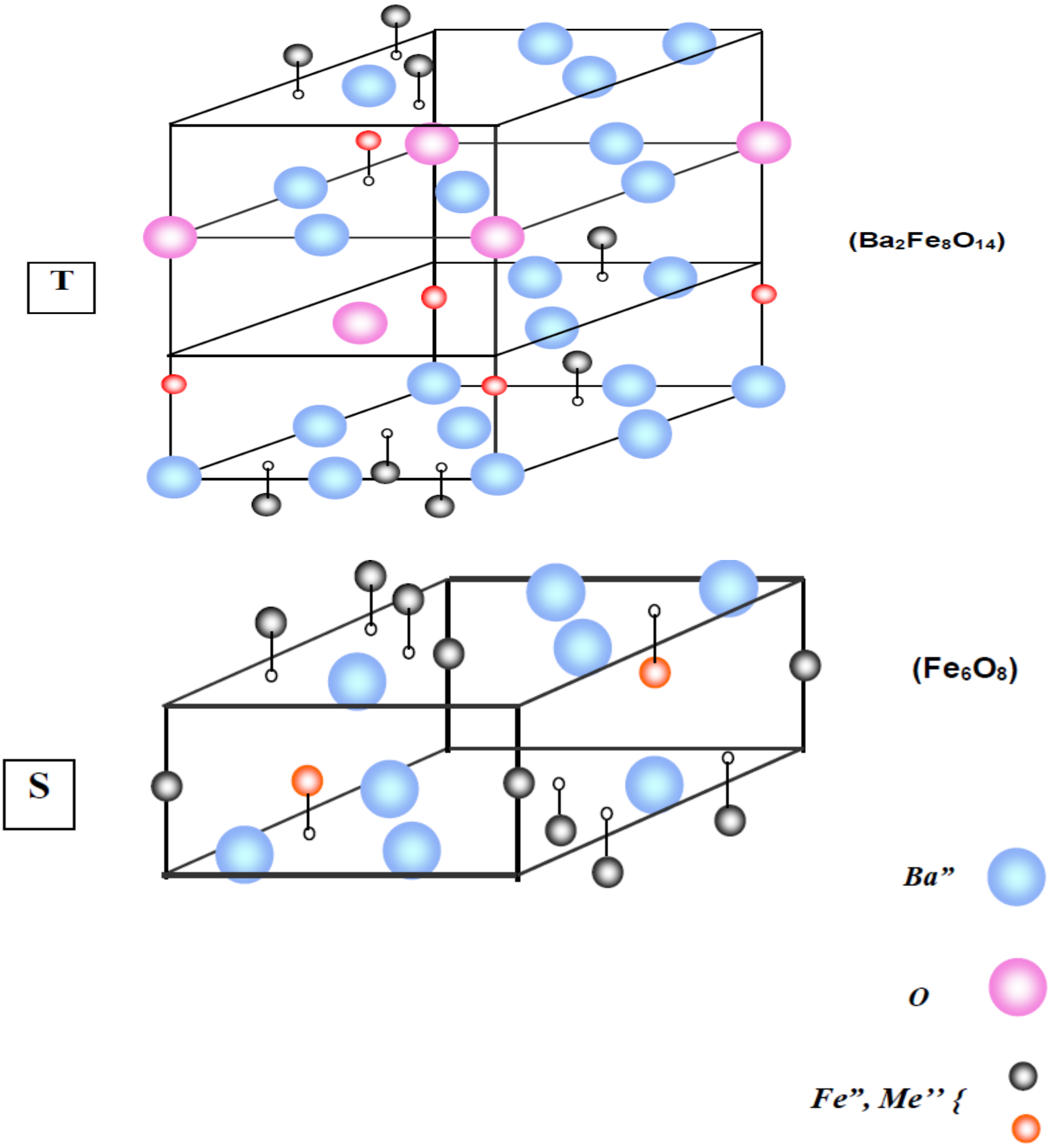

Figure-1: Basic S and T Blocks of hexagonal Y-Ferrites

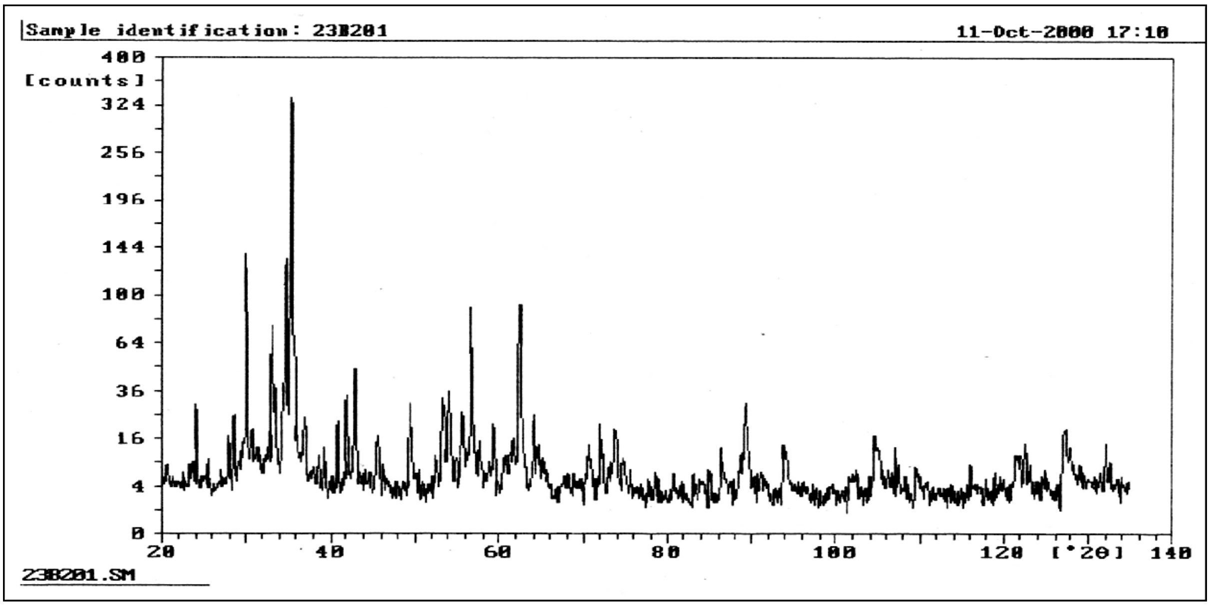

Fig.2 X-ray Diffraction Patterns of $Ca_2Zn_2Fe_{11}AlO_{22}$

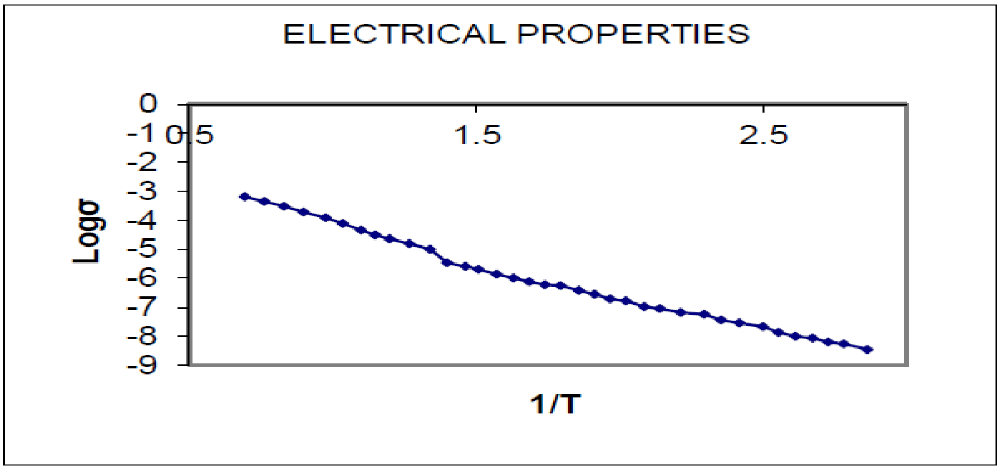

Fig -3: Variation of Logarithmic Conductivity with Inverse Temp For $Ca_2Zn_2Fe_{11}AlO_{22}$

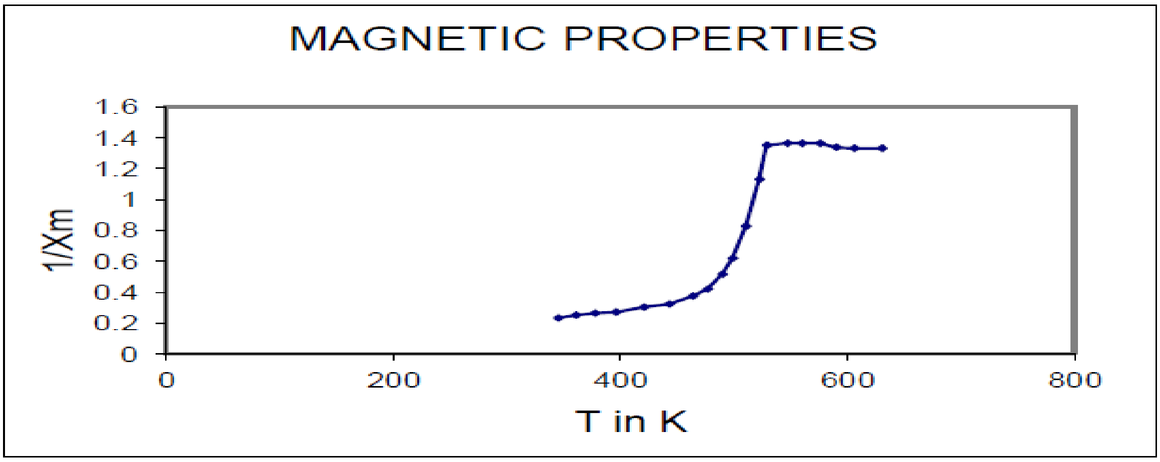

Fig - 4. Variation of Inverse Molar Magnetic Susceptibility with Temp $Ca_2Zn_2Fe_{11}AlO_{22}$

Sr. No.	**Compounds**	**Molecular weight**	**a (Å)**	**c (Å)**	**Volume Å^3**	**X-ray density (g/cm^3)**
1	**Ca2Zn2Fe11AlO22**	1204.18	5.907	44.013	1329.94	4.509

Table 1: Results of X-ray diffraction pattern

Sr. No.	**Activation Energy (Eg) in eV**		**Resistivity at room temp in Ω-cm**	**Curie Molar Constant CM**		**TC (K)**
	Ferri region	**Para region**		**CM Theoretical**	**CM Observed**	
1	0.185	0.238	0.22×10^9	48.19	48.02	529

Table 2: Activation Energy, Resistivity and Curie Molar Constant for Ca2Zn2Fe11AlO22

Result and Discussion:

The X-ray diffraction method has been used for studying the structure of compound Ca2Zn2Fe11AlO22. The X-ray diffraction pattern for the compound Ca2Zn2Fe11AlO22 is shown in Fig.2 with indexing of lines. The values of unit cell parameters **a** and **c** were calculated by standard method[15] and are shown in the Table-1. The density and cell volume of the sample is also given. The crystallographic data of the compound shows that the compound has Y- type hexagonal structure with the space group R 3 m (166) [16]. The plot of logarithmic conductivity verses inverse temperature for the compound is shown in Fig-3, which illustrates a linear decrease in log ☐ with increase in reciprocal temperature up to a certain temperature Tc, where a kink is observed and slope of the curve changes. Lotgering[17] also observed the similar behavior in magnetoplumbites. The compound is ferrimagnetic up to Tc and beyond that, it changes to paramagnetic. The activation energy of compound in the ferrimagnetic region is less than that of the paramagnetic region which is in the well agreement with the theory developed by Irkhin, Turov[18] and Satyanarayana[19]. This change can be explained on the basis of Verway's model[20]. According to this model, the change is due to exchange of electrons between Fe^{+2} and Fe^{+3} ions in the same element. The first change is due to hopping of electrons from Fe^{+2} to Fe^{+3} ions and the second change is due to formation of energy for Fe^{+2} ions on the octahedral sites. The activation energy in the ferrimagnetic and paramagnetic regions is calculated separately and given in Table-2.

The high activation energy in paramagnetic region is attributed from the contribution of excitation of electrons from Fe^{+2} ions within the basal to Fe $^{+3}$ ions within the octahedral sites of spinel blocks. The lowering of activation energy, in the ferrimagnetic region is attributed due migration of intrinsic electrons between iron ions on octahedral sites within the spinel block. The variation of electrical resistivity with temperature follows Wilson's law. The room temperature resistivity is obtained by extrapolating the curve and the value is found to be in the range of 0.22×10^{9} Ω-cm.

The plot of inverse molar susceptibility verses temperature for the compounds is shown in Figure-3. The value of Tc is investigated from molar susceptibility verses temperature curve. The result indicates that the compounds are ferrimagnetic in nature.

The experimental value of Curie Molar constants CM for the compound is calculated from the slope of the curves and is in agreement with theoretically calculated 'spin only value' of CM (Table-2.), implying that there is no change in the valency distribution of the compound due to substitution of ions[21]. The magnetic susceptibility depends on the density of magnetic ions and super exchange interaction between the cations in the compound[22].

The presence of non-magnetic ion La^{+3} increases the value of Curie temperature for **Ca2Zn2Fe11AlO22** and found to be 529 K.

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