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Effect of the trivalent substitution on structural, magnetic and electrical properties of SR-Y type hexaferrite

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ABSTRACT

The substitution of trivalent aluminium in Sr-Y type hexaferrite is considered to be an important for the enhancement of its magnetic and electrical properties. A series of single phase polycrystalline samples with chemical composition $Sr_2Zn_2Al_xFe_{12-x}O_{22}$ ($x = 2-10$) were prepared by high temperature solid state reaction technique. The formed samples were analyzed with the help of X-ray diffractometer for single phase without the traces of ambiguous reflections. It is found to have hexagonal Y type structure with space group $R3m$. the helium Picnometric real density nearly agrees with X ray density. The electrical conductivity and magnetic susceptibility measurement was carried out over the temperature range 400-800K. It shows semiconducting behavior with dual conduction mechanism for higher iron concentration. Magnetic study of the compounds was performed by Gouy's method. The Curie temperature T_C and Curie molar constant C_M of the compounds was found to be decreasing with increase in aluminium concentration.

Keywords: Hexaferrites, Trivalent substitution, XRD, magnetic susceptibility, electrical conductivity.

INTRODUCTION

Since the discovery of hexagonal ferrites [1], there has been an extensive study of ferrimagnetism of these compounds because of their direct utility in the field of materials science viz. permanent magnets, microwave devices etc. The entire family of hexagonal ferrites comprises a group of closely related rhombohedral and hexagonal structure having same basal sections but differing by stacking blocks along C axis.

Among these hexaferrite family, in the year 1956 Jonker first discovered Y type hexaferrite [2]. The structure of this ferrite belongs to the space group $R3m$ and is constructed from the stacking of the spinel block S, consisting of two oxygen layers and the so called T block composed of two barium containing oxygen layers sandwiched between two oxygen layers. The Y structure is designated as $(TS)_3$ where the index 3 means three formula units. The cations in the blocks occupy octahedral and tetrahedral voids between the oxygen layers in six sublattices. As the substitutions, processing route, development of microstructure, etc. drastically changes the properties of hexaferrites, several attempts have been made in this direction for further enhancement of direct utility by researchers. Initially the work was concentrated on basic structure $Ba_2Zn_2Fe_{12}O_{22}$ [3,4]. Later on few researchers reported the outcome with full substitution of strontium [5,6] and with different divalent Me^{2+} substitutions [7,8] for the improvement of their various properties with appropriate charge compensation as its unit cell contains 42 cations in their crystallographic

sites. With these substitutions these authors are successful in explaining the substitutional effects on magnetic and electric properties of Y type ferrite and confirmed that these ferrites also have the ferrimagnetic properties depending on superposition of Fe-O-Fe linkage.

Even though this hexaferrite is studied by using different divalent substitutions, very few attempts have been made with trivalent substitutions [9]. So in this article we have reported the substitution of iron with trivalent aluminium by varying the concentration of these ions in Y type strontium ferrite with the aim of analyzing effect of substitution on the structural, magnetic and electrical properties.

MATERIALS AND METHODS

A series of single phase polycrystalline samples with composition corresponding to the formula $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$ ($x = 2, 4, 6, 10$) were prepared by high temperature solid state reaction technique. The analar grade reagents SrCO_3 , Fe_2O_3 , ZnO and Al_2O_3 were mixed in proper molar ratio using A.R. grade acetone in agate mortar for about 7 to 8 hours to achieve accurate homogenization and uniform grain size. An intimate mixture of the reagents was palletized by adding 5 % Polyvinyl acetate as a binder. These pellets then introduced in electrically operated furnace and slowly heated to 700°C to remove the binder. The temperature then rose to 1100°C for the period of several days (120 hours). Then cooled down to 1000°C at $10^\circ\text{C}/\text{h}$ and to 500°C at $60^\circ\text{C}/\text{h}$ and then by natural way to room temperature. These processed ferrite pellets are finely powdered, sieved through fine sieve and used for further characterization.

This powdered sample was analyzed using Philips PW X ray diffractometer using Cu-K α radiation with wavelength 1.542 \AA for the confirmation of single phase formation. The X ray pattern was indexed, lattice parameters was calculated using a procedure given by Henry and Lipson [10]. The true density of the compounds was then performed on micrometrics multivolume helium Picnometer 1305. The magnetic susceptibility measurements were done by Gouy's method. [11] in the temperature range $400 - 800\text{K}$. The electrical conductivity σ was measured by determining the resistance of the compound using bridge type circuit developed in the laboratory using two probe upto 800K [12]. The voltage drop across a standard resistance was measured by digital multimeter having input impedance $10^9\Omega$.

RESULTS AND DISCUSSION

The series of compounds are prepared with aluminum as a trivalent substitutions for Fe^{3+} cations taking $x = 2, 4, 6$ and 10 respectively. From X ray diffraction studies (Fig.1) it is confirmed that the single phase Y type compounds are formed without any traces of unreacting oxides. The structural parameters of the series are shown in Table 1. The lattice parameters a and c both decreases with decrease in iron content. This is obvious as Al^{3+} ions (ionic radii 0.57 \AA) have smaller ionic radii than Fe^{3+} and hence it is clear that the lattice parameters are predominantly governed by the larger Fe^{3+} ions. It has been observed that prepared compounds with different aluminum substitutions results into considerable decrease in cell volume as compared with the cell volume of $\text{Sr}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ hexaferrite. Slight increase about 2 to 4% is seen in the real density measured by helium Picnometric method than by X-ray densities in the compounds except for $x=4$, where the variation is about 10% . This variation may be due to less porosity of this ferrite comparable to other aluminum substituted ferrite. Thus we can say that with suitable trivalent Al^{3+} substitutions, the ionic radii and site stabilization energies decides the site preference of these cations without change in crystal structure.

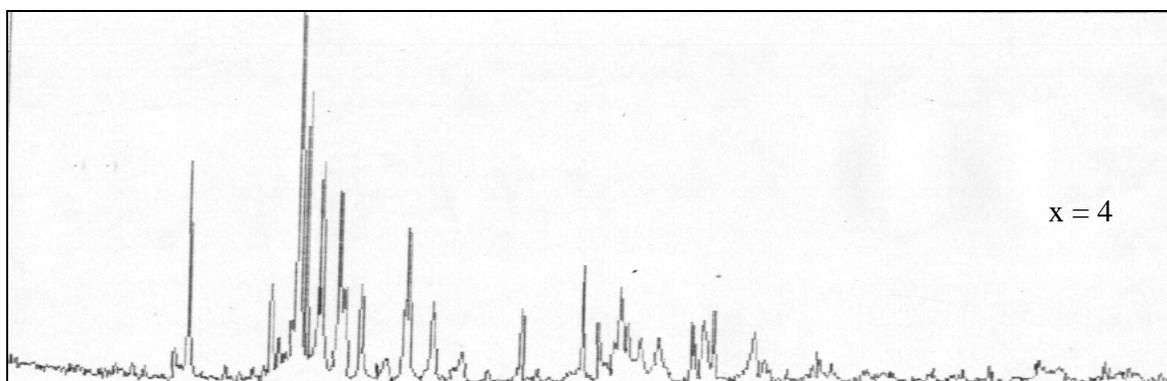
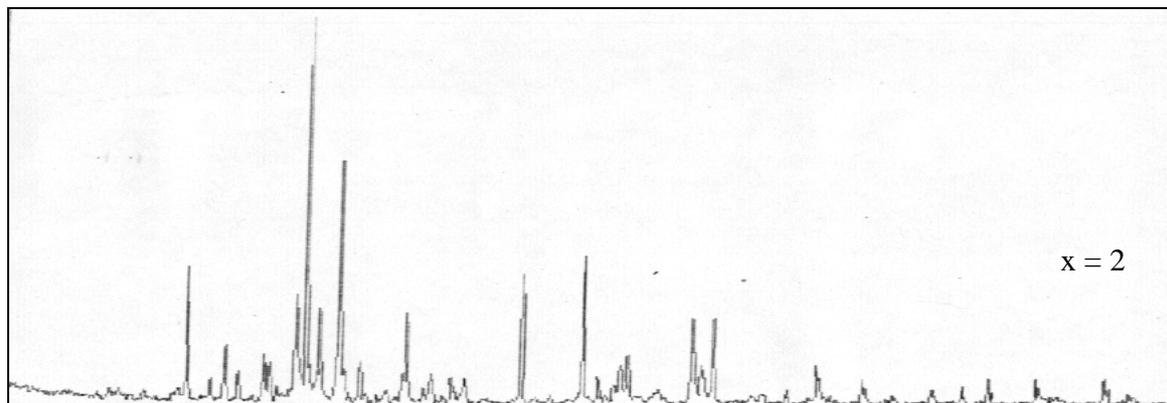
From the magnetic susceptibility results, first three compounds with $x = 2, 4$ and 6 are found to be ferrimagnetic at room temperature while the last one is paramagnetic above room temperature ($T_C = 301^\circ\text{K}$). The Curie temperature T_C , observed and theoretical values of C_M decreases linearly (Fig. 2) with increase in aluminium concentration. This linear decreasing change is due to the substitutions of non magnetic Al^{3+} ions for magnetic Fe^{3+} ions causing a reduction in total number of $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ exchange interaction. In Ba-Y hexaferrite divalent Zn cations are randomly oriented in both blocks on tetrahedral site $6c$. With complete replacement of Ba by Sr, the zinc ions deviate towards the $6c_{iv}^*$ ($z = 0.152$) position in the S block from the initial position $6c_{iv}$ ($z = 0.0428$) in the T block closest to the strontium ions freeing their places for iron ions. After aluminium substitutions, due to its smaller ionic radii the occupancy of these aluminium cations increases in the site $6c_{iv}$ ($z = 0.0428$) in the T block nearest to the Sr^{2+} cations results in to a reduction in total number of $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ exchange interaction. The theoretically calculated values of C_M for high spin state of Fe^{3+} ions along with orbital quenching is in fair agreement with

experimentally observed values indicating no need for the consideration of electron transfer. Thus from magnetic study it has been verified that the large portion of the aluminium ions are substituted for iron ions in the corresponding sublattices.

From the electrical conductivity measurements over 400 to 800 K all the compounds shows semiconducting behavior and obeys Wilson law [13]. The plot of logarithmic conductivity versus inverse temperature (Fig. 3) shows change in slope at Curie temperature for higher iron concentration. This change in slope clearly indicates that there is dual conductivity mechanism with different activation energies [14]. The activation energy in ferrimagnetic and paramagnetic regions are calculated separately and observed that the activation energy in ferrimagnetic region is less in paramagnetic regions. The compound with $x = 10$ shows paramagnetic behavior at room temperature with activation energy 0.581 eV (Fig. 4) from the linear portion of the plot. This compound has Curie temperature 301°K just below room temperature (room temperature is 303°K). This strong decrease in Curie temperature for higher aluminium concentration shows that some of the intersublattice interactions may strongly diminished [15]. The higher value of the activation energy (1.064 eV) is observed in the compound with $x = 4$ may be due to local distortion present in different sites in this compound, which may probably be due to site distribution differences of two non comparable ions such as Al and Fe in specific proportions as 1:2. The conduction in these ferrites is explained on the basis of hopping mechanism of the localized d electrons present in the lattice.

Table No. 1 : Structural parameters of the series $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$

Al ³⁺ concentration	Lattice parameter (Å)		Cell Volume (Å) ³	X ray density (gm/cc)	Density by helium picnometer (gm/cc)	Crystallite size (μm)
	a	c				
x = 2	5.773	44.263	1277.503	4.953	5.201	0.1663
x = 4	5.756	43.966	1261.468	4.788	5.317	0.2767
x = 6	5.732	43.909	1249.349	4.605	4.729	0.1663
x = 10	5.708	43.715	1233.435	4.198	4.364	0.0463



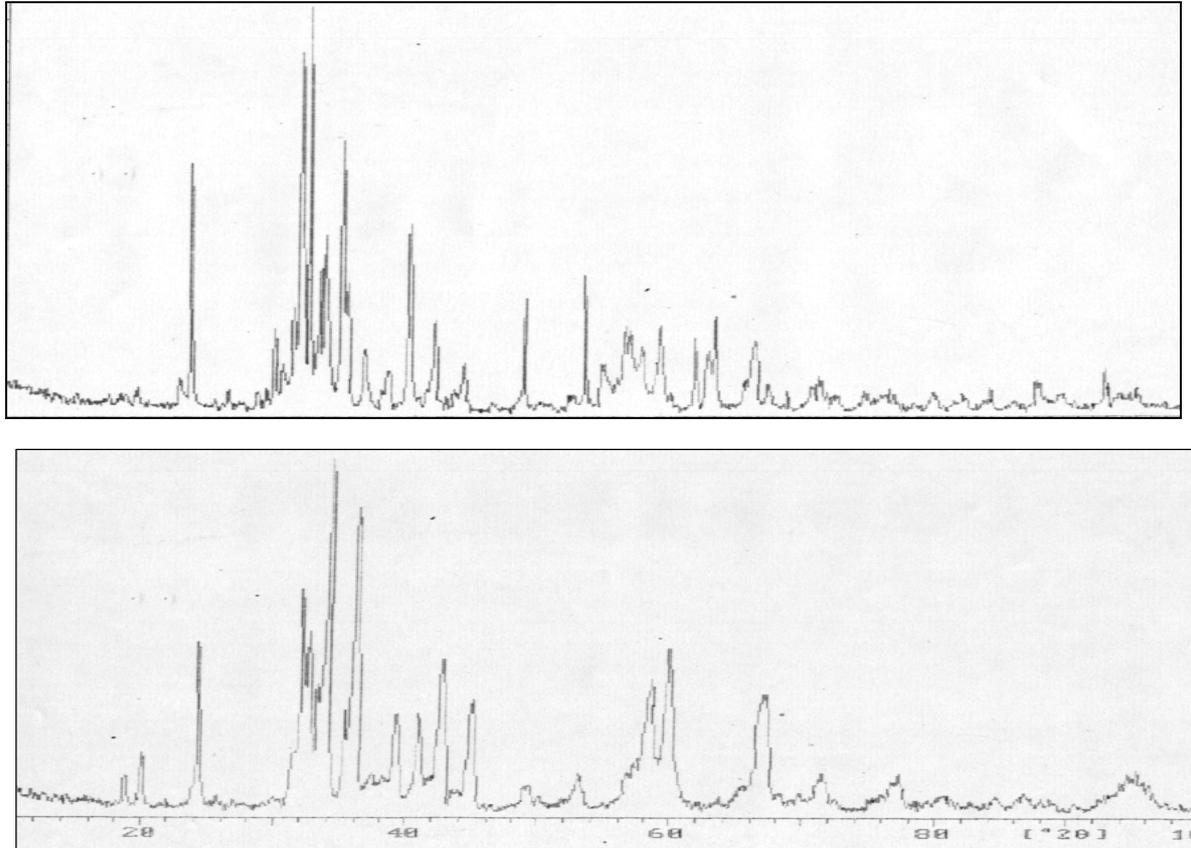
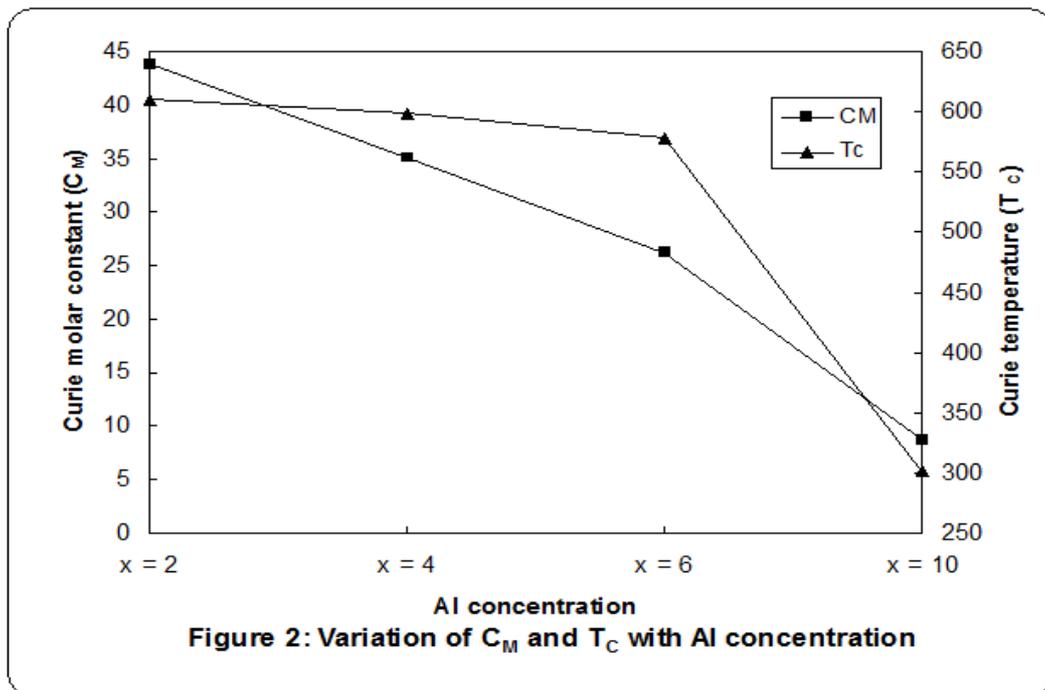


Figure 1: X ray diffraction pattern of $Sr_2Zn_2Al_xFe_{12-x}O_{22}$ hexaferrite.



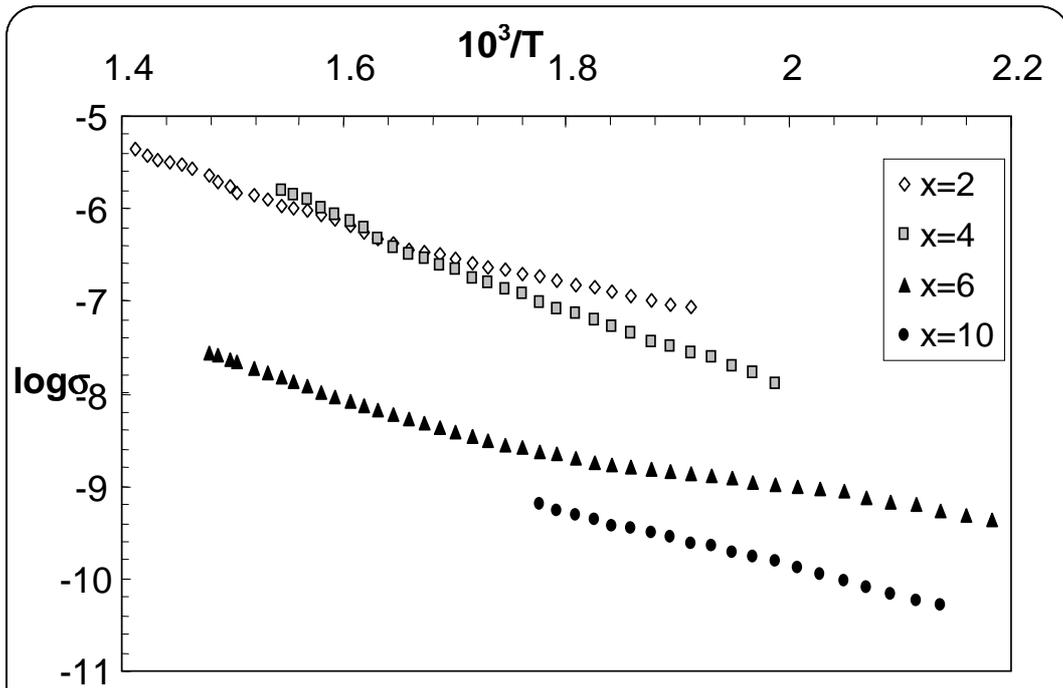


Figure 3 : Variation of electrical conductivity with temperature

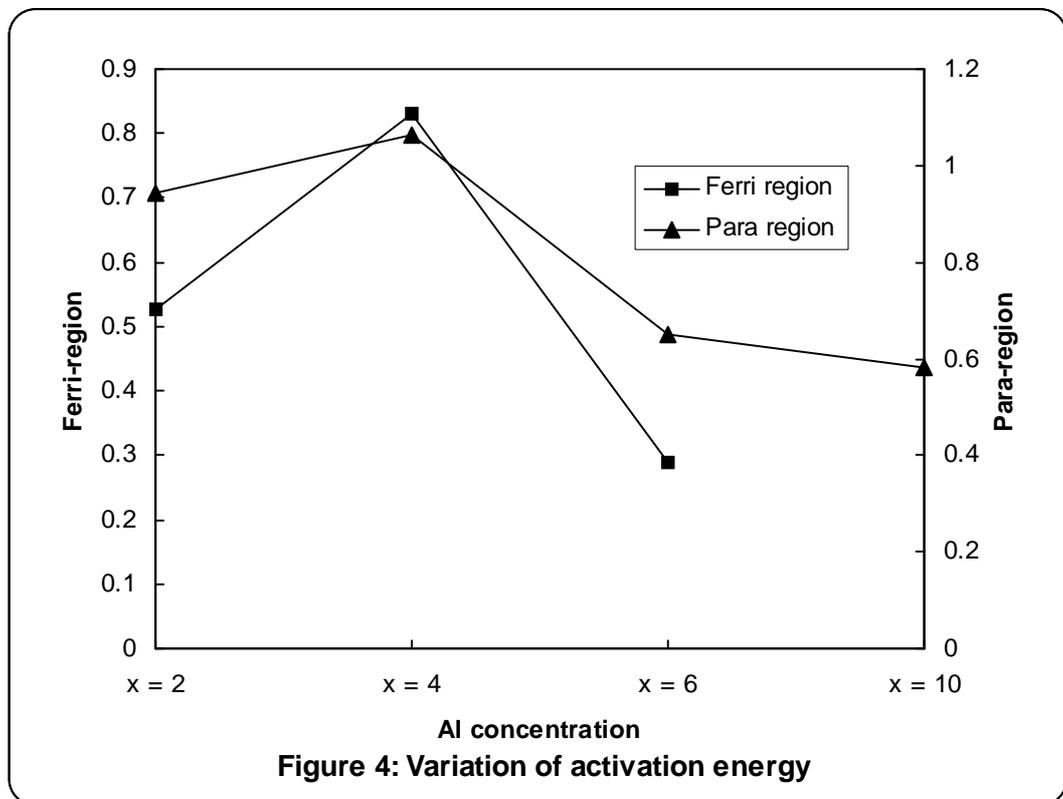


Figure 4: Variation of activation energy

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