Structural and Magnetic Properties of Al³⁺ Ion Doped Ca-Sr Ceramics Synthesized by Sol-Gel Auto-Combustion Technique

Suresh S Darokar

Shivaji Science College Congress Nagar, Nagpur-12, Maharashtra, India

Abstract: *An aluminium substituted calcium-strontium hexaferrite (M- type) compounds with the general chemical formula $Ca_{0.5}Sr_{0.5}Al_xFe_{12-x}O_{19}$ (x = 1 and 1.5) have been synthesized by sol-gel auto-combustion technique. The structural characterization of compound has been carried out from X-Ray diffraction powder pattern. The compounds are in single hexagonal phase without traces of uncertainly ambiguous reflection. From XRD pattern lattice parameters has recorded with doped aluminum element is a = 5.8357 Å and c = 22.1287 Å pertaining the space group $P6_3/mmc$ (No.194) conformed from JCPDS data. The mass density of the ferrites were found linearly varies and depends upon the mass and volume of sample. The X-Ray density has depends upon the lattice constant and molecular weight of the compounds. The average particle size was also estimated. The compounds were studies magnetically by using Guoy's method in the temperature range 300 to 800 K, the result shows that the compounds are paramagnetic in nature. The Curie temperature was work out.*

Keywords: M-type hexaferrites, molar constant, magnetic susceptibility .etc

1. Introduction

Magnetoplumbite ferrite (M -Type) attract more attention of many researchers over the years due to their various category of applications over wide frequency range, low cost and high performance [1]. In 1952, a new class of ferrites so called hexagonal ferrites with formula $MFe_{12}O_{19}$ having permanent magnetic properties were discovered. where M is the divalent alkaline metal cations and can be replaced by a suitable cations or their combinations [2]. Alkaline metal likes barium, strontium, calcium or lead. The calcium ferrite having general formula $CaFe_{12}O_{19}$ is one of the most important hard magnetic materials, widely used for above application. M-type are very useful for microwave application [3]. The magnetic and electric properties of the hexagonal ferrites can be altered by the doping of various cations at M (Ca, Sr, Ba, Pb). Several researchers have substituted many cations and their combinations in M-type hexagonal ferrites [4-6]. In this present work, literature review by many research workers with combination of Al^{3+} in calcium Strontium hexaferrite and that worked is carried out on the simultaneous combinational effect of these cations, namely Ca^{2+} and Sr^{3+} on electric, magnetic and other related properties of the M-hexaferrite, hence formed composition chemical formula $CaAl_xFe_{12-x}O_{19}$, Where X=1 and 1.5 was synthesized by sol-gel auto-combustion method with different ions concentration [8-9].

The M type ferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites (P63/mmc space group). The structure of M-type hexagonal is stacked alternatively by (S = Fe_6O_8) and hexagonal (R = $MFe_6O_{11}^{2-}$) layers. The O^{2-} ions exist as close packed layers, with M^{2+} substituting for an O^{2-} in the hexagonal layers. Number of Fe^{3+} ions in sub lattice of hexaferrites and their spin as shown in table- 1.

Table 1

Site	Geometry	No. of Fe^{3+} ions	Sign
12k	Octahedral	6	Up ↑
2a	Octahedral	1	Up ↑
4f₁	Tetrahedral	2	Down ↓
4f₂	Octahedral	2	Down ↓
2b	Trigonal bipyramidal	1	Up ↑

2. Experimental Techniques

An aluminium substituted calcium- strontium hexaferrite compounds with composition $Ca_{0.5}Sr_{0.5}Al_xFe_{12-x}O_{19}$ (x=1 and 1.5) have been synthesized by sol-gel auto-combustion method. The synthesis method involved the combustion of redox mixtures, in which metal nitrates acted as an oxidizing reactant and urea as a reducing reactant. The $Ca(NO_3)_2.4H_2O$, $Fe(NO_3)_3·9H_2O$, $Sr(NO_3)_2$ and $Al(NO_3)_3.9H_2O$ and urea $CO(NH_2)_2$, dissolved in 10ml of distilled water in a glass beaker. The solutions as prepared in beaker were mixed together to form a homogeneous aqueous solution. The aqueous solution was then heated onto the hot plate. After few minutes aqueous solution get converted into wet gel by evaporating the water. After the wet gel reaches the point of auto-combustion, it begins burning and becomes a solid which burns. The combustion is not completed until all the flammable substances are consumed and the resulting material is a loose substance exhibiting voids and pores formed by escaping gases during combustion reaction. The ash of aluminium substituted calcium strontium ferrite was obtained after complete combustion. This ash was then ground in in a pastoral mortal for three hours and then sintered in muffle furnace for four hours at 800°C temperature and cooled it , then crushed again for three hours get a fine powder of aluminium substituted calcium strontium hexaferrite is obtained.

3. Result and Discussion

In the present work of Calcium-Strontium hexaferrite is studied as $Sr_{0.5}Ca_{0.5}Fe_{11}AlO_{19}$. The ions in basic Ca-Sr compound Fe^{+3} can be replaced by Al^{+3}. In this case, substituted ions were chosen to keep charge neutrality and have to deep knowledge of internal variation of properties. In this ferrites the aluminium plays a dominant role in the property variations. The samples reported was synthesis by standard sol-gel auto combustion method. X-ray diffraction pattern of an investigated compound belongs to the hexagonal magnetoplumbite structure as shown fig(1) were obtained using X-ray diffractometer and pertain to space group $P6_3/mmc$ (194) from JCPDI data. The probable occupations of cations in differentsites in the lattice can be explained from the known oxidation states and observed for Curie temperature. The constitutional elements, viz. Fe, Al are trivalent states. The hexagonal M-structure with space group ($P6_3/mmc$) (No. 194), which confirms that phase belongs to magnetoplumbite(M type) indicating the crystal
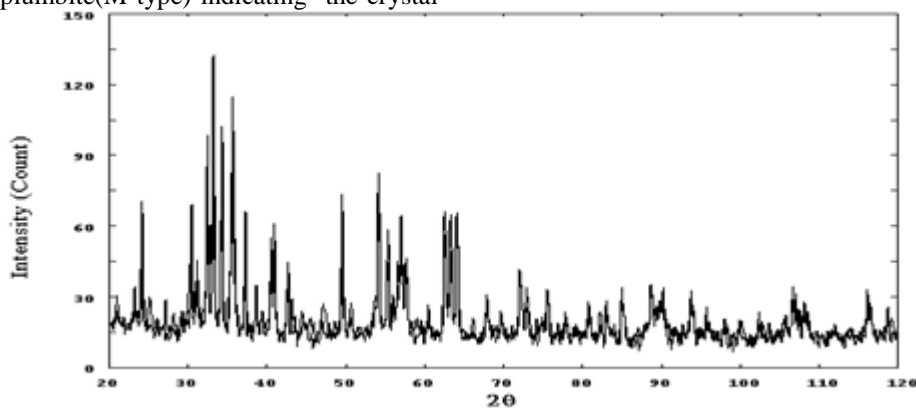
structure were single phase hexagonal magnetoplumbite after substitution with La^{3+} ions respectively. The lattice constant 'a' and 'c' of hexagonal calcium strontium ferrite were calculated using equation (1) .

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

Where h ,k, l are miller indices, d is interplaner distance.
The lattice parameter 'a' and 'c' was found to be 5.8357 and 22.1287 respectively.

Discussion of Al with Sr-Ca ferrite:
The composition was sintered in a polycrystalline state by a sol-gel auto combustion, by heating the mixture of the constituents nitrites. The single phase M-type compound can be obtained by heating in air at 800^oC. The formationwas tested by X-ray diffraction technique and consolidate data of XRD as shown in table- 2 and its pattern is shown in figure- 1

Figure 1: XRD Pattern of $Sr_{0.5}Ca_{0.5}Fe_{11}Al_1 O_{19}$

The replacement of Fe^{+3} ions by Al^{+3} ions has been investigated because of resemblance of the ionic radii. It is seen that the former ions are very easily replaced at any substitution ratio without changing the crystal geometry. The numerical values of lattice parameters and X-ray intensity is reported in table -2

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Table 2: X-Ray diffraction of ($Sr_{0.5}Ca_{0.5}Fe_{11}Al O_{19}$)
Lattice Parameter**:** a =5.8357 Å and c = 22.1287 Å

d_{obs} Å	d_{cal} Å	I_{obs}	h	k	l
3.6883	3.6883	26.2	0	0	6
2.9705	2.9774	8.2	1	0	6
2.7657	2.7662	30.6	0	0	8
2.7029	2.7092	100	1	1	3
2.5226	2.5226	68.5	2	0	0
2.4207	2.4255	12.3	1	0	8
2.2921	2.2952	1.7	2	0	4
1.8441	1.8441	34	0	0	12
1.8091	1.8028	0.6	2	1	4

d_{obs} Å	d_{cal} Å	I_{obs}	h	k	l
1.6971	1.6939	46	2	1	6
1.6648	1.6635	8.2	2	0	10
1.6316	1.6396	7.5	3	0	3
1.6012	1.609	11.9	3	0	4
1.4884	1.4887	26.8	2	0	12
1.4805	1.4847	15.4	3	0	7
1.4561	1.4564	26.8	2	2	0
1.4732	1.4753	12.8	0	0	15
1.4522	1.4532	13.2	2	2	1
1.3827	1.3831	1.9	0	0	16
1.3522	1.3546	3	2	2	6
1.3135	1.3161	11.1	1	1	15
1.3006	1.3017	2.8	0	0	17
1.2613	1.2604	4.3	1	0	17
1.2297	1.2294	1.4	0	0	18
1.1914	1.1944	3.4	1	0	18
1.1653	1.1647	3.9	0	0	19
1.1429	1.1429	5.4	2	2	12

The temperature dependence of the material measurement was made upto temperature 660K. The curve for the variation of χ_m versus temperature T (^oC) was in figure -2. The compound is paramagnetic in nature in the studied temperature range. The determined Curies temperature is calculated as 460^oK.
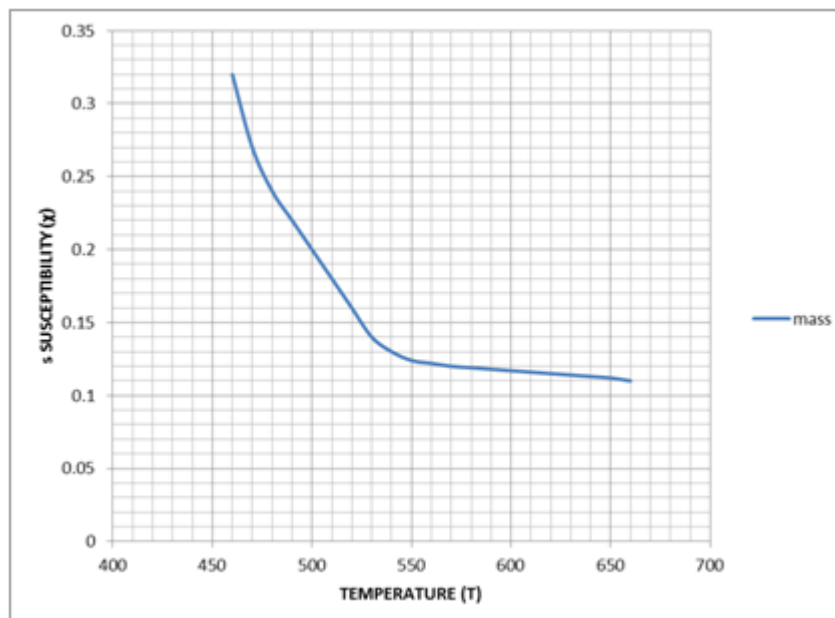
Figure 2: Magnetic Susceptibility of $(Sr_{0.5}Ca_{0.5}Fe_{11}AlO_{19})$

As the lattice contains both magnetic and non-magnetic ions with different site preferences. It is possible to guess the site distribution from Mossbauer experiment, and hypothecated that the Al^{+3}ions enter the 2a and 12k sites in lattice. Bertaut et.al. (1959) and Borker(1987) referring to the X-ray investigation. They came to the conclusion that Al^{+3} first occupy 2a-sites then 12k sites [10-11]. There assumptions are theoretically support by Rensen et.al.(1971)by Mossbauer studies. The presence of magnetic ion in the site 2a and 12k shows strong magnetic behavior[12].

In M type compounds, the orientation of the magnetic moment of the ferric ions in the crystal are generally aligned along the c-axis in antiparallel with each other. L.Neel (1948) and Anderson (1950) first considered from theoretically view point, that these alignments of magnetic ions can be realized by super change interaction through oxygen ion, which has also been proved from experimental facts. These exchange interaction are responsible for spin alignment [13-14]. In magnetoplumbite the interaction between two close sites, such as 2a-12k, 2a-4f1 and 4f1-12k are decisive for strong magnetic character. So, when Fe^{+3} ions in the 12k sub lattice are substituted by the non-magnetic Al^{+3} ions, weakening of the super exchange interaction between magnetic ions results in a fairly inclined paramagnetic nature. The presence of Al^{+3}ions in 2a and 12k sites in the lattice imply the decrease in interaction energy and thereby decrease in Curie temperature has been seen in the compound.

4. Conclusion

In the present work, an aluminium substituted calcium-strontium hexaferrite compounds with composition $Ca_{0.5}Sr_{0.5}Al_xFe_{12-x}O_{19}$ (x=1 and 1.5) have been synthesized by sol-gel auto-combustion method and checked the formation of ferrite containing Al^{+3} ions along with Fe^{+3} ions from XRD. The XRD confirms that calcium hexaferrite have hexagonal structure and single phase and values of lattice parameters '*a*' and 'c' of hexagonal unit cell. The compound have M-structure though the site distribution changes. No

changes occurs in the charge distribution is changed due to stoichiometric changes.

Magnetic susceptibility for higher concentration substitution of Al^{3+} in Ca-Sr hexaferrite give rise to paramagnetic nature and may be used as ceramic materials due to higher resistivity and they are paramagnetic nature over a wide range of temperature. As the temperature goes on increasing the susceptibility goes on decreasing that is the mass change is directly proportional to susceptibility.

5. Acknowledgement

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