Application as Radar Absorbing Material & Co-Relation between Properties of Mixed Ion Doped La-M Hexaferrite

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Abstract:

The concept & effort to develop radar absorbing materials (RAMs) has been gaining widespread interest to the researchers, mainly, working in the field of magnetic materials viz. hexaferrites. In this work, bulk M-hexaferrite with combined substitution of divalent ions Ca-Ba-Sr with trivalent La has been synthesized using standard ceramic method. Due to combined substitution of mixed valence ions the magnetic & conducting parameters found enhanced. The order of magnitude for dielectric constant lies in the range of 10^3 to 10^4& can favor to suppress microwave reflection. Following the truthiness of Iwauchi's relation, a relation between mobility (**μ**) & dielectric constant (**ε**) was tried to achieve.

Keywords: M-hexaferrite, Iwauchi's relation, mobility, dielectric constant

1. Introduction :-

The reduction of military platform radar cross-sections has been a major challenge since the Second World War. Possible solutions for reducing the radar signatures of targets include the design of objects with small cross sections or the use of radar absorbing materials (RAMs) for covering the metallic surface. The main problem in designing a magnetic absorber is related to the choice of the material, preferentially with control over some magnetic &dielectric properties, such as magnetic saturation (M_S), dielectric constant (ε) Seebeck coefficient(S) & electrical conductivity (σ). The use of Ba-M & Ca-M hexaferrites as RAMs has been widely cited in literature during the last two decades.[1-4]

Among the various reports on the dielectricproperty of pure & doped Ba & Sr-M hexaferrite, F.pereire et.al studied the dielectric constant for $Ba_xSr_{1-x}Fe_{12}O_{19}$ upto 1MHz& observed the decrease in dielectric constant from ~750 to ~150 for Ba-M hexaferrite, whereas in Sr-M hexaferrite it was from ~230 to ~60 with increase in frequency from 100Hz to 1MHz.Hussain et al &Makled et al reported a much higher dielectric constant of 959 &Iqbal et al plotted decrease for 221 to 183 for increasing Sr^{2+} ion in Sr-M hexaferrite at 1MHz.[5-8]

Again it came to knowledge thatmeager work carried out to co-relate different parameters of properties like thermoelectric, dielectric& magnetic, though the governing phenomenon are interlinked, in past time. As the electrical phenomenon in hexaferrites follow the same mechanism viz. hopping mechanism, a relation between dc electrical conductivity &dielectric constant was well established by

Iwauchi et al. However, both electrical conductivity (σ)&dielectric constant (**ε**) are electrical phenomenon measured with temperature & frequency respectively still the correlation holds good agreement. According to relation, the dielectric constant is inversely proportional to square root of resistivity i.e product of dielectric constant (**ε**)& square root of resistivity (√**ρ**)remains fairly constant. Moreover, Hudson (1968) showed that the dielectric measurements in ferrites are generally reflected in the resistivity measurements, where materials with low resistivity exhibiting higher value dielectric constant & vice versa.[9-10]

In the same way, present work devote,

1) individual or simultaneous substitution of ions having mixed valency with La^{3+} to compensate the charge valency & improve the magnetic, electric &dielectric behavior of M-hexaferrite, allowing their application as RAMs at various frequencies.

2) An endeavor to uncover the truthiness of Iwauchi relation & correlate properties.

2. Experimental Details

2.1 Sample preparation: The preparation of mixed ion doped M-hexaferrite with chemical formula $Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO_{19}$ (CSBFLO) (with x = 0.1, 0.25, 0.4; z = 0.1, 0.2, 0.3 & y = 0.2, 0.4, 0.6) was carried out via standard ceramic method. The AR grade oxides Fe_2O_3, La_2O_3, CaO, SrO, & BaO (Merck grade) were used as starting precursors for the synthesis of present series of compounds. The preparation process involved the mixing of oxides with respective stoichiometry & grounded together in agate mortar in an acetone medium. The synthesis was divided into two steps: Initially the mixture was calcinated at 773 K for 8 h in air followed by further mixing & rigorous grinding, & finally the mixture was thermally treated at 1430 K for 72 hr. The details of the method of the preparation have been given in earlier publications. [11, 12]

2.2 Measurements: X-ray diffraction patterns of $Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO_{19}$ hexagonal ferrites, under investigation, were obtained using Cu-Kα radiation on a Philips X-ray diffractometer (Model PW1732) within scanning range from 0^0 to 90^0. Electrical conductivity & thermoelectric measurement were done by standard two probe method using LCR meter. Dielectric parameters were measured by using samples in the pellet form (13 mm diameter) using a Quad-Tech make LCR meter in the frequency range of 10 Hz–2MHz at room temperature.

3. Result & Discussion

3.1 Structural Analysis: The XRD profiles of the M-hexaferrite samples with standard pattern are presented in fig.1. The recorded X-ray diffraction patternsof all the samples have shown the presence of reflection planes (006), (107),(114),(201),(108),(220), & (304) corresponding to predominant magnetoplumbite phase of hexaferrite family which belongs to the space group P63/mmc (No.194) as compared with standard pattern of M-hexaferrite from JCPDS data file no. 00-039-1433. Finally prepared samples were coded as R1 to R10 respect to substitution and its concentration. The analysis was deeply discussed in previously published paper. [11, 12,13]

3.2 Compositional variation of Carrier concentration (n), Dielectric constant (ε), Electrical conductivity (σ)&Mobility (μ): Fig.1**,** table-1& table-2reflect the graphical variation & values of carrier concentration, Seebeck coefficients &mobility at 358K temperature for samples respectively. The carrier concentration for these hexaferrites was calculated using the formula given by Morin & Gabella [14]

$$n = Nexp\left(-\frac{Se}{K}\right)$$

Where, S = Seebeck coefficient,

e = charge of electron,

K= Boltzman constant,

N = density of states

The computed values of carrier concentration were included in Table-2,enable us to inferred that the variation to carrier concentration, linearly corresponds to variation in Seebeck coefficient. The maximum value regards to sample R1, was also having the maximum value for Seebeck coefficient. Moreover, values of carrier concentration &Seebeck coefficient remains fairly constant over entire range.

Dielectric constant, electrical conductivity &mobility shows linear variation as observed from table-2&fig1represents variation in electrical conductivity &dielectric constant with respect to composition (sample codes).Thepeak value for parameters correspond to sample R9 having proportion of Ca^{2+}=0.4, Sr^{2+}=0.6 & La^{3+} = 0.3. The maximum value obtained, reflects formation of maximum number of ferrous ion which are involved in phenomenon of exchange interaction between $Fe^{2+}\leftrightarrow Fe^{3+}$ giving rise to maximum space charge polarization. It's due to solubility of La^{3+} ion, which resides at the grain boundaries, results in decrease of Fe^{3+} ion concentration & enhancement in conductivity which reflects n-type semiconducting behavior [15-16].

Whereas decrease in both electrical parameters for further samples attributes to enlargement in linear densities table-1 which reflects lower available space in unit cell for local displacement of charges, results in decrease in electron exchange mechanism i.e. space charge polarization.

3.3 Co-relation between Dielectric constant (ε) &Mobility (μ): The correlation between different properties was done by many researchers in past time. As the electrical phenomenon in hexaferrites follow the same mechanism viz. hopping mechanism, a relation between DC electrical conductivity &dielectric constant was well established by Iwauchi et al. However, both electrical conductivity &dielectric constant are electrical phenomenon measured with temperature & frequency respectively still the correlation holds good agreement. According to relation, the dielectricconstant is inversely proportional to square root of resistivity i.e. $\varepsilon = \frac{1}{\sqrt{\rho}}$.This reflects that the product $\varepsilon\sqrt{\rho}$ remains fairly constant. The values of ε& resistivity ρ for investigated CSBLF mixed hexaferrite are given in table-1,& can be understood that the product $\boldsymbol{\varepsilon\sqrt{\rho}}$ remains fairly constant in order of magnitude & obey Iwauchi relation.[9]

Keeping above mention relation, a relation is put forward in dielectric constant &mobility for the present investigating compounds. It was observed that square of dielectric constant is directly proportional to mobility. This reveals that product of $\frac{\varepsilon^2}{\rho}$ found fairly constant in order of magnitude.

The relation was established by taking the Iwauchi relation & the formula for conductivity in term of mobility.

$$\varepsilon = \frac{1}{\sqrt{\rho}}$$ **(Considering proportionality constant 1)**(1)

Further, $\sigma = ne\mu$ (2)

squaring equation (1)

$\varepsilon^2 = \frac{1}{\rho}$- But,

$\frac{1}{\rho} = \sigma$

Therefore, $\varepsilon^2 = \sigma$ (3)

Put in equation (2) $\varepsilon^2 = n.e\mu$

Where, n - carrier concentration & is found constant in order of magnitude (10^{22})

e- charge of electron

hence,

$\varepsilon^2 \alpha \mu$, $\frac{\varepsilon^2}{\rho}$ **= Fairly Constant**

The result was found true as observed in table 1.

Chemical Composition	Code	ε x 10^3	√ ρ	ε.√ ρ	μ x 10^{-9}(m^2/Vs)	ε^2 x 10^8	(ε^2/μ)x 10^{15} (m^2/Vs)$^{-1}$
$Ca_{0.1}Sr_{0.2}Ba_{0.7}Fe_{11.9}La_{0.1}O_{19}$	R1	8.54	4.25	36292.81	7.94	0.728633	9.17211
$Ca_{0.1}Sr_{0.4}Ba_{0.5}Fe_{11.9}La_{0.1}O_{19}$	R2	5.15	4.74	24435.32	3.16	0.265225	8.3932
$Ca_{0.1}Sr_{0.6}Ba_{0.3}Fe_{11.9}La_{0.1}O_{19}$	R3	7.36	3.73	27419.58	38.00	0.541696	1.42552
$Ca_{0.25}Sr_{0.2}Ba_{0.55}Fe_{11.8}La_{0.2}O_{19}$	R4	13.50	1.75	23550.85	151.00	1.82142	1.20624
$Ca_{0.25}Sr_{0.4}Ba_{0.35}Fe_{11.8}La_{0.2}O_{19}$	R5	12.27	1.49	18398.88	210.00	1.50651	0.717386
$Ca_{0.25}Sr_{0.6}Ba_{0.15}Fe_{11.8}La_{0.2}O_{19}$	R6	12.45	1.18	14793.78	416.00	1.54908	0.372376
$Ca_{0.4}Sr_{0.2}Ba_{0.4}Fe_{11.7}La_{0.3}O_{19}$	R7	18.08	1.16	21046.46	432.50	3.26886	0.755807
$Ca_{0.4}Sr_{0.4}Ba_{0.2}Fe_{11.7}La_{0.3}O_{19}$	R8	17.47	1.24	21714.18	379.00	3.05201	0.805279
$Ca_{0.4}Sr_{0.6}Fe_{11.7}La_{0.3}O_{19}$	R9	18.02	1.74	31439.37	197.30	3.2472	1.64582

$Ca_{0.4}Ba_{0.6}Fe_{11.7}La_{0.3}O_{19}$	R10	14.26	2.70	38540.54	86.70	2.03291	2.34476

Table1 - Co-relation between properties

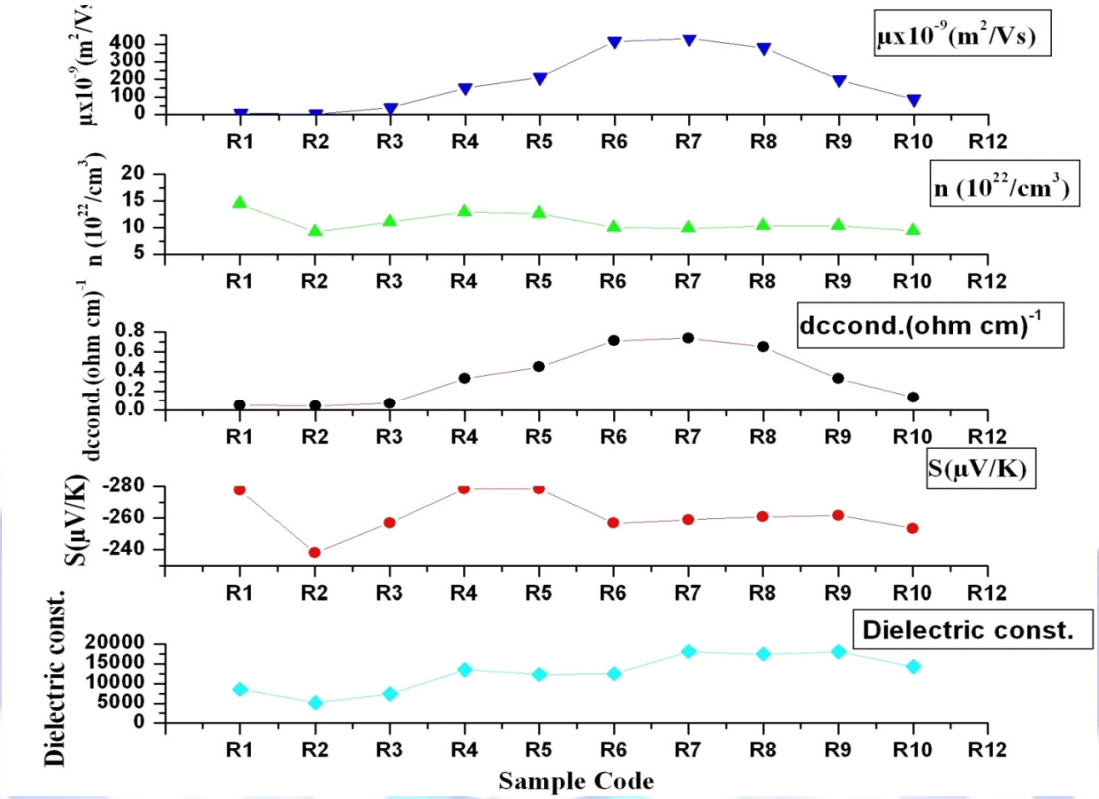

fig 1- relation between Electrical Parameters

In the above graphical representation fig.1, it is clear that the electrical parameters are showing similar kind of variation. The mobility, thermoelectric power &dielectric constant show fairly similar deviation as composition progress. It can be related with the basic theoretical background that the thermoelectric power is the result of change in EMF produces to the temperature difference over the two opposite surfaces of pallet of the samples. This is related to the number of produced charge carrier at the surfaces & can be referred as carrier concentration. It was obvious that enhancement in carriers concentration should increase the thermoelectric power of the compounds. Moreover, as discussed**,** the increment in the carrier concentration is dominantly due to the charge polarization, which leads to the phenomenon of dielectric polarization.

The variation in electrical resistivity & activation energy can be attributed to magnetic ordering & transition. The effect of magnetic transition on the electrical properties was observed by many workers viz. Sattar et.al, Josyulu et.al, Ahmed et.al&Patil et.al [18-21]. According to thermodynamic theory by Zemansky et.al, the magnetic transition belongs to second order transition which is accompanied by a change in the volume expansivity [22].The results observed in thermoelectric parameters & magnetic parameters in table-2can be explained with thermodynamic theory. The variation in volume changes the distance between the ions that are

responsible for the conduction process & hence alter the activation energy of resistivity. In addition to this the La ion resides at the grain boundaries & enhances the electron transfer between Fe^{2+}& Fe^{3+} which also accounts on the variation of thermoelectric power (S) for the samples, while the other substituted ions reside at the spinel block of hexagonal structure. [15-16]

Table -2 Co-relation between Electric, Thermoelectric & Magnetic Parameters

Sample Code	M_S (emu/g)	M_r (emu/g)	H_C (emu/g)	T_C(K)	S (μV/K)	n (10^{22} cm^{-3})	E_A(eV)	Vol. (cm^3)
R1	49.298	24.339	2307.5	723	-277.845	14.53	0.34	686.45
R2	57.88	30.44	2427.3	710	-238.098	9.17	0.312	669.54
R3	68.471	35.569	2904.6	707	-256.95	11.11	0.351	667.61
R4	55.61	23.671	1176.5	700	-278.459	12.96	0.28	668.97
R5	48.143	23.043	2074.1	692	-278.584	12.67	0.263	664.32
R6	42.32	22.897	2589.9	690	-256.822	10.01	0.268	664.32
R7	54.811	22.2	1074.9	686	-259.03	9.89	0.31	694.63
R8	43.381	19.91	1657.1	675	-260.781	10.34	0.248	695.71
R9	54.14	26.934	2101.8	697	-261.779	10.42	0.239	696.45
R10	52.35	21.67	1091.1	685	-253.482	9.44	0.265	696.76

4. Conclusion

- Successful preparation of mixed ion doped La-M hexaferrite below sintering temperature of 1200^0C using standard ceramic method.
- Prepared series of sample with mixed valance substitution possesses n-type semiconducting nature with low resistivity.This attributes to enhancement in the phenomenon like charge polarization & hopping mechanism due to mixing of ions of different valency.
- The dielectric& magnetic parameters are well improved then the previous reported, allow it to stand as available materialfor application as RAMs.
- The Iwauchi relation found true &a new relation i.e “square of dielectric constant is directly proportional to mobility” has observed & proved analytically as well as experimentally.This reveals that product of $\frac{\varepsilon^2}{\mu}$ found fairly constant in order of magnitude.

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