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Effect of simultaneous substitution of Ca-Ba-La in Sr-M hexagonal ferrites on thermoelectric and dielectric parameters

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The polycrystalline compounds with chemical formula $Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO_{19}$ (CSBFLO) were synthesized via standard ceramic method. The chemical phase analysis was carried out by X-ray powder diffraction (XRD) method, which confirms the formation of the magnetoplumbite phase, belongs to ferrite structure. The thermoelectric power studies of hexagonal ferrites of various compositions were investigated. The See-beck coefficient is negative for all the compositions showing that ferrites behave as n-type semiconductors. The value of the charge carrier's concentration has been computed from the observed values of the see-back coefficient. On the basis of these results an explanation to conduction mechanism for the properties like electrical conductivity & Dielectric constant is suggested.

Key Words: standard ceramic method, Thermoelectric power, Dielectric polarization, electrical conductivity.

Introduction

Hexaferrite is a class of hard magnetic material which is widely used in various industrial applications. Various members like W, Z, Y, X, U and Mhexaferrites belong to this family and they can be distinguished as per their stoichiometry. However, Mhexaferrites have gained more attention because of their special characteristic of being magnetoplumbite in nature which leads to greater structural stability compared to normal ferrites. They are generally represented by a chemical formula; MeFe₁₂O₁₉ where Me is the divalent metal cation and can be replaced by a suitable combination of mono, di, and trivalent cations. Among various hexaferrite members, Mhexaferrites are preferred as the permanent magnetic materials due to their cost effectiveness, reasonable electric & magnetic performances and wide availability of raw materials needed for synthesis [1].

The Hall effect and thermoelectric power studies are widely used in the interpretation of the conduction mechanism in semiconductors. However, in case of low mobility semiconductors such as ferrites, it is sometimes difficult to measure the Hall Effect; hence thermoelectric measurement is the only alternative. Moreover, the measurement of thermo-electromagnetic force (e.m.f) is simple and its sign gives vital information about the type of conduction in semiconductors whether they are n-type or p-type.

It is found that the Sr-M hexagonal ferrite with suitable amount of substitution of rare earth La³⁺ ion enhances magnetic character and it is continuously gaining important as permanent magnet material in microwave, small motors, magnetic recording material, & radar absorbing materials (RAMs) [2, 3, 11]. In addition, it shows promising for use as magnetic and magneto-optic recording media as well as in microwave devices [4, 5]. The Magnetic and Mossbauer studies of mixed Sr-M ferrites have been studied in detail by G.K. Thompson et.al and many researchers [6-10]. But the effect on electric, thermoelectric and dielectric parameters on such composition with variation of some more suitable doping find less room in survey. Also, to our knowledge depose information is available on thermoelectric power studies of combined substitution of Ca-Ba-La into Sr-M hexagonal ferrite in the literature. Hence in the present research plan an attempt to throw enough light on the conduction phenomenon, charge polarization and charge carrier concentration by performing electrical conductivity, dielectric and thermoelectric measurements of Ca-Ba-La, Sr-M hexagonal ferrite as a function of composition and temperature is carried out.

Experimental Details

Sample preparation

The preparation of polycrystalline compounds 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 Fe₂O₃, La₂O₃, CaO, SrO, and BaO

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(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 and 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 hrs in air followed by further mixing and rigorous grinding, and finally the mixture was thermally treated at 1430 K for 72 hrs. The details of the method of the preparation have been given in earlier publications. [11, 12]

Measurements

X-ray diffraction patterns of Ca_xSr_yBa_{1-x-y}Fe_{12-z}La_zO₁₉

hexagonal ferrites, under investigation, were obtained using Cu-K α radiation on a Philips X-ray diffractometer (Model PW1732) within scanning range from 0 ° to 90 °. Elenctrical conductivity and 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-2 MHz at room temperature.

Result and Discussion

Structural Analysis

The XRD profiles of the M-hexaferrite samples with



Fig. 1. XRD Patterns.



Fig .2. Variation of S, n and μ along with the sample code/ composition.



Fig. 3. Variation of thermoelectric power(S) with temperature.

standard pattern are presented in Fig. 1. The recorded X-ray diffraction patterns of all the samples have shown the presence of reflection planes (006), (107), (114), (201), (108), (220), and (304) corresponding to pure 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 00-039-1433. [11, 21] The detailed explanation over structural variation was given in our previous published paper. [11, 12]

Variation of See-beck coefficient with Composition

The graphical variation & values of See-beck coefficient (S) computed from the measured values of thermo-e.m.f. are given in Fig. 2 and Table 2, respectively. It can be seen from the table that the sign of the See-beck coefficient is negative for all compounds [13]. This reflects majority of n-type charge carrier i.e. electron and n-type semiconducting behavior. it was earlier expected that Fe^{2+} ion concentration will be slightly different for all substituted samples as the sample contain simultaneous substitution of other divalent ions along with La³⁺ ion (z = 0.1 to 0.3), and experimentally found values were in the range of 61 to 70 μ V/K, this provide a good support to our

assumption. This review enables us to conclude that equal amount of Fe³⁺ ions are replacing by Fe²⁺ ion. This alteration to Fe³⁺ concentration is attributed to varying amount of La³⁺ ion. As the presence of La³⁺ ions at the grain boundaries enhances the electron transfer between Fe²⁺ and Fe³⁺ which accounts on the lower absolute values. It was already coated that increasing La³⁺ substitution in sample results in decreases of Fe³⁺ ion concentration. [13]

Temperature dependence of thermoelectric power

The variation of thermoelectric power (S) with temperature is shown in Fig. 3. It can be seen that the value for thermoelectric power for all samples increases with increasing temperature. The negative value of thermoelectric power found over the entire range showed that the majority charge carriers are electrons [14]. It was well reported that the magnetic variations has a marked influence on thermoelectric property of hexagonal ferrites. It is known from thermodynamics that magnetic transition belongs to second order transition, is accompanied by volume expansivity [15]. Such expansion increases the distances between the ions that are responsible for conduction process and thermoelectric power. Moreover, the change in the behavior of thermoelectric power with the temperature may be due to magnetic transition. The detailed variation of magnetic parameters was provided into previously published paper but still for the sake of comparison we included the variation of magnetic saturation (M_S) in the Table 2. On account of our presented data for magnetic properties [12], we found the values of critical temperature ranging from 600 to 700 K for samples, and the thermoelectric variation was studied in the temperature range of 300 to 450 K, i.e. paramagnetic region for the samples. This difference in the temperature range restricts us to produce a comparative study of transition temperature of thermoelectric parameter and critical temperature of magnetic parameter.

Compositional variation of carrier concentration, dielectric constant, electrical conductivity and mobility

Fig. 2 and Table 2 give the graphical variation & values of carrier concentration, See-beck coefficients and mobility at 358 K temperature for samples, respectively. The carrier concentration for these hexaferrites was calculated using the formula given by morin and gabella [16]

$$n = N \exp \frac{Se}{K} \tag{1}$$

Where, S = See-beck coefficient,

e = charge of electron,

K = Boltzman constant,

N = density of states

The computed values of carrier concentration were

Code	X, Z			$a(A^{0})$	$c(\Lambda^0)$	$V(cm^3)$	D_X	D_M	Mol Wt	Porocity	a/c
	Ca	Sr	Ba	a (A)	C (A)	v (em)	(gm/cm^3)	(gm/cm^3)	1v101. W L.	rorocity	d/C
R1	0.1	0.2	0.7	5.8569	23.1070	686.45	5.32	4.13	1100.09	22.33	0.25
R2	0.1	0.4	0.5	5.8157	22.7836	667.35	5.42	4.02	1090.14	25.85	0.25
R3	0.1	0.6	0.3	5.8170	22.7823	667.61	5.37	3.99	1080.20	25.66	0.25
Code	X, Z		$a(\Lambda^{0})$	$a(\Lambda^{\circ})$	$V(am^3)$	D _X	D _M	Mal Wt	Borogity		
	Ca	Sr	Ba	a (A)	C (A)	v (cili)	(gm/cm^3)	(gm/cm ³)	1 v101. vv l.	rotocity	a/C
R4	0.25	0.2	0.55	5.8278	22.7442	668.97	5.43	3.96	1093.80	27.01	0.25
R5	0.25	0.4	0.35	5.8158	22.7633	666.78	5.39	3.87	1083.85	28.13	0.25
R6	0.25	0.6	0.15	5.8079	22.7410	664.32	5.36	3.83	1073.92	28.57	0.25
Code	X, Z					Dv	DM				
	Ca	Sr	Ва	a (A ^o)	c (A ⁶)	$V (cm^3)$	(gm/cm^3)	(gm/cm ³)	Mol.Wt.	Porocity	a/c
R7	0.4	0.2	0.4	5.8959	23.0741	694.63	5.19	3.97	1087.52	23.57	0.25
R9	0.4	0.6	0.0	5.8956	23.1369	696.45	5.09	3.87	1067.64	23.88	0.25
R8	0.4	0.4	0.2	5.8958	23.1108	695.71	5.14	3.81	1077.58	25.91	0.25
R10	0.4	0.0	0.6	5.9028	23.0910	696.76	5.23	3.89	1097.47	25.63	0.25

Table1. The structural properties of mixed M-hexaferrite samples.

Table 2. Electric, dielectric and thermoelectric properties of mixed M-hexaferrite samples.

Code	X, Z		E. (eV)	$\sigma_{-} = (\Omega \text{ cm})^{-1}$	s 10 ³	Ms(emu/a)	$S(\mu V/K)$	$n \times 10^{22}$	$\mu \times 10^{5}$	N/n	
	Ca	Sr	Ва	$L_A(cv)$	$O_{\rm DC}$ (32 CIII)	2 10	wis (ennu/g)	5 (μν/Κ)	(cm^{-3})	μ ^ 10	
R1	0.1	0.2	0.7	0.34	0.053	6.93	49.298	-70.759	1.03325	0.08062	-0.357
R2	0.1	0.4	0.5	0.31	0.054	5.03	57.88	-61.343	0.91702	0.02653	-0.309
R3	0.1	0.6	0.3	0.35	0.108	7.38	68.471	-65.551	0.96483	0.03996	-0.331
Code	X, Z		E (aV)	$\sigma = (0 \text{ cm})^{-1}$	$c 10^3$	$M_{c}(amu/a)$	S(uV/K)	$n \times 10^{22}$	10^{5}	N/n	
	Ca	Sr	Ba	$\mathbf{E}_{\mathbf{A}}(\mathbf{e}\mathbf{v})$	ODC (22 CIII)	6 10	TVIS (ennu/g)	5 (μ //Κ)	(cm^{-3})	$\mu \wedge 10$	
R4	0.25	0.2	0.55	0.279	0.420	8.56	55.610	-69.759	1.00531	0.18187	-0.352
R5	0.25	0.4	0.35	0.262	0.594	9.21	48.143	-69.526	0.99924	0.25191	-0.351
R6	0.25	0.6	0.15	0.268	0.664	3.96	52.98	-64.539	0.94041	0.4295	-0.325
Code	X, Z		E (aV)	σ (0 cm) ⁻¹	$c 10^{3}$	$M_{c}(amu/a)$	S(uV/K)	$n\times 10^{22}$	10^{5}	N/n	
	Ca	Sr	Ba	$L_A(ev)$	$O_{\rm DC}$ (32 CIII)	6 10	wis (enitu/g)	5 (μ //Κ)	(cm^{-3})	μ ^ 10	
R7	0.4	0.2	0.4	0.31	0.426	15.80	54.811	-64.641	0.93739	0.43347	-0.326
R9	0.4	0.6	0.0	0.234	0.979	18.01	54.140	-65.526	0.94996	0.6433	-0.330
R8	0.4	0.4	0.2	0.248	0.835	3.75	43.381	65.335	0.94832	0.38641	-0.329
R10	0.4	0.0	0.6	0.265	0.259	11.23	52.350	63.525	0.92673	0.08281	-0.320

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

Dielectric constant, electrical conductivity & mobility shows linear variation as observed from Table 2. The Fig. 4 and Fig. 5 represents variation in electrical conductivity & dielectric constant with respect to composition (sample codes).The peak 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 and enhancement in conductivity which reflects n-type semiconducting behavior [17-19].

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



Fig. 4. Variation of DC conductivity with sample code/composition.



Fig. 5. Variation of dielectric constant with sample code/composition.

decrease in electron exchange mechanism i.e. space charge polarization [20].

Temperature dependence of electrical conductivity and mobility

The variation of See-beck coefficient (S1 to S10), carrier concentration (n1 to n10) & mobility (µ1 to μ 10) for the sample code R-1 to R-10 respectively, over temperature range was represented in Fig. 3, Fig. 6 and Fig. 7. It was observed that all parameters showed increase with increasing temperature [13]. Theses parameters are basically electrical properties and it has been recognized that the same mechanism viz. exchange of electrons between Fe²⁺ and Fe³⁺ is responsible for them. It is clear from the theory of semiconductor that as temperature increases concentration of free charge carrier increases. This charge carrier ultimately enhances the conduction process inside the material. and as the samples were showing semiconducting behavior, It can be concluded that the electron exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ increases, results in the local displacement of charges, which is responsible for polarization and



Fig. 6. Variation of carrier concentration (n) with temperature.



Fig. 7. Variation of mobility (μ) with temperature.

conduction in hexaferrites, and ultimately increase of electrical conductivity, mobility & carrier concentration. **Conclusions**

- 1. Thermoelectric studies conclude that samples showed n-type semiconducting behavior over entire range of composition and temperature.
- 2. Enhancement in the conduction and polarization phenomenon follows appropriate mixing of divalent and trivalent substituted ions.
- 3. All the samples showed high values of conductivity, dielectric constant and mobility, highly applicative in formation of radar absorbing materials.

References

- J. I Kraschwitz, et al./ Mary Howe-grami, Encyclopedia of chemical Technology, 10 (1993) 381.
- 2. Y Kubota et al./, proceedings of 8th International conference on ferrites,Kyato (2000) 405-410.
- F Kools et al./, proceedings of 8th International conference on ferrites, Kyato (2000) 437.
- 4. F Hernadez-Gomex et al./, Physics B 320 (2002) 267.
- 5. M Sharrock et al./, IEEE Trans. Magn. 25 (1989) 4374.
- 6. G Thompson et al./, J. Appl. Phys. 73 (1993) 6295.
- 7. S Besenicar et al./, J. Magn. Magn. Mater. 101 (1991) 307.
- 8. G Wieseinger et al./ Phys. Stat. Sol. (a)189 (2002) 499.
- 9. R Pullar et al./, J. Mater. Res. 16 (2004) 3162.

- 10. B Saha et al./, J. Appl. Phys. 73 (1993) 6260.
- 11. JCPDS file no. 00-039-1433, International centre for diffraction DATA (ICDD).
- 12. R Mahadule et al./, Int.jour. of metals, 2013 (2013) 1-7.
- R Mahadule et al./,Int. Jour. Metall. & Material Sci. & Engg., 3 (2013) 93-96.
- 14. D Ravinder et al./ J. Alloy & Comp. 363 (2004) 68-74.
- 15. A Sattar et. al./ Egypt. J. Sol. 26 (2003) 2.
- 16. M Zemansky, Heat & Thermo., McGraw-Hill, P 460 (1968).
- 17. F Morin et al./, Phys. Rev. 99 (1955) 467.

- 18. N. Debnath et al./, IJENS 12 (2012) 49-52.
- 19. D selfert et al./, Journal of magnetism and magnetic material, 321 (2009) 4045-4051.
- 20. L. Khobragade et al./, Journal Materials & Metallurgical Engg.,1 (2011) 1-12.
- N. Rezlescu and E. Rezlescu et al./, Phys. Status Solidi A 23 (1974) 575-582.
- 22. D. Ravinder et al./, Material Letters 57 (2003) 4344-4350.
- 23. Anterpreet Singh et al./, Journal of ceramic processing research, 11 (2010) 241-249.
- 24. M.Giriya et al./, IJSER. 3 (2012) 30-36.