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DC conductivity studies of $SrMe^{2+}(Li^{1+}Fe^{3+})_{0.5}Fe_{16}O_{27}$ ferrites

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ABSTRACT

Lithium substituted W type ferrites having common chemical formula $SrMe(LiFe)_{0.5}$-W where Me is a divalent cation such as Zn, Ni, Cd, Cu, Fe were prepared by standard solid state reaction method and their dc electrical properties such as conductivity, activation energy were studied and the type of carriers responsible in each was determined from thermoelectric studies. The higher resistivity of the compounds $SrMe(LiFe)_{0.5}W$ where Me = Cu, Zn and Ni, suggests less presence of mixed valency cations on equivalent lattice. While with Me = Fe and Cd show low value due to the ferrous ions present on the octahedral sites along with ferric ions.

Keywords: W type ferrite, Lithium, Conductivity, Activation energy, Hopping.

INTRODUCTION

The critical literature survey revealed that the electrical properties of hexagonal [1,2,3] W-type ferrites are less studied compared to its magnetic properties. This may be due to the fact that they were developed initially as permanent magnet.[4,5,6,7] Today W-type ferrites are finding applications in many diverse fields like microwave and hence their electrical properties are also becoming important. Many attempts have been made to improve the properties of W ferrites by variety of substitutions. Though W-type ferrite does not contain any monovalent cation, hence a combination of monovalent cation with some multivalent cation for charge compensation may be substituted. With this idea in mind a new series of materials for permanent magnets $BaZn_{2(1-x)}(LiFe)_xW$ ferrites were developed for the first time by Mignot J. P. et. al.[8]. Afterward Ram S. and Joubert J.C.[9] reported synthesis and magnetic properties of $SrZn_2W$ ferrite using a partial $2Zn^{+2} = Li^{+1}\ Fe^{+3}$ substitution. Albanese G. et. al.[10] reported Mossbauer and magnetic study of $SrZnLi_{0.5}Fe_{0.5}W$ ferrite along with thermoelectric analysis, X-ray diffraction and Mossbauer measurements.

In the present work W type ferrites having common formula $SrMe(LiFe)_{0.5}$-W where Me is a divalent cation such as Zn, Ni, Cd, Cu, Fe were prepared and their electrical properties such as conductivity, activation energy and thermoelectric power were studied. Since the properties of ferrite depend on the interactions among the cations distributed over various sites, these were explained on the basis of the knowledge of site distribution of cations in the W type structure.

MATERIALS AND METHODS

The W-type compounds, in the present investigations were prepared using the standard solid-state reaction method.[11,12] AR grade oxides and carbonates were used as starting materials. Preparation of ferrites from Hexagonal family are usually difficult as compared to Spinel ferrites and especially the W-type ferrite is one of the most difficult one. This is due to the higher formation temperature and difficulty to get a pure product. The prolonged and continuous heating (1200 ^{o}C sintering temperature maintained for about 100 hours) used in present work resulted in better product formation as this has given sufficient time to the ions to diffuse. Also the lithium present, in these compounds might have facilitated the synthesis[9].

In the present work X-ray diffractometer with filtered Cu K_{α} radiation from X-ray tube, operating at 40 KV and 20 mA was used for identification of compounds. (Philipse PW 1710) From the X-ray graph, formation of hexagonal structure, corresponding to space group $P6_3/mmc$ or $D_6{}^4{}_h$ (No 194) was checked.[1]

Two-terminal method was employed for measurement of dc conductivity. The measurements were taken in the range from 150 ^{o}C to 500 ^{o}C. Finally graphs of ln σ against 1/T were plotted and from the slope of these graphs the activation energies for the compounds were calculated using the relation
$\Delta E = 8.617 \times 10^{-5} [\Delta (\ln (1/\sigma) / \Delta (1/T)]$

The thermoelectric coefficient measurements were carried out using two-probe set up fabricated in the laboratory. The measurements were taken in the temperature range 350^{o}K to 450^{o}K. The type of carriers responsible for conduction was determined in each of the compound from these studies.

In order to prepare pellet for the above observations the compound prepared was grounded to fine particle size in an agate mortar. The powder was mixed with 5% polyvinyl acetate solution made in A.R. grade acetone, as binder and mixed thoroughly. This mass was then transferred to a die and pressed under pressure of 5 tons per cm^2 using a hydraulic press. The pellets so prepared were then heated in a furnace up to 500 ^{o}C to remove the binder. After maintaining this temperature for few hours the pellets were slowly cooled to room temperature. In this way crack free pellets in the shape of a cylinder of small height were obtained. The end faces of the pellets, so prepared, were gently grounded over zero number sand paper to ensure smooth surfaces. The dimensions of the pellets were measured accurately. The smooth and flat parallel faces of the pellets were coated with uniform thin layer of silver paste to facilitate a good electrical contact with the electrodes. The silver paste was dried by heating the pellet slowly for few hours in air at 500 ^{o}C. The thin coating of silver paste thus formed was adherent and chemically inert. Pellets were stored in desiccators if found necessary.

RESULTS AND DISCUSSION

The consolidated data of lattice parameters, Molecular weights and X-ray densities derived from the X-ray diffraction study, for the compounds studied in the present work, is given in table no. 1. The formation of predominant W phase in all the compounds was confirmed from the X-ray study (figure No. 1).

The results of dc electrical conductivity study are shown in the form of plots of Ln of conductivity against inverse absolute temperature in figure no. 2. and compiled in the table no 2. It was observed that the conductivity increases with temperature in all compounds and follows Wilson's law $\sigma = \sigma_o \exp(\Delta E/kT)$ This indicates semi-conducting nature of the compounds The large values of resistivity and activation energy are attributed to the relatively low number of mixed valency state of an element on an equivalent lattice sites. The increase in conductivity with temperature is attributed to the greater overlap of orbitals due to the increased lattice vibrations. Since the overall distances get reduced during overlap, there is a greater probability of exchange of charges between the two overlapping ions. This increased exchange might have led to increase the conduction in the compound.

The various divalent cations may be categorized as per their atomic radii, masses, magnetic nature and most importantly their site preferences. The exchange interactions responsible for conduction mechanism depends on the overlapping of orbits and hence on actual locations of cations. Therefore the site distribution of these cations on various sites influences the conduction process and hence decides the conductivity of a W-type ferrite. As a result the conduction properties of the compounds prepared in the present work could be explained on the basis of distribution of cations.

The electrical properties of the $SrFe^{2+}(Li^{1+}Fe^{3+})_{0.5}W$ ferrite has been explained on the basis of the hopping of electrons in between the ferrous and ferric cations ($Fe^{2+} \rightarrow Fe^{3+}$) present on the octahedral sites. The small quantity of Li, though occupies some of the octahedral sites, there is enough space on these sites for the iron cations. It has been revealed from the Mossbauer and other studies that the divalent Fe^{2+} cations locate on the octahedral sites of S block.[13,14,15,16] Due to this, iron cations of mixed valency on the octahedral sites are developed, which facilitated the electrical conduction. The lowest value of room temperature resistivity for this compound, among all the compounds studied in present work, could be attributed to this phenomenon. Since resistivity and activation energy go hand in hand, this compound also shows lowest activation energy.

Since $(LiFe)_{0.5}$ contents along with Fe_{16} contents are fixed in all the compounds studied in the present work, the difference observed in electrical properties could be accounted to the variations in divalent cation. Therefore the resistivity and activation energies of the compounds in present study can be compared with the compound $SrFe(LiFe)_{0.5}W$ which was prepared simultaneously.

Ni^{2+} prefer octahedral sites.[17,18] The presence of Ni on octahedral sites favoured the mechanism of conduction[19] given by $Ni^{2+} + Fe^{3+} \rightarrow Ni^{3+} + Fe^{2+}$. The resistivity for this compound was found only moderately higher than $SrFe(LiFe)_{0.5}W$. The Fe^{2+} generated in the above reaction facilitates the conduction process. The substitution of Cu in the ferrite always shows increase in resistivity. They prefer octahedral sites in the W type ferrites.[20,21] Moreover Cu doping was found to increase lattice vacancies in ferrites such as Zn-W ferrite. As reported further, these would be anion vacancies rather than cation vacancies. These vacancies acted as centres of phonon scattering thus altering the conductivity. Sawadh P.S.[22] studied the electrical properties of Cu_2 –W ferrite and observed high resistivity at room temperature and high activation energy. This observation was explained on the basis of the decreased ferrous ions, due to substituted Cu, which decreases the number of hopping electrons, which in tern causes the increase of resistivity. The relatively high resistivity observed in Cu substituted Lithium W ferrite in comparison to $SrFe(LiFe)_{0.5}W$ compound studied in present work, could be explained on theses lines.

Zn ions prefer tetrahedral sites.[23,24,25] The presence of Zn ions also found to suppress the ferrous formation in the compound. This phenomenon might have taken place in $SrZn(LiFe)_{0.5}W$ and hence resulted in higher resistivity as compared to that of $SrFe(LiFe)_{0.5}W$.

Exceptional electrical behaviour was observed in the Cd substituted lithium W ferrite i.e. $SrCd^{+2}(Li^{1+}Fe^{3+})_{0.5}W$. The resistivity of Cd ferrite which was just little higher than that observed in case of $SrFe(LiFe)_{0.5}W$. The relatively low resistivity is attributed to the compensatory increase of number of ferrous ions at the octahedral sites due to the preferential occupation of Cd ions on tetrahedral sites.[26] Similar increase in population of ferrous ions due to presence of Cd in the S type ferrite was observed by Patil R.S. et.al.[27]

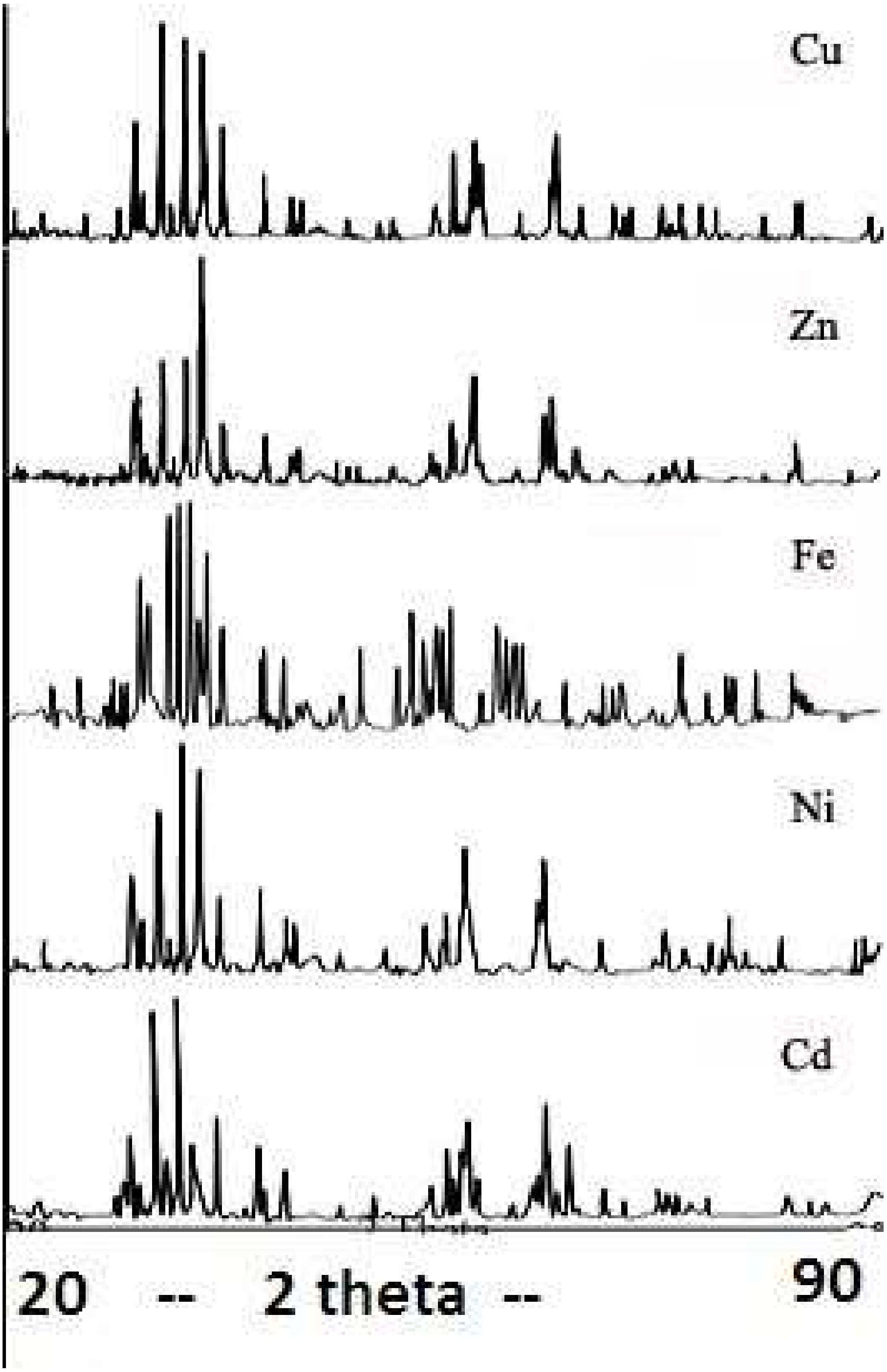
Thermoelectric studies were carried to know the type of carrier responsible for the conduction mechanism. It was found that the p type nature prevailed in W-type ferrites with Me = Zn, Cu, Ni and n type in W-types ferrites with Me = Fe^{2+} and Cd^{2+}. In these two compounds, presence of excess Fe^{2+} ions is considered responsible for the conduction mechanism. Hence hopping electrons takes part in conduction.

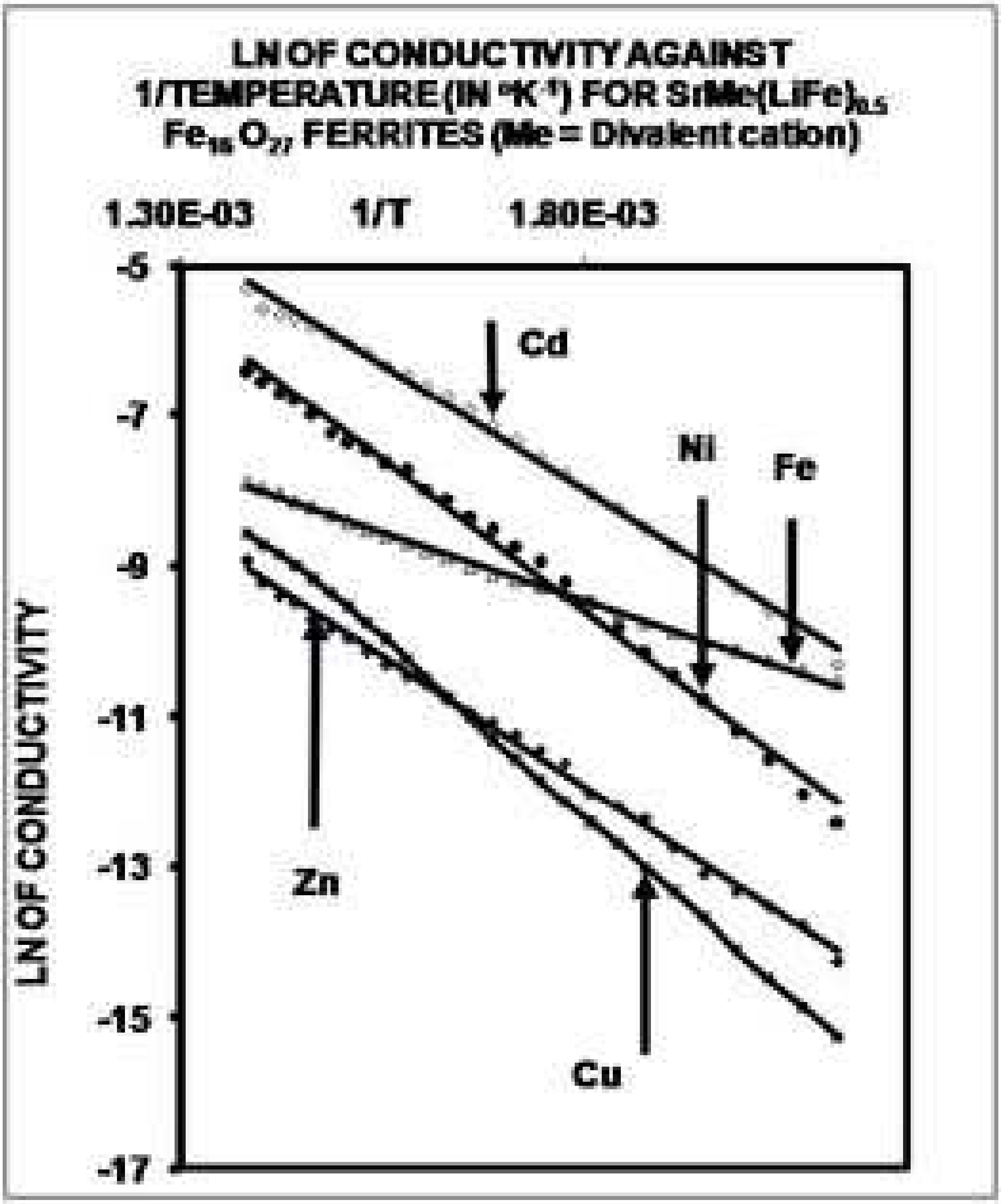
Table No. 1: Structural data of $SrMe(LiFe)_{0.5}$-W ferrites

Sr No	Sample	a Å	c Å	c/a ratio	Volume $(Å)^3$	Mol.Wt gm	Density gm/c.c
1	$SrZnLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	5.9048	32.8893	5.5699	993.110	1509.90	5.049
2	$SrNiLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	5.9030	32.868	5.5680	991.865	503.21	4.973
3	$SrCdLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	5.8955	32.8772	5.5767	989.628	1556.92	5.225
4	$SrCuLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	5.8985	32.8998	5.5777	991.304	1508.06	5.062
5	$SrFeLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	5.8857	32.7953	5.5720	983.872	1500.36	5.065

Table No. 2: Electric conductivity details of $SrMe(LiFe)_{0.5}$-W ferrites

Sr. No	Sample	Activation Energy E. eV	Resistivity		Type of carrier
			at 250 °C ohm.cm x 10^4	at R.T. ohm.cm x10^4	
1	$SrZnLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	0.610	34.7	300	p
2	$SrNiLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	0.813	3.5	50	p
3	$SrCdLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	0.601	0.633	6	n
4	$SrCuLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	0.821	24.8	900	p
5	$SrFeLi_{0.5}Fe_{0.5}Fe_{16}O_{27}$	0.310	1.29	5	n


Cu
Zn
Fe
Ni
Cd
20 -- 2 theta -- 90



CONCLUSION

The resistivity of the compounds SrMe(LiFe)$_{0.5}$W where Me = Cu, Zn and Ni is higher than the resistivity of SrFe(LiFe)$_{0.5}$W which suggests less presence of mixed valency cations on equivalent lattice. While the resistivity of the compounds SrMe(LiFe)$_{0.5}$W where Me = Fe and Cd show low value due to the ferrous ions present on the octahedral sites along with ferric ions and as a result the conduction takes place in the form of hopping of electron from ferrous to ferric ion.

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