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Preparation and thermoelectric properties of Cd^{2+} and Cr^{3+} substituted Magnesium ferrites

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ABSTRACT

The structural and thermo-electrical properties of Cd^{2+} and Cr^{3+} substituted are studied by synthesizing the spinel solid solutions series $\text{Cd}_x\text{Mg}_{1-x}\text{Fe}_{2-y}\text{Cr}_y\text{O}_4$. Spinel samples of this series with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 ; $y = 0, 0.05$ and 0.1 were prepared by double sintering ceramic method. X-ray diffraction (XRD) and FTIR absorption methods are used to obtain the structural characterization. The structural details like: lattice constant, A-O, B-O, r_A and r_B have been deduced through XRD data analysis. Lattice constant increases with Cd^{2+} concentration and decreases with Cr^{3+} concentration. These changes in lattice constant are attributed to the difference in ionic radii of Cd^{2+} , Cr^{3+} and Fe^{3+} ions. Seebeck Coefficient of each composition was measured in the temperature range 300 K to 750 K. The Seebeck coefficient is negative for all the compositions showing that these ferrites behave as n-type semiconductors. On the basis of these results, an explanation for the conduction mechanism in Cd^{2+} and Cr^{3+} substituted Magnesium ferrites are suggested.

Keywords: preparation of ferrites, Seebeck coefficient, TEP measurement.

INTRODUCTION

Usefulness of ferrites is determined by their physico-chemical properties, which found to be sensitive to the method of preparation and heat treatment during preparation [1]. Many researchers tried to prepare the ferrites by different methods, like

Chemical methods [2-4], microwave sintering method [5,6], Citrate precursor method [7], wet chemical method [8] and Sol-gel method [9] etc. The ceramic method found to be easiest method of preparation of ferrites in the bulk form. In this paper the results are presented of the ferrites prepared by double sintering ceramic method.

In case of magnetic materials such as ferrites, Seebeck coefficient (α) measurement gives better insight into the conduction mechanism. The sign of Seebeck coefficient gives the information regarding the type of charge carriers in the conduction mechanism. Nikolski [1] measured the thermoelectric power (TEP) of $\text{Mg}_x\text{Al}_{2-x}\text{FeO}_4$ ($x=0, 0.2, 0.4$ and 0.6) and observed that the compositions $x = 0$ and $x = 0.2$ shows n-type conductivity while remaining two compositions shows p-type conductivity. The measurement of Seebeck coefficient in Ni-Zn ferrites is reported in the literature [10,11]. Murthy et al [12], from the study of dc resistivity and TEP concluded that iron excess ferrites show n-type conductivity and those with iron deficient shows p-type conductivity. TEP in Gd^{3+} substituted Cu-Cd ferrites were studied by Kolekar et al [13]. Characterization and thermoelectric power studies of ferrites with

various substitutions was well documented [14-19]. Structural properties of Mg^{2+} and Al^{3+} co-substituted lithium ferrites were studied by Modi *et al* [16]. X-ray and infrared studies of chromium substituted magnesium ferrite was reported by Kawade *et al* [17] and found that, the lattice parameters decrease with Cr^{3+} substitution and the X-ray density decreases as Cr^{3+} content increases. The distance between magnetic ions in both octahedral and tetrahedral sites decreases with increase in Cr^{3+} . Infrared spectral studies of Zn-substituted Li-Mg ferrites were reported by Shaikh *et al* [20].

Following this introduction, the paper focuses on preparation, characterization and Seebeck coefficient study of $Cd_xMg_{1-x}Fe_{2-y}Cr_yO_4$ ferrite system.

MATERIALS AND METHODS

A series of ferrites with general formula $Cd_xMg_{1-x}Fe_{2-y}Cr_yO_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 ; $y = 0, 0.05$ and 0.1) were prepared by double sintering dry ceramic method using starting oxides Fe_2O_3 , $CdCO_3$, MgO and Cr_2O_3 (AR grade, LOBA Chemi India). These oxides were weighed on the single pan microbalance in the required molecular weight proportion and were mixed and milled thoroughly in agate mortar with acetone base for about 2 hours. The dried power was then transferred into clean and dry crucibles. The powder was presintered in a temperature-controlled furnace at temperature $700^\circ C$ for 12 hours. The temperature of the furnace was measured by using well-calibrated Chromel-Alumel thermocouple. The furnace was cooled at the rate of $80^\circ C$ per hour to room temperature.

For sintering process, the temperature was maintained at $1050^\circ C$ for 24 hours. The sintered compositions were then mixed with 5% PVA and again milled thoroughly.

The pellets of 1cm diameter and 4-5 mm in thickness were prepared by applying pressure of 7 tones/sq.cm using hydraulic press, for 5 minutes. These pellets were finally sintered at $1050^\circ C$ for 24 hours for better compaction. Using soft metal paper, pellets were polished.

The powdered samples of each composition was characterized by X-ray diffraction method (XRD) on Philips computerized X-ray diffractometer (PW 3710) using Cu-K α radiations. The samples were also characterized by IR absorption spectroscopy at room temperature, in the range of 350 cm^{-1} to 800 cm^{-1} by using FTIR spectrophotometer (Perkin -Elmer).

For the measurement of Seebeck coefficient (α), the pellet holder required was fabricated in the laboratory. This pellet holder has an auxiliary supply to its one end with which the temperature difference of 10 K is obtained between two ends. A Chromel- Alumel differential thermocouple was used to measure the temperature difference. The sign of Seebeck coefficient was decided from the polarity to the non-auxiliary end of the specimen, as the charge carriers diffuse from hot to cold parts [13].

RESULTS AND DISCUSSION

3.1 Characterization

Typical X-ray diffractogram is presented in Fig.1. Study of X-ray diffraction reveals that all the compositions under investigations were found to be face centered cubic spinel structure. The values of lattice constant 'a' for all the compositions are presented in table 1. From this table it is found that lattice constant increases with Cd^{2+} concentration. Such increase in the lattice constant due to addition of cadmium content is also reported in literature [13,21]. The increase in lattice constant is attributed to the difference in ionic radii of Cd^{2+} ion ($1.03A^0$) and Fe^{2+} ion ($0.67A^0$)[21]. On substitution on Cr^{3+} ion, the lattice constant found to decrease. This is also attributed to the difference in ionic radii of Cr^{3+} ion ($0.63A^0$) and Fe^{3+} ($0.67A^0$)[21]. The X-ray data is presented in table 1. From this table it is seen that tetrahedral metal-oxygen bond length (A-O) and cationic radius (r_A) increases with increase in Cd^{2+} content which suggest that the Cd^{2+} ion occupies A-sites. With the substitution of Cr^{3+} in Mg-Cd ferrites, octahedral metal-oxygen bond length (B-O) and ionic radius (r_B) found to decrease slightly. These observations conclude that substituted Cr^{3+} occupies B-sites. From the same table it is also seen that, the X-ray densities increases with substitution of Cd^{2+} and decreases with Cr^{3+} substitution. Such variations are also reported in the literature [17,21].

Typical IR absorption spectrum is presented in Fig.2. The far infrared spectra obtained at room temperature in the range 200 to 800 cm^{-1} shows two absorption bands. The high frequency band (ν_1) and low frequency band (ν_2) are assigned to the tetrahedral and octahedral complexes, respectively [17,20,22]. Table 2 lists the values of these absorption bands and force constants of tetrahedral (K_T) and octahedral site (K_O).

The force constant K_T is found to be greater than K_O in all compositions. With substitution of Cd^{2+} the force constant K_T decreases while K_O increases [17]. This is attributed to the increase in the A-O bond length with addition of Cd^{2+} , the energy required for breaking of longer bond is less. This supports the occupancy of Cd^{2+} on A sites. On substitution of Cr^{3+} the force constant K_O increases which is due to decrease in the B-O distance. The substituted Cr^{3+} ion occupies B sites, which causes decrease in B-O bond length. This supports the occupancy of Cr^{3+} ion at B sites[21].

3.2 Seebeck Coefficient (α)

Seebeck Coefficient (α) was determined by the equation,

$$\alpha = \Delta V / \Delta T$$

Where, ΔV is the change in thermo-emf

ΔT is the temperature difference between hot and cold end.

The plots of Seebeck coefficient versus temperature for all compositions under investigation are presented in Figs 3-5. From these figures it can be noted that, for all the compositions Seebeck coefficient is negative, exhibiting n-type of conductivity in these samples. Such type of conductivity is attributed to the hopping of electrons between Fe^{2+} and Fe^{3+} ions on octahedral sites,



Bhosale et al [23] and Ladgaonkar et al [24] reported similar results for CdFe_2O_4 and MgFe_2O_4 respectively.

On substitution of Cr^{3+} , Seebeck coefficient decreases due to occupancy of Cr^{3+} ions on B-sites. This results into decrease in Fe^{3+} ions on B-sites. The Cr^{3+} does not contribute to the hopping process but provides impedance to it and hence conductivity decreases resulting into decrease in Seebeck coefficient.

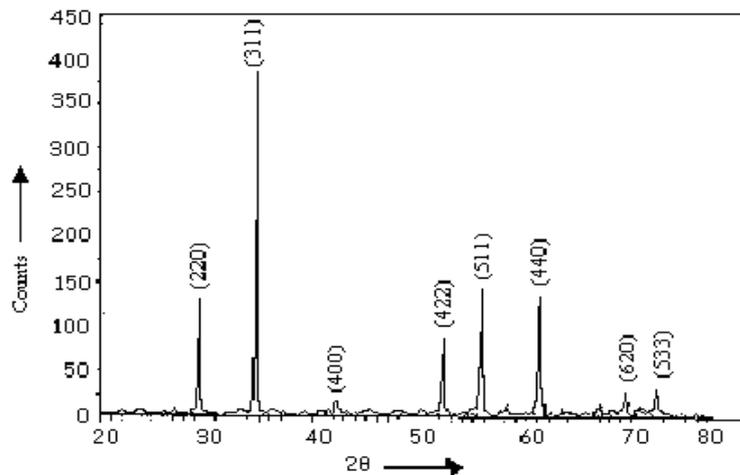


Fig. 1 Typical XRD Pattern of $\text{Cd}_x\text{Mg}_{1-x}\text{Fe}_{2-y}\text{Cr}_y\text{O}_4$ Ferrite System with $x=0.6$, $y=0$

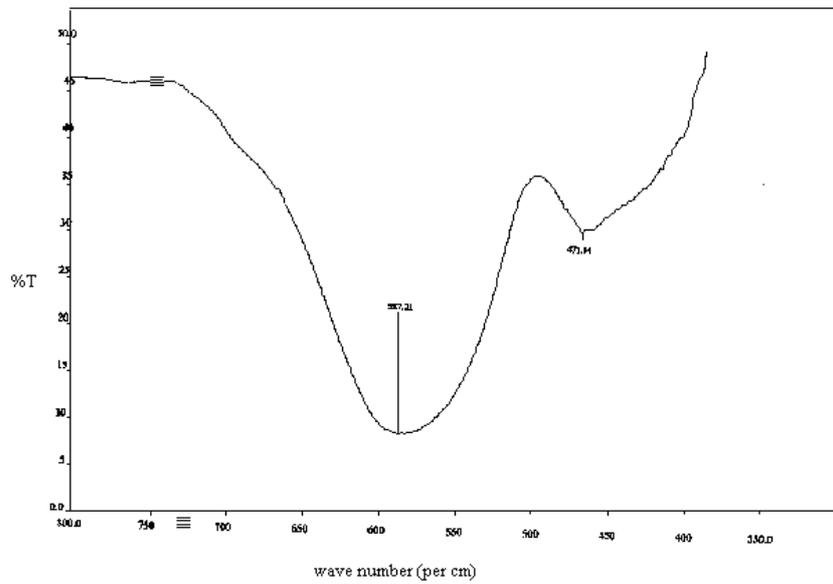


Fig. 2 Typical IR absorption spectrum of $Cd_xMg_{1-x}Fe_{2y}Cr_yO_4$ ferrite system with $x=0.4, y=0$

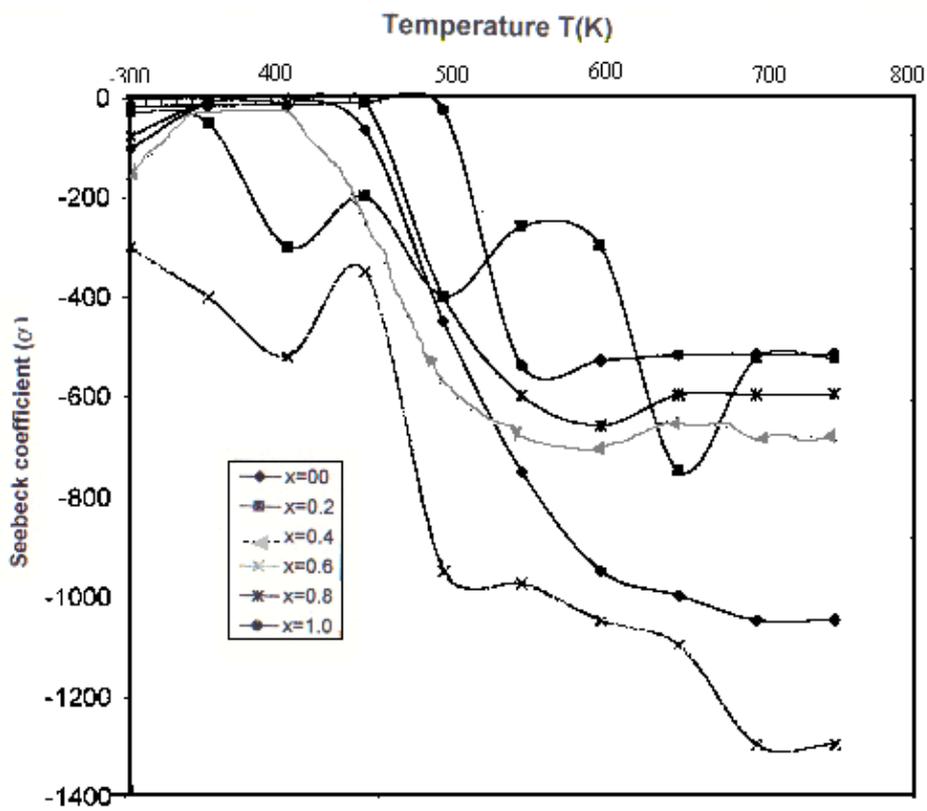


Fig. 3. Plot of Seebeck coefficient versus Temperature for the composition $Cd_xMg_{1-x}Fe_{2y}Cr_yO_4$ with $y=0.0$

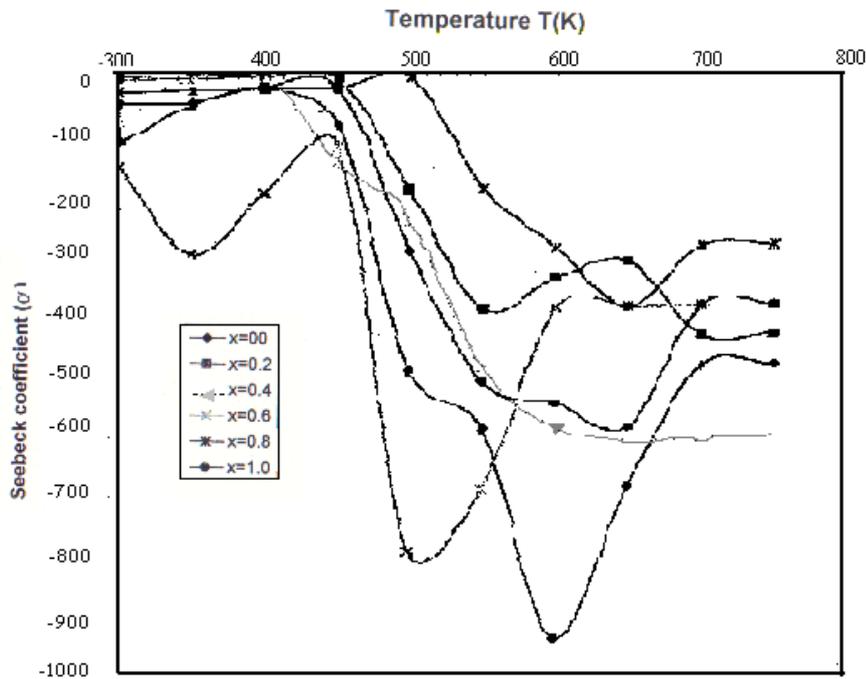


Fig. 4 Plot of Seebeck coefficient versus Temperature for the composition $Cd_xMg_{1-x}Fe_{2y}Cr_yO_4$ with $y=0.05$

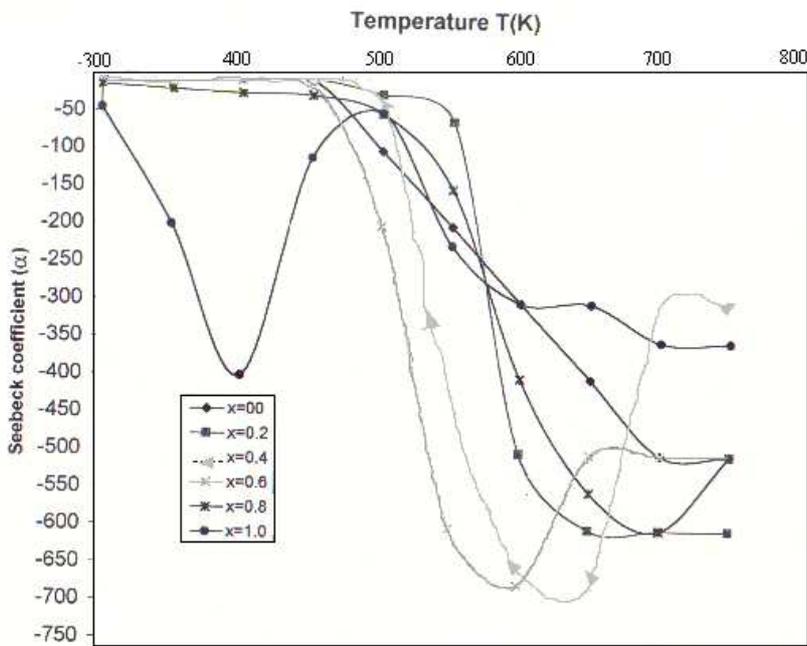


Fig. 5 Plot of Seebeck coefficient versus Temperature for the composition $Cd_xMg_{1-x}Fe_{2y}Cr_yO_4$ with $y=0.10$

Table 1 Structural parameters of Cd_xMg_{1-x}Cr_yO₄ ferrites system.

x	y	Lattice constant 'a' A ⁰	Ionic Radii r _A A ⁰	Ionic Radii r _B A ⁰	Bond Length A-O A ⁰	Bond Length B-O A ⁰	X-ray Density dx gm/cc
0.0	0.00	8.36	0.58	0.71	1.91	2.03	4.53
0.2		8.43	0.62	0.72	1.94	2.04	4.81
0.4		8.50	0.65	0.72	1.97	2.04	5.08
0.6		8.57	0.68	0.73	2.00	2.05	5.33
0.8		8.63	0.72	0.73	2.04	2.05	5.58
1.0		8.70	0.77	0.73	2.09	2.05	5.80
0.0	0.05	8.35	0.59	0.71	1.91	2.03	4.50
0.2		8.42	0.62	0.71	1.94	2.03	4.80
0.4		8.48	0.65	0.72	1.96	2.04	5.05
0.6		8.54	0.67	0.72	1.99	2.05	5.32
0.8		8.60	0.72	0.72	2.41	2.04	5.53
1.0		8.66	0.76	0.73	2.08	2.04	5.80
0.0	0.10	8.34	0.58	0.70	1.90	2.02	4.47
0.2		8.40	0.61	0.71	1.93	2.03	4.78
0.4		8.46	0.65	0.71	1.97	2.03	5.04
0.6		8.52	0.65	0.72	1.97	2.04	5.34
0.8		8.58	0.71	0.72	2.03	2.04	5.47
1.0		8.64	0.76	0.73	2.08	2.04	5.70

Table 2. Wave number and force constant of Cd_xMg_{1-x}Fe_{2-y}Cr_yO₄ ferrites system.

Compositions		Frequency of vibration cm ⁻¹		Force constants dynes/cm	
x	y	v ₁	v ₂	K _T	K _O
0.0	0.00	571	434	249880	118670
0.2		575	472	256528	125398
0.4		550	471	265079	124616
0.6		563	466	247099	118687
0.8		556	451	230809	107879
1.0		540	441	230809	105852
0.0	0.05	541	434	267160	118671
0.2		540	431	245313	124305
0.4		581	470	255312	124317
0.6		568	465	241916	120102
0.8		559	437	237581	1088891
1.0		550	457	238760	111010
0.0	0.10	623	423	279871	104042
0.2		604	425	279871	107072
0.4		590	471	265989	124643
0.6		586	467	265070	118712
0.8		574	456	255125	110103
1.0		559	439	237553	119801

CONCLUSION

Lattice constant increases with substitution of Cd²⁺ ions and on substitution Cr³⁺ ion, it found to decrease. The variations in lattice constant are attributed to the difference in ionic radii. A-O and r_A increases with increases in Cd²⁺ content, which suggest that the Cd²⁺ ion occupies A-sites. On substitution of Cr³⁺ ion, B-O and r_B found to decrease slightly suggesting substituted Cr³⁺ occupies B-sites. The far infrared spectra obtained at room temperature in the range 200 to 800 cm⁻¹ showed two absorption bands. With substitution of Cd²⁺ the force constant K_T decreases while K_O increases. On substitution of Cr³⁺ the force constant K_O increases. For all the compositions Seebeck coefficient is negative, exhibiting n-type of conductivity in these samples. Such type of conductivity is attributed to the hopping mechanism in the ferrites.

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