X-ray far IR characterisation and susceptibility study of Gd^{3+} substituted copper-cadmium ferrites

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Abstract   :   Polycrystalline ferrites of $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ (X = 0 0, 0 2, 0 4, 0 6, 0 8 and 1 0 for y = 0 0 and 0 1) are prepared by ceramic method and characterised by X-ray, IR, SEM and atomic absorption techniques. All the samples show cubic character except x = 0 0 for y = 0 0 and 0 1, which are tetragonal. The IR spectra show two strong absorption bands in the frequency range of 300 cm^{-1} to 700 cm^{-1} from which the values of force constant K_o and K_t have been calculated. The substitution of Gd^{3+} shifts the centre frequency of the bands, lowers R_A and R_B show increasing trend of K_o and K_t, which are explained on the basis of change of cation distribution distortion of co-ordination octahedra and surroundings of oxygen atom. The a c. susceptibility study shows M–D to S-D type change on substitution of Gd^{3+} in copper rich compounds alongwith an increase in the coercive force, decrease in the Curie temperature. However, for cadmium rich ferrites the domain structure remains unaltered and there is a decrease in Curie temperatures

1. Introduction

Metal ion doping in oxide spinels induces dopant ion size dependent changes in the magnetic character, site preference energy and bonding. The substitution of Zn and Cd in inverse spinels are extensively studied [1–3]. In addition to these, the substitution of multivalent cations have been carried out [4–7]. Soft ferrites consist of M–D, S–D and S–P type of domains, which decide the magnetic character. The domain structure of ferrites is found to alter on substitution. The substitution of Zn in $CuFe_2O_4$ changes domain structure from S–D to M–D [7]. Murty *et al* have used susceptibility study with temperature to understand the effect of substitution on magnetic behaviour [8,9]. The relation of grain size with domain

structure have been reported in literature [7,10]. Structural deformations, changes in bond lengths and force constants on doping in the ferrites can also be studied by IR spectroscopy [11]. In the present communication, we are reporting our IR spectroscopic and a.c. susceptibility study of Gd^{3+} substituted Cu–Cd ferrites.

2. Experimental

The ferrite samples of $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) for y = 0.0 and 10.1 are prepared by standard ceramic technique. The starting materials used were the A–R grade Fe_2O_3, Gd_2O_3, $CdCO_3$, and CuO. The calcination is carried out at 975°C for fortyeight hours in two cycles. All the samples are slow cooled. The characterisation is done by X-ray using filtered CuK_α radiations. The infrared absorption study is done by using computerised Perkin-Elmer (Model 783, resolution ± 2 cm^{-1}) IR spectrophotometer in the frequency range 200 cm to 800 cm^{-1} by KBr pellet technique. The chemical analysis of the constituent elements is carried out by using computerised Perkin-Elmer (Model 1301) Atomic Absorption Spectrophotometer. The measurement of initial susceptibility with temperature, in the range of 290 K to 713 K are carried out at a field of 5.0 Oe by double coil set up [12] and scanning electron microscopy is done using scanning electron microscope STEREOSCAN. (Model 250 MK3 Cambridge Instruments) in reflection mode.
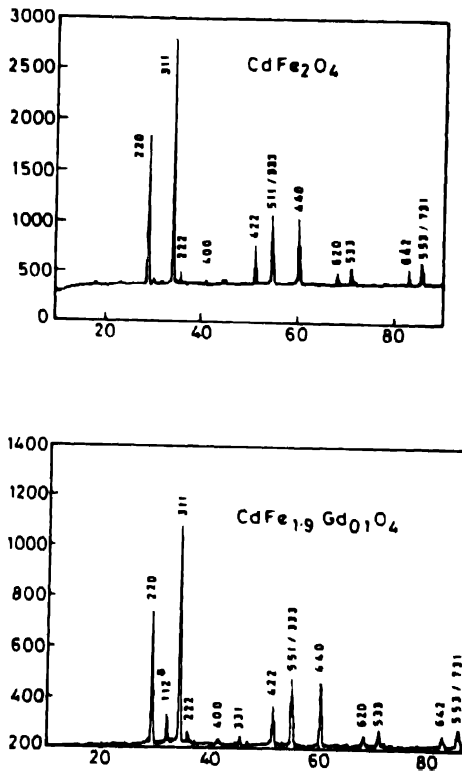

Figure 1. Typical X-ray diffractograms of polycrystalline powder samples.

3. Results and discussions

X-ray diffractograms of powder samples show that the compositions $x \geq 0.2$ for $y = 0.0$ and 0.1 are cubic spinels, while $x = 0.0$ for $y = 0.0$ and 0.1 are tetragonally distorted spinels with $c/a > 1$. The diffractograms of $y = 0.0$ compositions show allowed reflection peaks of *fcc* spinels for all the values of x. However, the compositions with $y = 0.1$ show an extra reflection of low intensity on lower angle side off (311) plane. Typical diffractograms of the compositions of $x = 1.0$ for $y = 0.0$ and 0.1 are presented in Figure 1. This reflection was identified as due to Gadolinium-iron oxide (GeFeO$_3$) phase of orthorhombic character (A.S.T.M. 15-198). The orthorhombic distortions in copper containing ferrites have been reported in literature [6,7]. In the present case, phase formation may be due to high reactivity of iron with Gadolinium at elevated temperature.

The calculation of lattice constant a and c is carried out at each reflection by comparing observed and calculated d spacings and allowed Miller indices (hkl) for cubic and tetragonal spinels. The lattice constant thus calculated for each plane are plotted against corresponding $(\cos2\theta /\sin\theta + \cos2\theta/\theta)$ of these reflections to cover information at higher angles. The straight line relation is obtained which can be extrapolated to intersect the a axis at $\theta = 90$.

Table 1. Lattice constant and cation distribution of Cd$_x$Cu$_{1-x}$Fe$_{2-y}$Gd$_y$O$_4$ (for $y = 0\,0$ and 0.1)

Composition		Lattice Constant (nm)	Cation distribution
x	y		
0 0	0 0	$a = 0\,825$ $c = 0\,870$	(Cu$_{19}$ Fe$_{81}$) [Cu$_{81}$ Fe$_{119}$] O$_4$
0.0	0.1	$a = 0.826$ $c = 0\,857$	(Cu$_{47}$ Fe$_{53}$) [Cu$_{53}$ Gd$_1$ Fe$_{137}$] O$_4$
0.2	0 0	$a = 0\,847$	(Cd$_2$ Cu$_{32}$ Fe$_{48}$) [Cu$_{48}$ Fe$_{152}$] O$_4$
0.2	0.1	$a = 0\,846$	(Cd$_2$ Cu$_{44}$ Fe$_{36}$) [Cu$_{36}$ Gd$_1$ Fe$_{154}$] O$_4$
0 4	0.0	$a = 0.853$	(Cd$_4$ Cu$_{17}$ Fe$_{43}$) [Cu$_{43}$ Fe$_{157}$] O$_4$
0.4	0 1	$a = 0\,851$	(Cu$_4$ Cu$_{21}$ Fe$_{39}$) [Cu$_{39}$ Gd$_1$ Fe$_{151}$] O$_4$
0 6	0.0	$a = 0.857$	(Cd$_6$ Cu$_{08}$ Fe$_{32}$) [Cu$_{32}$ Fe$_{168}$] O$_4$
0 6	0.1	$a = 0.856$	(Cd$_6$ Fe$_4$) [Cu$_4$ Fe$_{15}$ Gd$_1$] O$_4$
0 6	0 1	$a = 0.856$	(Cd$_6$ Fe$_4$) [Cu$_4$ Fe$_{15}$ Gd$_1$] O$_4$
0.8	0 0	$a = 0\,864$	(Cd$_8$ Fe$_2$) [Cu$_2$ Fe$_{18}$] O$_4$
0 8	0.1	$a = 0.863$	(Cd$_8$ Fe$_2$) [Cu$_2$ Gd$_1$ Fe$_{17}$] O$_4$
1.0	0.0	$a = 0\,869$	(Cd$_1$) [Fe$_2$] O$_4$
1.0	0.1	$a = 0.869$	(Cd$_1$) [Fe$_2$ Gd$_1$] O$_4$

The values of lattice constant thus obtained are presented in Table 1. The graph of lattice parameter a and c against cadmium content is as shown in Figure 2.

The variation of lattice parameter with the cadmium content obeys Vegard's law for $x \geq 0.2$. However, this behaviour is not observed for the compositions $x = 0.0$ to $x = 0.2$ due tetragonal distortions in cubic spinel where c/a is greater than unity. No appreciable change
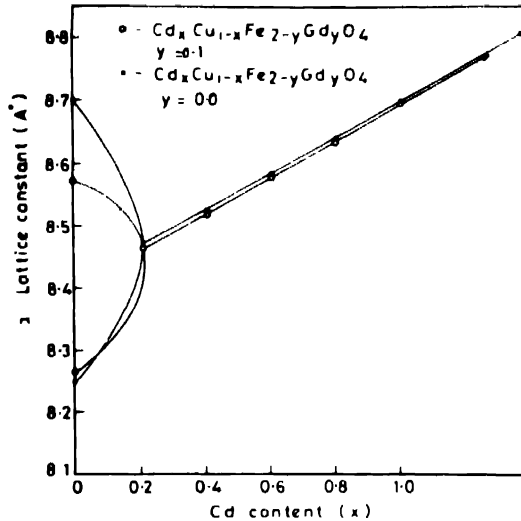

Figure 2. Dependence of lattice constants (a) and (c) on Cd-content (x) of the system $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.0$ and 0 1

in the value of lattice constant is observed on substitution of Gd^{3+}. However, the c/a ratio is found to be lowered on substitution of Gd^{3+}. It may be due to migration of Cu^{2+} to A site on substitution thereby decreasing the number of Cu^{2+} ions on B site which lowers the Jahn-Teller co-operative distortions [13]. This was also confirmed from our study [14] and can be seen from the cation distribution presented in Table 1.

The far infrared absorption spectra of all the samples show two strong absorption bands in the frequency range of 405 cm^{-1} to 605 cm^{-1} which are the characteristic bands of spinel structure [11,15]. From the IR absorption spectra we have measured the centre frequency of each band and used to calculate the force constants. The force constant K_t (tetrahedral) and K_o (octahedral) are calculated by the method of Waldron [11]. The calculations of bond lengths R_A (tetrahedral metal-oxygen) and R_B (octahedral metal-oxygen) are calculated by using the value of oxygen ion parameter, $u = 0.389$ for CdFe$_2$O$_4$ [16], $u = 0.380$ for CuFe$_2$O$_4$ [17] and observed value of lattice constant (a). The bond length R_A is less than R_B in all the compositions for $y = 0.0$ and 0.1 except for CdFe$_{2-y}$Gd$_y$O$_4$ ($y = 0.0$ and 0.1) which is in conformity with the previous workers [18].

The plots of force constant K_t and K_o against bond length R_A and R_B respectively for $y = 0.0$ and 0.1 are given in Figure 3. The force constant K_t is found to be greater than K_o which is rather expected because bond lengths R_B are greater than R_A except $x = 1.0$ for $y = 0.0$ and 0.1. However, increase of R_A with content of Cd^{2+} upto $x = 0.4$ shows increasing trend of force constant K_t since we expect the decrease of force constant with increase of

bond lengths. This behaviour is similar to oxides of metal with $26 \geq z \leq 29$ [19] and can be attributed to formation of strong bonds by oxygen in favourable conditions. The variation in the values of force constant K_o with R_B is small, because R_B is found to be almost constant in
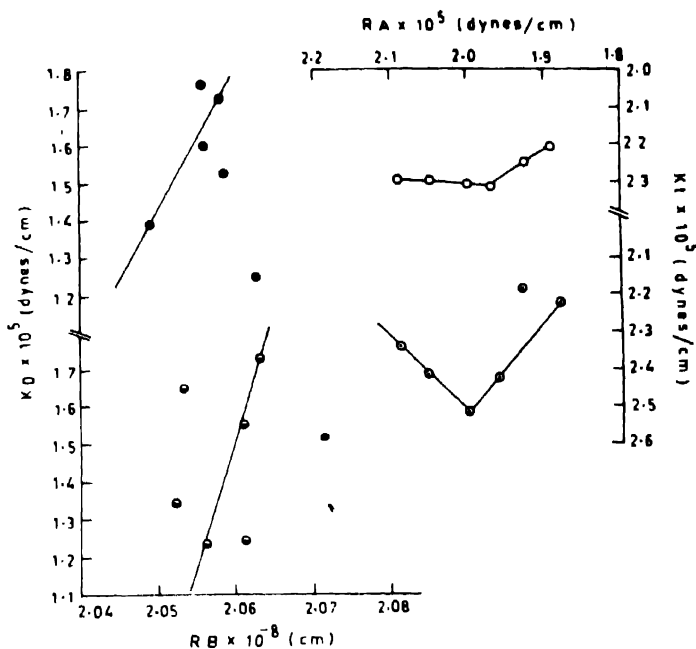

Figure 3. The plots of force constant K_t and K_o against bondlengths R_A and R_B of the system $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ for $y = 0.0$ and 0.1. Symbols : R_A Vs K_t $\circ$ $Y = 0.0$, R_A Vs K_t $\ominus$ $Y = 0.1$; R_B Vs K_0 $\ominus$ $Y = 0.0$; R_B Vs K_0 $\bullet$ $Y = 0.1$.

all the samples. This may be because of substitution of Cd^{2+} in $CuFe_2O_4$ occupies tetrahedral A site thereby replacing Fe^{3+} from A site to B site. Which is having comparable ionic size with Cu^{2+} and Fe^{3+} already sitting on B site. Therefore, R_B might be remaining almost unchanged. The values of R_A and R_B in copper rich ferrites are lower than cadmium rich ferrites because of the fact that $CuFe_2O_4$ is strong in covalent character. The decrease in bond-lengths corresponds to increase of covalent character [20].

On the substitution of Gd^{3+} it is observed that the bond lengths are slightly lowered so also the lattice constant and R_A, R_B while the force constants are increased. This may be due to the fact that ratio of ionic radius of (Gd^{3+}) to the ionic radius of oxygen (O_2^-) is greater than 0.73 therefore, Gd^{3+} requires eight fold coordination. In a spinel structure therefore, Gd^{3+} takes the positions of centre of the cube and thus distorts the tetrahedral and octahedral oxygen symmetry thereby affecting the lattice constant R_A, R_B the force constants and the centre frequency of the absorption bands.

The plots of bond-lengths and force constant are not exactly the straight lines as expected. It may be because of uneven distruction of Cu^{2+}, Jahn-Teller ion on A and B sites

of spinel structure, which can be immediately seen from the cation distribution proposed. The cation distribution proposed is presented in Table 1. The IR spectrum within the experimental range of frequencies and conditions do not show any band splitting thereby ruling out the possibility of presence of multivalence states of cations present in the system. However, some band broadening takes place on substitution which may be attributed to occupancy of cations with different character and valency, occupying the same site and the cation distribution presented in Table 1 supports this.

The chemical analysis by atomic absorption technique shows the presence of substituent cations in stoichiometric weight proportions. The microstructural aspects of the system are studied by scanning electron microscopy from which we have measured grain size and presented in Table 2. The grain size in cadmium and copper rich ferrites is higher than intermediate compositions. On substitution of Gd^{3+} the grain size is found to be reduced. Curie temperatures (T_c) are measured by Loroia and Sinha method [21] and are presented in Table 2, and also the T_c values from the susceptibility measurements $(T_c$ susceptibility). The values of calculated T_c from cation distribution proposed and blocking temperature T_B are also presented in Table 2.

Table 2. Curie temperature (T_c), blocking temperature (T_B), domain structure, and grain size data of $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ for $(y = 0\ 0$ and $0\ 1)$ ferrite system.

| Composition | | T_c | | | T_B | Domain | H_c | Grain |
| x | y | susceptibility K | Expt K | Cal K | K | structure | (Guass) | size (μm) |
		± 5K	± 5K	± 5K	± 5			
0.0	0 0	736	744	736	515	S–D	384 3	1 7294
0 0	0.1	710	739	665	410	S–D	700 28	0.8622
0.2	0.0	608	635	609	520	M–D	–	2 5297
0 2	0 1	576	625	522	500	M–D–S–D	–	1.2331
0 4	0 0	509	556	508	460	M–D	–	1.5225
0.4	0 1	467	507	445	423	M–D	–	1.0473
0 6	0.0	386	383	385	322	M–D	–	4.8296
0.6	0.1	367	330	393	318	M–D	–	0.8911

The plots of temperature dependence of normalised susceptibility (χ/χ_{RT}) are presented in Figures 4(a) and 4(b). The samples $x \geq 0.8$ are paramagnetic at and above 300 K therefore, the data of these compounds are not reported. From Figure 4(a) it can be seen that for compositions $x \geq 0.2 \leq 0.6$ for $y = 0.0$ and 0.1 the normalised susceptibility is independent of temperature up to blocking temperature T_B and beyond this it decreases sharply and reaches zero at Curie temperature (T_c). The sharp decrease of normalised susceptibility beyond T_B confirms the formation of homogeneous single phase compounds

[3]. The normalised susceptibility of $x = 0.0$ and $y = 0.0$ and 0.1 of as shown in Figure 4(b) is independent of temperature up to blocking temperature T_B and beyond it, it increases with
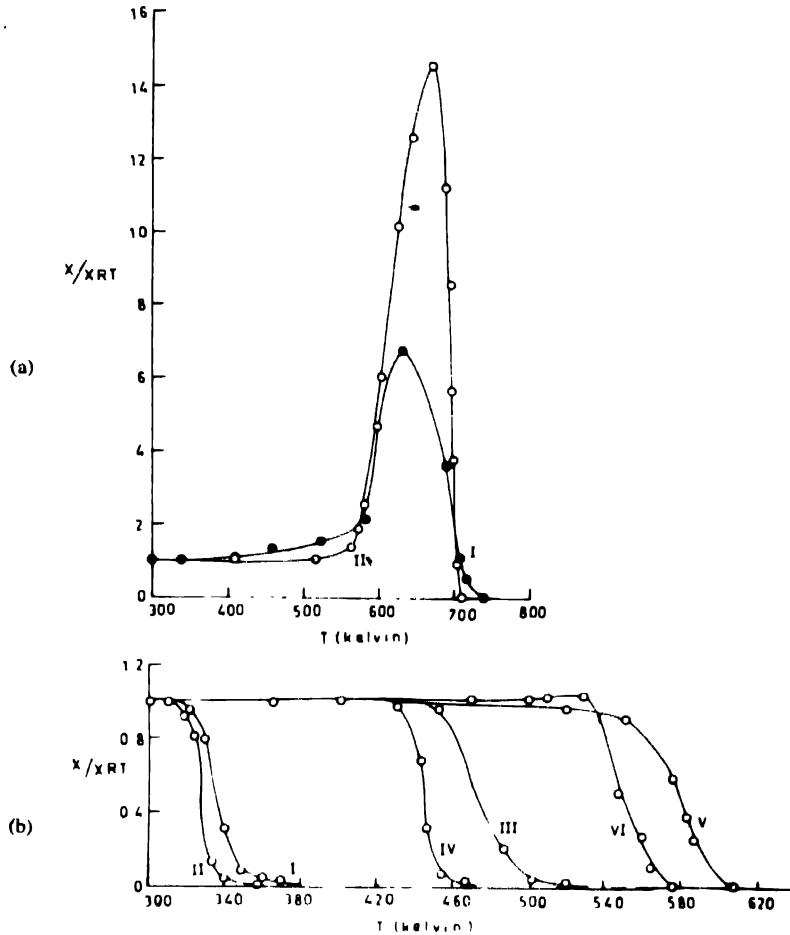

Figure 4. Temperature dependence of normalised susceptibility of $Cd_xCu_{1-x}Fe_{2-y}Gd_yO_4$ system Symbols . I ● $x = 0$, $y = 0$ 0; II ○ $x = 0$, $y = 0$ 1, (b) Symbols   I $x = 0$ 6, $y = 0$ 0, II $x = 0$ 6, $y = 0.1$, III $x = 0.4$, $y = 0$ 0, IV $x = 0.4$, $y = 0$ 1, V $x = 0.2$, $y = 0$ 0, VI $x = 0$ 2, $y = 0.1$

temperature and then decreases sharply and reaches zero at Curie temperature. The composition $x = 0.2$ for $y = 0.1$ also shows marginal increase in normalised susceptibility beyond T_B.

The dependence of normalised susceptibility on temperature is mainly decided by the nature of domains and the structure of the materials. If the normalised susceptibility is independent of temperature upto T_B and sharp decrease beyond T_B shows presence of Multi-Domain (M–D) particles in the compounds [3,10]. The compositions $x \geq 0.2 \leq 0.6$ for $y =$

0.0 and 0.1 show the presence of M–D particles while a sharp rise in normalised susceptibility of $x = 0.0$ for $y = 0.0$ and 0.1 beyond T_B and below T_c shows presence of Single-Domain (S–D) particles. The peak in the normalised susceptibility is attributed to S–D to S–P (Super Paramagnetic) transitions. The similar behaviour is observed for Cu–Zn ferrite [3] and Co–Ge ferrites [10].

The substitution of Cd in the lattice of $CuFe_2O_4$ for $x \geq 0.2$ changes S–D to M–D particles similar to Cu–Zn [3]. However, the substitution of Gd^{3+} enhances the S–D behaviour of copper ferrites presence of S–P particles in the system show high coercive force (H_c) which has its origin in the presence of anisotropy in these compounds [10]. The values of grain diameters obtained from SEM analysis are presented in Table 2, which supports the high values of H_c for the compositions $x = 0.0$ for $y = 0.0$ and 0.1.

Substitution of Gd in Cu–Cd ferrites thus changes M–D to S–D type in copper rich compositions, increases the coercive force and lowers the Curie temperatures (T_c) and the magnetic character of the material in general.

Acknowledgment

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