

Novel Existence of canted Spins on Octahedral Sites of $Cd_xMg_{1-x}Fe_2O_4$ Ferrites as a Third Active Mode of Vibrations

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Abstract: Polycrystalline ferrites $Cd_xMg_{1-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6$ and 1.0) were prepared by standard ceramic technique and characterized by X-ray, SEM, IR absorption and Mössbauer technique. X-ray analysis shows that the samples have single-phase cubic spinel structure. SEM study revealed that all ferrite samples are crack-free having well packed continuous grain structure with well defined grain boundaries. Two distinct absorption bands ν_1 and ν_2 in $MgFe_2O_4$ arising from intrinsic vibrations on tetrahedral A-site and octahedral B-site is observed. Addition of Cd^{2+} in the host lattice resembles the shifting of & broadening of ν_2 up to $x=0.4$, While for $x \geq 0.6$ third active mode of vibration ν_3 in the frequency range 335 cm^{-1} to 340 cm^{-1} , well separated from ν_2 , is clearly observed. Saturation magnetization was determined for obtaining information about the Yaffet-Kittle angles at 300 K. The variation of n_B with Cd^{2+} content suggested the existence of predominating Y-K model for $x \geq 0.6$, while Neel's two Sub-lattice models applicable up to $x \leq 0.4$. The canting of spins explains the fundamental third active mode of vibrations in Mg-Cd ferrites satisfactorily.

Keywords: Ferrites; IR Spectra; Vibrational mode; Magnetization; Canted spins; Y-K angles.

1. Introduction

Magnesium is often an ingredient in commercial soft ferrites [1]. The Substitution of Zn^{2+} and Cd^{2+} in such inverse spinels are extensively studied [2-7] and studies of aluminium substitution in copper, cobalt and mixed ferrite [8]. The electric and magnetic properties of the ferrites are strongly dependent on their physical structure. In particular, the far-infrared spectra of the ferrite can give the informational not only about the position of the ion in the crystal but also the vibrational mode [9]. In certain mixed ferrites, increasing content of divalent metal ion gives rise to structural changes within the lattice without affecting the spinel structure of the ferrite as a whole. The far-infrared spectral study has proved to be useful and effective tool in the investigation of structural properties of the mixed ferrite. The structural, electrical properties of copper and cobalt ferrite are studied by researchers [10-13]. In the present communication the data on magnetization and IR results are reported.

2. Experimental

Stoichiometric polycrystalline ferrites of the system $Cd_xMg_{1-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6$ and 1.0) was prepared with AR grade Fe_2O_3 , $CdCO_3$ and MgO by standard ceramic method. The samples were sintered at 1000°C for 48 hr. The slow cooled powder samples were characterized by X-ray diffraction technique. Scanning Electron Microscopy of the fractured surface of the ferrite pellet samples was done. The saturation magnetization measurements for all ferrites samples were carried out at 300 K using the high field loop tracer described elsewhere [14]. Infrared absorption spectra were carried out on IR spectrometer computerized Perkin-Elmer model 783 by K-Br window.

3. Results and Discussion

Powder X-ray diffractometry reveals the single-phase cubic spinel structure of the ferrites and well-defined reflection are observed without any ambiguity. The variation of the lattice constants with Cd^{2+} obeys Vegard's law (Fig.1), which suggests that the substituted Cd^{2+} ion preferentially occupies on tetrahedral (A) site. X-ray data obtained is verified from International data of the Inorganic phases (ASTM-22-1063 for $CdFe_2O_4$ and ASTM-17-465 for $MgFe_2O_4$), and found it in close agreement. Scanning electron microscope studies reveal that all ferrites sample have crack-free and well-packed continuous grain structure with well-defined grain boundaries shown in fig.2. Average grain size of sample is estimated and presented in table 1.

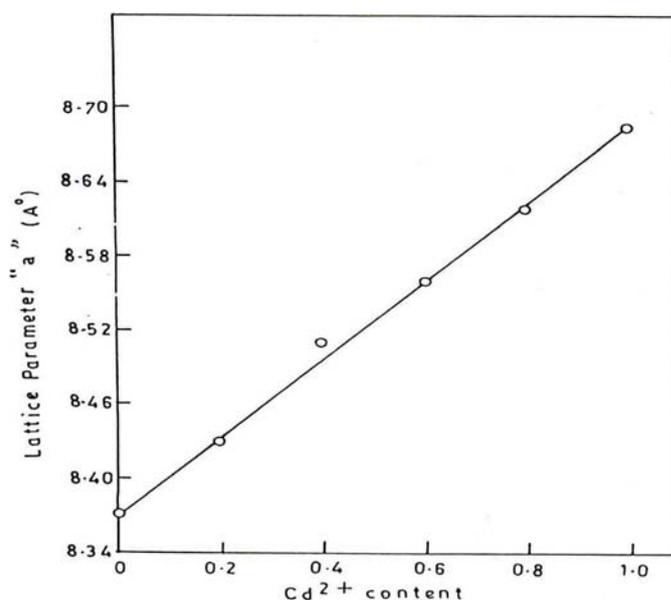


Figure 1: Variation of lattice constant with Cd^{2+} content

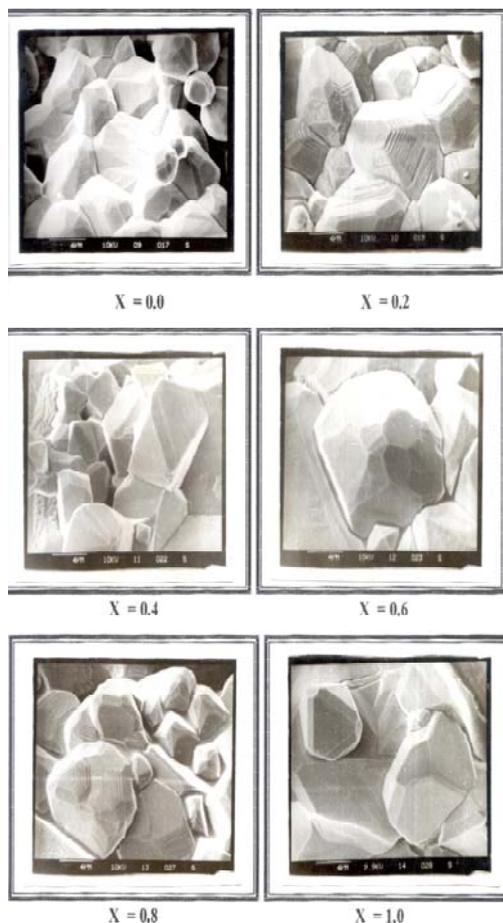


Figure 2: SEM of Cd_xMg_{1-x}Fe₂O₄ Ferrite System

The saturation magnetization per formula unit in the Bohr Magneton (n_B) are calculated and presented in table 2. However MgFe₂O₄ is almost inverse spinel [15], Cu²⁺, Co²⁺ Cd²⁺ preferentially occupies tetrahedral (A) site [16-18]. The Cation distribution in all the ferrites is estimated and presented in the table 2. From figure 3, the n_B variation with Cd²⁺ content evidently suggest the existence of canted spins in Mg-Cd ferrite which is in accordance with the previous report [19, 20]. Y-K angles have been calculated from formula, $n_B = M_B \cos \alpha_{YK} - M_A$ discussed elsewhere [21] and presented in table 2. Niessen [22] non co-linear model was applied to calculate resultant on B sub-lattice. B sub-lattice splits into two sub-lattice B₁ and B₂ having magnetic moments and making an angle α_{YK} with their resultant ($2 \alpha_{YK}$ being the angle between the moments on B₁ and B₂). Resultant on B sub-lattice is calculated as,

$$B = \sqrt{[B_1^2 + B_2^2 + 2 B_1 B_2 \cos(\alpha_{YK})]}$$

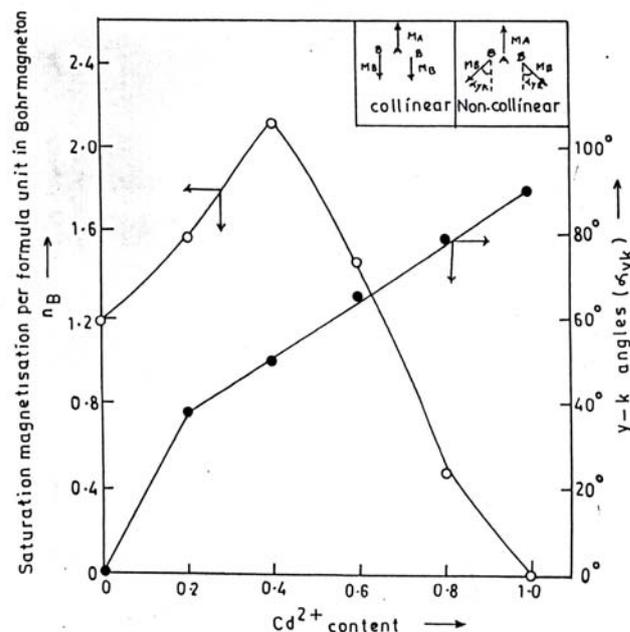


Fig. 3 Dependence of saturation magnetisation per formula unit in Bohr magneton (n_B) with Cd²⁺ content in MgCd Ferrite system.

IR absorption spectra show two distinct absorption bands ν_1 at 585cm⁻¹ and ν_2 at 420cm⁻¹ for MgFe₂O₄. This result closely agrees with previous report [23]. A close inspection of fig.4 shows that the absorption band ν_1 is shifted towards lower frequency side & ν_2 becomes broad. The broadening of ν_2 band is found to increase with increase of Cd²⁺ contents up to X= 0.4, while a third band ν_3 in the frequency range 335 cm⁻¹ to 380 cm⁻¹, well separated from ν_2 band is clearly observed for X ≥ 0.6. Replacements of Fe³⁺ by Cd²⁺ on tetrahedral site gives rise the shifting of ν_1 band towards lower frequency side in accordance with theoretical prediction [24]. Reddy et al [25] have reported the shifting of the band towards higher frequency side due to replacements of Mn²⁺ by lighter weight Mg²⁺. In our case as the Cd²⁺ ion is higher in weight than Fe³⁺ ion, therefore a shift toward lower frequency side could be expected and the results in good agreement. Braber et al [26] have been reported the splitting of band near 700cm⁻¹ in Mn_xFe_{3-x}O₄ ferrites. Naik [27] and Sagare [28] have observed the splitting around 600cm⁻¹ in Li-Cu and Li-Cd ferrites respectively. Dallal et al [29] in 1990 have Predicted that shoulder splitting could be observed due to presence of John-Teller ion. V.R.K. Murty et al [30] have reported ν_3 band in Ni-Zn ferrite and variation of band position was ascribed to change in Fe-O bond distance in two crystal lattices. Josyulu et al [31] have reported ν_3 band in Co-Zn ferrites and from intensity variation it was assigned due to divalent metal oxygen complex. K.V.S. Badarinath has observed the third band very close to ν_2 in Al³⁺ substitute MgFe₂O₄ ferrite and assigned due to trivalent octahedral substitution. Increase in intensity was reported due to increasing Al³⁺ content in MgAl_{2x} Fe_{2-2x} O₄ ferrite Kunal Modi et al [32] reported the existence of local canted spins in Al³⁺ substituted magnesium ferrite. It has been noticed by Tarate [33] that, the nature of intrinsic vibrations of tetrahedral group and

octahedral sites and to smaller extent on the tetrahedral voids in the spinal structure. The addition of Cd^{2+} ions in the sample up to $X = 0.4$ increases the $Y - K$ angles so also the broadening of the ν_2 band. However when $X > 0.4$ with increasing angle (α_{YK}) and ν_3 band as separate identity in close vicinity of the ν_2 band.

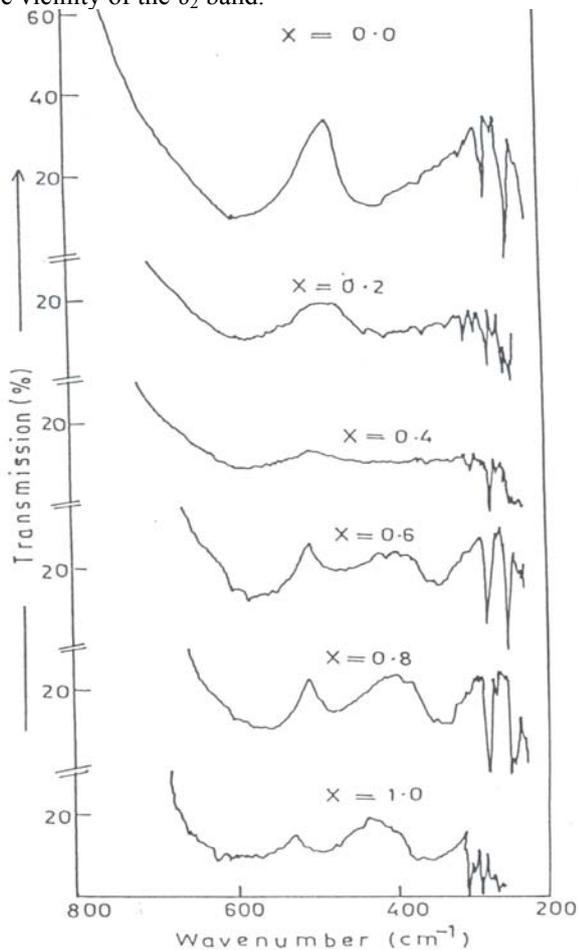


Figure 4: IR Spectrum of $\text{Cd}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system

4. Conclusions

Third fundamental active mode of vibrations ν_3 band observed in Mg-Cd ferrite is assigned due to canted spins where Y-K three Sub-lattice model Predominating. Absent of ν_4 band suggests the lattice vibrations under experimental conditions are insignificant.

5. Acknowledgement

One of the Author (B.R.K) is thankful to U.G.C., New Delhi for the award of fellowship for Ph .D course as a teacher fellow.

6. Future Scope

Micro-structure of ferrites depends up on preparation technique. There is a scope to reduce the particle size by adopting a preparation technique like wet chemical precipitation method, sol-gel method etc and see the interesting further results for electrical and magnetic properties.

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Author Profile



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Table 1: Structural and IR data of Cd_xMg_{1-x}Fe₂O₄ mixed ferrites

Cadmium Content (x)	Lattice Constant a A ⁰	X-ray Density D _x gm/cm ³	Average Grain size D μm.	Fundamental Active Mode Of Vibrations		
				v ₁ cm ⁻¹	v ₂ cm ⁻¹	v ₃ cm ⁻¹
0.0	8.372	4.527	3.98	585	420	---
0.2	8.430	4.825	4.00	580	410	---
0.4	8.512	5.066	4.38	575	410	---
0.6	8.560	5.355	5.23	570	480	350
0.8	8.618	5.613	6.22	565	482	350
1.0	8.682	5.847	9.62	595	495	350

Table 2: Cation Distribution and magnetization data Cd_xMg_{1-x}Fe₂O₄ Ferrite System

Cd Cont. (x)	Cation Distribution	Magnetisa-tion σ emu/gm	M _s (Gauss)	n _B Bohr Magneton
0.0	Cd ₀ Mg _{0.1183} Fe _{0.8817} ^A [Mg _{0.8817} Fe _{1.1183}] ^B O ₄	33.01	112.8	1.1425
0.2	Cd ₂ Mg _{0.0946} Fe _{0.7054} ^A [Mg _{0.7054} Fe _{1.2946}] ^B O ₄	40.54	149.5	1.5772
0.4	Cd ₄ Mg _{0.0710} Fe _{0.5290} ^A [Mg _{0.5290} Fe _{1.4210}] ^B O ₄	50.12	198.8	2.1118
0.6	Cd ₆ Mg _{0.0473} Fe _{0.3527} ^A [Mg _{0.3527} Fe _{1.6763}] ^B O ₄	32.68	164.2	1.4801
0.8	Cd ₈ Mg _{0.0237} Fe _{0.1763} ^A [Mg _{0.1763} Fe _{1.8237}] ^B O ₄	9.80	51.2	0.4749
1.0	Cd ₁ Mg _{0.0000} Fe _{0.0000} ^A [Mg _{0.0000} Fe _{2.0000}] ^B O ₄	0.00	0.00	0.0000