Novel Existence of canted Spins on Octahedral Sites of Cd\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) Ferrites as a Third Active Mode of Vibrations

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Abstract: Polycrystalline ferrites Cd\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) (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 MOssbauer 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 \(\nu_1\) and \(\nu_2\) in MgFe\(_2\)O\(_4\) 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 \(\nu_2\) up to x =0.4, While for x \(\geq\) 0.6 third active mode of vibration \(\nu_3\) in the frequency range 335 cm\(^{-1}\) to 340 cm\(^{-1}\), well separated from \(\nu_2\), 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\(_x\)Mg\(_{1-x}\)Fe\(_2\)O\(_4\) (x = 0.0, 0.2, 0.4, 0.6 and 1.0) was prepared with AR grade Fe\(_2\)O\(_3\), 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\(_2\)O\(_4\) and ASTM-17-465 for MgFe\(_2\)O\(_4\)), and found it in close agreement. Scanning electron microscopic 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.
The saturation magnetization per formula unit in the Bohr Magneton (nB) 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. From figure 3, the nB 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, nB = 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 \( \alpha_{YK} \) with their resultant (2 \( \alpha_{YK} \) being the angle between the moments on B₁ and B₂). Resultant on B sub-lattice is calculated as,

\[
B = \sqrt{B_1^2 + B_2^2 + 2B_1B_2 \cos (\alpha_{YK})}
\]

IR absorption spectra show two distinct absorption bands \( \nu_1 \) at 585 cm⁻¹ and \( \nu_2 \) at 420 cm⁻¹ for MgFe₂O₄. This result closely agrees with previous report [23]. A close inspection of fig. 4 shows that the absorption band \( \nu_1 \) is shifted towards lower frequency side & \( \nu_2 \) becomes broad. The broadening of \( \nu_2 \) band is found to increase with increase of Cd²⁺ contents up to \( X = 0.4 \), while a third band \( \nu_3 \) in the frequency range 335 cm⁻¹ to 380 cm⁻¹, well separated from \( \nu_2 \) band is clearly observed for \( X \geq 0.6 \). Replacements of Fe³⁺ by Cd²⁺ on tetrahedral site gives rise the shifting of \( \nu_1 \) 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. Brabet et al [26] have been reported the splitting of band near 700 cm⁻¹ in MnₓFe₃₋ₓO₄ ferrites. Naik [27] and Sagare [28] have observed the splitting around 600 cm⁻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 \( \nu_1 \) 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 \( \nu_3 \) 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 \( \nu_1 \) in Al³⁺ substitute MgFe₂O₄ ferrite and assigned due to trivalent octahedral substitution. Increase in intensity was reported due to increasing Al³⁺ content in MgAl₂ₓFe₂₋₂ₓO₄ 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 $\upsilon_2$ band. However when $X > 0.4$ with increasing angle ($\alpha_{YK}$) and $\upsilon_3$ band as separate identity in close vicinity of the $\upsilon_2$ band.

Figure 4: IR Spectrum of CdxMg$_{1-x}$Fe$_2$O$_4$ ferrite system

4. Conclusions

Third fundamental active mode of vibrations $\upsilon_3$ band observed in Mg-Cd ferrite is assigned due to canted spins where Y-K three Sub-lattice model Predominating. Absent of $\upsilon_4$ 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.

References


**Author Profile**

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| Table 1: Structural and IR data of Cd$_{x}$Mg$_{1-x}$Fe$_2$O$_4$ mixed ferrites |
|----------------------------------|---------------|-----------------|-----------------|-----------------|
| Cadmium Content (x)             | Lattice Constant a ($\text{Å}$) | X-ray Density $D_{X}$ ($\text{gm/cm}^2$) | Average Grain size $D$ ($\mu$m) | Fundamental Active Mode Of Vibrations $\nu$ |
| 0.0                             | 8.372         | 4.527           | 3.98            | 585 $\nu_1$ cm$^{-1}$, 420 $\nu_2$ cm$^{-1}$, 408 $\nu_3$ cm$^{-1}$ |
| 0.2                             | 8.430         | 4.825           | 4.00            | 580 $\nu_1$ cm$^{-1}$, 410 $\nu_2$ cm$^{-1}$, 405 $\nu_3$ cm$^{-1}$ |
| 0.4                             | 8.512         | 5.066           | 4.38            | 575 $\nu_1$ cm$^{-1}$, 415 $\nu_2$ cm$^{-1}$, 400 $\nu_3$ cm$^{-1}$ |
| 0.6                             | 8.580         | 5.355           | 4.23            | 570 $\nu_1$ cm$^{-1}$, 430 $\nu_2$ cm$^{-1}$, 350 $\nu_3$ cm$^{-1}$ |
| 0.8                             | 8.618         | 5.613           | 6.22            | 565 $\nu_1$ cm$^{-1}$, 480 $\nu_2$ cm$^{-1}$, 350 $\nu_3$ cm$^{-1}$ |
| 1.0                             | 8.682         | 5.847           | 9.62            | 595 $\nu_1$ cm$^{-1}$, 495 $\nu_2$ cm$^{-1}$, 350 $\nu_3$ cm$^{-1}$ |

| Table 2: Cation Distribution and magnetization data Cd$_{x}$Mg$_{1-x}$Fe$_2$O$_4$ Ferrite System |
|----------------------------------|---------------|-----------------|-----------------|-----------------|
| Cd Cont. (x)                     | Cation Distribution | Magnetisation $\sigma$ emu/gm | $M_s$ (Gauss) | Bohr Magneton $\mu_B$ |
| 0.0                             | Cd$_{0.1183}$Fe$_{0.8817}$O$_4$ | 33.01 | 112.8 | 1.1425 |
| 0.2                             | Cd$_{0.0946}$Fe$_{0.7054}$O$_4$ | 40.54 | 149.5 | 1.5772 |
| 0.4                             | Cd$_{0.0710}$Fe$_{0.5290}$O$_4$ | 50.12 | 198.8 | 2.1118 |
| 0.6                             | Cd$_{0.0473}$Fe$_{0.3527}$O$_4$ | 32.68 | 164.2 | 1.4801 |
| 0.8                             | Cd$_{0.0237}$Fe$_{0.1763}$O$_4$ | 9.80  | 51.2  | 0.4749 |
| 1.0                             | Cd$_{0.0000}$Fe$_{2.0000}$O$_4$ | 0.00  | 0.00  | 0.0000 |