X-ray, IR and SEM studies on some Li-Cd ferrites

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Abstract:

Lithium-Cadmium ferrites with general formula $\text{Li}_{0.5-x/2} \text{Fe}_{2.5-x/2} \text{Cd}_x \text{O}_4$ (with $x = 0, 0.1, 0.2, \dots, 0.7$) were prepared by standard ceramic method. X-ray diffraction studies confirms single phase formation and lattice parameters were calculated. The crystal structure is cubic and lattice parameter increases with increasing Cd content. The infrared absorption (IR) spectra of all the samples were recorded in the range $200\text{-}800\text{ cm}^{-1}$ at room temperature in the KBr medium. Lithium ferrite shows four principal bands and some shoulders have been observed. The force constants K_t and K_o were calculated using Waldron's analysis. Scanning electron microscopy studies shows increase in grain size up to $x = 0.1$ and then the grain size decreases with increase in cadmium content.

Keywords: Ceramic oxides, Ferrites, Lithium ferrites

1. Introduction

Ferrites are interesting and technological important materials that have been extensively studied and used for decades [1]. The use of ferrites has very well been established in many branches of telecommunications and electronics engineering embracing a very wide diversity of composition, properties and applications [2]. Hoffman reported that Lithium (Li) ferrite is magnetic with a spinel crystal structure [3]. Li ferrite possesses high curie temperature of about 650°C , high electrical resistivity [4], a square loop hysteresis [5]. Substitutions in Li ferrites makes materials suitable for the requirement of microwave devices [6].

2. Preparation and Characterization

The standard ceramic method was used for the ferrite samples with general formula $\text{Li}_{0.5-x/2}\text{Fe}_{2.5-x/2}\text{Cd}_x\text{O}_4$ where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ and 0.7 using high purity AR grade Li_2CO_3 , CdO and Fe_2O_3 . These powders were weighed in the required mole proportions on a semimicro balance having least count of 0.001mg and were mixed thoroughly in an agate mortar in acetone medium. This powder was presintered at 700°C for 10 hours in a glow bar furnace in air medium. Then the furnace was cooled slowly. The presintered powder was then ground in an agate mortar in acetone medium. The fine powder of the resultant ferrites was obtained by sieving them through a 100-micron mesh. The mixture was then compressed in the form of pellets by using a die of 1 cm . diameter and by applying a pressure of about 7 to 8 tonnes per square inch for 2 minutes. To reduce the lithium loss the samples were fired at 950°C for 20 hours in air medium. The samples were furnace cooled.

For x-ray diffraction and IR absorption studies, the pellets were again grounded and sieved powder was used.

3. X-ray diffraction studies

In our case diffraction patterns were recorded by using Philips PW-1710 diffractometer with $\text{CuK}\alpha$ radiation with wavelength $\lambda = 1.5418\text{ \AA}$. All the samples were scanned within the range 2θ between 15° to 85° . The diffractograms were indexed in the light of the crystal

structure of a natural spinel MgAl_2O_4 by taking prominent line corresponding to (311) plane. The diffraction pattern of the sample with $x = 0.1$ is shown in figure 1. The Table 1 shows values of the lattice parameter for different values of 'x'. All the sample shows cubic spinel structure. The observed and calculated 'd' values are in good agreement for all indexed planes. For Li- ferrite the value of lattice parameter has been confirmed to be $8.33 \text{ \AA}$ by many workers [7,8]. Our value of lattice parameter viz. $a = 8.324 \text{ \AA}$ in case of Li- ferrite agrees well with these reported values. Figure 2 shows the variation of the lattice constant with cadmium content in the sample. The lattice parameter increases linearly with the increasing Cd content obeying the Vegard's law. This increase in lattice parameter is explained on the basis of cation distribution and size difference of component ions.

The cation distribution of Li ferrite having inverse spinel structure is given by

West and Blankenship have shown that when a nonmagnetic ion like Zn^{2+} is substituted in Li-ferrite, it prefers A-site transferring Fe^{3+} ions to octahedral site[9]. Hence the cation distribution in our case, which is Cd substituted Li-ferrite can be written as

In the present case Cd ions with large ionic radius ($0.97 \text{ \AA}$) replace Fe^{3+} ions having ionic radius $0.69 \text{ \AA}$ on the tetrahedral site. Consequently, lattice parameter increases with increasing Cd content. Reddy et al reported slightly higher values of lattice parameter for the sample with $x = 0.2, 0.4$, and 0.6 . [10].

4. Infrared absorption studies

The Infrared absorption spectra of the samples in the range $200\text{-}800 \text{ cm}^{-1}$ were recorded at room temperature on PerkinElmer IR spectrometer (Model 783) in the KBr medium. IR spectra of the samples studied in the present case are shown in the Figure. The spectrum of pure Li-ferrite possesses four principal bands in the range $200\text{-}800 \text{ cm}^{-1}$ which are usually observed for mineral spinel [11,12]. Along with these four principle bands some shoulders have also been observed. The position of the principle bands along with the shoulders for these samples are shown in the Table 2. Table shows the values of the force constants K_t and K_o along with the bond length R_A and R_B . The force constants K_t and K_o were calculated using Waldron's analysis [13].

The first principle band (U_1) for Li- ferrite is at about 810 cm^{-1} and it is found to shift towards 570 cm^{-1} as the Cd^{2+} content increases. The bandwidth of the absorption band also goes on increasing with the increase in Cd^{2+} content. In the mixed spinel ferrite, a tetrahedral site is occupied by both Cd^{2+} ions and Fe^{3+} ions with decreasing concentration of Fe^{3+} by $1-x$. This causes a charge imbalance at tetrahedral sites and probably makes oxygen ion shift towards the Cd^{2+} ions, which results in increase of force constant. Due to this reason the central frequency (U_1) shows decreasing trend from 610 cm^{-1} to 570 cm^{-1} with increase in Cd content in Li-ferrite. Waldron attributed the (U_1) band to the intrinsic vibrations of the tetrahedral group. Thus, it is clear that $\text{Cd}^{2+}\text{-O}^{2-}$ complex are responsible for the occurrence of the (U_1) band.

The (U_2) absorption band for Li ferrite is observed at 480 cm^{-1} . As the Cd content increases U_2 band shifts from 480 cm^{-1} to 430 cm^{-1} and its intensity also decreases. It is found to be minimum and reduce to mere shoulders for $x = 0.2$. For the remaining samples for which $x > 0.2$ the U_2 band reappears with increasing bandwidth. The shifting of U_2 values from 480

cm^{-1} to 430 cm^{-1} with increase in x is also due to charge imbalance at the octahedral site. Similar behaviour for U_1 and U_2 bands is reported by earlier investigators [14,15,16,17]. Decreasing intensity for the sample with $x = 0.1$ and 0.2 is due to migration of Fe^{2+} ion from tetrahedral site to octahedral site. Reappearance of U_2 band for the samples with $x > 0.2$ is due to increasing concentration of Fe^{3+} ions on octahedral site. Hafner attributed U_2 band due to presence of $\text{Fe}^{3+}\text{-O}^{2-}$ complexes at the octahedral site [18]. Potakova et al have reported displacement and decrease in intensity of U_2 band in case of Zn^{2+} doped in highly ferrous nickel ferrites [19]. Reddy et al in case of pure Lithium and Li-Ni ferrite reported decrease in intensity and disappearance of U_2 band [20].

U_3 absorption band in present case is found for the samples up to $x = 0.4$. For the remaining samples U_3 band is absent. For these samples the concentration of Li^{1+} goes on decreasing by $0.5 - x/2$ on the octahedral site. Therefore, U_3 band can be attributed to the $\text{Li}^{1+}\text{-O}^{2-}$ metal complexes at the octahedral site.

Frequency of U_4 band depends on the mass of the tetrahedral cation and is assigned to vibrations of tetrahedral metal ion [21,22]. In the present case, the intensity of U_4 band is lowest among all the IR bands and is observed only for the samples up to the value of $x = 0.3$. The reason for absence of U_4 band for the samples having $x > 0.3$ is that at the tetrahedral site the concentration of Fe^{3+} decreases by $1-x$. Thus, the vibrational band U_4 band may be attributed to the presence of $\text{Fe}^{3+}\text{-O}^{2-}$ ions at the tetrahedral site.

Potakova et al have shown that existence of side band can be considered as evidence for the presence of Fe^{2+} ions [23]. Similar Splitting and disappearance of IR absorption bands has been reported by Reddy et al in case of Li-Ni and Li-Ti ferrites [24,25].

Scanning electron microscope of the samples were recorded at Regional sophisticated Instrumentation Centre Nagpur using Model Cambridge Stereoscan S-250 MKII. Figure 4 shows the SEM micrographs of the samples with $x = 0, 0.1$. The data on composition and grain size is shown in Table 4. The variation of grain size with composition is shown in Figure 5. It is found that grain size increases with increase in Cd content up to $x = 0.1$. On further addition of Cd with $x = 0.3, 0.5, 0.7$ the grain size decreases.

Table 1 shows values of the lattice parameter (a) for different values of 'x'.

Sr. No.	x	Lattice parameter (a) $\text{\AA}^0$
1.	0.0	8.324
2.	0.1	8.364
3.	0.2	8.4328
4.	0.3	8.4533
5.	0.4	8.5123
6.	0.5	8.5266
7.	0.6	8.6006
8.	0.7	8.644

Table 2 Data on lattice vibration frequencies and side bands for $\text{Li}_{0.5-x/2}\text{Fe}_{2.5-x/2}\text{Cd}_x\text{O}_4$ ferrites

x	U_1	U_{1s}	U_2	U_{2s}	U_3	U_{3s}	U_4	U_{4s}
0.0	610	560	480	450	400	380	340	310
0.1	605	--	480	--	400		360	310
0.2	600	--	480	425	400	380	360	310
0.3	590	--	470	410	400	--	360	--
0.4	590	--	460	440	400	--	--	--
0.5	580	--	440	--	--	--	--	--
0.6	570	--	410	--	--	--	--	--
0.7	570	--	400	--	--	--	--	--

Table 3 Bond lengths and force constants for $\text{Li}_{0.5-x/2}\text{Fe}_{2.5-x/2}\text{Cd}_x\text{O}_4$ ferrites

x	$R_A \text{ \AA}^0$	$R_B \text{ \AA}^0$	Force Constants	
			$K_t \times 10^5$	$K_O \times 10^5$
0.0	2.005	2.084	1.38	2.76
0.1	2.014	2.093	1.46	2.70
0.2	2.030	2.110	1.52	2.64
0.3	2.035	2.115	1.51	2.54
0.4	2.049	2.130	1.49	2.53
0.5	2.053	2.134	1.40	2.44
0.6	2.071	2.152	1.24	2.35
0.7	2.081	2.163	1.20	2.34

Table 4 Composition and grain size of $\text{Li}_{0.5-x/2}\text{Fe}_{2.5-x/2}\text{Cd}_x\text{O}_4$ ferrites

X	Grains size (μ_m)
0.0	0.98
0.1	2.35
0.3	1.50
0.5	1.30
0.7	0.97

Figure 1. X-ray diffraction pattern of Li-Cd ferrite with $X = 0.1$

Figure 2 Variation of lattice parameter with Cd content

Figure 3. IR absorption spectra of Li-Cd ferrites.

$X = 0$

$X = 0.1$

Figure 4. SEM of Li-Cd ferrite with $X = 0$ and $X = 0.1$

Figure 5 shows variation grain size with Cd content.

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