Microstructural and Magnetic Property Analysis on La Ions in Cu-Zn Ferrites

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Abstract. Lanthanum substituted Cu-Zn ferrite $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($x=0\sim0.09$) powders have been prepared by a sol-gel. XRD results indicate that the production of a single cubic phase of ferrites, the lattice parameter first increase and then decrease, but the average crystallite size decrease with the substitution La^{3+} ions. SEM shows that the ferrite powers are nanoparticles, and calculate the distribution of Fe^{3+} ion between in A- and B-sites in the crystal lattice, according to two sets of Mössbauer spectrum line of absorption peak surrounded by the ratio of the area. The saturation magnetization increases with particle bigger size, the biggest saturation magnetization intensity is $Cu_{0.7}Zn_{0.3}Fe_2O_4$.

1. Introduction

Cubic spinel ferrites have attracted much attention due to their potential applications in many technical fields [1-3]. Thomas Mathew *et al.* [4] investigate the $Cu_{1-x}Co_xFe_2O_4$ ferrospinels prepared by a coprecipitation method. It noticed that the basicity of the system decreases with increasing x value. Sarah Briceno *et al.* [5] studied the structural, catalytic and magnetic properties of $Cu_{1-x}Co_xFe_2O_4$. They discuss that the magnetizition of Cu-Co ferrites decreases with the less magnetic moment of Cu^{2+} ions. P.P.Hankare *et al.* [6] researched the effect of sintering temperature on the properties of Cu-Co ferrites. In this work, $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($x=0\sim0.09$) powders were prepared by the sol-gel method. Our aim of this study is to research the varication structural and magnetic properties of $Cu_{0.7}Zn_{0.3}Fe_2O_4$ ferrite by replacement small amounts of lanthanum.

2. Experiment section and Synthesis

Rare earth ions substituted cobalt ferrite $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($x=0\sim0.09$) powders were prepared by a sol-gel auto-combustion method. The XRD, SEM, MPMS and Mössbauer spectrometer were used to investigate the microstructure and magnetic properties of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$.

3. Results and discussion

3.1. XRD patterns analysis

Fig.1 shows the XRD pattern of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($0\leq x\leq0.09$) ferrites. All the samples are single phase and all diffraction peaks can be indexed to the cubic spinel structure of $CuFe_2O_4$ (JCPDS card

no.34-0425). It noticed that there is no impurity phase in the patterns when x=0.00 and 0.01.There is a obvious impurity peak between (220) and (311) main peak, and the impurity diffraction peak intensity are increase with the content x increase when $x \geq 0.03$. The impurity phase is the $LaFeO_3$ through the peak searching of Jade 5.0.The reasons for this phenomenon may be that less lanthanum doped completely into crystal lattice form spinel structure.But doping excessive lanthanum there is a impurity phase formation on the crystal boundary when $x \geq 0.03$. The precipitation effect will be more obvious with the increase of lanthanum [7, 8].
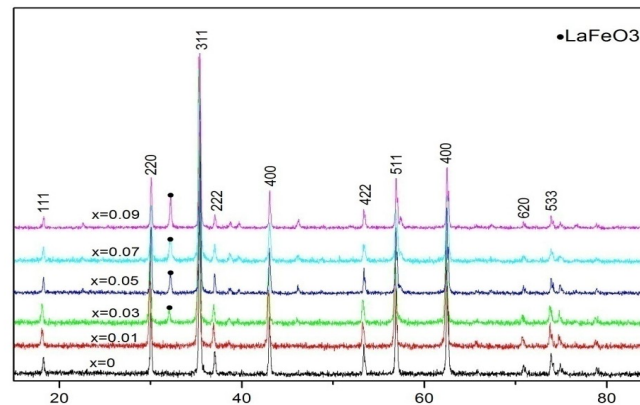

Figure 1. X-ray diffraction patterns of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ calcined at 950°C for 3h.

It observed that the lattice constant of the samples will be first increase and then decrease in Table 1. The maxmum value of lattice constant is getted when x=0.03 and the minimum value of lattice constant is obtained when x=0.09. When a small amount of lanthanum completely into the crystal lattice to form spinel structure, due to the ionic radius is larger than be replaced iron ion radius, the lattice expansion occurs, which resulted in increased lattice constant. From the XRD analysis shows that when x=0.03 the adding lanthanum began to excess, there are a few in the formation of grain boundary precipitates $LaFeO_3$ impurities, has certain extrusion effect to the crystal lattice, but the effects of the stress is larger than the extrusion swell, so the lattice constant continue to increase. When continue mixed with lanthanum, the impurtit on the grain boundary produce the extrusion stress is greater than the getting into the internal lanthanum stress, prompting the lattice constant is reduced, so the lattice constant getting minimum value when mixed with most lanthanum. The change of the grain size D without certain regularity. But overall, the grain sizes of most samples are decrease when the rare earth ions doped. The change of grain density has certain relevance with lattice constant and the grain size.

Table 1. The parameters of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ samples in the XRD patterns.

Content(x)	a(Å)	$\rho(g/cm^3)$	D(nm)
0	8.40292	5.1841	66.5
0.01	8.42019	5.1522	57.5
0.03	8.42049	5.1517	48.9
0.05	8.40376	5.1825	73.6
0.07	8.40212	5.1800	47.1
0.09	8.40054	5.1885	69.4

3.2. Structures and grain size
Fig.2 shows the SEM micrographs of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ (0, 0.01, 0.03, 0.05). The particles are big and spherical when x=0.00. At the same time, the grain boundary is more obvious. When $x \geq 0.01$,

the grain size of particles smaller and number of pores decreases. Distinctly, the grain boundary increasly blurred and there is a significant phenomenon of reunion. Fig.3 shows the particles size distribution of $Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.01}O_4$ ferrites anneled at 950°C. It noticed that the particle size is 92.2~108.8nm mostly, the average particle size of powder sample is 132.80nm, the smallest size is 59.00nm, the largest diameter is 224.16nm.

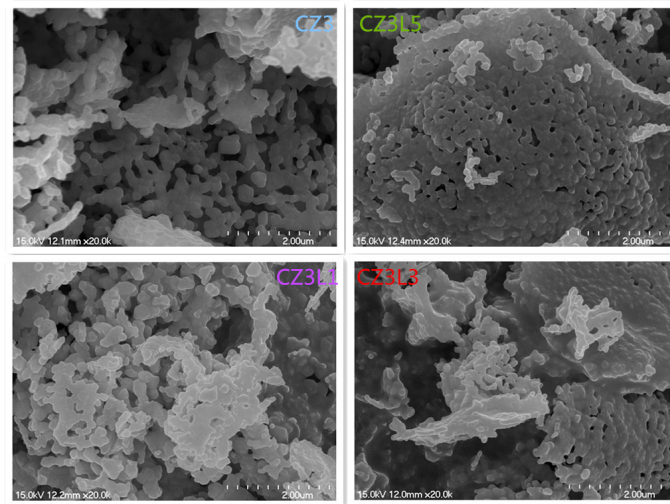**Figure 2.** SEM of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($CZ_{0.3}L_x$).

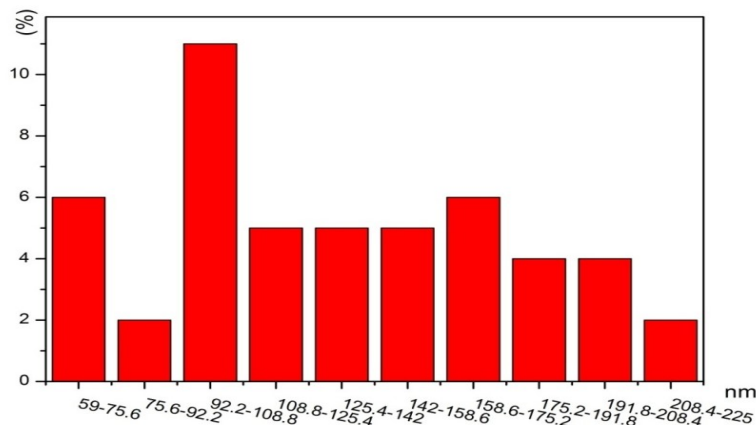**Figure 3.** Size distribution of $Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.01}O_4$.

3.3. Mössbauer spectroscopy anaysis

The Mössbauer spectra of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ (x=0, 0.01, 0.09) ferrites are shown in Fig.4. It can be seen from the Table 2 that the isomeric shift values of the A- and B-sites are in the range of 0.2~0.4mm/s. Because of three valence state of iron ions isomeric shift values are generally 0.2~0.5mm/s [9, 10], so there is only ferric iron in the crystal lattice. Mössbauer spectra of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ is two normal Zeeman-split sextets, which display ferrimagnetic behavior.
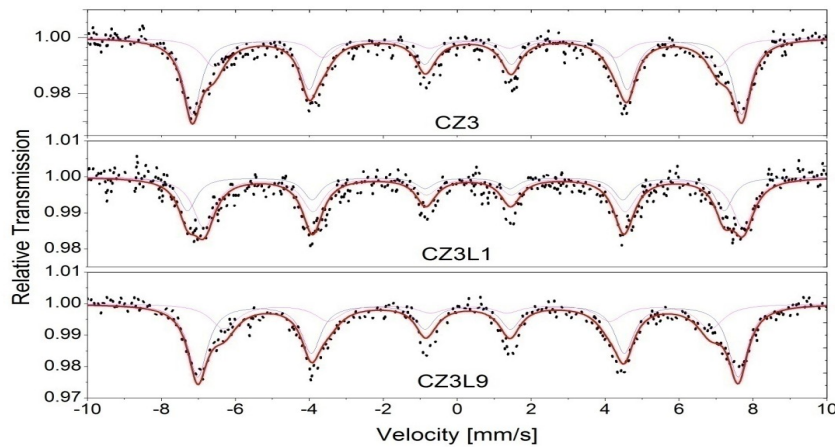
Figure 4. Mössbauer spectra of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($CZ_{0.3}L_x$, x=0, 0.01, 0.09) ferrites.

Table 2. Mössbauer parameters of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ (x=0~0.09) ferrites calcined at 950℃.

Content(x)	I.S.(mm/s)		Q.S.(mm/s)		H_{hf}(T)		A_0(%)	
	A	B	A	B	A	B	A	B
0	0.2766	0.2865	-0.032	-0.079	46.10	42.36	66.9	33.1
0.01	0.2658	0.3783	0.121	-0.315	46.21	38.92	64.8	35.2
0.03	0.2993	0.3261	0.012	0.009	45.88	39.90	65.2	34.8
0.05	0.2975	0.3923	0.020	0.119	45.50	40.38	68.1	31.9
0.07	0.2841	0.3598	0.014	-0.023	45.33	40.79	71.4	28.6
0.09	0.2851	0.2884	0.004	-0.049	44.80	45.00	74.7	25.3

At the same time, with the increase of lanthanum adding quantity, the isomeric shift values are increased which are compared to the not mixed with copper zinc ferrite. Because the increase is not obvious so that it shows that lanthanum into the lattice have not significant influence to the density of s electron which is outermost layers of Fe^{3+} [11]. Quadrupole splitting value and symbol respectively are on the behalf of the ball symmetry of the deformation size and the direction of the deformation. It shows that the Fe^{3+} coordination environments are better around in all samples of symmetry. Because the Q.S values of the A- and B-sites are relatively are very small. It illustrates that the doping lanthanum has no influence on the lattice symmetry. We can calculate the distribution of Fe^{3+} ion between in A- and B-sites in the crystal lattice according to two sets of Mössbauer spectrum line of absorption peak surrounded by the ratio of the area from Table 2. We found that the Zn^{2+} (0.74 Å) tend to occupy A-site and the rare earth La^{3+} (1.034 Å) ionic radius is larger, more inclined to occupy larger B-sites. Meanwhile, it need consider that the two facts of crystal structure and chemical equilibrium price. At the end, after calculating the results shows in the Table 3.

Table 3. The distribution of iron ions between in the A- and B-sites.

Samples	A:B[/%]	Chemical formula
$Cu_{0.7}Zn_{0.3}Fe_2O_4$	33.1/66.9	$(Zn_{0.30}Cu_{0.04}Fe_{0.66})_A[Cu_{0.66}Fe_{1.34}]_BO_4$
$Cu_{0.7}Zn_{0.3}Fe_{1.99}La_{0.01}O_4$	35.2/64.8	$(Zn_{0.30}Fe_{0.70})_A[La_{0.01}Cu_{0.7}Fe_{1.29}]_BO_4$
$Cu_{0.7}Zn_{0.3}Fe_{1.97}La_{0.03}O_4$	34.8/65.2	$(Zn_{0.30}Cu_{0.02}Fe_{0.68})_A[La_{0.03}Cu_{0.68}Fe_{1.29}]_BO_4$
$Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.05}O_4$	31.9/68.1	$(Zn_{0.30}Cu_{0.08}Fe_{0.62})_A[La_{0.05}Cu_{0.62}Fe_{1.33}]_BO_4$
$Cu_{0.7}Zn_{0.3}Fe_{1.93}La_{0.07}O_4$	28.6/71.4	$(Zn_{0.30}Cu_{0.14}Fe_{0.56})_A[La_{0.07}Cu_{0.56}Fe_{1.37}]_BO_4$
$Cu_{0.7}Zn_{0.3}Fe_{1.91}La_{0.09}O_4$	25.3/74.7	$(Zn_{0.30}Cu_{0.22}Fe_{0.48})_A[La_{0.09}Cu_{0.48}Fe_{1.43}]_BO_4$

It noticed that there are two characters from the Table 3. Firstly, the Fe^{3+} ions in the distribution of A bit quantity has been reduced and at the same time the occupancy of Fe^{3+} in B-site presents the increasing trend with the increase of amount of lanthanum adding [12]. Because the larger ionic radius of La^{3+} occupy the B-site; In addition, the ionic radius of Cu^{2+} and Fe^{3+} are almost. On the basis of satisfy the valence state of balance, it will force some Cu^{2+} from B-site to A-site causing the distribution changes of Fe^{3+} between in the two crystal lattice; Secondly, the Cu^{2+} ions are all in the B-sites when $x=0.01$. In the absence of incorporation before La^{3+} ion distribution can be seen in most of the occupied Cu^{2+} B-site, only a few Cu^{2+} ions occupy the A-site. When the incorporation of 0.01, the La^{3+} directly into the crystal lattice and occupy the B-site, forcing Fe^{3+} to migrate from B-site to A-site. So the result indirect handful of the Cu^{2+} migrated from the A-site to B-site.
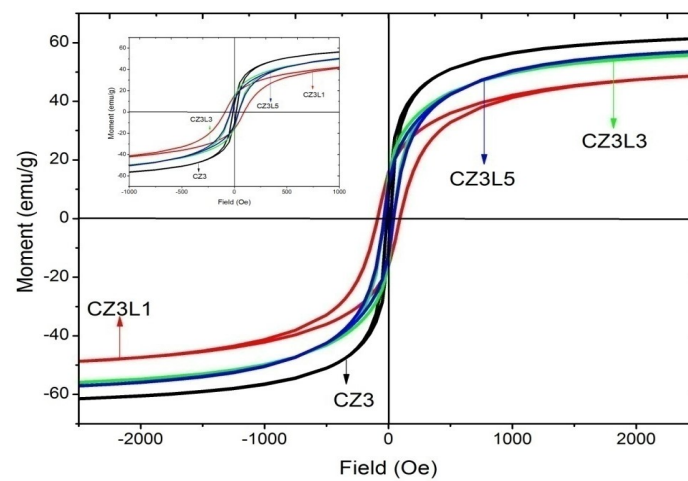
3.4. Magnetic property of particles

Figure 5. Hysteresis loops of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($CZ_{0.3}L_x$, x=0, 0.01, 0.03, 0.05) ferrites.

Fig.5 shows hysteresis loops of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ ($x=0$, 0.01, 0.03, 0.05) at room temperature. The magnetization of all samples nearly reaches saturation at the external field of 2000Oe. Among them, the top left corner of the figure shows a qualitative comparison of each sample coercivity size from the Table 4. The largest saturation magnetization is 64.8 emu/g when $x=0$. The smallest value of saturation magnetization is 53.3emu/g when $x=0.01$. Meanwhile, the biggest coercivity is 75.5Oe when $x=0.01$. The others have same valus coercivity (25Oe). The above results are basically consistent with the XRD and Mössbauer spectrum measurement results. $Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.05}O_4$ particle have the bigger size from the results of XRD. The basic conform to the saturation magnetization increases with particle bigger size. But the biggest saturation magnetization intensity is $Cu_{0.7}Zn_{0.3}Fe_2O_4$. Because $Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.05}O_4$ has the impurity of $LaFeO_3$ phases in the lattice, residing in the grain boundary form of internal stress which influence the saturation magnetization. It shows that $Cu_{0.7}Zn_{0.3}Fe_{1.99}La_{0.01}O_4$ is into the lattice of La^{3+} added to the critical value from XRD analysis result, so its saturation magnetization is the largest.

Table 4. The magnetic parameters of $Cu_{0.7}Zn_{0.3}Fe_{2-x}La_xO_4$ (x=0, 0.01, 0.03, 0.05).

Samples	M_s (emu/g)	H_c (Oe)	M_r (emu/g)
$Cu_{0.7}Zn_{0.3}Fe_2O_4$	64.8086	25.1231	7.74308
$Cu_{0.7}Zn_{0.3}Fe_{1.99}La_{0.01}O_4$	53.3464	75.5048	15.6428
$Cu_{0.7}Zn_{0.3}Fe_{1.97}La_{0.03}O_4$	59.5698	25.1532	14.7939
$Cu_{0.7}Zn_{0.3}Fe_{1.95}La_{0.05}O_4$	60.7086	25.1683	11.5695

4. Conclusion

The Cu-Zn ferrite particles were prepared by sol-gel method, the results of XRD anysis that the all samples are single cubic ferrits phase. There is an obvious impurity phase of $LaFeO_3$ between (220) peak and (311) peak. The intensity of impurity phase is increased with the incorporation. The lattice constant first increase and then decrease with the x value increase. The average crystal size has ruleless law when x value increase. The SEM anysis indicates that the distribution of samples particles size are very good. Meanwhile, the crystallization of samples is very well. The average crysal size of particles are refined because of the crystallined temperature rise when the La^{3+} dopping. The dopping La^{3+} will cause a new distribution of Fe^{3+} between A- and B-sites. So the magnetic field of A-site will increase but the magnetic field of B-site will decrease. There is only ferric ion in the crystal lattice from the anysis of I.S. The saturation magnetization is not obvious influenced by the La^{3+} incorporation. The coercivity has a biggest values when x=0.01.

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