Crystallographic and Magnetic Properties of Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$ Ferrite

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This study examined the crystallographic and magnetic properties of vanadium-substituted lithium cobalt titanium ferrite, Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$. Ferrite was synthesized using a conventional ceramic method. The samples annealed below 1040°C showed X-ray diffraction peaks for spinel and other phases. However, the sample annealed above 1040°C showed a single spinel phase. The lattice constant of the sample was 8.351 Å, which was relatively unaffected by vanadium-substitution. The average grain size after vanadium-substitution was 13.90 μm, as determined by scanning electron microscopy. The Mössbauer spectrum could be fitted to two Zeeman sextets, which is the typical spinel ferrite spectra of Fe$^{3+}$ with A and B sites, and one doublet. From the absorption area ratio of the Mössbauer spectrum, the cation distribution was found to be (Co$_{0.2}$V$_{0.2}$Fe$_{1.6}$)[Li$_{0.7}$Ti$_{0.2}$Fe$_{1.1}$]O$_4$. Vibrating sample magnetometry revealed a saturation magnetization and coercivity of 36.9 emu/g and 88.6 Oe, respectively, which were decreased by vanadium-substitution.

Keywords: Li-Co-Ti-V ferrite, Mössbauer spectroscopy, saturation magnetization, coercivity

1. Introduction

It was recently reported that vanadium has an interesting effect on the crystallographic and magnetic properties of ferrites. It was found that the grain size and porosity initially increase and then decrease with increasing vanadium concentration in Li$_{0.5+t}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{2-2t}$O$_4$ ferrite up to t=0.1. It was also shown that the Curie temperature and saturation magnetization change with increasing vanadium concentration. Moreover, the addition of V$_2$O$_5$ to certain ferrites, such as Li ferrite, Mn-Zn ferrite and Ni-Cu-Zn ferrite, allowed a decrease in sintering temperature and promoted densification and grain growth [1-4]. The crystallographic and magnetic properties of vanadium-substituted and doped ferrites were previously examined [5, 6].

Lithium ferrite shows a high Curie temperature, the squareness shape of the hysteresis loop, and high electric resistivity. In addition, its properties are quite sensitive to the type and amount of substituents, methodology of preparation, sintering temperature and atmosphere used in its preparation [7, 8]. Cobalt ferrite is a well-known hard magnetic material that has been studied in detail due to its high coercivity (5.40 kOe), moderate saturation magnetization, remarkable chemical stability and mechanical hardness [9]. The crystallographic and magnetic properties of Ti$^{4+}$ substituted cobalt ferrite powders of Ti$_{0.2}$Co$_{1.8}$Fe$_4$O$_4$ annealed at various temperatures ranging from 473 K to 1073 K were reported. The magnetic properties showed that an increase in annealing temperature led to a decrease in coercivity and an increase in the saturation magnetization [10]. V$_2$O$_5$ has a low melting point of 670°C and promotes sintering if present as a liquid phase on the grain boundaries. However, it evaporates during prolonged sintering, leaving the ferrite grain boundaries without a large excess of a V$_2$O$_5$-rich phase.

In this study, Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$ was synthesized at different annealing temperatures to clarify the crystallographic and magnetic properties of vanadium substituted Li-Co-Ti ferrite. The crystallographic and magnetic properties were examined by x-ray diffraction (XRD), scanning electron microscopy (SEM), Mössbauer spectroscopy and vibrating sample magnetometry (VSM).

2. Experimental Method

The vanadium-substituted lithium cobalt titanium ferrite powder, Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$, was prepared using a conventional ceramic method. The Li$_2$O, CoO, TiO$_2$, Fe$_2$O$_3$, and V$_2$O$_5$ powders used were all of 99.9% purity. After drying the powders at 120°C for 2 h, the mixtures

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were pressed into pellets using a hydraulic press at 8 ton/cm². The pellets were then sintered in a furnace and annealed at 800°C for 6 h, which was followed by a second annealing process at various temperatures for 6 h. The samples were used in powder form for XRD, SEM, Mössbauer spectroscopy, and VSM.

The powder samples were analyzed by XRD at room temperature using CuKα (λ = 1.5418 Å) radiation. The surface microstructure was observed by SEM at room temperature. The Mössbauer spectra were obtained using a conventional electromechanical-type Mössbauer spectrometer with a ⁵⁷Co source (10 mCi) in a rhodium matrix. The magnetic properties were measured using a VSM.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the vanadium-substituted lithium cobalt titanium ferrite, Li₀.7Co₀.2Ti₀.2V₀.2Fe₁.7O₄, at various annealing temperatures. At annealing temperatures < 1040°C, the XRD pattern showed peaks consistent with a typical spinel structure with additional peaks, which were assigned to Fe₂O₃. However, above 1040°C, all the XRD peaks were consistent with those of a typical spinel structure. Therefore, the samples annealed at temperatures > 1040°C were used in this study. The lattice constant a, as calculated from the observed interplanar spacing d value, was 8.351 Å, which indicates that the lattice constant is relatively unaffected by vanadium substitution (the lattice constant for non vanadium substituted ferrite, Li₀.₅Co₀.₂Ti₀.₂Fe₂O₄, is 8.349 Å). As reported previously [1], this was explained by the composition formula, where one Fe³⁺ ion (0.67 Å) is replaced with 0.5 Li⁺ and 0.5 V⁵⁺ with an average ionic radius of 0.665 Å (the ionic radii of Li⁺ and V⁵⁺ are 0.74 Å and 0.59 Å, respectively).

Fig. 2 shows SEM images of the Li₀.₇Co₀.₂Ti₀.₂V₀.₂Fe₁.₇O₄ sample at x 2000 magnification. The average grain size and/or morphology of the Li-Co-Ti ferrite was reported to be strongly dependent on the amount of vanadium present in the samples during annealing [5]. As the level of substitution increased, some larger grains were embedded in finer grains, and the number of these grains increased with increasing size. The average grain size of the Li₀.₇Co₀.₂Ti₀.₂V₀.₂Fe₁.₇O₄ sample was 13.90 µm, which is larger than the average grain size of non vanadium substituted Li₀.₅Co₀.₂Ti₀.₂Fe₂O₄ (3.04 µm).

Mössbauer spectroscopy is used to examine the microstructural properties of substituted systems, e.g. ferrites, in a way that XRD and SEM cannot. Fig. 3(a) and (b) show the Mössbauer absorption spectrum for the vana-
Fig. 3. Mössbauer spectrum of (a) the non vanadium ion-substituted Li<sub>0.5</sub>Co<sub>0.2</sub>Ti<sub>0.2</sub>Fe<sub>2.1</sub>O<sub>4</sub> and (b) the vanadium ion-substituted Li<sub>0.7</sub>Co<sub>0.2</sub>Ti<sub>0.2</sub>V<sub>0.2</sub>Fe<sub>1.7</sub>O<sub>4</sub> at room temperature.

Table 1. Room temperature Mössbauer parameters of (a) non vanadium substituted lithium cobalt titanium ferrite, Li<sub>0.5</sub>Co<sub>0.2</sub>Ti<sub>0.2</sub>Fe<sub>2.1</sub>O<sub>4</sub> and (b) vanadium substituted lithium cobalt titanium ferrite, Li<sub>0.7</sub>Co<sub>0.2</sub>Ti<sub>0.2</sub>V<sub>0.2</sub>Fe<sub>1.7</sub>O<sub>4</sub>. $H_{hf}$ is the magnetic hyperfine field, $QS$ is the quadrupole splitting, and $IS$ is the isomer shift relative to the metallic iron. The area ratio (A/B) and doublet represent the Mössbauer spectra absorption area ratio of the A and B sites, and doublet.

<table>
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<th>spectrum</th>
<th>$H_{hf}$ (kOe)</th>
<th>$QS$ (mm/s)</th>
<th>$IS$ (mm/s)</th>
<th>Area ratio (A/B, doublet)</th>
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<td>A site</td>
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<td>484.7</td>
<td>−0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>(b) sextet</td>
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<td>482.2</td>
<td>−0.219</td>
<td>0.002</td>
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<td>(b) doublet</td>
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where a small amount of vanadium and cobalt can go into the B site.

The magnetic properties of the samples were determined at room temperature using a vibrating sample magnetometer. Fig. 4 shows the hysteresis curve of (a) the non vanadium ion-substituted Li$_{0.5}$Co$_{0.2}$Ti$_{0.2}$Fe$_{2.1}$O$_4$, and (b) the vanadium ion-substituted Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$.

The saturation magnetization ($M_S$) of the vanadium ions substituted Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$ was 36.9 emu/g, and the coercivity ($H_C$) was 88.6 Oe. The lower saturation magnetization of the sample compared to that of the non vanadium ion-substituted ferrites (for Li$_{0.5}$Co$_{0.2}$Ti$_{0.2}$Fe$_{2.1}$O$_4$, the $M_S$ is 41.6 emu/g) can be understood based on the nonmagnetic vanadium and lithium ion substitution. Because the coercivity is inversely proportional to the grain size [1], the lower coercivity of the sample than that of the non vanadium ion-substituted ferrites (for Li$_{0.5}$Co$_{0.2}$Ti$_{0.2}$Fe$_{2.1}$O$_4$, the $H_C$ is 120.4 Oe) can be understood based on the large grain size.

4. Conclusion

The crystallographic and magnetic properties of vanadium-substituted lithium cobalt titanium ferrite, Li$_{0.7}$Co$_{0.2}$Ti$_{0.2}$V$_{0.2}$Fe$_{1.7}$O$_4$, were investigated. Ferrite was synthesized using a conventional ceramic method. The samples showed a single phase with a spinel structure at annealing temperatures $> 1040^\circ$C with a lattice parameter of 8.351 Å. The lattice parameter was relatively unaffected by vanadium substitution. The average grain size of the sample increased to 13.90 µm due to vanadium substitution. The Mössbauer spectra could be fitted with two Zeeman sextets, which is the typical spinel ferrite spectra of Fe$^{3+}$ with A and B sites, and one doublet. From the absorption area ratio of the Mössbauer spectrum, the cation distribution was determined to be (Co$_{0.2}$V$_{0.2}$Fe$_{0.6}$)[Li$_{0.7}$Ti$_{0.2}$Fe$_{1.1}$]O$_4$. The saturation magnetization and coercivity was 36.9 emu/g and 88.6 Oe, respectively, which were reduced by vanadium substitution.

Acknowledgements

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References