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Magnetic and Mössbauer Studies on α–Fe_2O_3–Li_2O System

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A study has been made of the structural and thermal phase behavior of the mixed system $\alpha-Fe_2O_3$–xLi_2O with a view toward investigating the changes occurring in the properties of different compositions due to substitution of diamagnetic Li^+ for Fe^{3+} at B sites in the inverse spinel lattice. This also indicates whether the addition of Li_2O, over and above that ($x = 0.2$) required for the formation of the spinel $LiFe_5O_8$, enters the substitutional or interstitial sites. Characterization by X-ray powder diffraction, initial magnetic susceptibility, magnetic hysteresis, Mössbauer spectroscopy, and differential thermal analysis clearly indicates that Li^+ does not enter the spinel lattice, but forms a biphasic system $LiFe_5O_8$ and $LiFeO_2$, which are not miscible.

Introduction

$\alpha-Fe_2O_3$–xLi_2O system attracted considerable attention as lithium ferrite ($x = 0.2$), one of the products of the system, found technological application because of its square loop properties coupled with thermal stability (*1–3*). It is an inverse spinel with cation distribution as $(Fe^{3+})\,[Li^{+}_{0.5}Fe^{3+}_{1.5}]O_4^{2-}$. Most of the studies were concentrated on the correlation of electrical and magnetic properties with deviation from stoichiometry due to lithium and oxygen loss (*4*) and to some extent with phase transition behavior (*5*). While studies have been made on $\alpha-Fe_2O_3$–xLi_2O systems where $x < 0.2$ (*6*) and $x = 2.0$ (*7*), little information is available on the range $0.2 < x < 1.0$. It is of interest to determine whether Li^+, which is diamagnetic and has the same ionic radius (0.68 Å) as Fe^{3+} (0.70 Å), substitutes Fe^{3+} from B sites or enters as interstitials, as well as to determine the influence of the amount of additions in the intermediate range on the magnetic properties.

This note deals with a study of the effect of varying molar ratios of the constituent oxides, viz., $\alpha-Fe_2O_3$ and Li_2O through analyses of magnetic susceptibility, hysteresis, Mössbauer spectroscopic measurements, and differential thermal behavior data.

Experimental

Specimens corresponding to the molar ratios of $\alpha-Fe_2O_3$–xLi_2O where $x = 0.2$, 0.4, 0.6, 0.8, and 1.0 were prepared by the conventional ceramic technique, by intimately mixing the required amounts of $\alpha-Fe_2O_3$ and Li_2O (as Li_2CO_3), pressing into the form of a pellet, heating at 1170–1200°K for 2 days in the furnace, and cooling in air under normal conditions. A nominal analysis showed that the sublimation loss of lithium was negligible. The X-ray powder diffraction patterns of finely powdered samples were recorded using Cu*K*α radia-

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tion with Ni filter ($\lambda = 1.5418$ Å) for characterization of the products. The incremental susceptibility in a small ac magnetic field may be defined as $\Delta M/\Delta H$. When ΔH is very small the magnetization changes are reversible and the ratio $\Delta M/\Delta H$ is called initial or reversible susceptibility (χ_i). For any magnetic material, this reversible magnetic susceptibility increases or remains steady with increase of temperature up to a certain stage and then decreases sharply to zero at the Curie temperature(T_c). The measurements were done on an apparatus, the details of which are given by Likhite (*8*). The *B–H* measurements were done on a ac electromagnet-type hysteresis loop tracer with a maximum field of 2000 Oe. The saturation magnetization was measured using electrolytically pure Ni pellet as standard (53.4 emu/g). The room temperature Mössbauer spectra were recorded using ^{57}Co/Cr source in a constant-velocity spectrometer with a single-channel analyzer. The spectrometer was calibrated using standard absorbers such as sodium nitroprusside and iron foil. The DTA analyses of the various compositions were carried out at temperatures up to 1100°K in an apparatus fabricated in our laboratory. The heating rate was maintained at 6°C/min.

Results and Discussion

From the X-ray powder diffraction patterns, the specimens corresponding to $x = 0.2$ and 1.0 were characterized as $Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$, respectively, by comparison with ASTM powder diffraction data. However, for $x = 0.4$ to 0.8, it was rather difficult to characterize in a straightforward manner whether the compositions were single or multiphased solutions or two phased solid solutions, as the important X-ray reflections for most of the possible phases ($Li_{0.5}Fe_{2.5}O_4$, $LiFeO_2$, and Fe_3O_4) overlapped. The above ambiguity was resolved from magnetic measurements. The thermal variation of initial susceptibility (Fig. 1) showed insignificant variations among different compositions, with identical Curie temperature, T_c (943 ± 5°K), corresponding to that reported for $Li_{0.5}Fe_{2.5}O_4$ (*9*, *10*). The constancy of T_c in different compositions indicated that added Li_2O in going from $x = 0.2$ to 0.8 did not enter the lattice of $Li_{0.5}Fe_{2.5}O_4$ as this would be expected to decrease T_c due to the weakening of superexchange interactions of the type *A*–O–*B*. This suggests the existence of some other lithium compound, probably $LiFeO_2$, and that there is no solid solution among these phases.

The saturation magnetic moment σ_s (Table I) decreased with increase in x from 0.2 to 0.8. Assuming the existence of two phases, viz., $Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$, theoretical saturation magnetic moments were computed from the following reaction stoichiometries:

$$x = 0.4 \qquad 10\,Fe_2O_3 + 4\,Li_2O \rightarrow 6\,Li_{0.5}Fe_{2.5}O_4 + 5\,LiFeO_2 \tag{1}$$

$$x = 0.6 \qquad 10\,Fe_2O_3 + 6\,Li_2O \rightarrow 4\,Li_{0.5}Fe_{2.5}O_4 + 10\,LiFeO_2, \tag{2}$$

$$x = 0.8 \qquad 10\,Fe_2O_3 + 8\,Li_2O \rightarrow 2\,Li_{0.5}Fe_{2.5}O_4 + 15\,LiFeO_2. \tag{3}$$

The calculated and the observed values (Table I) were found to be in good agreement.

As a supplement to the above studies, the room temperature Mössbauer spectra were recorded (Fig. 2). For $x = 0.2$, the spectrum consisted of a six-line pattern with isomer shift of +0.345 mm/sec (with respect to Fe) and H_{eff} of 510 kOe. This could be assigned to $Li_{0.5}Fe_{2.5}O_4$ (*11*). The spectrum corresponding to $x = 1.0$ consisted of a central doublet (IS = +0.32 mm/Δ, ΔQ = 0.52 mm/sec) and could be assigned to $LiFeO_2$ (*12*). For the intermediate compositions the sepectra indicated the presence of both $Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$ phases. Assuming the recoil free fraction to be the

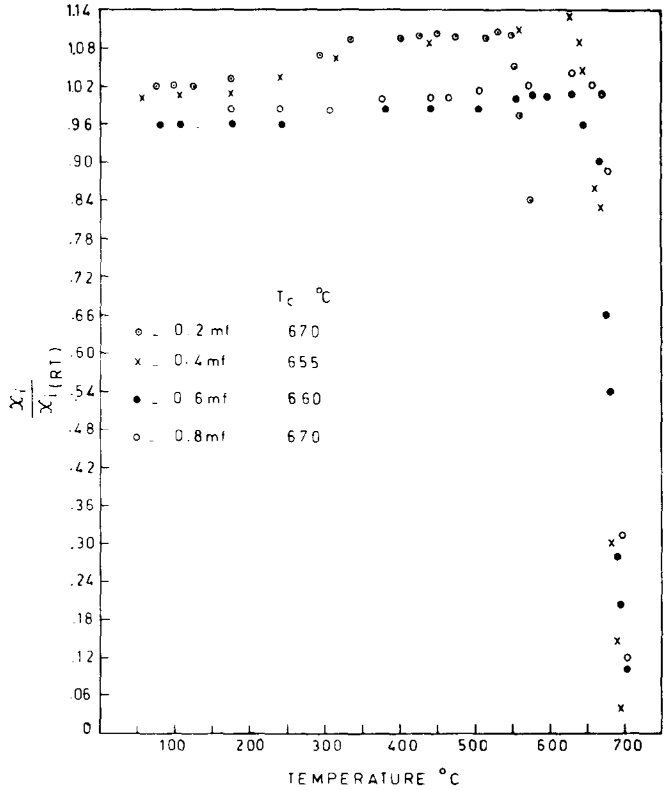

FIG. 1. Variation of normalized initial susceptibility with temperature.

same for both phases, the areas under the magnetically split component (A_{hfs}) and the central doublet (A_{cd}) were computed. The ratios of the areas (2.5 for 0.4; 0.77 for 0.6; and 0.24 for 0.8) which give the relative amount of the two phases present were found to be in agreement with the proposed reactions (3.0 for 0.4; 1.0 for 0.6; and 0.33 for 0.8).

$Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$ are known to undergo different crystallographic modifications depending on the mode of preparation. In the case of $Li_{0.5}Fe_{2.5}O_4$, the two modifications, cubic ordered ($a = 8.329$ Å)

TABLE I

CORRELATION BETWEEN COMPOSITION OF PHASES AND MAGNETIC DATA

$Fe_2O_3xLi_2O$ where x is	Composition of phases based on reaction	Amount $Li_{0.5}Fe_{2.5}O_4$/product (g)	Saturation magnetization (emu/g) Theor	Saturation magnetization (emu/g) Exptl
0.2	$Li_{0.5}Fe_{2.5}O_4$	1.0	—	63.05
0.4	$6Li_{0.5}Fe_{2.5}O_4$–$5LiFeO_2$	0.724	45.62	47.63
0.6	$2Li_{0.5}Fe_{2.5}O_4$–$5LiFeO_2$	0.466	27.97	28.40
0.8	$2Li_{0.5}Fe_{2.5}O_4$–$15LiFeO_2$	0.226	14.21	16.62
1.0	$LiFeO_2$	—	—	—

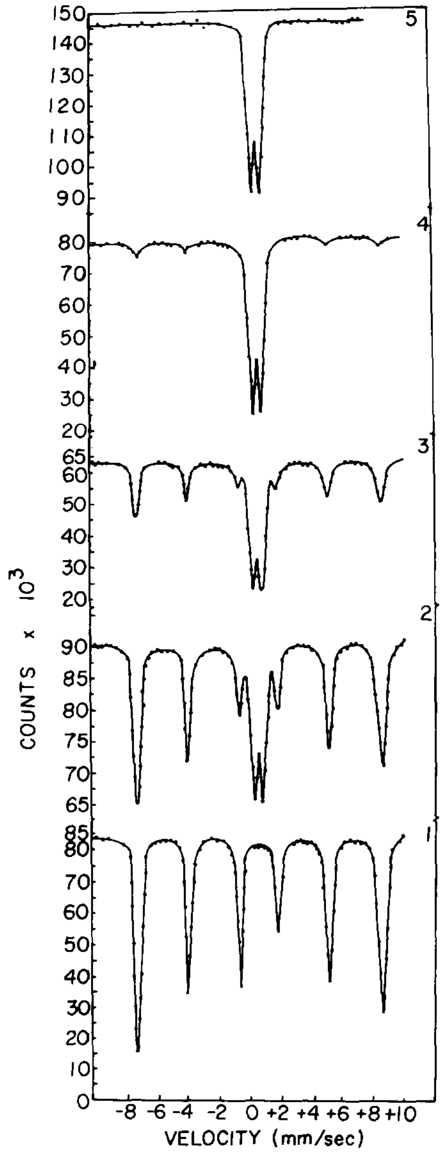

FIG. 2. Mössbauer spectra of $\alpha-Fe_2O_3-xLi_2O$ system. (1) $x = 0.2$; (2) $x = 0.4$; (3) $x = 0.6$; (4) $x = 0.8$; (5) $x = 1.0$.

and cubic disordered ($a = 8.332$ Å), of the cations at *B* sites are not distinguishable by X-ray (*5*) and Mössbauer methods (*11*). However, differential thermal analysis exhibits order–disorder transition. An endothermic peak centered at 1023 ± 5°K, which is close to the reported value of 1030°K (*5*), has been observed for the specimen with $x = 0.2$, which is reversible on cooling. Thus $Li_{0.5}Fe_{2.5}O_4$ is characterized as cubic ordered. $LiFeO_2$ is reported to crystallize in three modifications as disordered cubic, ordered tetragonal, and low-temperature tetragonal form (*12*). Since no peak was observed, $LiFeO_2$ is characterized as cubic disordered which is in agreement with X-ray and Mössbauer results.

Conclusions

(i) Addition to Li_2O to stoichiometric $Li_{0.5}Fe_{2.5}O_4$ did not result in the substitution of Fe^{3+} by Li^+ from *B* sites, but a separate phase $LiFeO_2$ was found to be formed ($LiFe_5O_8 + 2\,Li_2O = 5\,LiFeO_2$). Hence, there is a limit to the solubility of Li_2O in Fe_2O_3, with $Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$ being the limiting cases. (ii) There was little miscibility of the two phases, viz., $Li_{0.5}Fe_{2.5}O_4$ and $LiFeO_2$.

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