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ELECTRICAL CONDUCTIVITY IN LiFe$_5$O$_8$ CERAMICS

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For Reference

Not to be taken from this room
Lithium ferrite ($\text{LiFe}_5\text{O}_8$) is a very promising magnetic material\textsuperscript{1,2} for use in computer memory systems. It is ferrimagnetic and has an inverse spinel structure. Electrical conductivity which is directly related to power loss of the system during use is an important physical property. The electrical conduction of lithium ferrite has not been clearly defined. Reported resistivity data\textsuperscript{3-5} vary from a few ohm-cm to values many orders of magnitude higher. The primary problem in defining the electrical properties of lithium ferrite is the difficulty in controlling the sample composition during processing. Lithium ferrite loses both oxygen and lithium during sintering.\textsuperscript{1,2,6} In this laboratory, a packing powder technique\textsuperscript{7,8} used extensively for the processing of PZT ceramics was employed to control the material loss from lithium ferrite during sintering. The purpose of this investigation was to determine the D.C. resistivity of polycrystalline lithium ferrite as a function of stoichiometry and temperature.

In order to make a series of samples with known deviation from the stoichiometric composition, $\text{LiFe}_5\text{O}_8$ powder was mixed with proper proportions of $\text{LiFeO}_2$ or $\text{Fe}_2\text{O}_3$ powder, ball milled and dried. The powder was then pressed into disks and sintered at $1150^\circ\text{C}$ for two hours in 1 atmosphere $\text{O}_2$ using $\text{LiFe}_5\text{O}_8$ as a packing powder.\textsuperscript{8} Densities of all specimens were above 98% of the theoretical density.
DC bulk resistivity was measured by using a guard ring method. Sputtered gold electrodes were used to insure ohmic contact. The contact resistance was negligible. Thermoelectric power measurements were made to determine the type of charge carrier contributing to the conduction process. Measurements were made from room temperature to 300°C. The surfaces of all the sintered samples were ground to a depth sufficient to eliminate any inhomogeneity due to surface reactions before electrodes were applied.

The influence of composition on the resistivity of LiFe₂O₈ at different temperatures is shown in Fig. 1. Resistivity always drops while moving from the LiFeO₂ doped region into the Fe₂O₃ doped region. This is due to the increasing Fe²⁺ content on the octahedral sites. Because both Fe²⁺ and Fe³⁺ are in octahedral sites, electron hopping from Fe²⁺ to Fe³⁺ acts as the primary charge transfer process. While moving from the Fe deficient region (LiFeO₂ doped) into the Fe excess region (Fe₂O₃ doped), more Fe²⁺ ions are created and contribute to charge transport. The resistivity decreases with increasing Fe₂O₃ in the composition. Measurement of the thermoelectric voltage showed that electron conduction dominated in all samples. This is consistent with n-type charge carriers due to the Fe²⁺ ions. The resistivity value increases while moving away from the near stoichiometric region for Fe₂O₃ doped samples. This is probably due to a second phase developing or disordering. Fe²⁺ on the octahedral site tends to introduce disorder into the system. This disorder may decrease the mobility of the charge carrier and thus increase the resistivity.
In Fig. 2 all the resistivity data at a given temperature were normalized to that of the stoichiometric composition at that temperature. For a single type of charge carrier, the conductivity is proportional to the product of the concentration of the charge carrier and its mobility. The concentration of the charge carrier (Fe$^{2+}$) for a particular composition should remain constant in the temperature range where the measurements were made. The shift of the curve with temperature as shown in the figure is clearly an influence of the mobility term.

The temperature dependence of the resistivity for various compositions is shown in Fig. 3. The resistivity decreases with increasing temperature. Normalization of all the resistivity data of a fixed composition with the room temperature resistivity should indicate only the mobility effect. As shown in Fig. 3, mobility divided by temperature follows an exponential relation with temperature which is similar to the mobility expression proposed for charge carrier hopping among like ions in the inverse spinel ferrite CoFe$_2$O$_4$. The activation energy of mobility for each composition (as shown in Fig. 4) was calculated from the data in Fig. 3. It is shown that the activation energy does not change significantly through the stoichiometry region, which clearly indicates that the conductivity change through that region is primarily due to the change in carrier concentration. In fact, the conductivity appears to increase linearly with the amount of dopent in the near stoichiometric region as shown in Fig. 1.

In summary, data have been presented to show the influence of stoichiometry (which affects the carrier concentration) and temperature (which affects the carrier mobility) on the DC resistivity of lithium
ferrite. The exponential temperature dependence of the electrical resistivity is in good agreement with the electron hopping model. The electrical conduction occurs by thermally activated electron hopping between the octahedral Fe$^{+2}$ and Fe$^{+3}$.

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REFERENCES


FIGURE CAPTIONS

Fig. 1. The influence of composition on the resistivity of LiFe$_5$O$_8$ at different temperatures.

Fig. 2. Normalized resistivity of LiFe$_5$O$_8$ as a function of composition. $\rho_b$ indicates the bulk resistivity.

Fig. 3. Normalized resistivity for various compositions of LiFe$_5$O$_8$ versus temperature. $\rho_b$ is the bulk resistivity at temperature $T_b$. $\rho_0$ is the bulk resistivity at room temperature $T_0$.

Fig. 4. Activation energy for mobility of charge carriers as a function of composition.
Fig. 1
Fig. 2

$P_b/P_{\text{stoich.}}$

Mole % LiFeO$_2$ \quad Mole % Fe$_2$O$_3$

T = 20°C

100°C

300°C

Stoich.

XBL749-7217
LiFe$_5$O$_8$ doped with:

- $5\%$ Fe$_2$O$_3$
- $3\%$ Fe$_2$O$_3$
- $1\%$ Fe$_2$O$_3$
- undoped
- $3\%$ LiFeO$_2$
- $5\%$ LiFeO$_2$

$\frac{P_0}{P_b}$ vs $\frac{T_b}{T}$

Fig. 3
Fig. 4
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