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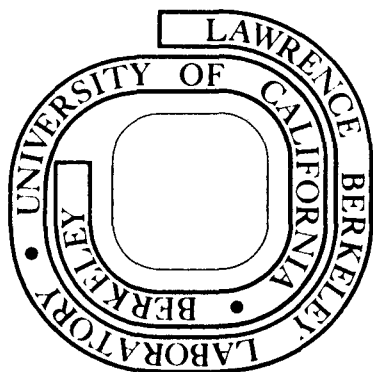
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INFLUENCE OF NiO AND NiFe₂O₄ DOPANTS ON THE PROCESSING
AND PROPERTIES OF LITHIUM FERRITE SPINEL

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ABSTRACT

Polycrystalline compacts of lithium ferrite doped with controlled amounts of NiO or NiFe₂O₄ were sintered using a stoichiometric packing powder under one atmosphere oxygen pressure. Both the dopants had only a slight effect on the densification. NiO favored discontinuous grain growth, whereas NiFe₂O₄ suppressed it. DC resistivity was affected significantly by the addition of minute amounts of either of the two dopants. The coercive force decreased with the addition of NiO, whereas it increased with the addition of NiFe₂O₄.

I. Introduction

In the processing of spinel ferrites, selective additions play an important role in the control of sintering, microstructure and the final magnetic properties. Dopants may modify the sintering behavior and the microstructure, which in turn, may influence the properties of the final ceramic. On the other hand, some dopants may directly influence the electrical and magnetic properties through other parameters, without influencing the densification or microstructure. In the case of lithium ferrite, it has been demonstrated that small additions of nickel,¹ zinc,² nickel and zinc,³ and manganese,^{4,5} significantly improve the hysteresis loop squareness. However, none of these studies investigated the influence of the dopants on the densification and microstructure. In a recent study⁶ carried out in this laboratory, it was noted that, depending on the atmosphere of sintering, dopants like NiO, MgO or TiO₂ can enhance the grain growth rate in lithium ferrite. It was further noted that the extrinsic defects introduced by these dopants may not have a significant effect on the densification compared to that due to the intrinsic defects in the composition. Thus it was felt necessary that to explain the effect of the dopants on the electrical and magnetic properties (like dc resistivity or hysteresis loop parameters), one should also take into consideration the influence on the densification and microstructure. In this investigation, a systematic study of the influence of varying amounts of NiO and NiFe₂O₄ dopants on the densification, microstructure, dc resistivity and B-H loop parameters has been made. Thermogravimetry and X-ray diffraction were used to characterize the chemical changes during the processing.

II. Experimental Procedure

The preparation of the lithium ferrite (LiFe_5O_8) powder was identical to that described in an earlier paper.⁷ NiFe_2O_4 powder was prepared by using reagent grade NiO and Fe_2O_3 as the starting material. Mixing was done in a neoprene lined ball mill for 48 h using isopropyl alcohol and teflon balls. The alcohol was evaporated and the mixture was calcined at 950C for 5 h in air. The calcined powder was milled and was recalcined at 1000C for 4 h in 1 atm O_2 .

A controlled amount of NiO or NiFe_2O_4 was added to the lithium ferrite powder and the mixture was mixed for 24 h in isopropyl alcohol. For the thermogravimetric runs, a second calcination of the powder mixture was carried out at 800C for 6 h in 1 atm O_2 .

Specimen size and its preparation for the sintering runs are the same as described earlier.⁷ Most of the sintering runs were made at 1150C for 2 h in 1 atm O_2 using a stoichiometric packing powder.⁷

The techniques for the property measurements⁷ and the weight loss apparatus and the experimental conditions associated with the thermogravimetric runs are described elsewhere.⁸

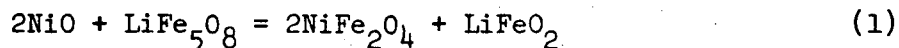
III. Results and Discussion

(1) Densification and Microstructure

In Fig. 1 the sintered densities of the doped specimens have been plotted against the amount of dopants after sintering at 1150°C for 2 h. For both NiO and NiFe_2O_4 , a drop in density is observed. In the case of NiO , this drop in density is probably due to the beginning of discontinuous grain growth with increasing amounts of NiO (Fig. 2). Discontinuous grain growth would cause a larger amount of pores to be entrapped

within the grains, thus leading to a lower final density.

The occurrence of discontinuous grain growth with increasing NiO content can be accounted for by the hypothesis that NiO reacts with LiFe_5O_8 following the reaction,



thereby forming LiFeO_2 in the specimen. In cases where NiO remains in solid solution with lithium ferrite, oxygen vacancies should be formed with excess cations in the interstitials. In either of the above cases where either oxygen vacancies or LiFeO_2 or both are formed, enhanced grain growth would be favored.⁷ The proposed reaction (reaction 1) can be supported through the thermogravimetric analysis of NiO containing compositions. LiFeO_2 , if formed, would alter the weight loss behavior of the powder significantly.⁸ In Fig. 3, weight loss data in mgs/mole of powder of 3 and 10 mol% NiO in lithium ferrite have been plotted against temperature, along with that for stoichiometric lithium ferrite in constant heating rate runs (the temperature was continually increased at the rate of 3 C/min). The weight loss behavior was identical to those of excess LiFeO_2 (in LiFe_5O_8) compositions.⁸ The equilibrated weight loss values (where equilibrium was achieved at each temperature by continuing the experiment for sufficiently long times) for 5 and 10 mol% NiO containing lithium ferrite have been plotted against $1/T$ in Fig. 4 along with those for 5 mol% LiFeO_2 in LiFe_5O_8 and 1 mol% Fe_2O_3 in LiFe_5O_8 . It is interesting to note that NiO dopants in the composition retards the initial weight loss in the same way as is observed

for excess LiFeO_2 (in LiFe_5O_8) compositions. The fact that 10 mol% NiO in LiFe_5O_8 and 5 mol% LiFeO_2 in LiFe_5O_8 compositions exhibit nearly identical weight loss behavior is in agreement with reaction 1, which suggests 2 moles of NiO react to form 1 mole of LiFeO_2 .

Further support of reaction 1 can be obtained through the X-ray studies of the specimen surfaces sintered at 1150C for 2 h in 1 atm O_2 and using stoichiometric packing powder. In Fig. 5, the I_{311}/I_{400} ratio (both planes are for the spinel phases Fe_3O_4 and LiFe_5O_8 ; the (200) peak of LiFeO_2 overlaps with the (400) peak of the spinel phases) has been plotted against the dopant content in the composition. Decreasing spinel content (as is evident from the decreasing I_{311}/I_{400} ratio) on the surface with increasing NiO dopant in the composition is identical to that observed for specimens with excess LiFeO_2 in the composition.⁷ It has already been reported⁷ that under the above experimental conditions, excess LiFeO_2 in the sample composition leads to a surface phase with very little spinel.

A "self decoration effect," as was observed by Lessoff and Childress⁹ on the thermally etched surfaces of polycrystalline lithium ferrite, is also evident on the micrographs of 5 and 10 mol% NiO containing compositions (Fig. 2). A similar effect was also observed in lithia rich compositions (Fig. 6), but was never noted in cation deficient materials.

NiFe_2O_4 dopant gives significantly different results than that of a NiO dopant. Microstructural studies revealed uniformly small grains

with pores exclusively in the grain corners for all compositions (Fig. 7). This may be due to a slight cation deficiency in the ferrite composition¹⁰ and therefore it can be assumed that the density drop, as has been observed with the addition of NiFe_2O_4 (Fig. 1), is due to a retarded densification rate. The cation deficiency may be due to a slight lithia loss or to a slightly cation deficient starting composition which could not be controlled or detected during its preparation. Thermogravimetric data for an equilibrated run with 5 mol% NiFe_2O_4 in LiFe_5O_8 is shown in Fig. 4. The close correspondence between the data for this composition and for the 1 mol% Fe_2O_3 in LiFe_5O_8 indicates the probable cation deficiency in the mixed ferrite composition. X-ray data in Fig. 5, where the I_{311}/I_{400} ratio has also been plotted for NiFe_2O_4 containing compositions, shows predominantly a spinel phase on the sintered surfaces of the specimens. This is also indicative of a cation deficiency.⁷

(2) DC Resistivity

In Fig. 8, dc resistivity values for sintered specimens have been plotted against the amount of dopants (NiO or NiFe_2O_4). In both cases the resistivity dropped sharply with minute additions of the dopant followed by a rapid increase with increasing amount of the additions. In the case of the NiO dopant, where reaction 1 leads to excess LiFeO_2 in the composition, the initial drop in the resistivity value is somewhat surprising. This drop was not observed in LiFeO_2 excess compositions sintered under identical conditions. This discrepancy can be accounted for by the assumption that at least part of the NiO dopant (less than or equal to 1 mol% NiO which is equivalent to 0.5 mol%

LiFeO_2) goes into solid solution with the lithium ferrite composition. This forms excess oxygen vacancies which may act as the current carriers in the anion deficient side.^{11,12} Beyond the solubility limit, the resistivity would tend to rise because of the appearance of a second phase. In the previously presented data⁷ the minimum LiFeO_2 content in the lithia rich side (1 mol% LiFeO_2) is apparently above the solid solubility limit and therefore no resistivity drop was observed on the anion deficient side.

Another plausible explanation for this resistivity drop could be due to the solution of NiO which destroys the octahedral ordering in lithium ferrite. Since disordered compositions are known^{2,11,13} to have a lower resistivity than that of the ordered specimens, this loss of ordering in the composition may lead to a drop of the resistivity value.

Addition of minute amounts of NiFe_2O_4 also lowers the resistivity value significantly (Fig. 8). This also may be due to the disordering of the lithium ferrite composition. The subsequent increase in resistivity with further additions of NiFe_2O_4 cannot be due to a second phase because secondary phases were not detected in the mixed ferrite compositions. Thus this increase may simply be due to the decrease in density or to nickel ferrite which, in general, has a higher resistivity than that of lithium ferrite.¹⁴

(3) B-H Loop Parameters

Wijn et al.¹ first reported that the squareness ratio R_s of lithium ferrite can be improved markedly by the addition of Ni^{+2} in the system. The R_s value for all the specimens in this study was better than 0.85

and with the addition of NiO or NiFe_2O_4 , slight improvement in the squareness was achieved. In Fig. 9, the coercive force (H_c) has been plotted against the amount of dopant. A NiO addition enhances the grain growth and thus the H_c value dropped significantly with increasing NiO content in the composition. NiFe_2O_4 dopant decreases the sinter density and also the grain size was small (in fact, the lower density specimens had a smaller grain size as is evident in Fig. 7) and therefore the value increased with increasing amounts of NiFe_2O_4 .

Maximum induction values (B_{max}) decreased slightly with NiO or NiFe_2O_4 addition.

IV. Summary and Conclusions

Both NiO and NiFe_2O_4 dopants influenced the densification of LiFe_5O_8 and microstructure of the sintered lithium ferrite. NiO favored discontinuous grain growth. It is concluded that NiO reacts with lithium ferrite to form NiFe_2O_4 and LiFeO_2 . Experimental evidence is presented to support the reaction. The effect of NiFe_2O_4 dopant on the densification and microstructure is assumed to be due to the slight cation deficiency in the composition.

Data are also presented relating dc resistivity and B-H loop parameters with the amount of dopants and the results are discussed in terms of compositional defects and microstructure.

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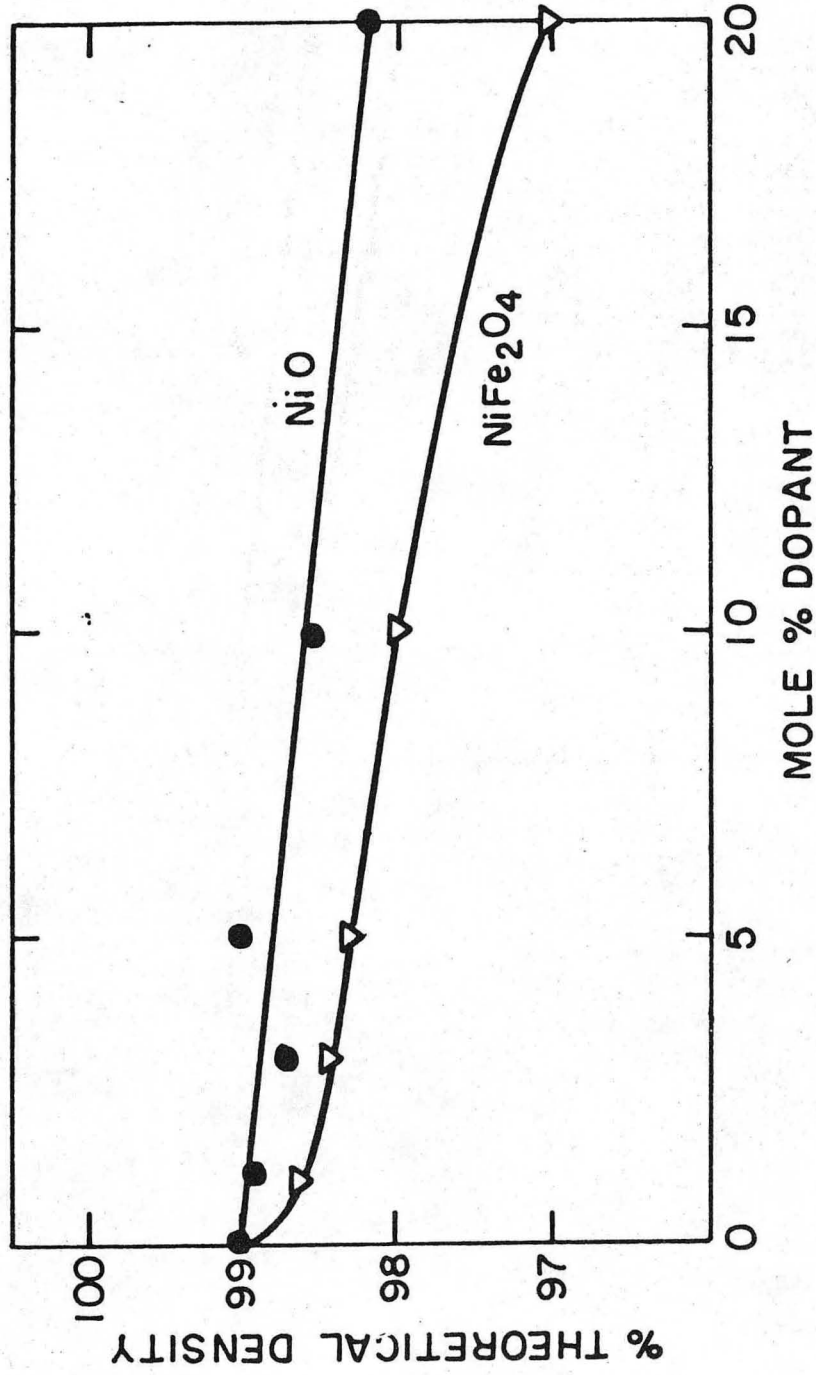
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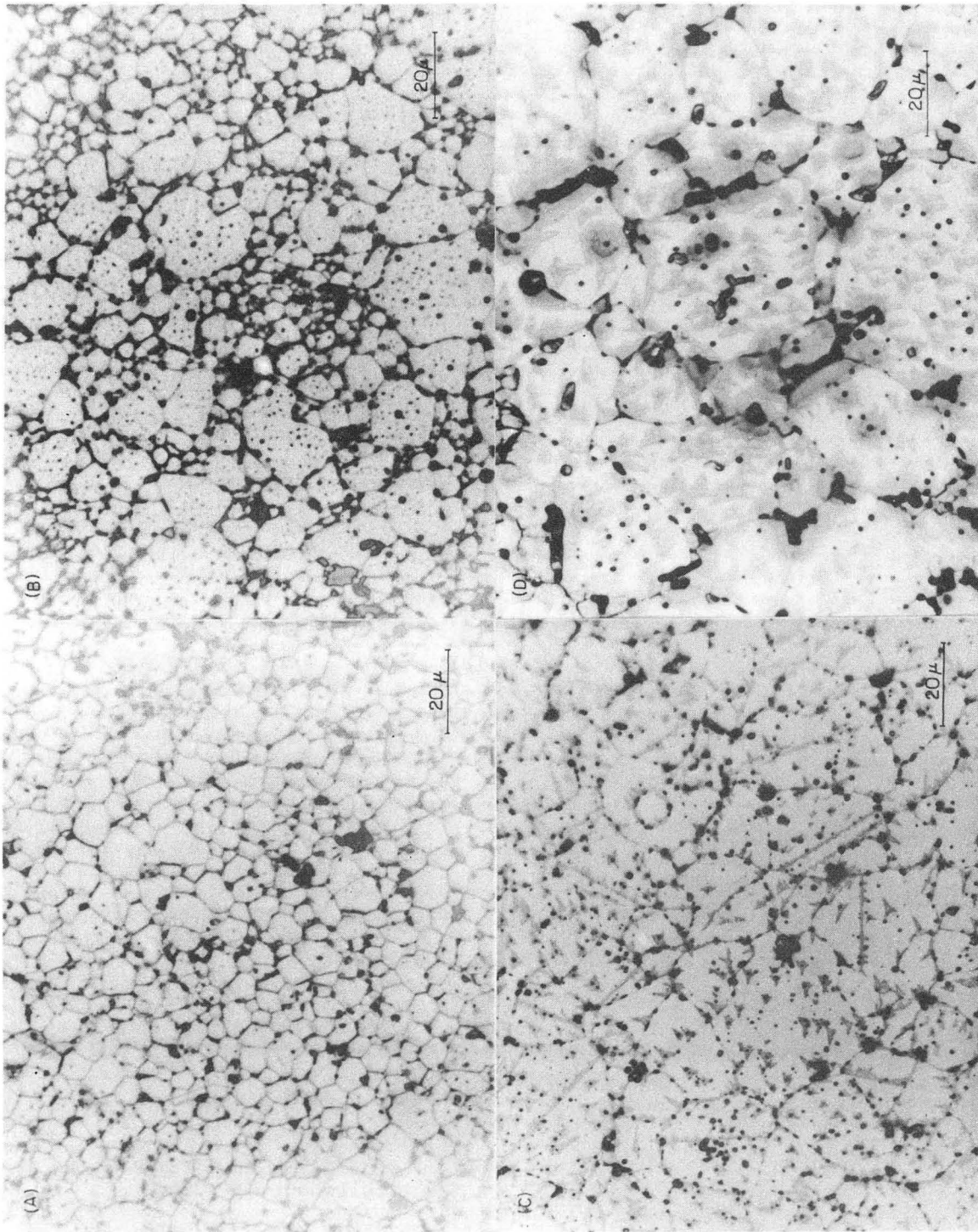
Figure Captions

- Fig. 1. Dependence of the sinter density on the amount of dopants. Sintering runs were done at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder.
- Fig. 2. Influence of NiO dopant on the microstructure of the specimens sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder. (A) 1 mol% NiO, (B) 3 mol% NiO, (C) 5 mol% NiO, (D) 10 mol% NiO.
- Fig. 3. Weight loss data in air for constant heating rate runs for lithium ferrite compositions with varying NiO content.
- Fig. 4. Equilibrated weight loss data for various compositions. Equilibration was always achieved in air.
- Fig. 5. X-ray data for doped specimens sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder.
- Fig. 6. Microstructure of a specimen of composition (LiFe₅O₈ + 3 mol% LiFeO₂) sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder.
- Fig. 7. Influence of NiFe₂O₄ dopant on the microstructure of the specimens sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder. (A) 1 mol% NiFe₂O₄, (B) 10 mol% NiFe₂O₄, (C) 20 mol% NiFe₂O₄.
- Fig. 8. Influence of dopants on the bulk resistivity of the specimens sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder.
- Fig. 9. Influence of dopants on the coercive force (H_c) of the specimens sintered at 1150°C for 2 h in 1 atm O₂ and using stoichiometric packing powder.



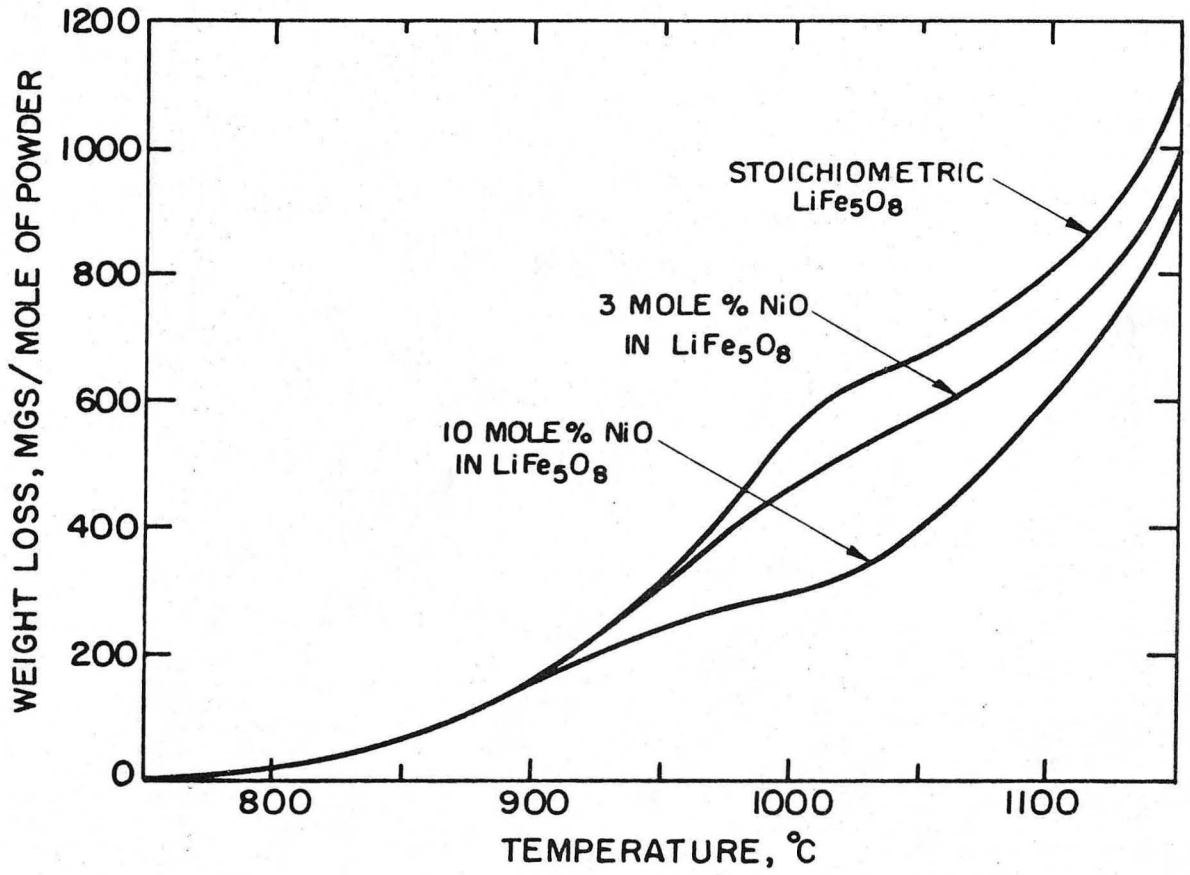
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Fig. 1



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Fig. 2



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Fig. 3

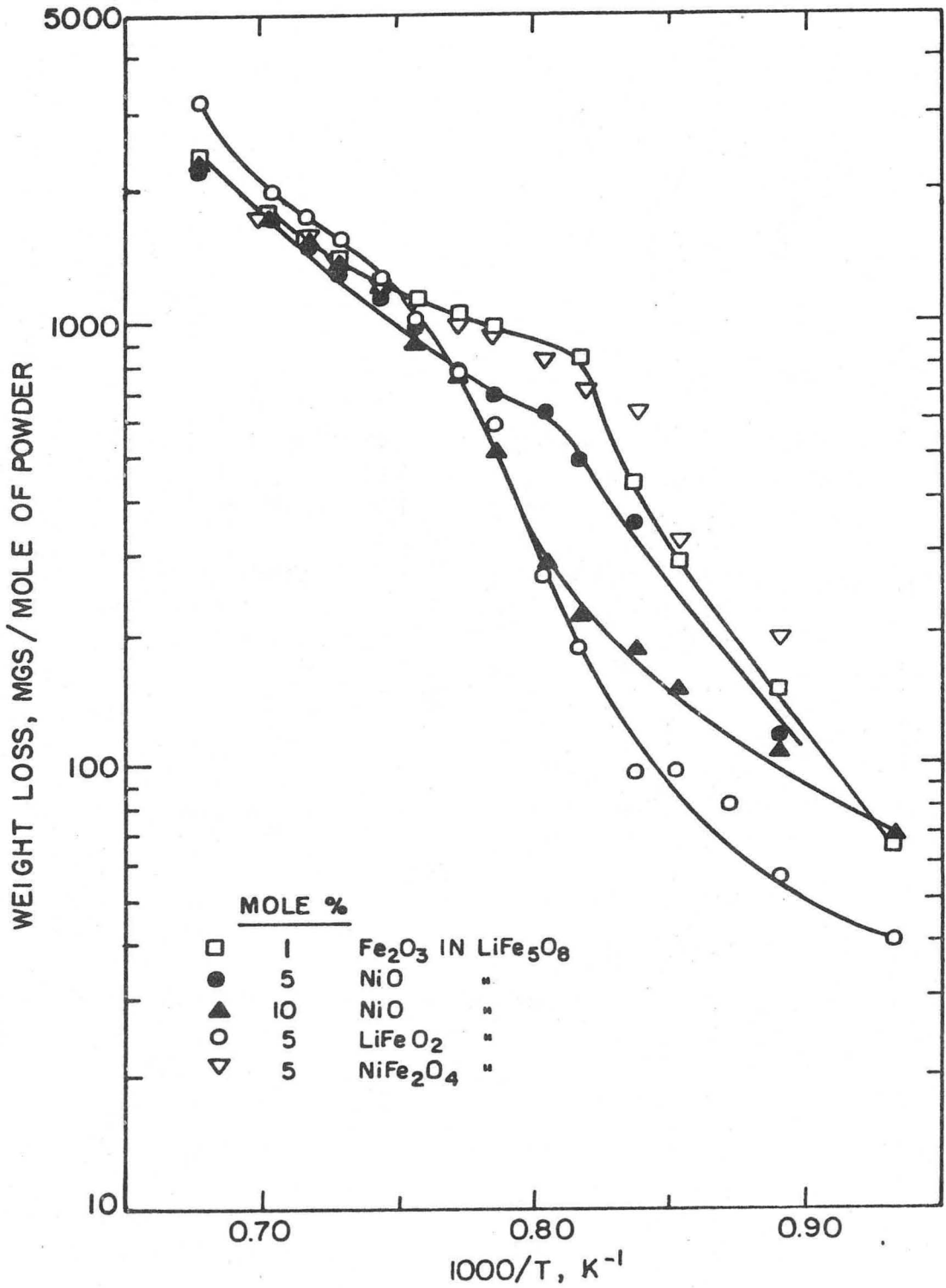
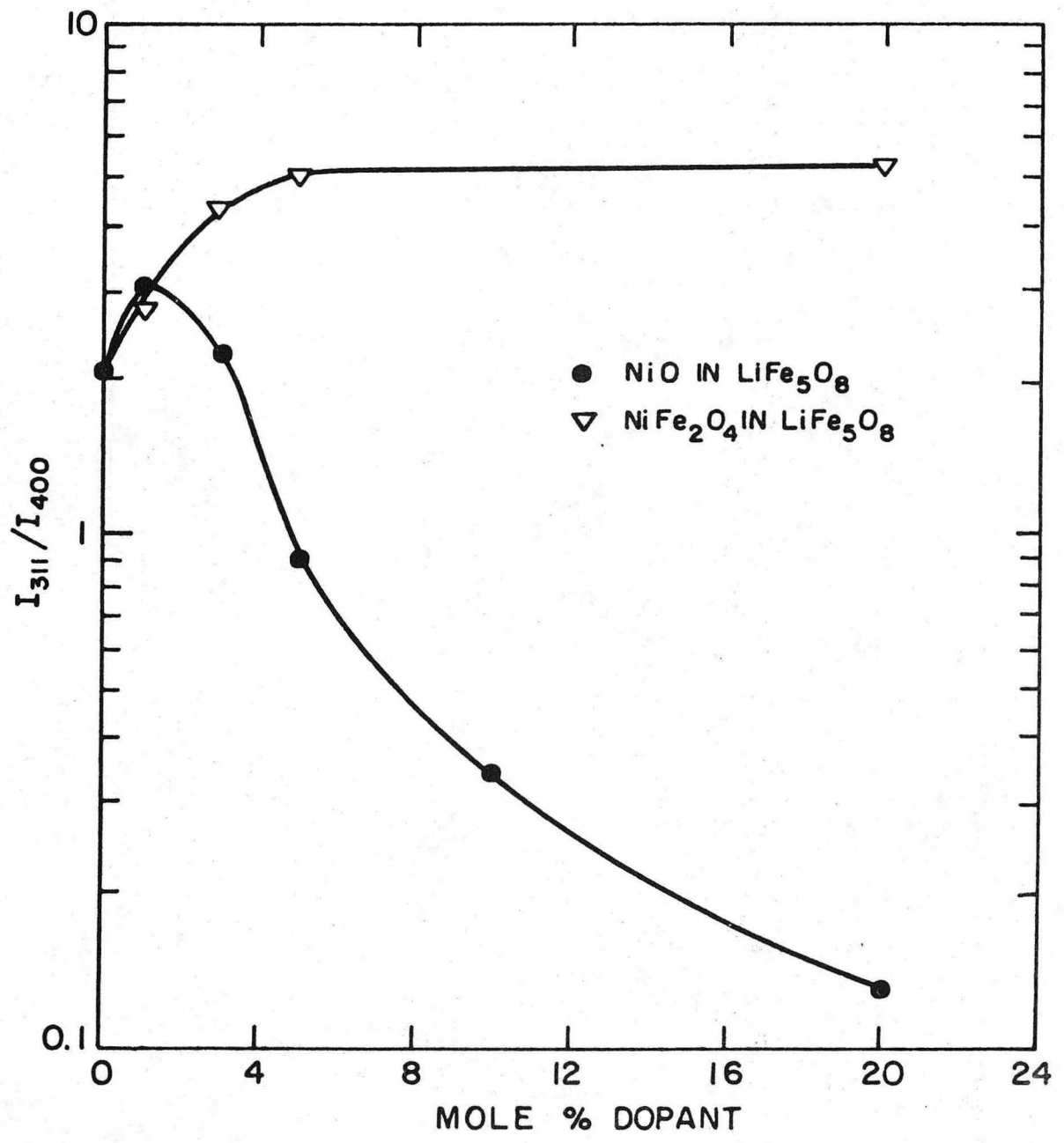
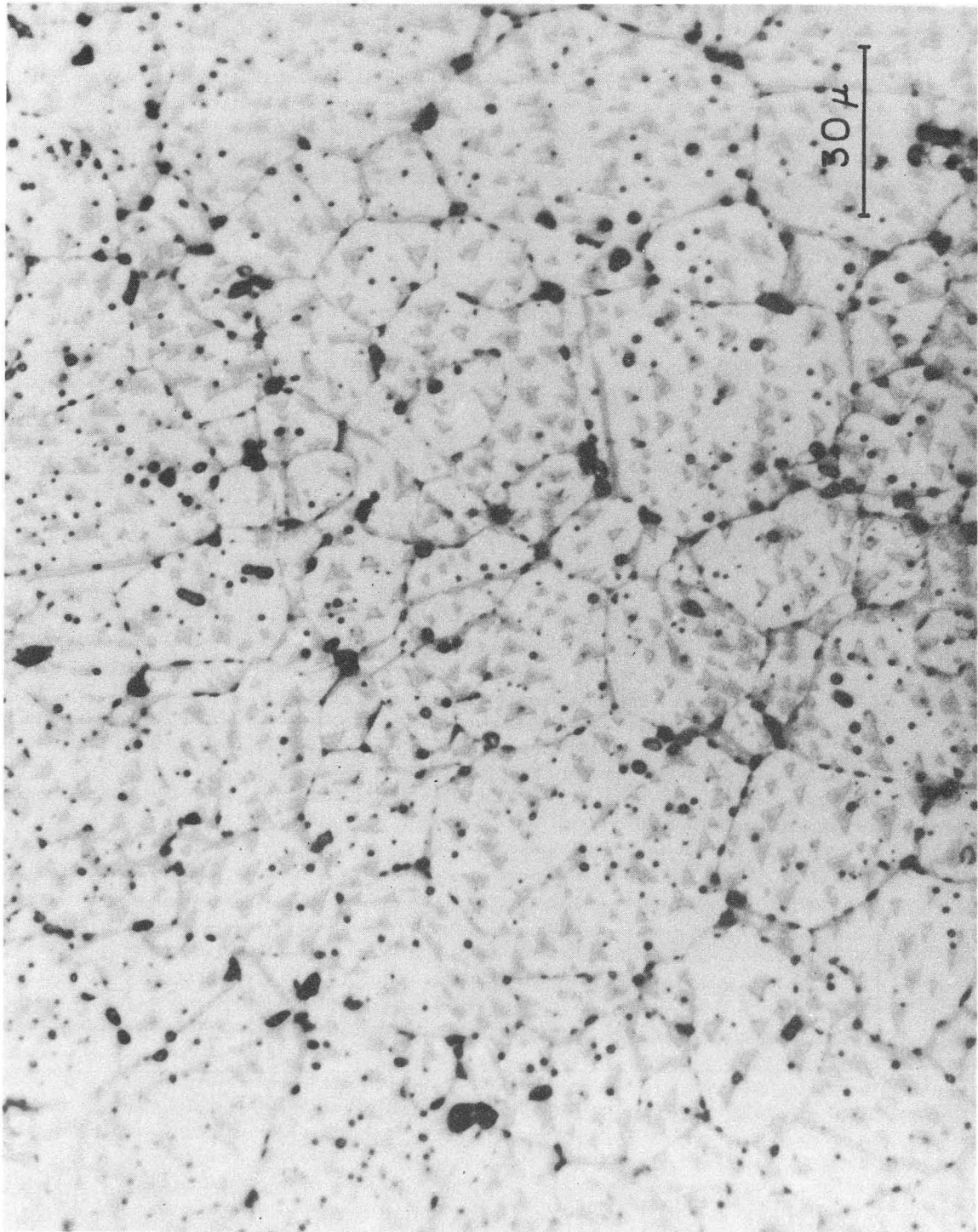


Fig. 4



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Fig. 5



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Fig. 6

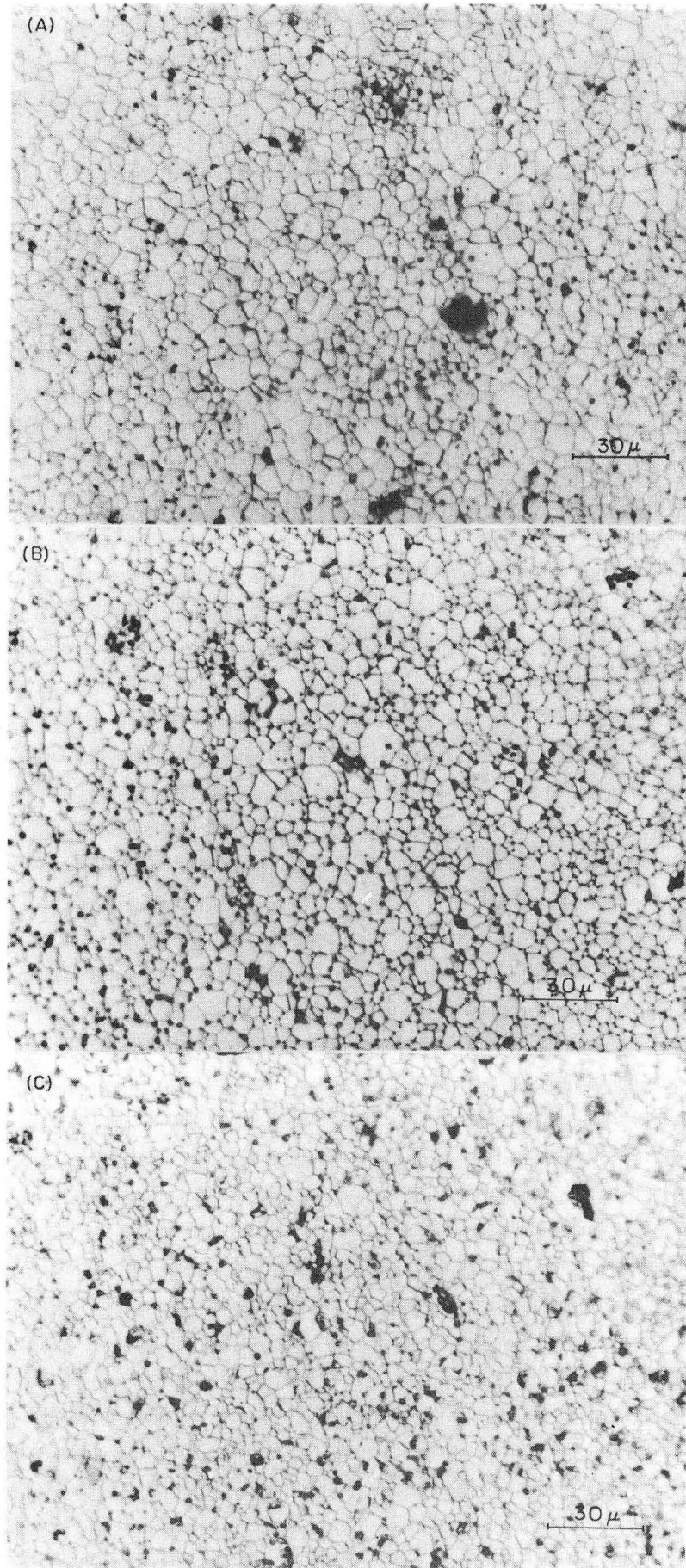
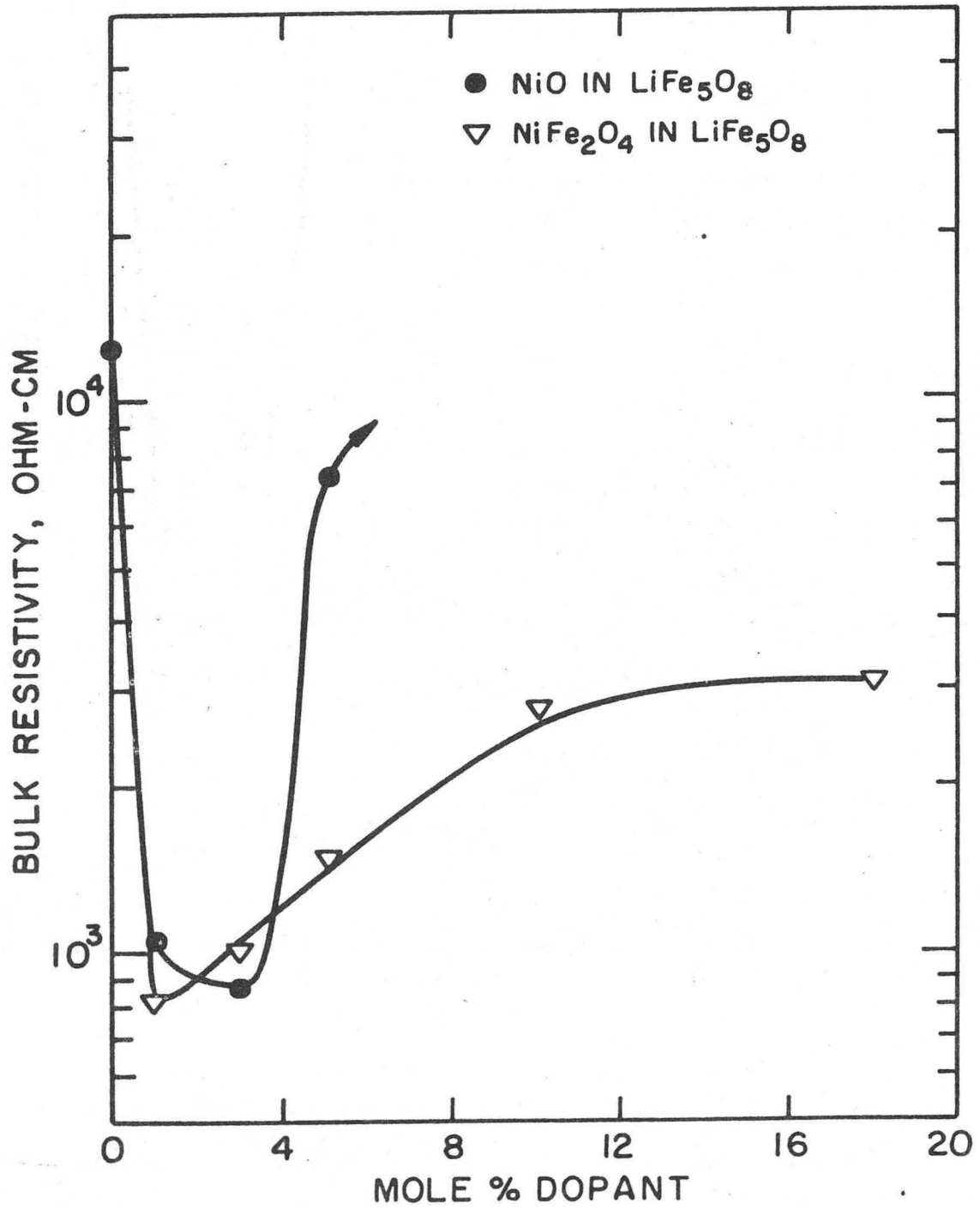
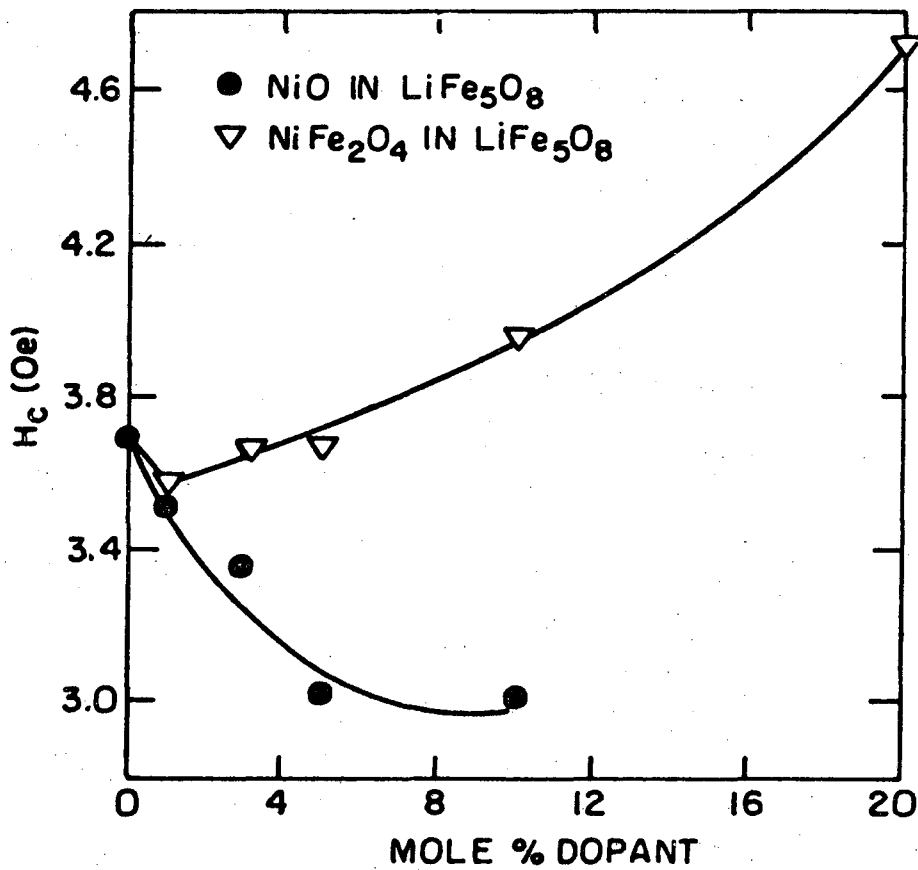


Fig. 7 XBB 739-5467



XBL 739-1840

Fig. 8



XBL 739-1841

Fig. 9

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