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Publication Date

1973-09-01

Submitted to J. Amer. Cer. Soc.
as a Note

LBL-2245
Preprint

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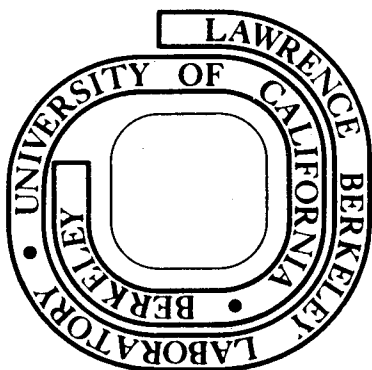
G. Bandyopadhyay, A. M. Lacy, and
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September 1973

Prepared for the U. S. Atomic Energy Commission
under Contract 7405-ENG-48

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DENSIFICATION AND GRAIN GROWTH IN
DOPED LITHIUM FERRITE SPINEL

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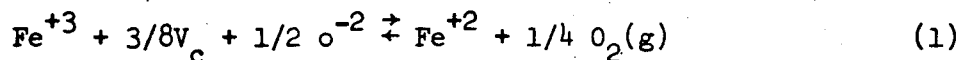
In processing of ceramic materials, it is very often desirable to add small amounts of selected additions to control the sintering, microstructure developed, and the physical and chemical properties. In the case of lithium ferrite, selective additives play a crucial role in developing a useful magnetic square loop material.¹⁻⁵ The purpose of this note is to report the influence of some common additives like NiO, MgO, TiO₂ and SiO₂ on the densification and grain growth behavior of lithium ferrite with respect to the sintering time, temperature and atmosphere. The sintering runs were done using a packing powder method⁶ where the specimens were buried deep into a packing powder composition to control the lithium loss. A high oxygen atmosphere was used to control the oxygen loss.

Lithium ferrite (LiFe₅O₈) powder was prepared from reagent grade Li₂CO₃ and α-Fe₂O₃. The method of preparation is identical to that described in a previous paper.⁶ Suitable amounts of dopants (NiO, MgO, TiO₂ or SiO₂) were added during the mixing of raw materials for better homogeneity after calcination. Three different packing powder compositions were used: (a) pure LiFe₅O₈, (b) LiFeO₂ + LiFe₅O₈ (2:1 mole ratio), and (c) LiFe₅O₈ + Fe₂O₃ (2:1 mole ratio). One of these packing powders was used during the sintering runs to control the lithium loss.

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Density was measured by geometric means and the grain size measurement was made from micrographs taken by scanning electron microscopy.

In Figure 1 log porosity vs log time is plotted for various sintering runs carried out in two different packing powder compositions and at two different temperatures (1000°, and 1100°C). These data were presented previously,⁶ and there it was concluded that a significant difference in the cation vacancy concentration in the composition depending on the packing powder led to the large density difference at 1000°C. However, at higher temperatures (e.g. at 1100°C) a large part of these excess cation vacancies can be lost by the loss of oxygen through the reaction,⁷



and thus packing powder may not influence the density significantly unless the oxygen loss can be eliminated. Thus there is an insignificant density difference at 1100°C depending on the packing powder relative to that observed at 1000°C.

In Fig. 2 similar plots with NiO, MgO, TiO₂ and SiO₂ doped specimens (1 mol% in each case) have been drawn along with that of the undoped lithium ferrite composition. It is interesting to note that NiO, MgO and TiO₂ doping do not affect the intrinsic sintering behavior significantly, although a slight improvement in the densification can be achieved. The influence of the packing powder on these compositions at 1000°C is equally strong as it was for the undoped specimens. This

suggests that in NiO, MgO or TiO₂ doped compositions, the nonstoichiometry introduced by the atmospheric conditions has a far greater effect than the extrinsic defects introduced by the dopants. The case of SiO₂ doping is somewhat different from the others. Apparently it forms a liquid phase as has been confirmed by the microstructural studies. Thus the sintering process in the SiO₂ doped specimens becomes more dependent on the amount and nature of liquid rather than on the defect structure of the solid.

At 1100°C the densification behavior in all the specimens is more independent of the packing powder similar to that noted for the undoped specimens (Fig. 1). The densification data at 1100°C with a lithia rich packing powder have been omitted intentionally from Fig. 2 in order to keep the figure simple. At 1100°C SiO₂ doping again exhibited a maximum enhanced densification.

In Fig. 3 log grain size vs log time has been plotted for specimens of various compositions and sintered in 1 atm O₂ with various packing powder compositions. It is noted that at 1000°C, all the data points for undoped, NiO, MgO, TiO₂ or SiO₂ doped specimens sintered in lithia rich or Fe₂O₃ rich packing powder at 1 atm oxygen, can be represented by a single straight line with a slope of 1/3. Despite significant density difference, these specimens showed an identical grain growth behavior. Furthermore, the density was always less than 90% (Fig. 2) which indicates the presence of an open pore structure in these specimens. Thus it is most reasonable to assume that the grain growth mechanism operative in these specimens is the same as was suggested by Greskovitch and Lay⁸ in their experiments with high porosity Al₂O₃ compacts. They suggest

neck growth between particles and the migration of the boundary followed by possible spheroidization of the remaining single particle. However, at 1100°C, deviation from a single straight line occurs with NiO, MgO, or TiO₂ doped specimens sintered in a high lithia packing powder and in 1 atm O₂ (Fig. 3). It should be noted that the above compositions (NiO, MgO, or TiO₂, doped LiFe₅O₈) sintered in Fe₂O₃ rich packing powder and 1 atm O₂, and undoped specimens sintered in either packing powder and 1 atm O₂, still follow the same single straight line without any apparent change in slope. SiO₂ doping led to rapid discontinuous grain growth in both packing powder compositions producing a microstructure with pores entrapped within the grains.

An enhanced grain growth rate with NiO, MgO or TiO₂ dopants in lithia rich atmosphere may be due to the change in the grain growth mechanism as a result of the change in the defect structure of the system. NiO or MgO in solution with lithium ferrite should create oxygen vacancies, whereas TiO₂ should form excess cation vacancies. Anion deficiency in ferrites favors discontinuous grain growth^{6,7} and thus enhanced grain growth with NiO or MgO doping is not unexpected. On the other hand, a cation deficiency should lead to a small grain microstructure with pores exclusively in the grain corners.^{6,7} But contrary to that, TiO₂ doping enhances the grain growth even more than does NiO. Thus it is evident that further analysis is necessary to understand the grain growth behavior in the doped lithium ferrite system in relation to the sintering atmosphere.

ACKNOWLEDGMENT

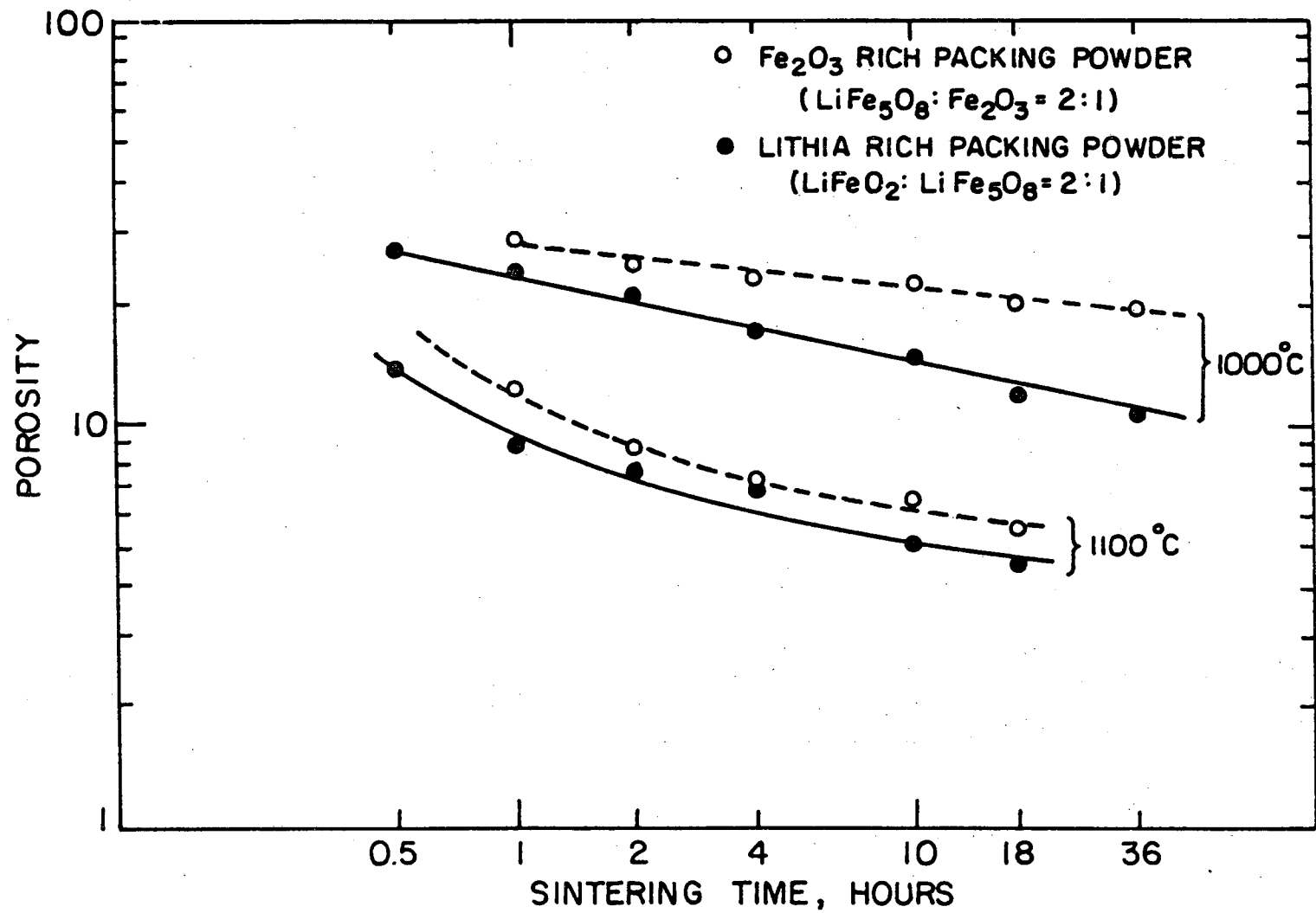
This work was done under the auspices of the United States Atomic Energy Commission.

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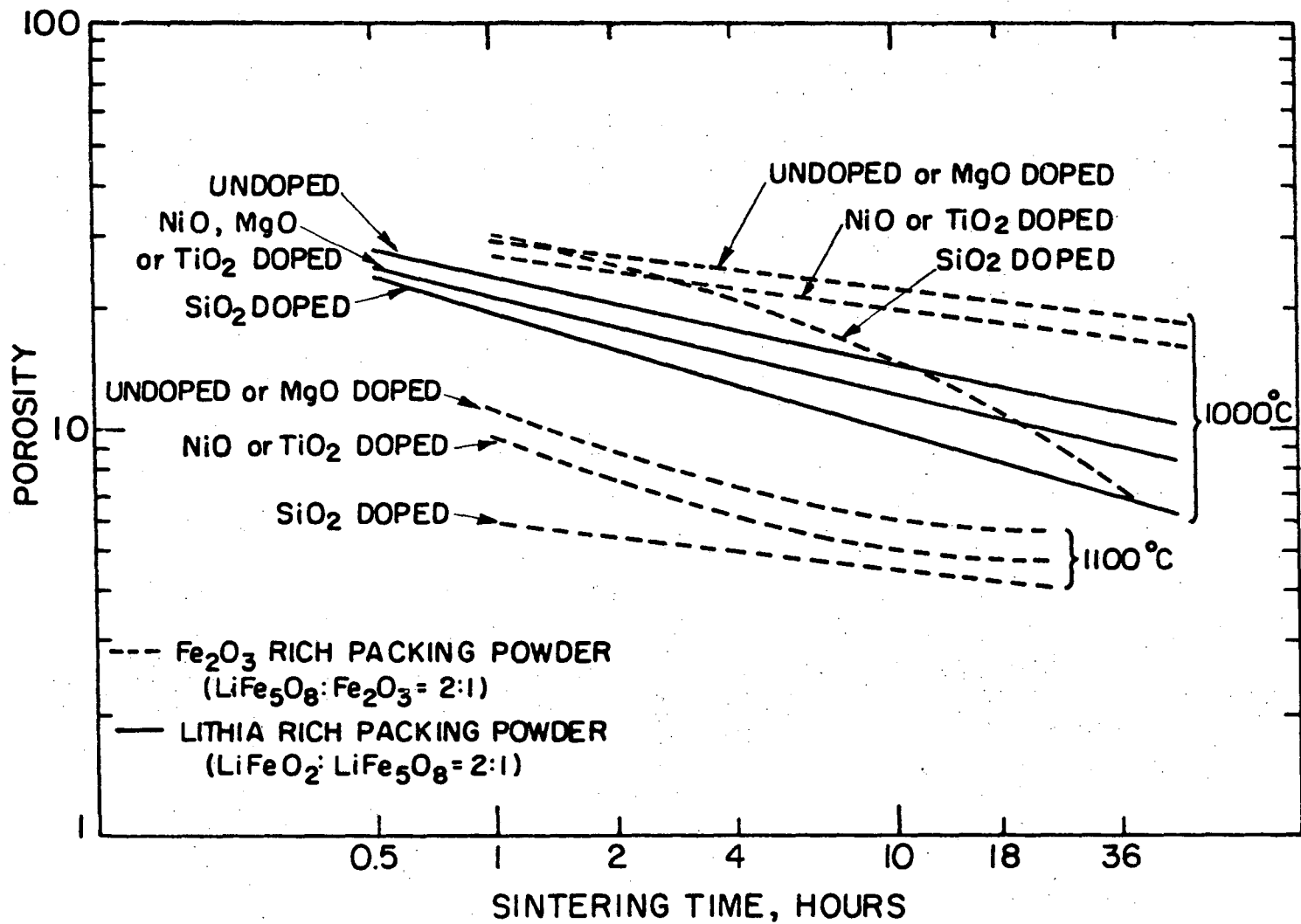
FIGURE CAPTIONS

- Fig. 1. Porosity-time relationship for some isothermal sintering runs of stoichiometric specimens in two different packing powder atmospheres and at 1 atm oxygen.
- Fig. 2. Porosity-time relationship for doped lithium ferrite compositions sintered isothermally in packing powder and at 1 atm O₂.
- Fig. 3. Grain size-time relationship for pure and doped lithium ferrite compositions sintered isothermally in packing powder and at 1 atm O₂.



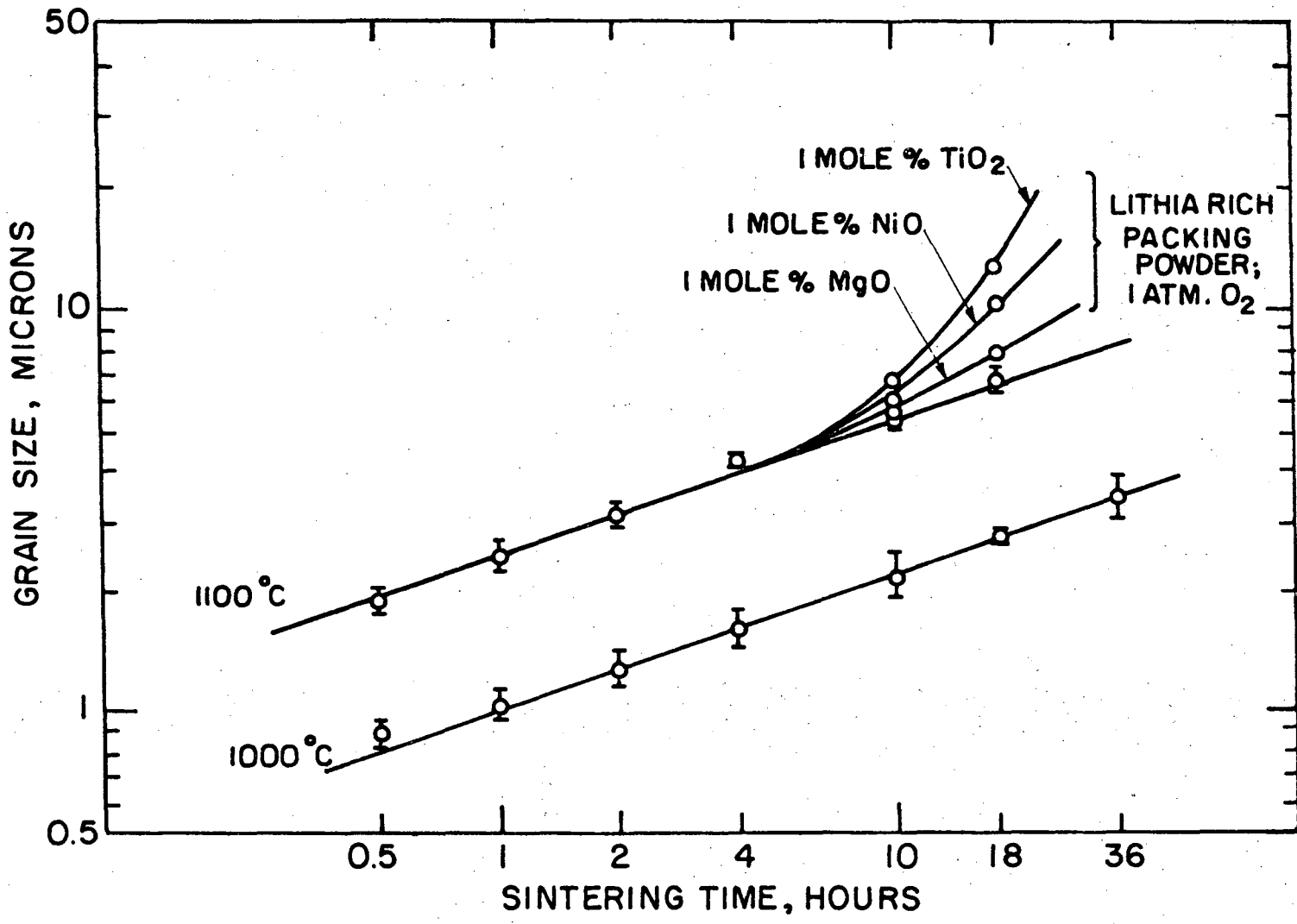
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Fig. 1



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Fig. 2



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Fig. 3

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