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FINE PARTICLE LI-FERRITE FOR APS MILLIMETER-WAVE PHASE SHIFTER.(U)
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Research and Development Technical Report

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# FINE PARTICLE LI-FERRITE FOR APS MILLIMETER-WAVE PHASE SHIFTER

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December 1977



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Powders composed of spheroidal particles 0.5-0.6 micrometer average size have been synthesized by rapidly quenching melts in the system lithium carbonate-boron oxide-iron oxide. The flow characteristics of the powders are adequate to fabricate Li-ferrite ceramic bodies by arc-plasma-spraying (APS) the powders. Post annealing leads to densification and grain growth with concomitant decrease in coercive force and increase in magnetization and remanence. Inversions in x-ray diffraction line intensity disappears with APS and annealing, yielding

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-20. Abstract (cont'd)

expected cation distribution. The inadvertent introduction of zinc accounts for the observed inverse relationship between magnetic moment and Curie temperature. The synthetic powder process requires further refinement to improve powder flow characteristics.

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TABLE



FIGURES

# FINE PARTICLE Li-FERRITE FOR APS MILLIMETER-WAVE PHASE SHIFTER

## INTRODUCTION

The arc-plasma-spraying (APS) process can be a cost-effective method for the fabrication of mm-wave ferrite phase shifters.[1] A rapid deposition rate and dense deposit are achieved if the feed powder upon passing through the APS gun becomes molten.[2] To achieve this, the powder must exhibit certain well-defined characteristics. It must be free flowing with submicron grain size because the most dense ferrite develops from submicron grains.[3] Agglomeration of particles is always present. The powder fed through the gun is composed of particle clusters whose size and distribution influence its flow character through the gun. A reasonable goal is a powder with 90% of its clusters < 37 μm, (400 mesh). Powders with good flow characteristics have been produced by flame spray and fluid bed techniques as well as by grinding fully sintered ferrite bodies, but these processes were found to be costly.[1]

Submicron particles of many ferrites have been produced by coprecipitation,[4] however, preparation of $LiFe_5O_8$ has not been reported. Wickham[5] has synthesized $LiFe_5O_8$ in molten salts from $Li_2CO_3$ and $Fe_2O_3$. Shirk and Buessem[6] have prepared submicron barium ferrite by quenching glasses in the system $B_2O_3$-BaO-$Fe_2O_3$. In this article, we report the APS deposition of $LiFe_5O_8$ from powders prepared by rapidly quenching melts in the system $Li_2CO_3$-$B_2O_3$-$Fe_2O_3$.

## POWDER SYNTHESIS

The following amounts of the indicated reagent were mixed together and loaded into a 500-ml platinum crucible; 8 mole % $Fe_2O_3$ (0.096 kg), 42 mole % $B_2O_3$ (0.221 kg), and 50 mole % $Li_2CO_3$ (0.278 kg). All constituents were reagent grade. The total charge was 0.595 kg which produced about 0.100 kg of $LiFe_5O_8$ powder. The crucible was heated to 1223-1273°K in an induction coil. The liquidus for this composition is just below 1173°K. When a homogeneous melt was perceived, the melt was poured down an aluminum inclined plane onto a copper hearth in the case of LS-2 or quenched directly into water for all others. The solid was then digested in hot 15% by volume nitric acid for 30 hours. After decanting to remove acid (pH ∿ 7), the powder was dried at 383°K. All samples were milled for 15-20 minutes to break up clumps. Four different batches were prepared and APS ferrites produced from each. In Table I the characteristics of each powder, APS parameters and magnetic properties are listed. Only Sample No. LS-7b-1 was leached in water until no

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1. W. Wade and R. Babbitt, AIP Conf. Proc. No. 34, 282-285 (1976).
2. R.W. Babbitt, Amer. Cer. Soc. Bull. 55, June 1976.
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4. T. Sato, M. Sugihara, and M. Sato, J. Chem. Soc. Japan 65, 52 (1962).
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6. B.T. Shirk and W.R. Buessen, J. Am. Cer. Soc. 53, 192-196 (1970).

lithium or boron was detected. It was then leached in hot acid for 2 hours. LS-3c-1 and LS-7b-1 were treated with acetone and $BiCl_3$, dried and heated at 773°K for 2-3 hours. The grain size was determined with a scanning electron microscope (SEM). The particle cluster size was determined with a sonic sifter.[7]

## MEASUREMENTS

Lithium ferrite powder was arc-plasma-sprayed onto $Li_2TiO_3$ substrates to form Li-ferrite ceramic bodies. Toroids were fabricated with an ultrasonic cutter. Hysteresis data ($H_c$ and $B_r$) were made with a standard 1000-cycle loop tracer in fields up to 5 times $H_c$. Density measurements were according to ASTM procedure C 376-56. Saturation magnetization was measured with a PAR vibrating sample magnetometer between 4.2°K and $T_c$ in fields up to 1.6T. Curie temperatures were determined by Arrott plots and magnetic moments $[\mu(H=\infty, T=0^oK)]$ by extrapolation of saturation magnetization from 4.2° to 0°K.

## RESULTS

Sample LS-2 powder, which was quenched more slowly than the other samples studied, had an average grain size of 1-2 μm. All other samples were water quenched and are typified by Fig. 1, a scanning electron micrograph, in which the average grain size is 0.5-0.6 μm but with some particles as large as 5 μm. The morphology is spheroidal. The first major objective, submicron particles, was achieved (Table I).

While the powders exhibited all the x-ray powder diffraction lines (no additional lines were ever noted), for lithium ferrite there was a complete inversion of intensities in 400 and 311 lines. In addition, the ratio of 400/220 before APS was 2.8 compared with 6.1 after. This ratio is sensitive to cation distribution[8] between octahedral and tetrahedral sites and reflects the presence of lithium on tetrahedral sites in powders before APS. Upon arc-plasma-spraying, the intensities of these lines came within 90% of the standard inverse pattern. After annealing for 5 hours at 1223°K, these intensities were within 98% of the standard inverse intensity.

In addition to the need for cation redistribution, post-annealing serves to increase the grain size and densify the ferrite. The former reduces the coercive force while the latter increases $B_r$ and $4\pi M_s$ (Table I). Particle size distribution shows a nearly exponential decrease from 2 to 14 μm for all annealed samples. Figure 2, a scanning electron micrograph of a fractured surface, indicates that while the average particle is ∿ 3 μm, a large volume is occupied by grains 10-12 μm in size. It should also be noted that most of the porosity is intergranular not intragranular.

Surprisingly, an inverse relationship between Curie temperature and magnetic moment was observed (Table I). In Fig. 3, the saturation magnetization is plotted for three samples, LS-3a-1, LS-3c-1, and LS-2. The inverse effect is quite obvious. All samples have $T_c$ less than the literature value of 943°K[9] although LS-2 is within 13 degrees of that value.

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7. J.J. Mitchell, ECOM Technical Report 4472, February 1977.

8. F. Bertant, Comptes Rendus 230, 213 (1950).

9. J. Smit and H.P.J. Wijn, Ferrites (Wiley, New York, 1959) p. 107.

Electron microprobe analysis indicated zinc present in LS-3a-1, LS-3c-1, and LS-7b-1. The following compositions, assuming Zn on tetrahedral sites, were determined: $(Fe_{0.938}Zn_{0.062})\ (Li_{0.469}Fe_{1.531})O_4$ for LS-3c-1 and $(Fe_{0.969}Zn_{0.031})\ (Li_{0.484}Fe_{1.516})O_4$ for Ls-3a-1.

The zinc present in the Li-ferrite originates from the metal quench containers from which zinc was dissolved by the action of alkaline solutions and is apparently retained by the ferrite in spite of thorough washing and acid treatment. This zinc retention is due to the large active surface of the fine ferrite particles. The magnetic moments calculated from these compositions, 3.10 $\mu_B$ for LS-3c-1 and 2.74 $\mu_B$ for LS-3a-1, are both somewhat larger than observed (Table I). The Curie temperatures are compared with values extrapolated from the literature.[10] The agreement here is somewhat better than that for the magnetic moments.

Increased moments could be produced by $Fe^{2+}$ arising from lithium loss during APS or annealing.[11,12] This would be most probable for LS-3c-1 in which the APS gun ran the hottest, approached the substrate the closest, and the oxygen flow was the slowest. The observed effect is, however, primarily due to the presence of zinc.

## CONCLUSION

A method has been developed for the synthesis of submicron average grains of lithium ferrites. Increase in percent of particles with a cluster size < 37 μm is still required for optimum APS gun control. This needs to be achieved by improved powder processing. With improved powder flow through the APS gun, lower gun currents and greater deposition distance will be attained. The coercive force on the one hand and the remanence and saturation on the other show an opposite dependence on particle size. Both will have to be considered in optimizing the particle size. The zinc, which is absorbed onto the active ferrite surfaces, finds its way into spinel tetrahedral sites upon melting and resolidifying during the APS process and by diffusion during annealing. The inadvertent addition of zinc can be eliminated by using plastic liners or containers in quenching. However, zinc will be added systematically to the melts for incorporation into the ferrite to increase $B_r$, $4\pi M_s$, and density to achieve a higher figure of merit for phase shifters at higher frequencies.[13]

## ACKNOWLEDGMENTS

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13. P.D. Bala, G.M. Argentina, W.E. Courtney, G.F. Donne, and D.H. Temme, IEEE Trans. Mag., MAG-8, 83 (1972).

TABLE I

APS LITHIUM FERRITE FROM QUENCHED FLUX MELT POWDERS

| Sample No. | LS-2 | LS-3a-1 | LS-3c-1 | LS-7b-1 |
|---|---|---|---|---|
| **Powder** | | | | |
| Av. grain size μm | 1-2 | 0.5-0.6 | 0.5-0.6 | 0.5-0.6 |
| % of batch with cluster size <37 μm | 60 | 25 | 32 | 45 |
| **As Sprayed (APS)*** | | | | |
| $H_c$ (A/m) | 1410 | 1230 | 1210 | 740 |
| $B_r$ ($Tx10^{-4}$) | 124 | 411 | 584 | 1417 |
| **Post Annealed *** | | | | |
| $H_c$ (A/m) | 33.0 | 29.7 | 25.7 | 37.0 |
| $B_r$ ($Tx10^{-4}$) | 1048 | 1964 | 1200 | 2447 |
| T/t ($^oK$)/(hr) | 1273/19 | 1223/5<br>1060/0.5 | 1223/5<br>1060/0.5 | 1223/5 |
| d ($kg/m^3 10^3$) | 3.90 | 4.20 | 3.73 | 4.16 |
| $4\pi M_s$ ($Tx10^{-4}$) | 2820 | 3400 | 3300 | 3950 |
| $\mu(H=\infty, T=0^oK)$ ** | 2.30 | 2.56 | 3.05 | |
| $T_c$(K) (Obs.)<br>(Lit.)10 | 930<br>943 | 879<br>875 | 842<br>830 | |
| Av. grain size μm | 5.5 | 3.07 | 3.50 | |
| **APS Deposition Parameters** | | | | |
| I (A) | 320 | 320 | 350 | 340 |
| d ($mx10^{-2}$) | 7.00 | 5.72 | 5.72 | 6.02 |
| Ar/He($m^3/s$) | 3.53/0.236 | 3.53/0.236 | 3.53/0.236 | 3.53/0.236 |
| $O_2$/feed ($m^3/s$) | 5.89/6.69 | 7.07/6.29 | 2.75/4.32 | 3.54/5.89 |

* Measure at $297^oK$

** Bohr magnetons

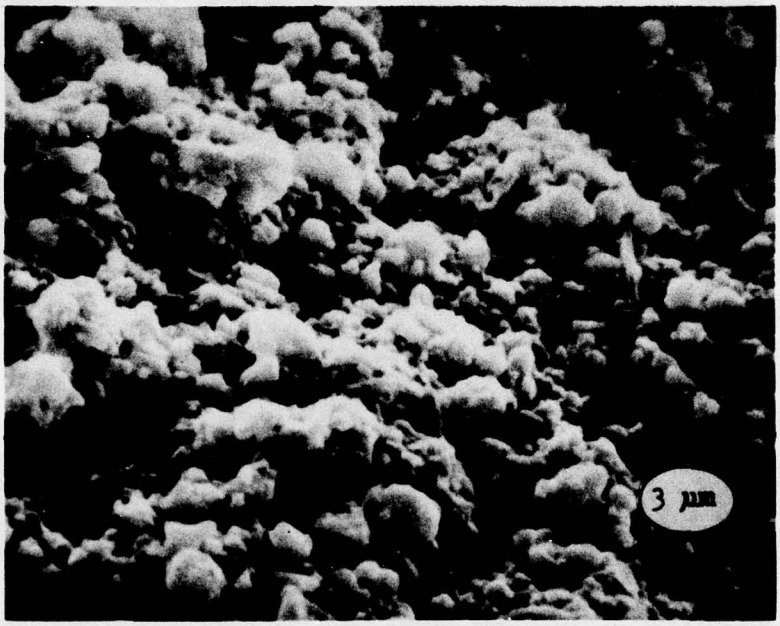
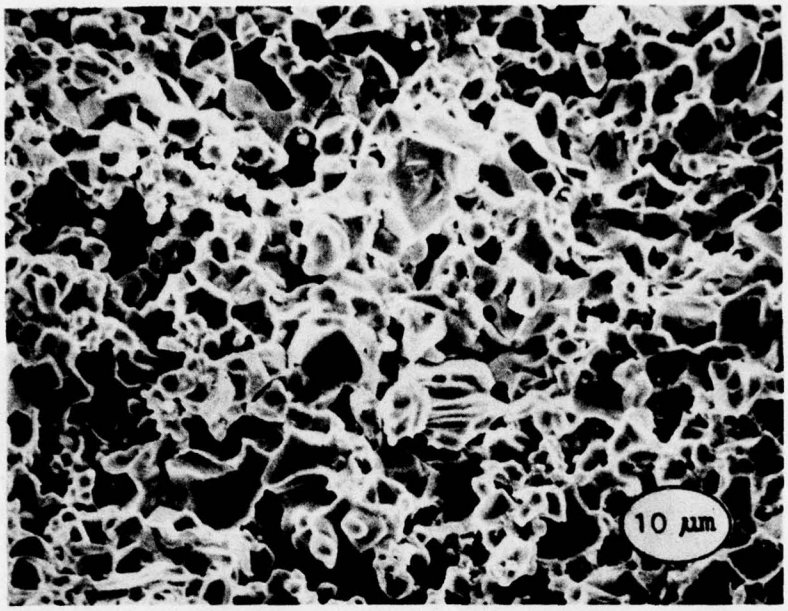


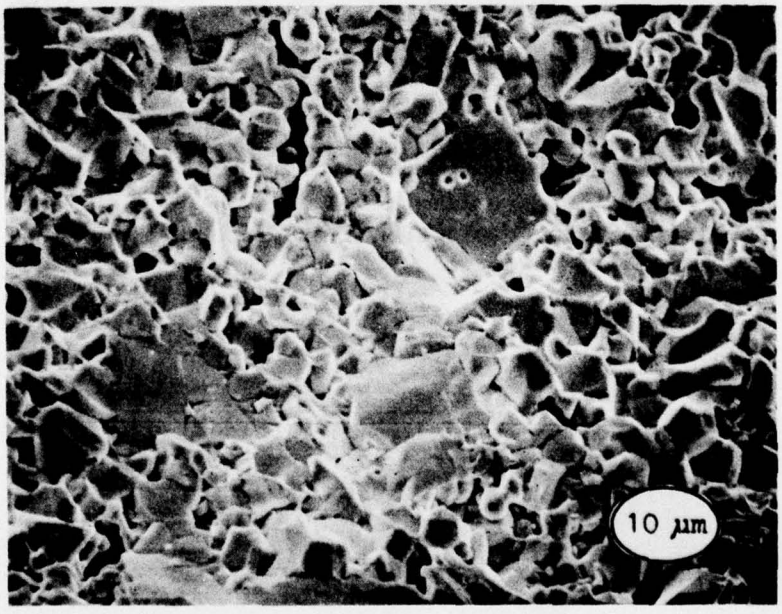

Fig. 1. Scanning electron micrograph of submicron grain size powder.

A




A. Sample No. LS-3a-1

B




B. Sample No. LS-3c-1

Fig. 2. Scanning electron micrograph of fractured annealed APS ferrite.

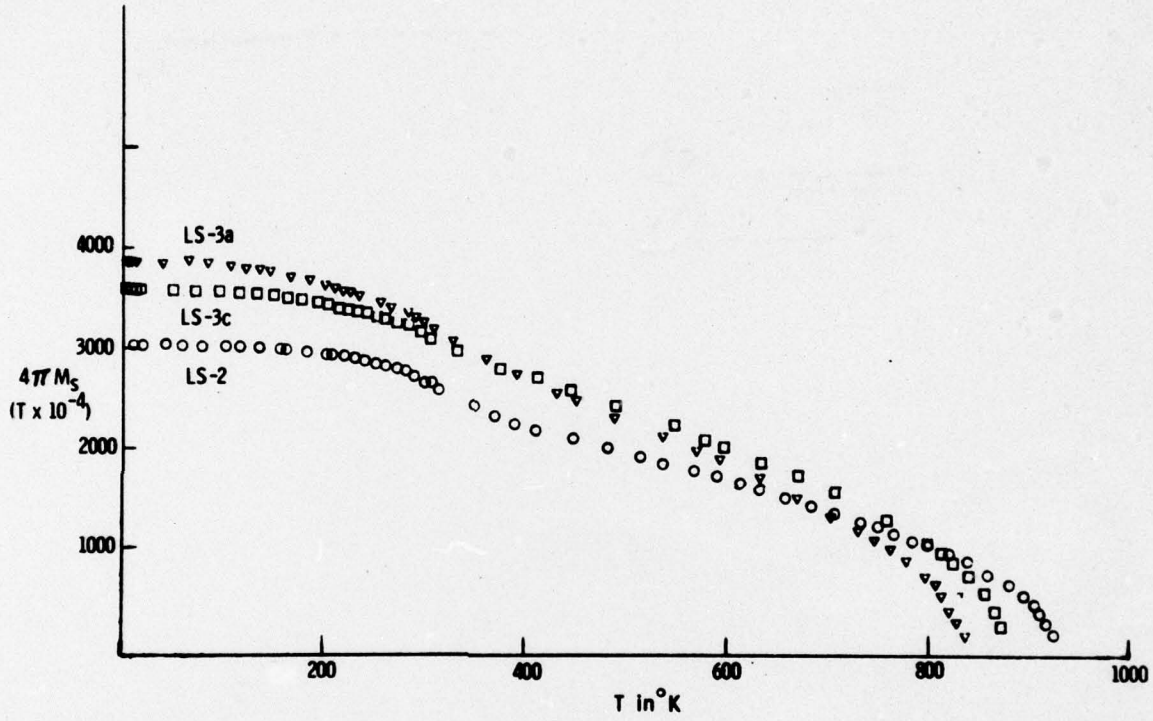



Fig. 3. Saturation magnetization versus temperature.