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Citation: Journal of Applied Physics **69**, 4053 (1991); doi: 10.1063/1.348415
View online: http://dx.doi.org/10.1063/1.348415
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/69/7?ver=pdfcov
Published by the AIP Publishing

Microwave dielectric loss studies on lithium-zinc ferrites

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(Received 11 July 1990; accepted for publication 6 December 1990)

Microwave dielectric parameters are measured for lithium-zinc ferrites with chemical formula $Li_{0.5-x/2}Fe_{2.5-x/2}Zn_xO_4$ ($x = 0.0$, 0.1, 0.3, 0.5, 0.6). All the samples except $x = 0.5$, show an increase in the dielectric loss with temperature. A relaxation-type mechanism is observed for $x = 0.5$. The results are compared with the low-frequency dielectric constant and loss.

I. INTRODUCTION

Lithium ferrites have emerged as a good substitute for the expensive garnets in the fabrication of microwave-latched devices[1] due to their properties such as higher squareness and remanence ratio, superior temperature stability of saturation magnetization, low intrinsic linewidth, and low magnetic losses far from resonance. The microwave magnetic properties have been widely studied.[2,3] However the results of dielectric studies of these materials at microwave frequencies are not available. The present note is aimed at discussing the results of temperature variation of microwave dielectric loss of zinc-substituted lithium ferrite.

II. EXPERIMENT

The samples with chemical composition $Li_{0.5-x/2}Fe_{2.5-x/2}Zn_xO_4$ ($x = 0.0$, 0.1, 0.3, 0.5, 0.6) were prepared by double-stage sintering. The samples are denoted as A,B,C,D, and E. The samples were fired at 900 °C to reduce the lithium loss.[4] In order to ensure good densification 0.2 wt % of bismuth-oxide flux material was added. The single phase nature of the samples was confirmed by x-ray diffraction.

dc electrical conductivity was measured using a two-probe technique with a Keithley electrometer (Model 610) and ac dielectric measurements were carried out with a GR 1615 capacitance bridge. The accuracy of ac and dc conductivities is $\pm 2\%$ and $\pm 4\%$, respectively. The microwave dielectric parameters were measured using a TE_{105}-mode rectangular cavity at 9150 MHz. The experimental setup consisted of a standard x-band test bench, comprising an X-13 klystron, isolator, attenuator, directional coupler, and magic Tee. One end of the collinear arm was connected with the cavity and the other end was terminated with a matched load. The detector mount was fixed at the E-arm of the Tee. This arrangement acted as the reflection-type cavity for easy temperature variation. The cavity was thermally isolated using a stainless-steel waveguide. An HP frequency counter (model 5352B) was used for the frequency measurement. The frequency measurement ensured an accuracy of $\pm 5\%$. The sample in the form of a thin rod was introduced at the center of the cavity and parallel to the electric-field maximum. The dielectric constant and loss are calculated from the resonant frequency and half-power-width frequencies.[5] More detailed discussion on the theory and measurement is reported in the literature.[6] The measurements were carried out from 300 to 650 K.

III. RESULTS AND DISCUSSION

The values of the dielectric constant and loss at 20 KHz and 9150 MHz, together with the dc conductivity data, are tabulated in Table I. The variation of dc conductivity and ac conductivity at 20 kHz with inverse of absolute temperature is shown in Figs. 1 and 2, respectively. The temperature variation of dielectric loss at microwave frequencies is shown in Fig. 3.

The frequency dependence of dielectric properties is usually explained by Koop's two-layer model of Maxwell–Wagner-type relaxation.[4] Grain boundaries in ferrites have different electrical properties from those of grains. This model assumes that grains with low conductivity separate the grains which are relatively good conductors. A large decrease in the dielectric constant and loss with frequency validates the two-layer model assumption. The hopping motion of electron is believed to occur through a thermally activated process. Consequently conductivity and the dielectric loss should increase with temperature. The temperature dependence of the conductivity is expressed as[7]

$$\sigma = \sigma_0 \exp(-E/KT), \tag{1}$$

where E is the activation energy. The experimental values of dc and ac conductivities which have accuracies of $\pm 2\%$ and $\pm 4\%$, respectively, are fitted into Eq. (1) for the determination of activation energy. Figures 1 and 2 indicate the validity of the above mechanism. The change of slope in the log σ vs $1/T$ plot is found to occur for many ferrites[8] indicating two parallel conductivity mechanisms with differing activation energies. In the present case the temperature corresponding to this change in the conductivity mechanism is different from the Curie temperature. The respective activation energies corresponding to the lower- and higher-temperature regions E_1 and E_2 for ac and dc conductivities are tabulated in Table II.

A high activation energy always goes hand in hand with high resistivity of the ferrite at room temperature, so

TABLE I. The value of dielectric constant and loss at 20 KHz and 9150 MHz and dc electrical conductivity at 300 K.

Sample	σ_{dc} (Ω^{-1} cm^{-1})	ϵ' at 20 kHz	ϵ'' at 20 kHz	ϵ' at 9150 MHz	ϵ'' at 9150 MHz
A	8.23×10^{-8}	1593.0	810.0	14.85	0.16
B	8.70×10^{-6}	2430.0	767.0	14.21	0.19
C	1.68×10^{-7}	168.4	105.0	14.14	0.13
D	1.71×10^{-7}	43.1	18.9	13.90	0.09
E	4.50×10^{-6}	1700.0	3921.0	14.52	0.17

it is important to analyze the conductivity results. The conductivity of lithium ferrite mainly depends on the temperature of preparation. The loss of lithium and presence of Fe^{2+} are the causes for this dependence. Conflicting reports on the conductivity of lithium ferrites are available[4,9,10] in the literature. The results of Kishan *et al.*[4] indicate that the addition of zinc to undoped lithium ferrite produces a marked increase in resistivity. The resistivity further increases with increasing zinc up to the concentration of 0.4 atom/formula unit, but then decreases for a sample with higher zinc content. The results of West and Blankenship[9] show the reverse trend for the annealed samples whereas the resistivity for the samples which are not annealed increases linearly. Rezlescue *et al.*[10] have observed that the resistivity increases with increasing concentration of Zn^{2+}. Another factor that can influence the conductivity is the ionic disorder in the *B* site.[11] The 1:3 order of Li and Fe^{3+} ions can be disturbed either by quenching the samples from 1000 K or by zinc doping. So it is worthwhile to compare the results of zinc-containing samples leaving the undoped lithium ferrite. The decrease in conductivity with zinc content may be due to the de-

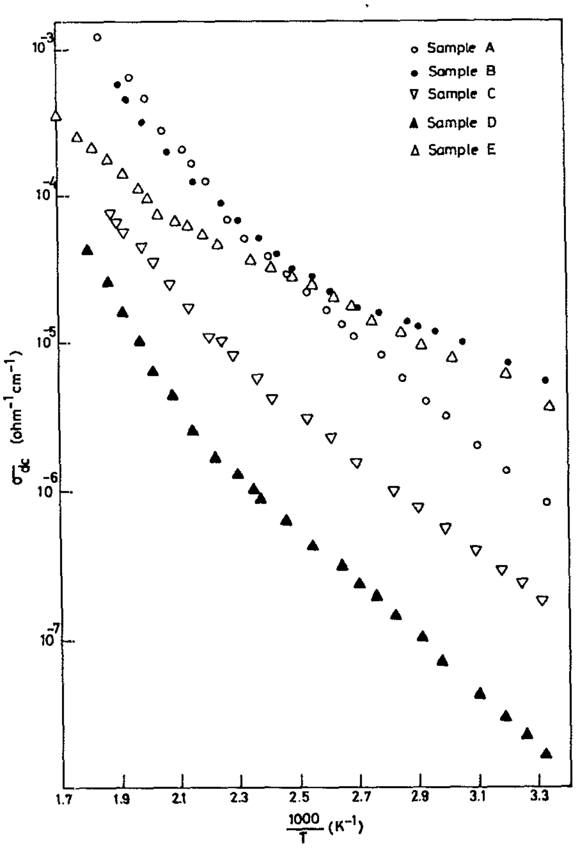

FIG. 1. dc conductivity vs inverse of temperature.

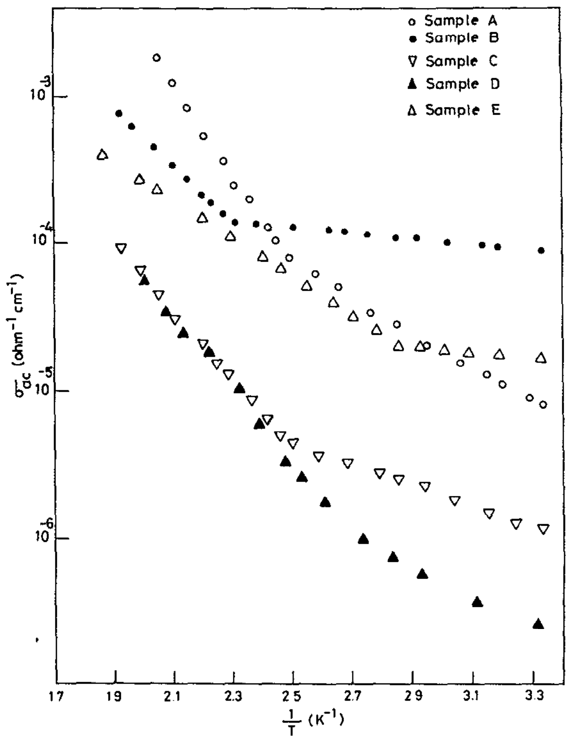

FIG. 2. ac conductivity vs inverse of temperature.

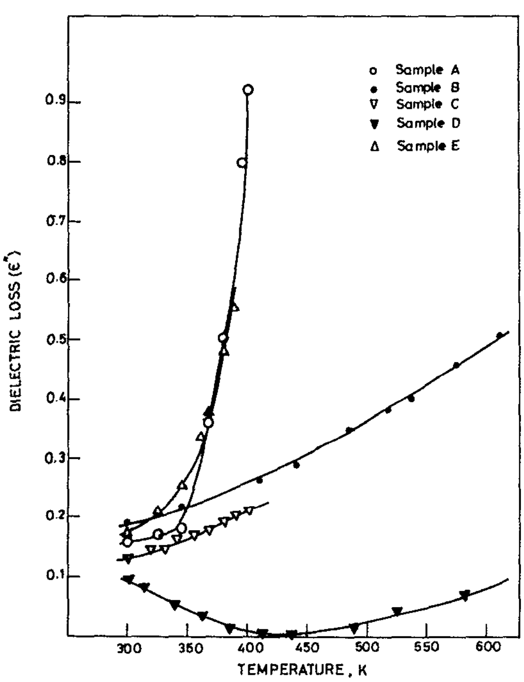

FIG. 3. Microwave dielectric loss vs temperature.

TABLE II. Activation energies E_1 and E_2 for ac and dc conductivities in eV.

Sample	E_1 (ac)	E_2 (ac)	E_1 (dc)	E_2 (dc)
A	0.23	0.60	0.35	0.53
B	0.04	0.41	0.16	0.40
C	0.14	0.45	0.28	0.61
D	0.21	0.46	0.36	0.70
E	0.20	0.26	0.20	0.38

crease in the lithium loss at the lower lithium content. In the Li-Zn ferrites, Zn loss is also possible during sintering.[12] Hence the possibility of ferrous content and enhancement of conductivity is more probable for higher zinc content. Whereas in the lower zinc content, the effect of Li volatilization is more significant in explaining the conductivity data. Koop's two-layer model also explains the variation of ac conductivity with frequency. It has been observed that the conductivity increases with frequency and attains constant value at very high frequency. The low and high activation energies are the natural consequences of the above variation of conductivity with composition.

At the microwave frequency, in all the samples except for sample D an increase in dielectric loss with temperature is observed. The behavior exhibited by sample D is similar to the results of Bethe and Verweel,[13] for Mg-Mn-Al-Zn ferrites and garnets. A relaxation-type process was observed by Samakhvalov, Ismailov, and Obukhov[14] for Ni-Zn ferrite with various amounts of ferrous ions and by Mizhushima and Iida[15] for Mn ferrites. Temperature variation studies of dielectric loss at the low-frequency region for Mn-Zn ferrite and magnetite also showed a relaxation-type process.[16,17]

Samakhvalov and co-workers[14] have observed that on reducing the ferrous content, the dielectric constant decreases and so does the value of dielectric maximum, while the temperature of this maximum shifts towards the higher-temperature side. It is well known that the preparation of lithium containing spinel is very critical because of the lithium oxide volatility. This leads to an enhanced dielectric loss due to the presence of Fe^{2+} content. From the dc and low-frequency dielectric results on these samples, it is obvious that the traces of ferrous ion content that is responsible for hopping loss is least for sample D. The observed decrease in the dielectric loss with temperature might be due to the portion of the relaxation curve and for the other samples the same is expected to occur at lower temperature.

ACKNOWLEDGMENT

Financial assistance from CSIR, New Delhi, is gratefully acknowledged.

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