DIELECTRIC PROPERTIES AND AGING OF MODIFIED LEAD TITANATE CERAMICS

B.K. Mukherjee*, H.D. Wiederick*, N. Maffei+ and E.S. Prasad+

*Department of Physics, Royal Military College, Kingston, Ontario,
Canada K7K 5L0
+B.M. Hi-Tech Inc., P.O. Box 97, Collingwood, Ontario, Canada L9Y 3Z4

ABSTRACT

Modified Lead Titanate Ceramics have shown considerable promise for use in underwater transducers. We have produced good quality ceramics with the general formula $(Pb,Ca)TiO_3-Pb(Co,W)O_3$. The material has a large tetragonal distortion and shows good piezoelectric properties. We have studied the dielectric properties of the material over a wide range of temperatures and frequencies. The material behaves like a good ferroelectric with a first order transition at 225°C. A preliminary study of its aging characteristics indicates that the dielectric properties of the material are reasonably stable.

I. Introduction

After the discovery of the piezoelectric properties of Barium Titanate, attention was focussed on other similar materials and lead titanate was reported to be a ferroelectric in 1950. It was found that lead titanate can form from the solid state reaction of lead oxide, PbO, and titanium dioxide, TiO_2, at a temperature as low as 360°C. Unfortunately pure lead titanate breaks up into a powder when cooled through the Curie temperature. However, small amounts of some additivies, such as calcium, inhibit cracking by reducing the spontaneous strain and keeping the grain size small. It is thus possible to produce good quality ceramics and calcium-modified lead titanate has shown considerable promise for use in underwater transducers[1]

B.M. Hi-Tech Inc. have produced good quality ceramic research specimens with the general formula:

$$(Pb,Ca)TiO_3 - Pb(Co,W)O_3 \quad .$$

The material has large tetragonal distortion and a c/a ratio of 1.14; this reduces the radial mode of vibration and the material shows good piezoelectric properties with a d_{33} value of about 65, thickness mode electromechanical coupling of 42% and a radial mode coupling of 4 to 6%. Owing to the complexity of solid solution formation and the critical processing parameters required to produce stable ceramics with high tetragonal distortion, it is important to know the electrical characteristics of the material. We have measured the dielectric properties of two specimens, of slightly differing compositions, produced by B.M. Hi-Tech Inc. and designated by them as BM322 and BM323. We are also studying the aging characteristics of the specimens and some of our preliminary observations are presented here.

II. Experimental Results

Our basic experimental arrangement is shown in Fig. 1. An Apple IIe microcomputer was used to remotely control a Hewlett Packard Model 4192A Low Frequency Impedance Analyser. Data obtained by the analyser was transmitted to the computer via the IEEE488 bus and recorded on floppy disc. The data was later manipulated by custom software which allowed the graphs to be generated on the plotter.

Both our specimens, BM322 and BM323, showed very similar behaviour and we present results pertaining to the BM322 specimen only.

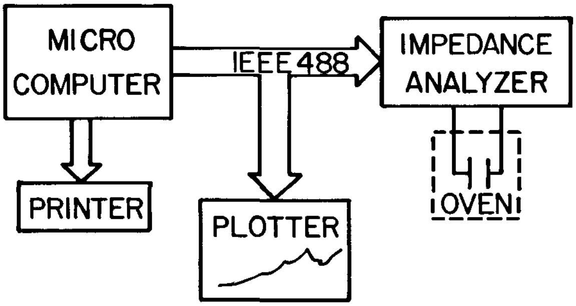

Fig. 1 Schematic of our experimental set-up.

Fig. 2 shows the inverse of the low frequency dielectric constant as a function of temperature

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at three different frequencies. A clear phase transition from the ferroelectric to the paraelectric phase occurs at 225°C for all three frequencies. This compares with a transition temperature of 492°C obtained by Remeika and Glass for lead titanate crystals.[2] Just above the transition temperature, the dielectric constant follows the Curie-Weiss law with Curie constant $C = 3.6 \times 10^5$ K. The ratio of the slope just below the transition to that just above is -5.85 which suggests that the transition is of the first order (Devonshire's theory[3] suggests a ratio of -8 for a first order transition and a ratio of -2 for a second order transition).

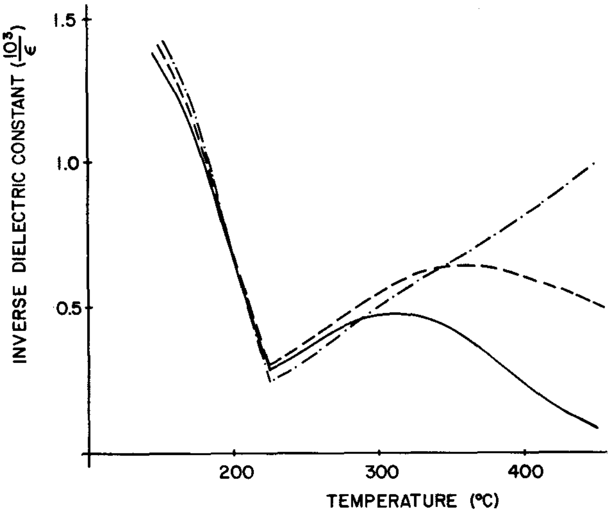

Fig. 2 Variation of the inverse of the dielectric constant as a function of temperature at three frequencies: full line 1 KHz, dashed line 100 kHz, dots and dashes 1 MHz.

Our measurements of dissipation in the specimen show that the loss factor increases steadily with temperature at lower frequencies but at 1 MHz there is an absorption peak corresponding to the phase transition. These results indicate that dc conductivity plays a dominant role in the dielectric behaviour of the material at lower frequencies whereas at higher frequencies the material shows a resonance type of behaviour. Further evidence of this can be seen in the variation of dielectric constant with frequency which is shown in Fig. 3. There is a dispersion in the megahertz frequency range at all temperatures and there is an additional dispersion in the lower frequency end at higher temperatures. We also note that Fig. 2 shows departures from the Curie-Weiss law behaviour for low frequencies at high temperatures, which suggests that the dispersion at low frequencies is due to contributions of a non-ferroelectric nature.

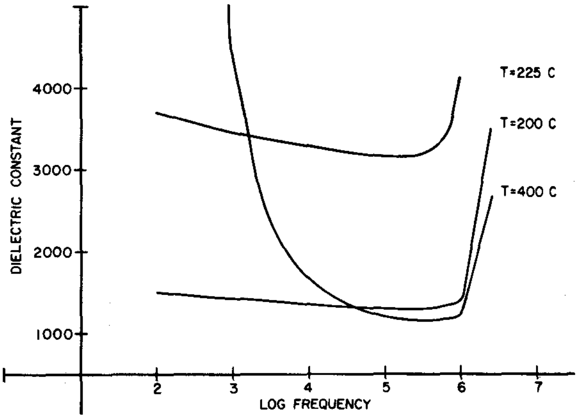

Fig. 3 Variation of the dielectric constant as function of frequency at three different temperatures.

In Fig. 4 we show the variation of the imaginary impedance as a function of the real impedance at three different temperatures. The 400°C curve is close to being circular which indicates a single relaxation time while the curves at other temperatures are skewed arcs and indicate a distribution of relaxation times.

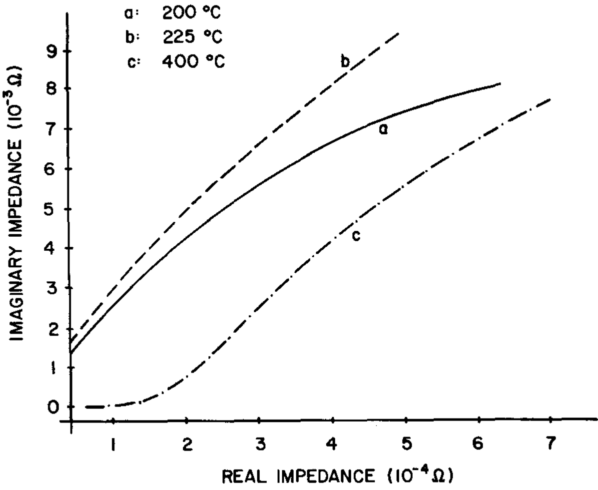

Fig. 4 Variation of the imaginary impedance as a function of the real impedance at three different temperatures.

Our observations could perhaps be described by a model with a resonant circuit and a temperature dependent load. The resonance, observed at around the megahertz frequency range, would be due to ferroelectric domains and associated domain wall motion. The dc conductivity of the specimen acts as the temperature dependent load on the resonance circuit. Such a circuit would show load dependent pass band behaviour similar to our observations.

We have also commenced a study of the aging behaviour of the specimens. Some preliminary results on the variation of the capacitance and the thickness mode resonance frequency at 30°C is shown as a function of time in Fig. 5 and Fig. 6 respectively. For these measurements the origin of time has been taken at 24 hours after polarization. Our observations show a 1.2% change in the dielectric constant per time decade and a 0.7% change in the resonance frequency per time decade. A more complete characterization of aging in these specimens is underway and will be reported later.

III. Acknowledgements

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IV. References

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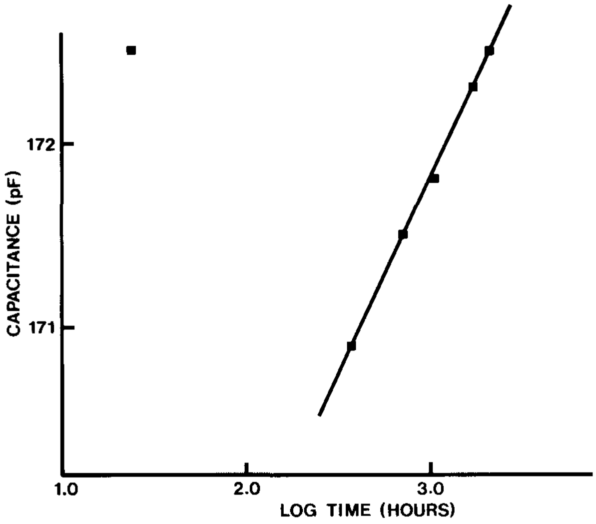

Fig. 5 Variation of the specimen's capacitance with time.

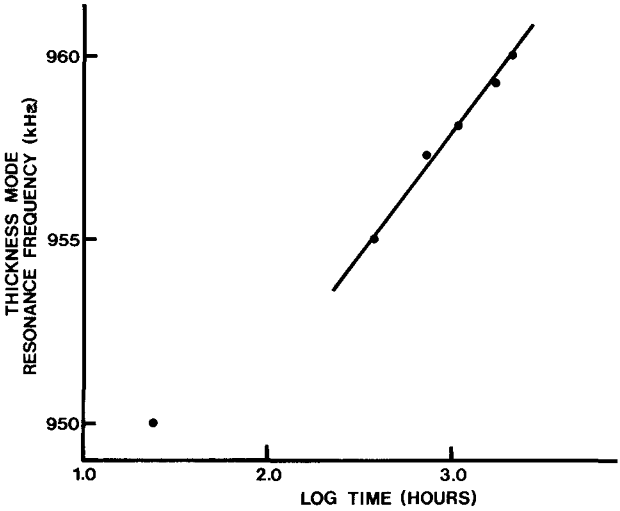

Fig. 6 Variation of the thickness mode resonance frequency of the specimen with time.