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# Dielectric Behaviour of Lead Nitrate with its Phase Transition

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The dielectric constant of lead nitrate is measured between the temperature range 35 to 110 ºC. In present measurement, it has been found that the compound has lower value of dielectric constant below 38 °C while it rises upto the value of 1200 around 40 °C, after which it decreases upto the value of 400 at about 75 °C, with some intermediate fluctuations. After 75 °C the dielectric constant increases with temperature almost linearly upto 110 °C. When the behaviour of compound is studied in cooling cycle, then pronounced hysteresis is found with certain intermediate fluctuations. The results have been explained on the basis of crystal structure changes and the possibility of free internal rotation of nitrate groups with in the crystal lattice at elevated temperature.

**Key Words: Dielectric Constant, Ferroelectricity, Phase transitions.**

## INTRODUCTION

The anomalous dielectric properties of amorphous materials discovered on ceramic specimen around 1943 by different group of scientists in different countries. The ferroelectric activity in amorphous crystals were reported in 1945-46 by Von Hippel and co-workers[1] and independently by Wul and Goldman[2]. The dielectric propreties of single crystals were investigated extensively by Merz[3], subsequentaly Cross[4] and a number of other authors extended and improved the results obtained by Merz. It is clear from the temperature dependence of dielectric constant of $BaTiO_3$ like crystals that, it is different corresponding to its different phase. As in the orthorhombic phase, where the crystal generally consists of a mixture of domains with different orientations of polar axis, one might at first expect that the measured values of the dielectric constant fluctuate around a certain mean value.

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It is also noted that the dielectric constant exhibits pronounced anomalies at the transitions from tetragonal to orthorhombic and from orthorhombic to rhombohedral states. Since these are transitions between ordered states, one may observes thermal hysteresis in both cases over a temperature span of about 10-15 °C[5,6]. In many crystals, it is also observed that in the cubic phase, the dielectric constant follows the Curie-Weiss law at or above the room temperature. This temperature may vary according to the purity and defects of crystals[7]. The room temperature dielectric constant of the sample, however increseas as samples are annealed at higher temperature[8].

We have studied the dielectric behaviour of lead nitrate between the temperature range 35 to 110 ºC. It is found that the dielectric constant approaches to the value of 1200 at around 40 °C. This high value of dielectric constant in the compound is perhaps due to the structural phase change in it. Above this temperature the dielectric constant of sample decreases upto the value of 400 around 75 °C with certain fluctuations. These fluctuations are due to surface defects and trap centres in samples. Above 75 °C the dielectric constant of sample increases linearly with temperature it is perhaps due to the rotation of nitrate group within the crystal lattice.

## EXPERIMENTAL

The compound has been procured from E. Merck (India), Mumbai. The chemical was grinded into the fine powder in a agate mortar, avoiding direct sunlight and preferably the most of the sample preparation was done at night. The pellets were prepared with compression machine (Flextural Testing Machine CAT No. AIM-313, S.No.91070 AIMIL Associated, India), having pressure range 0-10 tonne wt/cm$^2$. A suitable die was used having rectangular cross-sectional area of the piston = 2.33 cm$^2$.

The polishing of the pellets has been done to obtain smooth parallel surface for electrode formation. The polishing of the crystal introduces electrical charges inside the material. These charges and strains are to be removed, which we did by the process of annealing of the sample. In this process the pellets were kept in a suitable furnace at nearly two-third of their melting points for sufficient times (generally 8-10 h). The most of the irreproducibility was removed by annealing and therefore this process was necessarly done. The electrodes were formed using colloidal silver paints.

The sample holder loaded with pellet is kept into the furnace such that it lies near to the middle part of the furnace. A good quality thermometer, precisely calibrated is used to record the temperature. This thermometer is adjusted with the help of stand in such a way that it touches the metallic part of sample holder to record the exact temperature of sample.

The usual substitution method *i.e.* with and without the specimen in suitable sample holder is used[9]. The sample holder was directly fastened to the capacity measuring unit (Zenith M 92 A).

## RESULTS AND DISCUSSION

Lead nitrate is colourless solid and has cubic structure. It has refractive index 1.782 and specific gravity 4.53. The melting point of compound is 470 °C. However the measurement has been taken upto the moderate high temperature available in the furnace. The variation of dielectric constant *vs.* temperature plot for heating and cooling cycles has been shown in Figs. 1 and 2, respectively. The electrode used was colloidal silver paint. The transition in heating cycle occur around 40 °C with some fluctations, during the transition dielectric constant vary from 1200 to 400, in the measured temperature range 40 to 75 °C. The dielectric constant of sample starts to increase after the temperature 75 °C, more or less linearly. This trend is also found in the cooling cycle curve with pronounced hysteresis (Fig. 2). However the fall is very sharp at 35 °C and thereafter, the dielectric constant increases almost linearly with small fluctuations, as it is shown in Fig. 2. The high dielectric constant data at about room temperature (ε = 1200) is found in both the heating and cooling curves; however there is some anomaly due to the surface defects and trap centres.

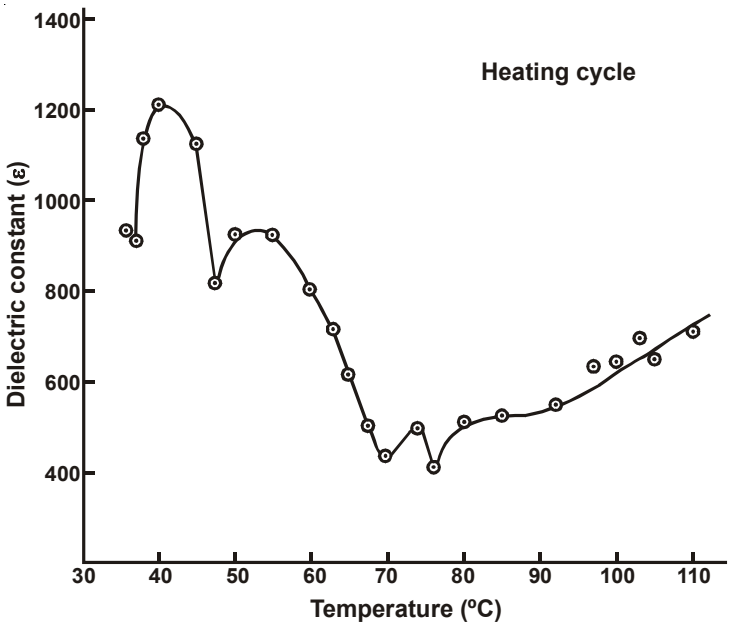


Fig. 1. Variation of dielectric constant of $Pb(NO_3)_2$ pellet with temperature, p = 5 ton/2.33 $cm^2$

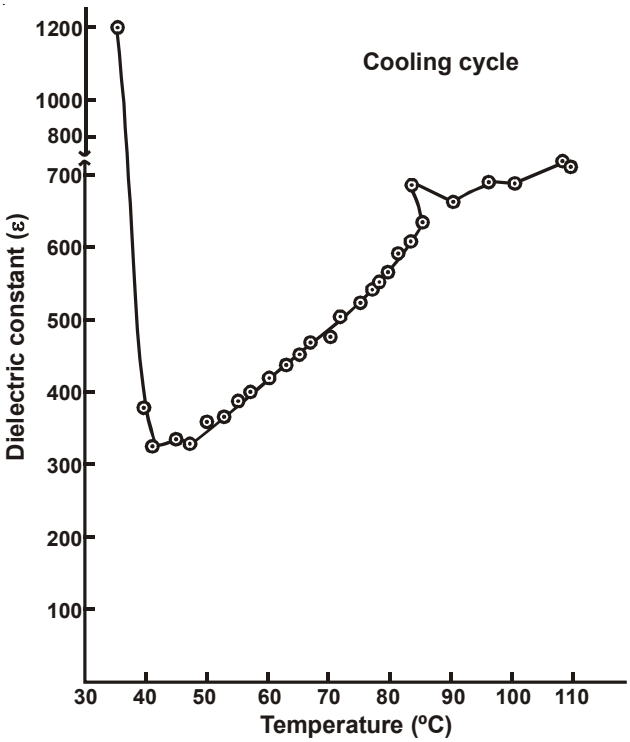


Fig. 2. Variation of dielectric constant of $Pb(NO_3)_2$ pellet with temperature, p = 5 ton/2.33 $cm^2$

The behaviour of dielectric constant of $Pb(NO_3)_2$ with the variation of temperature can be explained in context to its structural phase change and rotation of nitrate groups within the crystal lattice at elevated temperatures. The crystal structure of solid lead nitrate is in such a way that the compound crystallizes in the cubic system with the lead atoms in a face centred cubic system. The two nitrate groups lie above and below lead atoms at the same distance to the plane containing lead atoms. Above 35 °C the dielectric constant of lead nitrate follows the Curie-Weiss law approximately (Fig. 2) and the dielectric constant decreases inversely as the difference between the temperature and Curie temperature as it is also observed in case of barium titanate[10]. Actually ferroelectric transition in $Pb(NO_3)_2$ this temperature dipole moment develops due to the displacement of lead atom from its position, which causes the crystal change from cubic to tetragonal, similar as it is in case of barium titanate[11]. After the transition temperature the fluctuation in dielectric behaviour can be explained by flip-flopping of polar regions, in fact the orientation of dipoles, corresponds to the flip-flopping of polar region under external electric field

in the microscopic mechanism for high temperature relaxation polarization. At high temperature the density and moment of dipoles are small, so the interaction between the dipoles can be ignored and behaviour can be explained with the relaxation polarization.

After the 75 °C the dielectric constant start to increase linearly as shown in the Fig. 1 in heating cycle. This behaviour can be explained by considering rotational motion of nitrate group within the crystal lattice at the elevated temperatures. Perhaps when nitrate groups start to rotate with the crystal lattice then dipoles are formed again, which increases polarization with increase in temperature as it is reported by Gupta *et al.*[12] in case of nickel nitrate.

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## REFERENCES

1. V. Hippel, A. Breckenridge, R.G. Chesley and L. Tisza, *Ind. Eng. Chem.*, **38**, 1097 (1946).
2. B. Wul and I.M. Goldman, *Compt. Rend. Acad. Sci V.R.S.S.*, **46**, 139 (1945); **49**, 177 (1945); **51**, 21 (1946).
3. W.Z. Merz, *Phys. Rev.*, **76**, 1221 (1949).
4. L.E. Cross, *Phil. Mag.*, **44**, 1161 (1953).
5. W. Kanzig and N. Maikoff, *Helv. Phys. Acta*, **24**, 343 (1951).
6. M.E. Drougard and D.R. Young, *Phys. Rev.*, **95**, 1152 (1954).
7. F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon Press, New Yark, p. 112 (1962).
8. A.M. Glass, K. Nassau and J.W. Shiever, *Appl. Phys.*, **48**, 5213 (1977).
9. R.N. Gupta and M. Misra, *Indian J. Pure Appl. Phys.*, **19**, 1151 (1981).
10. J.A. Gonzalo and B. Jimenez, Ferroelectricity; Fundamental Collections, Wiley-VCH Verlag, Weinheim, p. 1622 (2005).
11. H.D. Megaw, *Trans. Faraday Soc.*, **42**, 224 (1946).
12. R.N. Gupta, G.K. Gupta, S. Yadava and K.S. Upadhyay, *J. Purv. Acad. Sci.*, **11**, 96 (2005).

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