Dielectric property of lead phthalocyanine

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Abstract. Dielectric constant and dissipation factor of lead phthalocyanine have been experimentally studied here as functions of frequency and temperature. Dielectric constant increases by one order of magnitude with temperature showing pyroelectric behaviour. It is explained that molecular distortion leads to increased dielectric constant.

1. Introduction

Lead phthalocyanine (PbPc) (tetraphthalonitrile) has lead chains along one crystallographic direction (Ukie 1973). It is found to be semiconducting (Ukie 1975; Frauenheim *et al* 1984).

Electrical resistivity of lead phthalocyanine in the form of thin films remains constant down to 4·2 K (Ukie 1975). Here we report dielectric property of this quasi one dimensional conductor.

2. Experimental

Lead tetraphthalonitrile (phthalocyanine) was prepared by refluxing lead monoxide with phthalonitrile from solution in nitrobezene (figure 1). The material was prepared from PbO and phthalonitrile powders both of which were amorphous. Thus PbPc was prepared in amorphous form. After that it was ground in a mortar to remove grains due to moisture and it was compressed in a high pressure die. So PbPc pellets were amorphous and not polycrystalline. A sample holder as shown (figure 2) was used for measurement of capacitance. The dielectric constant was evaluated from $C = C_0 \varepsilon$ where $C_0 = \varepsilon_0 A/d$. ε_0 is dielectric constant of air, A the area of pellet of PbPc and d the thickness of the pellet $\{\Sigma(100\,\text{Hz}) = 93$ at $40°\text{C}\}$. Capacitance and dissipation factors (dielectric loss) were measured using multifrequency LCR meter of Hewlett Packard Co.

3. Results and discussion

Both capacitance and dissipation factors are plotted against frequency and temperature (figures 3–6). The capacitance was found to increase in the range 40°C–300°C at 1 kHz. This temperature dependence reveals pyroelectric behaviour. When dielectric constant varies with temperature and remnant polarization takes place, then it is called a pyroelectric material (Tareev 1974).

There can be several contributions to dielectric constant viz. (i) ionic polarizability, (ii) interstitial polarization, (iii) electronic polarizability of atoms, (iv) lattice polarization,
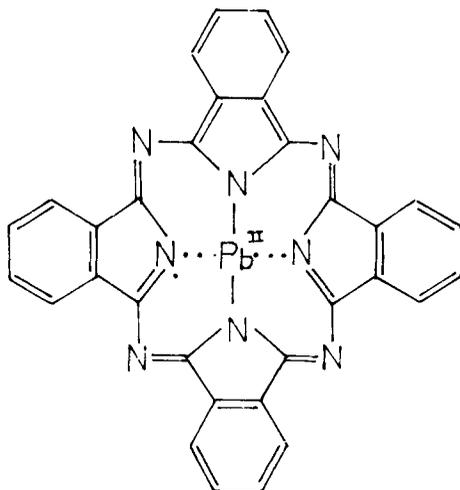
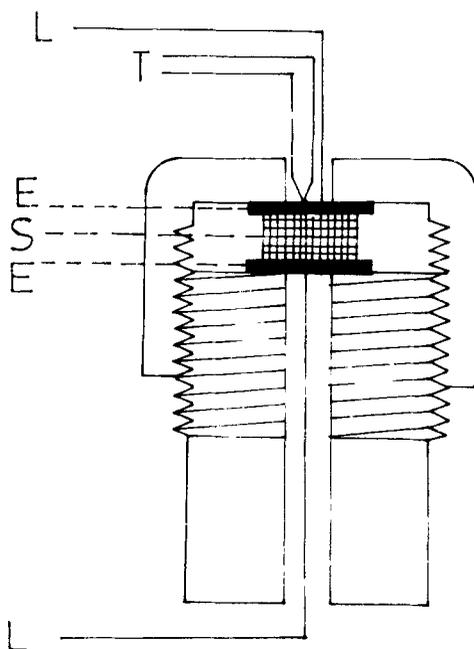**Figure 1.** Molecular structure of lead phthalocyanine.

Figure 2. Sample holder for capacitance measurement.

(v) molecular polarizability and (vi) ferroelectric transition. We discard the possibility of ion core polarizability because in that case dielectric constant should not change with temperature.

Interstitial polarization is also discarded because of homogeneous and amorphous pellets which are a continuous medium. The contribution from electronic polarizability is negligible because in that case variation of dielectric constant with frequency
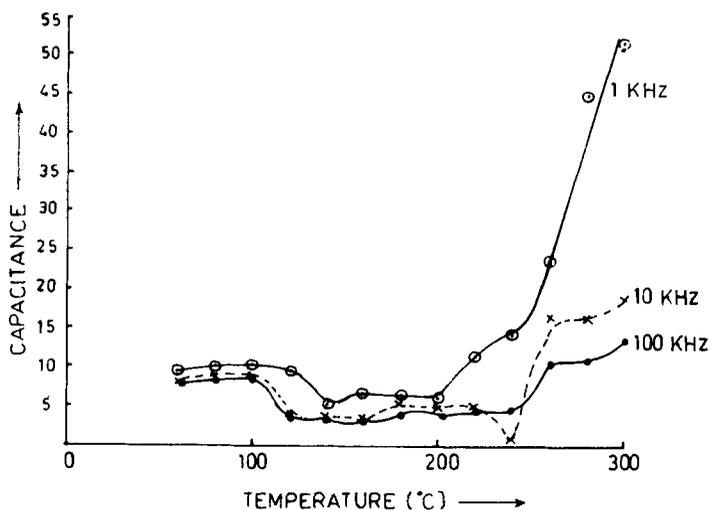
Figure 3. Temperature dependence of dielectric constant (capacitance is in pf).
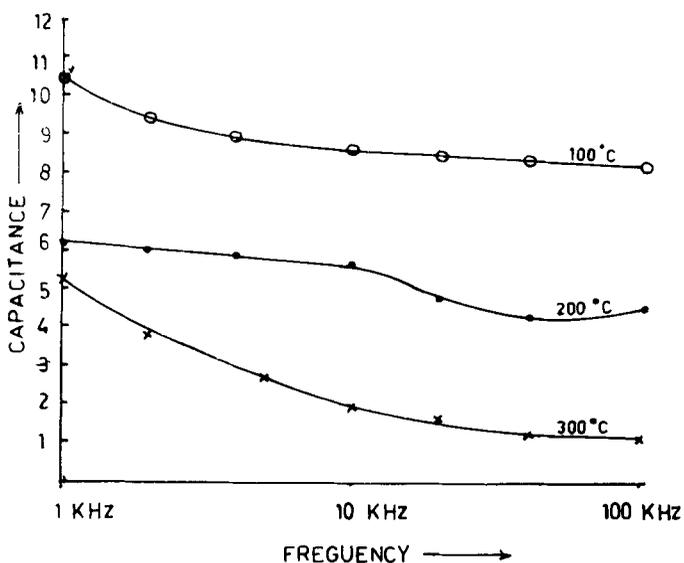

Figure 4. Frequency dependence of dielectric constant (capacitance is in pf).

should be very large. But it is not large (figure 4). Lattice polarizability is also not possible because of neutral molecules of PbPc in each unit cell. Also ferroelectric transition is discarded because change is only one order of magnitude and because of absence of two types of ions. Dielectric constant does not arise from localization of electrons.

There is no strong electron–phonon interaction along lead chains because of large band gap (Frauenheim *et al* 1984). Phonon generation at high temperature should increase dielectric constant due to phonon drag. Therefore, phonon drag does not localize charge carriers. Dielectric constant is not found to increase with frequency and
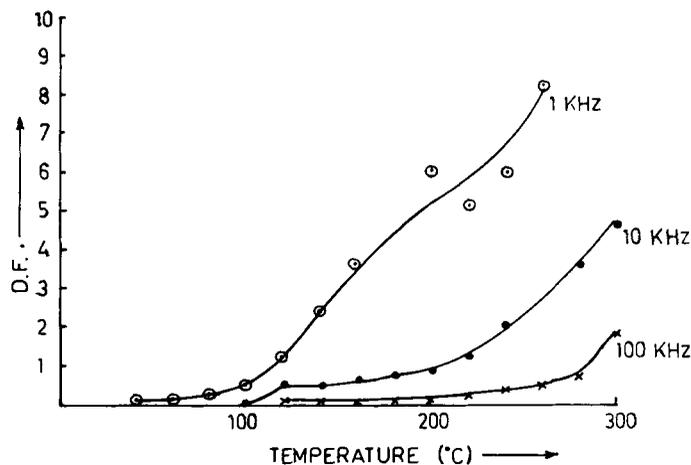
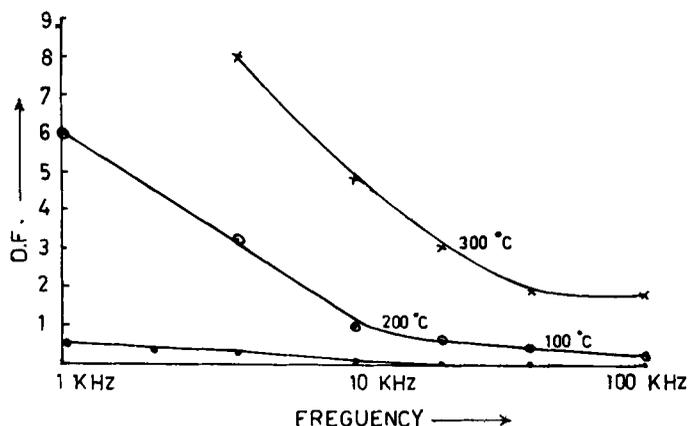**Figure 5.** Temperature dependence of dissipation factor.

Figure 6. Frequency dependence of dissipation factor.

this discards the possibility of any kind of dispersion. Also there are no localized states along lead chains in which case a trap-limited localization governs.

In an inductor or capacitor the DF is the cotangent of the phase angle α or the tangent of the loss angle ε. In low loss components, it is almost equal to power factor $\cos\alpha$ and can be given approximately by $\sigma/2\pi f E$. The dissipation causes free oscillations to be damped and removes sharpness of cut off in filters. This is the displacement polarization energy. The dissipated energy goes to heating effect.

Dissipation factor varies very similar to dielectric constant with temperature and frequency. It decreases by one order of magnitude with frequency showing considerable dispersion at 300°C.

One possibility is molecular polarizability. Two electrons in PbPc molecule show correlated motions and pairing as suggested for such a molecule (Kampas 1970). These electrons are in $5d_{x^2-y^2}$ orbital (figures 5a and b). Molecule of PbPc is distorted in a $5d_{x^2-y^2}$ $6S^1$ or $6P^1$ transition because of phonon absorption at higher temperature.
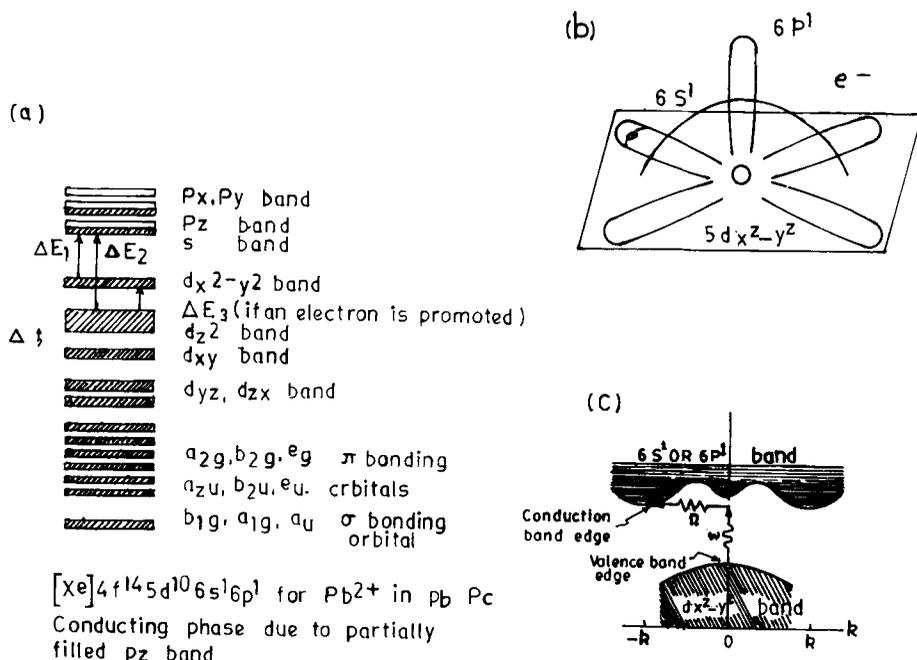
(b)

(a)

Px,Py band
Pz band
s band

ΔE_1 ΔE_2

dx^2-y^2 band
ΔE_3 (if an electron is promoted)
dz^2 band
d_{xy} band

Δ

d_{yz}, d_{zx} band

a_{2g}, b_{2g}, e_g π bonding
a_{zu}, b_{2u}, e_u.   orbitals
b_{1g}, a_{1g}, a_u σ bonding
                             orbital

$[Xe]4f^{14}5d^{10}6s^16p^1$ for Pb^{2+} in Pb Pc
Conducting phase due to partially
filled Pz band

(c)

6 S^1 OR 6P^1 band

Conduction
band edge

Valence band
edge

dx^2-y^2 band

$-k$ 0 k

Figure 7. (a) Band structure of PbPc, (b) $5d_{x^2-y^2} \to 6S^1$ or $6S^1$ transition and (c) indirect band gap.

This is an intermolecular transition. Orthogonality of the orbitals is related with relative shift of conduction and valence band along wave-vector axis. This leads to an indirect transition involving a phonon absorption (figure 5c). Molecule is left in polarized or deformed state involving quinonoid resonance. Each distorted molecule has large dipole moment in this excited state and electrons are decoupled with optical phonons of intramolecular vibrations. Conducting lead chains are embedded in a medium of high dielectric constant as required in excitonic mechanism of high temperature superconductivity (Davis *et al* 1976).

Phonon energy can be calculated from uncertainty relation as

$$E_P = (\Delta P)^2/2m,$$

where $\Delta P \cong \hbar/\Delta x$ and x is half of the diagonal size of molecule for $d_{x^2-y^2} \to 6P$ transition (figure 7). This comes out to be 0.03 eV which is approximately the same energy as thermal energy supplied between 40°C and 300°C.

There is hybridization of $d_{x^2-y^2}$ orbital of Pb^{2+} ion with orbital of phthalocyanine ligand. This is why molecular size is involved in the above calculation. Actually a π-electron of the ligand transits to $6S$ or $6P$ orbital of Pb^{2+} ions leaving the molecule in distorted state. Molecule stops resonating freely. Electron absorbs phonon with which it has strong coupling. Electron carries away momentum of a molecule in the sense that momentum associated with resonances and vibrations is lost. The distorted molecule is left in a polarized state and has large dipole moment. This increases the overall dielectric constant. Charge carrier migrates to neighbouring mole by carrying away momentum associated with vibrations.

4. Conclusion

There is molecular distortion at high temperature which increases dielectric constant of lead phthalocyanine.

Acknowledgement

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