

UDC 538.9

DOI: 10.33910/2687-153X-2020-1-3-87-92

## Dielectric polarisation in naturally disordered trilead tetroxide $\text{Pb}_3\text{O}_4$

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**For citation:** Avanesyan, V. T., Baranova, E. P., Chursina, K. A. (2020) Dielectric polarisation in naturally disordered trilead tetroxide  $\text{Pb}_3\text{O}_4$ . *Physics of Complex Systems*, 1 (3), 87–92. DOI: 10.33910/2687-153X-2020-1-3-87-92

**Received** 9 June 2020; reviewed 9 July 2020; accepted 10 July 2020.

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**Abstract.** The paper presents the results of an experimental study of trilead tetraoxide  $\text{Pb}_3\text{O}_4$  binder layers and their dielectric properties. The study revealed polarisation processes in low frequency range associated with structure peculiarities in the  $\text{Pb}_3\text{O}_4$  compound. The study established the dependence of dielectric properties on temperature and frequency of the applied field. The complex dielectric response of layer samples was measured under various AC drive and DC bias conditions. The paper provides an explanation for the influence of the simultaneous AC and DC voltages on dipole and Maxwell–Wagner polarisation in  $\text{Pb}_3\text{O}_4$ . It is assumed that there is an impact of interfacial barriers in the polycrystalline structure. The paper discusses the role of lone pair (LP) electrons  $\text{Pb}^{2+}$  in polarisation properties of trilead tetraoxide compound.

**Keywords:**  $\text{Pb}_3\text{O}_4$ , dielectric polarisation, Maxwell–Wagner polarisation, polycrystalline structure, dielectric response.

### Introduction

Electret materials mentioned in literature include two major types, i.e. organic polymers and inorganic dielectrics (Sessler 1987). Although organic materials such as Teflon show excellent electret properties when applied to microphones, their fabrication is still scarce and hardly compatible with the integrated–circuit technology. In recent years, inorganic oxide materials have been widely investigated to solve this problem. A long-standing interest of researchers, who have been studying the lead oxide system over the last decades, reflects its technical value as well as its complex and still unclear physical behaviour.

The trilead tetraoxide composition has attracted considerable interest recently due to its high resistance with large density of deep traps suggesting that this material is suitable for electret applications. Moreover, a practically interesting problem lies in the fact that polarisation and conductivity in this oxide system are closely connected with electret and photoelectric properties (Avanesyan 1999; Avanesyan et al. 1999; Avanesyan et al. 2002).

The high–resistivity lead oxide electret systems with  $\text{Pb}^{2+}$  cations are of interest as well because their  $6s^2$  LP electrons cause asymmetric oxygen coordination, often resulting in acentric or even polar crystal structures. According to Galy et al. (Galy et al. 1975), the LP is an intermediate state between an inert spherical  $ns^2$ –type orbital, which is centred on the nucleus, and a non-bonded hybridised–orbital lobe, which is not spherical but localised far from the atomic nucleus. This orbital of two electrons is encountered in compounds containing ions with an appropriate valence.

The present work deals with the study of dielectric properties and AC conductivity of the  $\text{Pb}_3\text{O}_4$  binder layers. The study explore the possibility of using the LP concept for a better understanding of polarisation properties of trilead tetraoxide.

### Experiment

Fine powder of  $\text{Pb}_3\text{O}_4$  was added to organic-silicon binder and stirred vigorously to make a homogeneous suspension. Then it was placed between a clean aluminium plate and an aluminium film by successive evaporation to form a cell for capacitance measurement. The experimental samples had a thickness of 50...100 micrometers. Dielectric dispersion was studied by using a precision impedance meter E7-20 with measuring voltage  $U = 0.04$  V. Dielectric measurements of polycrystalline  $\text{Pb}_3\text{O}_4$  binder layers were performed in the frequency range  $f = 10...10^6$  Hz.

The mentioned device was used for AC conductivity measurement as well. The samples were mounted in a dark chamber that could be evacuated in order to control the sample environment, which was found extremely important for the reproducibility of the experimental results. The heating of samples in an interval of temperatures  $T = 293...400$  K was carried out with a rate of about 1.5 K/min. Temperature was measured with a calibrated copper–constantan thermocouple.

### Results and discussion

In practice, the dielectric is often subjected to the simultaneous action of AC and DC voltages (Rapos, Calderwood 1974). Such study can be useful from a practical point of view. It can also provide additional characterisation of dielectric polarisation. Such experimental measurements were carried out in this study. The typical results of the observed fractional change variation in capacitance (correspondingly in dielectric permittivity) and dielectric losses ( $\tan\delta$ ) with temperature at constant frequency of the applied field  $f = 10^3$  Hz are presented in Fig. 1, 2.

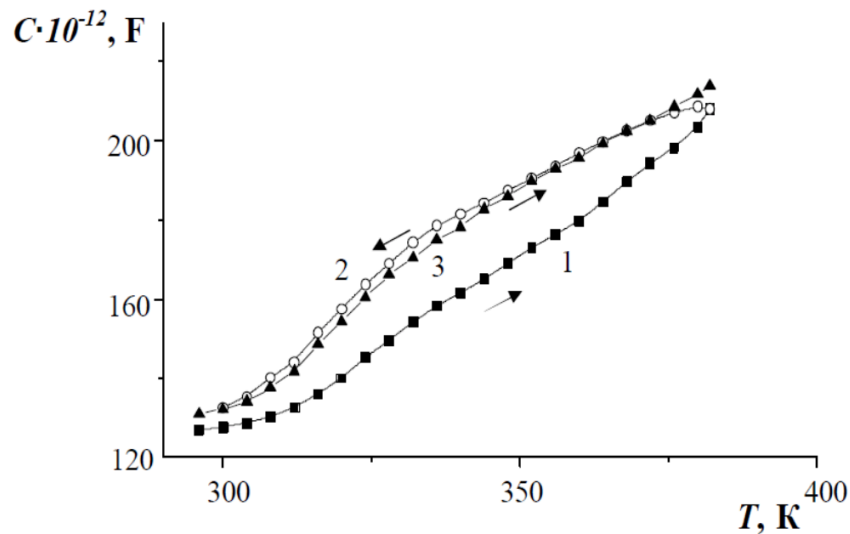


Fig. 1. Temperature dependence of  $\text{Pb}_3\text{O}_4$  binder layer capacitance without (curves 1, 2) and with additional bias voltage  $U_{dc} = 10$  V (curve 3). Arrows specify the direction of temperature change when heated or cooled

The findings indicate that the values of  $C$  increase very slowly at low temperatures. As the temperature rises, the values of  $C$  increase relatively rapidly towards higher temperatures. The application of AC voltage to  $\text{Pb}_3\text{O}_4$  layer samples reaches a peak in the  $\tan\delta$  vs. temperature dependence near 325 K, accompanied by an increase in  $C$  and  $\tan\delta$ , and shifts to low temperature when DC voltage is simultaneously applied. The results of dielectric measurements on polycrystalline samples of the  $\text{Pb}_3\text{O}_4$  compound showed thermal hysteresis caused by changes occurring in the grain boundaries during thermal cycling.

Electrical conduction in  $Pb_3O_4$  binder layers also shows marked dispersion with temperature. The activation energy  $\Delta E$  for conductivity relaxation was evaluated from the  $f$  c vs.  $1000/T$  log plot and made up the value of  $\Delta E = 0,56$  eV (for temperatures below  $T = 320$  K) and  $\Delta E = 0,02$  eV (for temperatures above  $T = 320$  K).

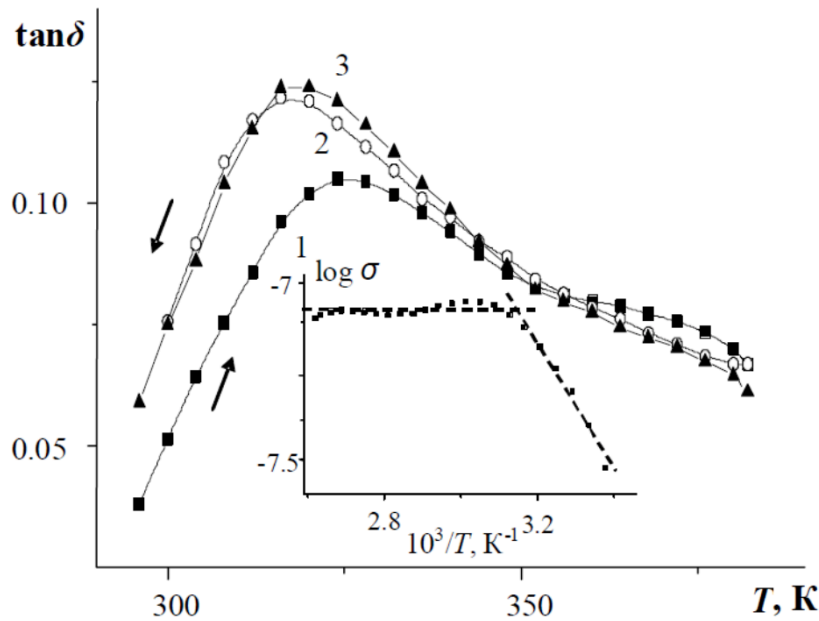


Fig. 2. The  $\tan\delta$  temperature dependence of  $Pb_3O_4$  binder layers with (curve 3) and without (curves 1, 2) additional bias voltage  $U_{dc} = 10$  V. Arrows specify the direction of temperature change when heated or cooled. The insert shows the temperature dependence on the AC conductivity

The dielectric permittivity, as calculated from the measured capacitance and losses ( $\tan\delta$ ) of  $Pb_3O_4$  layer structures in an investigated range of frequencies, exhibited strong frequency dependence (Fig. 3). The influence of the frequency factor indicates the relaxation nature of dielectric polarisation. It is possible to assume that this is an “apparent” permittivity influenced by the density distribution of charge carriers.

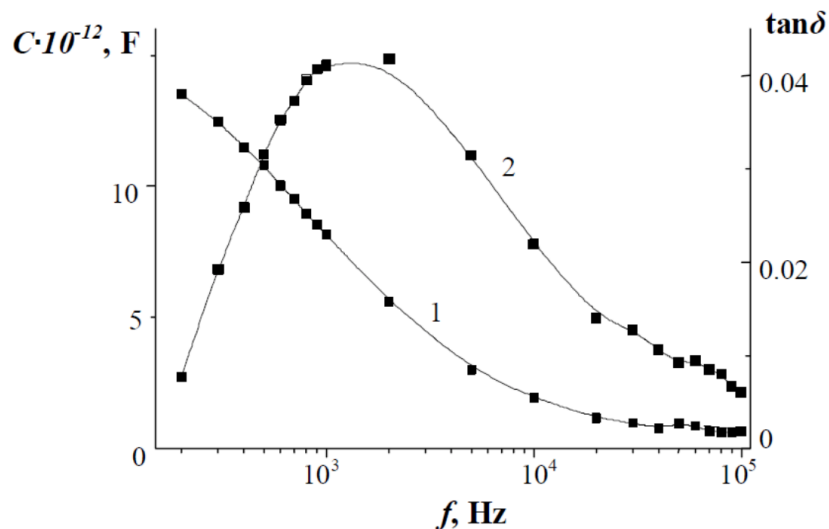


Fig. 3. Frequency dependence of the  $Pb_3O_4$  binder layer capacitance (curve 1) and  $\tan\delta$  (curve 2) at  $T = 293$  K

The imposition of AC and DC electric field possibly causes the deformation of an intergranular potential barrier and by that the orientation of the charged particles in primary direction occurs. The number of particles detained by barriers can change, thus decreasing the total dipole moment of the relaxing particles system. The average magnitude of the angle that the dipole makes with the applied field is reduced by the presence of a DC field. The torque, which an applied AC field is able to exert on the dipole, is thereby reduced; therefore, the polarisation brought from the given AC field is smaller in the presence of a DC field.

The results outlined above can be explained also on the basis of space charge formation near the barriers of polycrystalline structure. A possible reason for this behaviour of dielectric parameters may be the presence of some number of trapped electrons in defect states. The migration of the polycrystalline structure defects in an electrical field modulates an interface potential barrier and can influence the formation of a spatial charge. The presence of a DC field and an AC field at the same time causes an asymmetrical barrier. The structure defects migration of the polycrystalline  $Pb_3O_4$  oxide composition related to the LP of  $Pb^{2+}$  cations modulates the intergranular barrier, and thus may have a marked effect on the formation of a spatial charge.

The growth of the energy barrier  $\Delta E$  increases relaxation time in accordance with the formula  $\tau = \tau_0 e^{\Delta E/kT}$  and causes the shift of the  $\tan\delta$  peak to low temperatures. It can be concluded that dielectric relaxation is caused by jumping of particles (electrons or ions) between nearest-neighbour sites under AC electric field and that successive jumping between nearest-neighbour sites under DC electric field causes DC conduction.

The strong correlation between conductance and capacitance in the frequency range under investigation can be demonstrated by plotting Cole–Cole plot of  $C \tan\delta$  vs.  $C$  over the appropriate frequency range (Fig. 4) with frequency as a parameter. It seems reasonable to say that the observed low frequency dispersion is the result of non–Debye relaxation mechanism with continuously distributed relaxation times. The AC conductivity at  $T = 293$  K shows strong frequency dependence according to the relation  $\sigma_{\omega}(\omega) = A\omega^s$ .

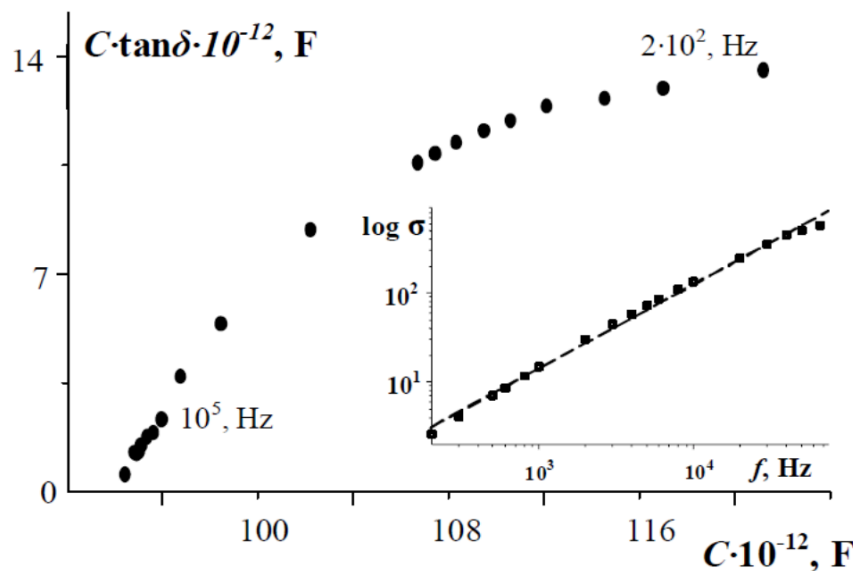


Fig. 4. Complex Cole–Cole plot of dielectric components for  $Pb_3O_4$  binder layer.  $T = 293$  K. The insert shows the frequency dependence of conductivity

The value of the exponent  $s$  obtained from the linearity of  $\log\sigma$  against  $\log f$  was found as 0.69 that can be dealt with the hopping mechanism.

In order to clarify the origin of dielectric dispersion observed in  $Pb_3O_4$  layers, the equivalent circuit based on the Maxwell–Wagner model (Jonsher 1996) was investigated by taking into account the microstructure of samples. It is considered that the microstructure of  $Pb_3O_4$  consists of  $Pb_3O_4$  grains and intergranular layers where each  $Pb_3O_4$  grain is three-dimensionally separated by this layer. The equivalent circuit for such an idealised model can be assumed as shown in Fig. 5a. The circuit consists of two blocks

of resistance and capacitance:  $R_1$  and  $C_1$  are resistance and capacitance of intergranular layer;  $R_2$  and  $C_2$  are resistance and capacitance of  $Pb_3O_4$ , respectively. The simplified equivalent circuit of the sample can be represented by a parallel  $R_c$  network as shown in Fig. 5b. Here each element  $C_e$  and  $R_e$  is defined experimentally and is connected to parameters of grains and intergranular layers by:

$$C_e = \frac{\omega^2 R_1^2 R_2^2 C_1 C_2 (C_1 + C_2) + R_1^2 C_1 + R_2^2 C_2}{\omega^2 R_1^2 R_2^2 (C_1 + C_2)^2 + (R_1^2 + R_2^2)^2}, \quad (1)$$

$$R_e = \frac{\omega^2 R_1^2 R_2^2 (C_1 + C_2)^2 + (R_1 + R_2)^2}{\omega^2 R_1 R_2 (R_1 C_1^2 + R_2 C_2^2) + R_1 + R_2}, \quad (2)$$

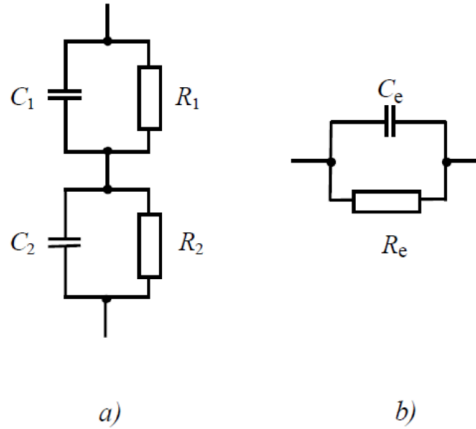


Fig. 5. Equivalent circuit model for  $Pb_3O_4$  structure: (a) with an intergranular layer ( $R_1, C_1$ ) and grain ( $R_2, C_2$ ), (b) the simplified equivalent circuit

Equations (1) и (2) define frequency dependence of the sample capacity and resistance. To simplify the analysis of  $C_e$  and  $R_e(f)$  functions we can assume that  $R_1 \gg R_2$  in view of amorphous and crystal phase distinction. In the low temperatures region, the inequality and relations are fair:

$$\omega\tau_{1L} \gg \omega\tau_{2L} \gg 1, \quad (3)$$

where  $\omega = 2\pi f, \tau_i = R_i C_i$ ;

$$C_{eL} = \frac{C_1 C_2}{(C_1 + C_2)}; \frac{1}{R_{eL}} = G_2 \left( \frac{C_1}{C_1 + C_2} \right), \quad (4)$$

where  $G_2 = \frac{1}{R_2}$  and the resistance  $R_{eL}$  is defined by crystal phase conductivity of a sample. The high temperatures region can be described as:

$$1 \gg \omega\tau_{2H} \gg \omega\tau_{1H} \quad (5)$$

$$C_{eH} = C_1; \frac{1}{R_{eH}} = G_1, \quad (6)$$

where  $G_1 = \frac{1}{R_1}$ , but the capacity and the resistance of the sample are defined in parameters of an amorphous phase. The situation in the range of intermediate temperatures can be expressed as:

$$\omega\tau_1 \gg 1 \gg \omega\tau_2, \quad (7)$$

$$C_{eL} < C_{eH} < C_{e2}; \frac{1}{R_{e2}} = G_1 + (\omega^2 C_1^2 / G_2). \quad (8)$$

In the latter the magnitude of  $C_e$  increases and the conductivity includes a component which decreases along with the temperature growth. This can also result in a positive factor of resistance. The positive resistance coefficient, in particular, may be attributed to the relaxation in barrier layers due to the formation of acceptor states on the surface of grains. It was found that  $Pb^{2+}$  in some materials could act as hole traps to give  $Pb^{3+}$  centers (Robertson et al. 1993). As a matter of fact, the parallel between structures and conductivities of  $Pb_3O_4$  is striking; therefore, it supports the idea of the relationship between lone pair disposition and conductivity. The specified phenomenon within the framework of the discussed model is caused by the change of a ratio between active and reactive components of intergranular layer conductivity.

The inspection of the structure geometry in the oxide semiconductor in question shows that all cationic sites display typically distorted coordinations usually found in  $Pb^{2+}$  oxides, where the presence of localised  $6s^2$  LP electrons determines the occurrence of short metal–oxygen interactions only on the opposite side with respect to  $6s^2$  localised electrons. Chemical bonding in complexes with inert pair of  $ns^2$  ions is largely determined by  $s$ – $p$  mixing (Avanesyan 1999; Galy et al. 1975). Hence, the LP takes part in the chemical bonding and cannot be considered as an inert pair. Thus, the unshared  $ns^2$  electron pair causes a tendency for the instability to antisymmetric distortions of lattice elements and their environment. The large defined value of the trilead tetraoxide dielectric constant ( $\epsilon \sim 25$ ) is related to the high polarisability of  $Pb^{2+}$  cations in which the LP causes a non-spherical change of distribution around these cations.

## Conclusion

The dielectric information is obtained, including electric characteristics of polycrystalline  $Pb_3O_4$  binder layers. The influence of DC voltage bias on dielectric response of  $Pb_3O_4$  layers in the temperature interval  $T = 293 \dots 400$  K is established. Thus, the greatest changes occur at high temperatures and low frequencies of a measurement field. Experimental results and theoretical considerations suggest that the dielectric dispersion observed in polycrystalline  $Pb_3O_4$  layers can be attributed to the nature of interlayer Maxwell–Wagner polarisation with a distribution of relaxation times.

Therefore, besides bond formation, non-bonding lone pairs can play a key role in determining polarisation properties of oxide semiconductors. This approach is sufficient for the molecular design of new electret materials and for the better understanding of electrets on a molecular scale.

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