

Structural and dielectric properties of $\text{Pb}(\text{Li}_{1/4}\text{Dy}_{1/4}\text{W}_{1/2})\text{O}_3$

S BERA and R N P CHOUDHARY

Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India

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Abstract. The polycrystalline samples of $\text{Pb}(\text{Li}_{1/4}\text{Dy}_{1/4}\text{W}_{1/2})\text{O}_3$ have been synthesized by high-temperature solid-state reaction techniques. Room temperature X-ray diffraction (XRD) studies of the compound provided preliminary structural data, and hence formation of a single phase desired material was confirmed. Detailed studies of dielectric constant (ϵ) and loss ($\tan \delta$) as a function of frequency (100 Hz to 10 kHz) at room temperature (298 K) and also as a function of temperature (liquid nitrogen to 403 K) at 10 kHz suggest that the compound undergoes a ferroelectric phase transition of diffuse type.

Keywords. High-temperature solid state reaction; X-ray and dielectric properties; diffuse phase transition.

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1. Introduction

The complex compound, lead-lithium dysprosium tungstate, $\text{Pb}(\text{Li}_{1/4}\text{Dy}_{1/4}\text{W}_{1/2})\text{O}_3$, (hereafter PLDW) belongs to the perovskite family of general formula ABO_3 (A = mono or divalent, B = tri, tetra, penta or hexavalent ions). Since the discovery of ferroelectricity in BaTiO_3 [1], a large number of pure, or complex oxides of different structures have been studied in search of a new material with optimum properties for ferroelectric or related devices [2–7]. Among them, Pb-based compounds such as PbTiO_3 , PbZrO_3 , $\text{Pb}(\text{ZrTi})\text{O}_3$ etc. have been found very useful for wide ranging applications [8–10]. Extensive literature survey on Pb-based ferroelectric compounds revealed that some of the compounds of $\text{Pb}(\text{M}_{1/4}\text{R}_{1/4}\text{X}_{1/2})\text{O}_3$ (M = alkali ions, R = rare-earth ions, X = W or, Mo) family have ferroelectric property [11], but not much work has been done on those reported and other members of the family. We undertook a study on structural, electrical, thermal and spectroscopic properties of some members of the family [12–14] and found their interesting behaviour. In this paper we report preliminary structural and detailed dielectric properties of PLDW.

2. Experimental

The polycrystalline samples of PLDW were prepared by a standard high-temperature solid-state reaction technique from the raw materials: PbO (99·99% pure, Aldrich Chemical Co.), Li_2CO_3 (99% S.D. Fine chem. Pvt. Ltd., India), Dy_2O_3 (99·99%, Indian Rare-Earth) and WO_3 (AR grade, BDH, England) in a suitable proportion. Those oxides and carbonates were thoroughly mixed in agate-mortar in alcohol for 10 h and dried. The dried powders were calcined in alumina crucible at 873 K for 15 h. The process of calcination and mixing was repeated till fine homogeneous powder of

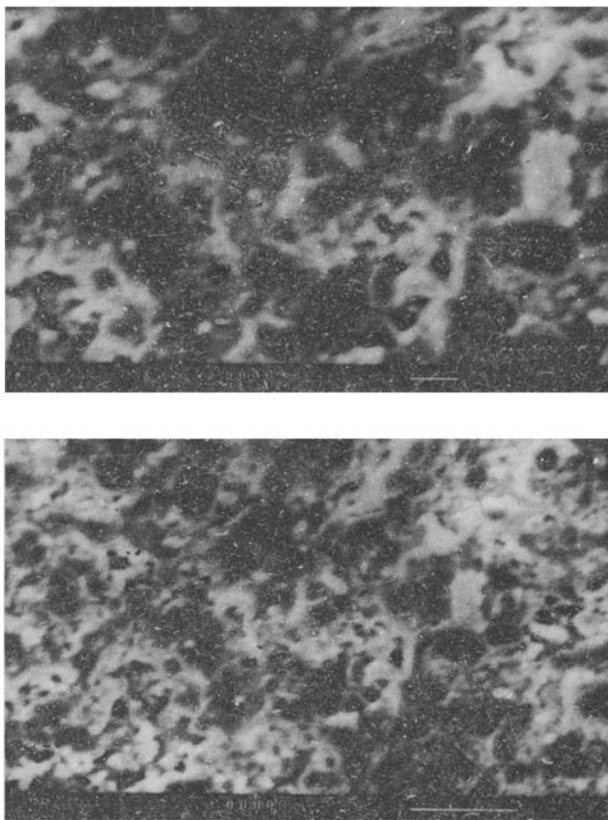


Figure 1. Scanning electron micrograph of PLDW pellet sintered at 900 K for 2 h [(a) 3 μm (b) 10 μm .]

PLDW was obtained. The formation and quality of the compound were checked with X-ray diffraction technique. Some cylindrical pellets of diameter 11.2 mm and thickness 1–2 mm were made under the isostatic pressure ($6 \times 10^7 \text{ kg/cm}^2$) using a hydraulic press. These pellets were then sintered in air atmosphere at 893 K for 10 h in alumina crucible. After polishing and grinding, both the flat surfaces of some pellets were electroded with air drying silver paints for electrical measurements. The density of the pellets obtained was approximately 95% of its theoretical value. This is consistent with compactness of the particles as seen in SEM photographs (figure 1), at two different magnifications which helped to estimate the grain size, shape and homogeneity.

The X-ray diffractograms of the FLDW pellet sample were taken with FeK_α radiation ($\lambda = 1.9364 \text{ \AA}$) in a wide 2θ range ($20^\circ \leq 2\theta \leq 110^\circ$) with Philips powder diffractometer (PW 1710, Holland).

The dielectric constant (ϵ) and loss ($\tan \delta$) were obtained on sintered and electroded pellet samples as functions of frequency (500 Hz to 10 kHz) and temperature (liquid nitrogen to 403 K) using GR-1620 capacitance measuring assembly. The reliability of the data was checked repeating the experiments with different instruments (LCR-High Tester, Hioki 5530 Japan) in the same physical conditions.

Structural and dielectric properties

Table 1. Comparison of observed and calculated d -values (\AA) of some reflections of PLDW at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
1	1	1	4.7360	4.7360	11
0	2	0	4.0892	4.0892	3
2	1	1	2.9013	2.9013	100
1	2	4	2.4786	2.4776	6
2	0	4	2.3718	2.3748	3
2	1	5	2.0562	2.0570	20
2	1	7	1.6801	1.6810	25
1	2	8	1.5855	1.5851	2
2	2	8	1.4558	1.4552	7
2	5	3	1.3916	1.3911	1
2	0	10	1.3032	1.3033	7

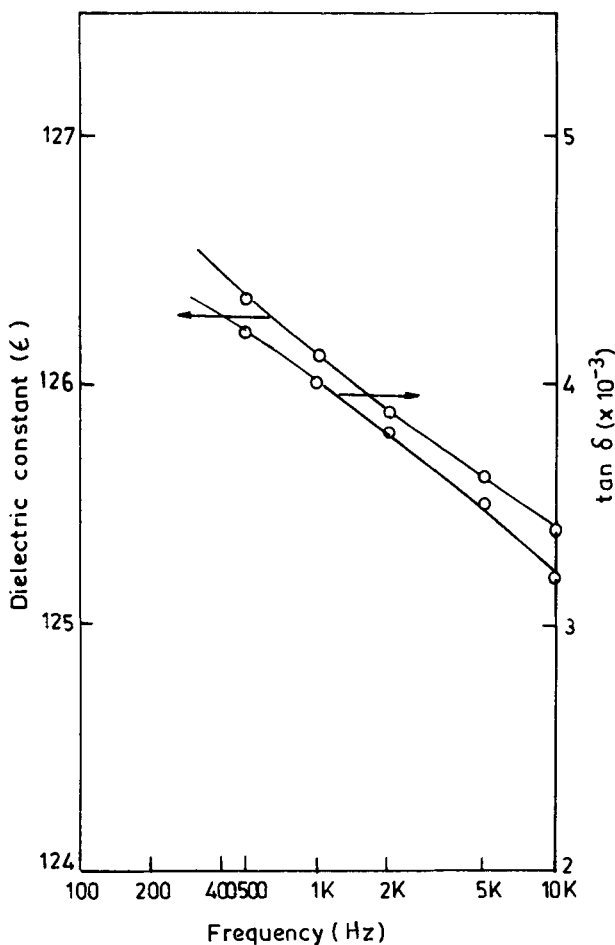


Figure 2. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of PLDW as a function of frequency at room temperature (298 K).

3. Results and discussion

All the peak-profiles of the sample were indexed with different cell configuration. Out of them, a suitable cell with its lattice parameters was selected. The lattice parameters were then refined using a least-squares technique. Using refined cell parameters, indexed reflections and wavelength of FeK α radiation, interplanar spacings (d) of all the reflections were calculated and compared with their observed values (table 1). A good agreement between calculated and observed d -values suggests that the compound is orthorhombic with lattice parameters: $a = 6.3582 (10) \text{ \AA}$, $b = 8.1786 (10)$, $c = 14.2888 (10) \text{ \AA}$. It was not possible to find out the space group with very limited data. The linear particle size (L) of the sintered sample, calculated for strong, medium and weak reflections, scattered in wide 2θ range using Scherrer's equation [15] was approximately 25 nm which is consistent with the values obtained from particle size analyser.

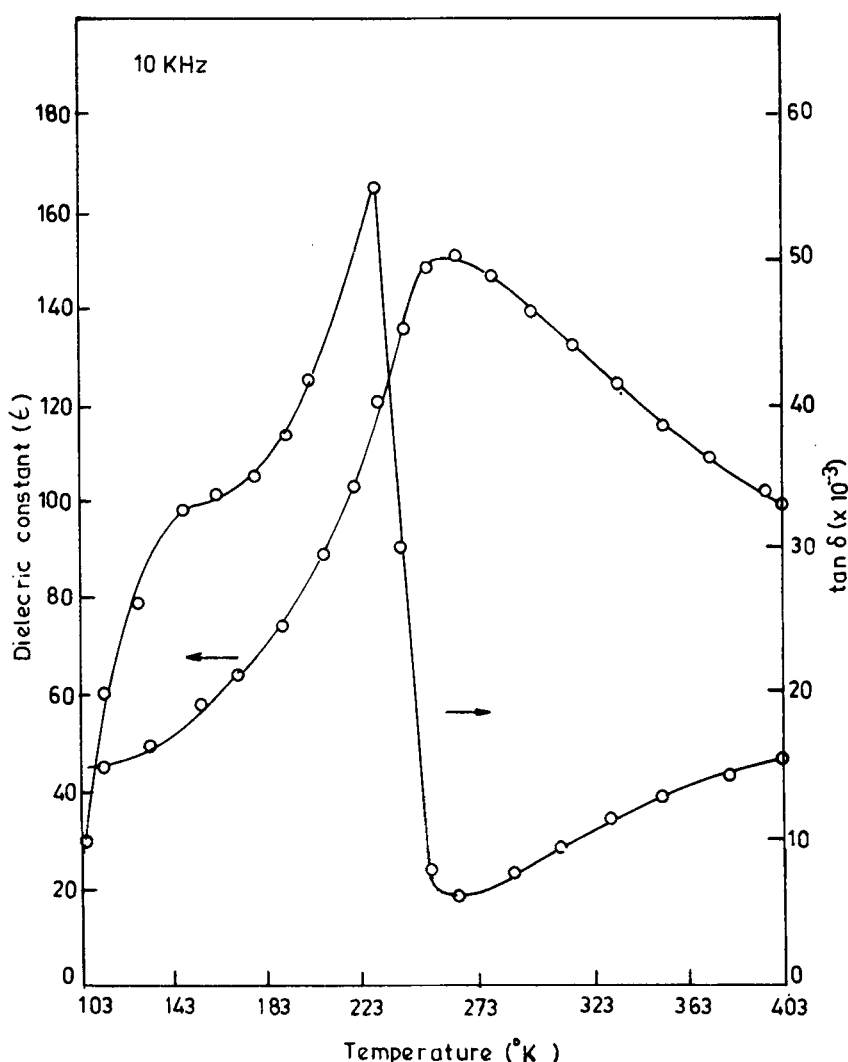


Figure 3. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of PLDW as a function of temperature at 10 kHz.

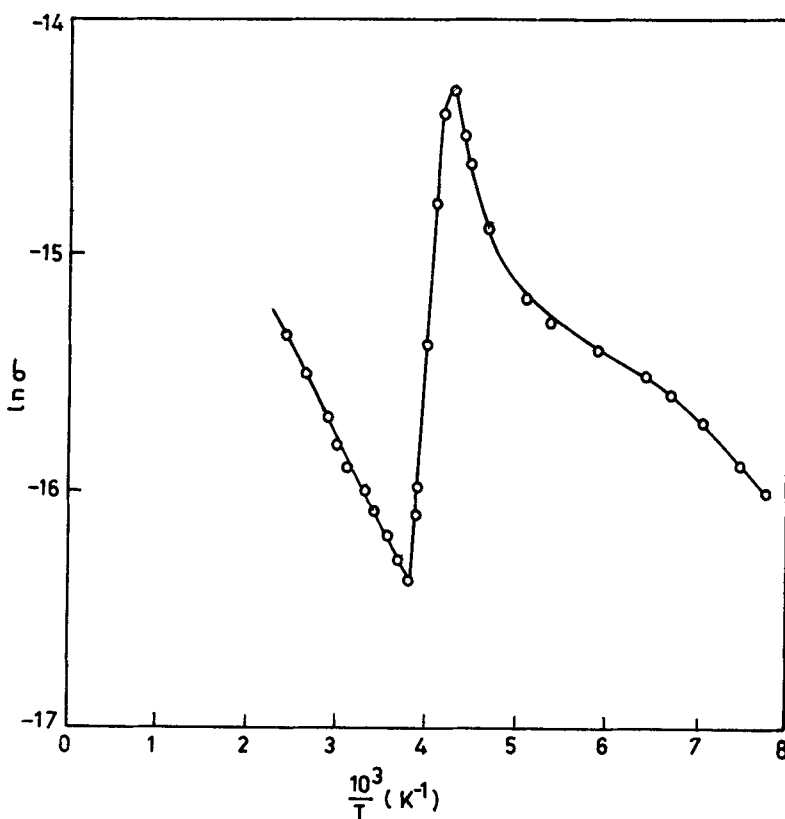


Figure 4. Variation of conductivity ($\log \sigma$) as a function of inverse of absolute temperature ($1/T$) of PLDW.

Figure 2 gives the variation of ϵ and $\tan \delta$ with frequency. Both these parameters show the normal behaviour of dielectrics because they decrease very slowly (from $\epsilon = 126.34$ (at 500 Hz) to 125.38 at 10 kHz), $\tan \delta = 0.0042$ to 0.003.

Figure 3 shows the variation of ϵ and $\tan \delta$ with temperature. The dielectric constant increases asymptotically. With rise in temperature, ϵ reaches its maximum value of 138 (at 10 kHz) at 263 K and then it starts decreasing almost linearly to 95 at 416 K. But $\tan \delta$ shows abnormal behaviour. It first increases with its maximum value at temperature 230 K and then it drops to minimum at 253 K and then starts increasing slowly. This type of variation has been observed in KNbO_3 ceramics [16] also. As the transition temperature in PLDW was found below room temperature ($T_c = 263$ K), we do not expect any hysteresis loop at room temperature in the paraelectric phase. Further it is not possible to get proper hysteresis loop in our complex lossy ceramic samples in the low temperature phase. However, we have confirmed the reported ferroelectric phase transition in some members of the family on the basis of dielectric anomaly. We have also observed dielectric anomaly in other members of the family [12–14] which is consistent with the ferroelectric phase transition.

Figure 4 shows the variation of ac electrical conductivity (i.e. $\log \sigma$) with inverse of temperature ($1/T$). It shows the change in slope at 262 K which corresponds to the transition temperature of the sample. The activation energy (E_A) was calculated using the formula $\sigma = \sigma_0 \exp(-E_A/K_B T)$, where K_B is the Boltzman constant of value

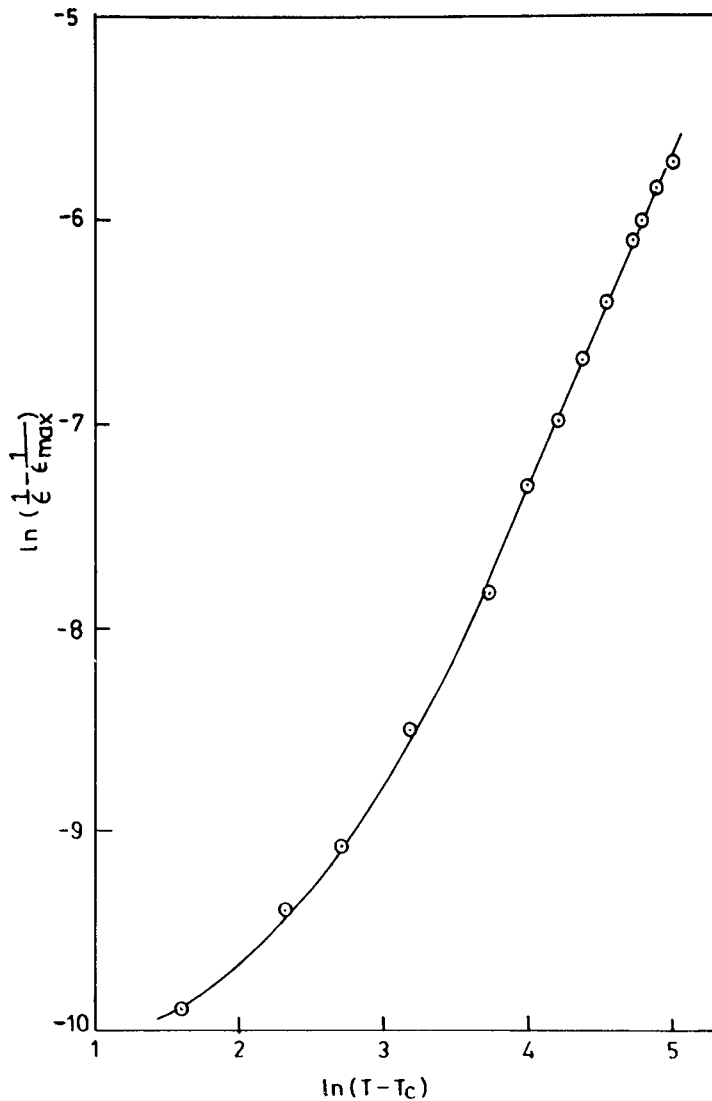


Figure 5. Variation of $\log(1/\epsilon - 1/\epsilon_{\max})$ with \log of temperature difference $(T - T_c)$ of PLDW.

0.06 eV. The value of activation energy is comparable to the other members of this family.

In figure 5, we have plotted $\log(1/\epsilon - 1/\epsilon_{\max})$ vs. $\log(T - T_c)$ which indicates the diffuseness of phase transition. The diffusivity (γ) calculated from formula [17]

$$\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}}\right) \propto (T - T_c)^\gamma$$

was 1.5 which shows the diffuse/relaxor behaviour of the compound.

Finally it is concluded that the complex compound PLDW has ferroelectric phase transition below room temperature and its dielectric constant and loss of the material are quite different from the other members of the family [12-14].

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