



Phase Transition in Tl_2TeO_4

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Abstract. A polycrystalline sample of thallium telurate, Tl_2TeO_4 , was prepared by a solid-state reaction technique. Preliminary X-ray structural study of the compound reveals the formation of single phase orthorhombic compound at room temperature. Detailed studies of dielectric constant as function of temperature and frequency suggest that the compound undergoes two phase transitions at 3°C and 272°C. Variation of dc resistivity with temperature shows that the conductivity of the material increases with the rise in temperature.

Keywords: dielectrics, incommensurate-commensurate phase transition, orthorhombic structure

1. Introduction

Since the discovery of successive or multiple phase transitions in BaTiO_3 in 1945, a large number of simple or complex compounds of different structural families have been examined in the past, but no compound with this type of phase transitions have been found so far. However, in last decade, ferroelectric properties with different types of successive phase transition (i.e., commensurate-incommensurate) in Rb_2ZnCl_4 [1] was observed. This compound with K_2SO_4 type structure, undergoes successive phase transition from a high-temperature normal phase (I) to a ferroelectric commensurate phase (III) via the incommensurate modulated phase (II) [2–5]. A normal phase belongs to the orthorhombic system with space group $\text{Pm}cn$. In the incommensurate phase, crystal lattice is modulated along c -axis with wave vector $q = (1/3 - \delta)c_0^*$ where c_0^* = reciprocal unit cell parameter in the normal phase. The ferroelectric phase is caused by locking into a commensurate value ($\delta = 0$) of $q = 1/3c_0^*$. The space group of ferroelectric phase is $\text{P}2_1cn$ and spontaneous polarization develops along b -axis [6–7]. This type of sequence phase transition was observed in a few compounds of A_2BX_4

(A = monovalent ions, BX_4 = divalent tetrahedral complex such as SeO_4^{2-} , ZnCl_4^{2-} , X = Cl, Br, I) family. Therefore, in order to check the existence of successive phase transitions with the above characteristics we have carried out preliminary structural and detailed dielectric and spectroscopic investigations of the $\text{A}^{2+}_2\text{B}^{6+}\text{O}^{2-}_4$ (B = S, W, Mo, Te, Se) compounds. In this paper, we report phase transition in the Tl_2TeO_4 compound, on which not much work has been reported so far.

2. Experimental Details

The polycrystalline Tl_2TeO_4 compound was prepared by a solid-state reaction technique using raw materials, thallium carbonate Tl_2CO_3 (99.9% M/s Aldrich Chemical Co. Inc) and tellurium TeO_2 oxide in an air atmosphere. These materials were thoroughly mixed in an agate mortar for 2 h. The mixed powder was calcined in an air atmosphere at 873 K for 5 h. The calcined powder was grounded and recalcined at 873 K for 6 h. The finally recalcined fine powder was used to make pellets of 10 mm diameter and 1–2 mm thickness under a pressure of $6 \times 10^7 \text{ Kg/m}^2$ using a hydrolic press. Polyvinyl alcohol (PVC) was used as a

binder which was burnt out during sintering. The pellets were then sintered at 900° K for 4 h in an alumina crucible to reduce the porosity of the green pellets. The formation of single phase Tl_2TeO_4 compound was checked by X-ray diffraction (XRD) technique.

For the preliminary structural studies, X-ray powder diffractogram (XRD) of the compound was recorded at room temperature with a X-ray diffractometer (Rikagu, Japan) with CuK_α radiation ($\lambda = 1.5418\text{\AA}$) in a wide ranges of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 100^\circ$) at a scanning rate of $2^\circ/\text{min}$. The dielectric constant (ϵ) and loss tangent ($\tan \delta$) of the compound were measured as a function of frequency (400 Hz to 10^4 kHz) at room temperature and as a function of temperature (-150 to 400°C) at a fixed frequency of 10 kHz over a small temperature interval using a GR 1620 AP capacitance measuring assembly in conjunction with a laboratory-made three-terminal sample holder which compensated any stray capacitance. As the dielectric loss ($\tan \delta$) was becoming very high at lower frequencies with rise in temperature, all the dielectric measurements were conducted only at 10 kHz (i.e., maximum limit of our GR Bridge). As the purpose of our measurements (i.e., to detect phase transition) was limited, this measurement at higher frequency was not conducted. The temperatures were measured using a chromel-alumel thermo-couple. The dc volume resistivity of the pellet sample was measured as a function of electric field at room temperature and as a function of temperature at a constant electric field using a Keithley-617 programmable electrometer. The temperature of the sample was recorded using chromel alumel thermo-couple with an accuracy of $\pm 2^\circ\text{C}$.

3. Results and Discussion

The sharp and single peaks of XRD pattern showed the formation of single crystalline phase compound. All the high, medium and low intensity and angle peaks were indexed in different (unit) cell configurations and crystal systems with the help of a standard computer program package (POWDIN). Finally, a suitable unit cell was selected on the basis of the best agreement in observed and calculated d values. The selected cell parameters were refined by least-squares method. These are: $a = 10.562(1)\text{\AA}$, $b = 8.700(1)\text{\AA}$ and $c = 9.794(1)\text{\AA}$. A good agreement found between

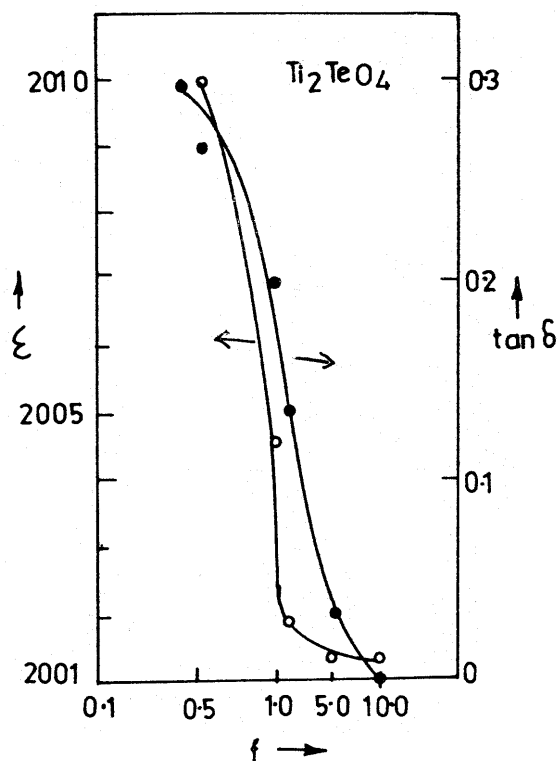
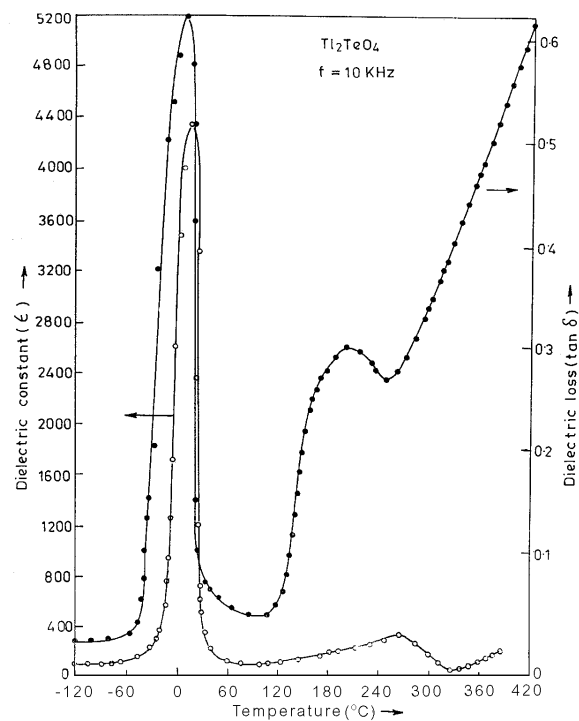
observed and calculated d -values (Table 1) suggests that the material has orthorhombic crystal structure at room temperature. However, with the limited number of reflections and crystal data it was not possible to uniquely determine the exact space/point group of the compound. The coherently scattered particle size of the pellet sample was calculated from each XRD reflection using Scherrer's equation: $P = K\lambda/\beta_{1/2} \cos \theta_{hkl}$ where K is an arbitrary constant with best possible values of 0.89, $\beta_{1/2}$ is the half peak width for each hkl reflection and θ_{hkl} is its Bragg angle. The average value of this particle size was 280\AA .

At room temperature frequency dependence of dielectric constant (ϵ) and loss tangent ($\tan \delta$) of the material is shown in Fig. 1. Decrease of ϵ and $\tan \delta$ with increase of frequency is noted as a normal dielectric behavior of Tl_2TeO_4 . The variation of ϵ and $\tan \delta$ of the compound with temperature (-150°C to 400°C) is shown in Fig. 2. A dielectric anomaly was observed between 12°C and 15°C , with maximum $\epsilon_{\text{max}1}$ at $T_i = 13^\circ\text{C}$, and again another between 271°C and 275°C (ϵ_{max} at 273°C). T_1 corresponds to the transition temperature (T_C) from the ferroelectric phase (commensurate) to the incommensurate phase and T_2 corresponds to the transition temperature (T_C) from incommensurate to the normal paraelectric phase as compared to the sequential phase transitions of the other members of A_2BX_4 family. The first phase transition is sharper than the second one. At higher temperatures (above T_i), increase of ϵ and $\tan \delta$ with temperature was found falling only over a short range of temperature, and then increases rapidly with rise in temperature. The increase in ϵ at this stage may be due to the space charge polarization as observed in other ceramic samples [8,9]. This extraordinary situation makes it difficult to accurately infer if the phase transition about T_i has any amount of relaxation. Even with a poled sample, it was not possible to obtain a proper hysteresis loops as a function of temperature. As a result, it was not possible to conclude experimentally, the commensurate-incommensurate phase transitions in the compound. However, by analogy with other compounds of the family, it is suggested that this compound also has sequential/successive commensurate-incommensurate phase transition. A single crystal work is planned to confirm this feature.

An electrical conductivity σ_{ac} was calculated from the relation $\sigma_{ac} = \omega\epsilon_0\epsilon \tan \delta$ at different temperatures where ω = angular frequency, ϵ = relative

Table 1. Comparison of some observed and calculated d -values (in Å) of some reflections of Tl_2TeO_4 at room temperature

hkl	d_{obs} (Å)	d_{cal} (Å)	I/I_0
120	4.0224	4.0224	22
300	3.5208	3.5208	30
024	3.2672	3.2672	40
205	3.1646	3.1676	10
016	3.0792	3.0847	20
215	2.9689	2.9765	40
125	2.8227	2.8215	100
026	2.6292	2.6286	60
008	2.4747	2.4742	40
035	2.3442	2.3395	35
041	2.1611	2.1621	12
501	2.1034	2.1006	16
430	1.9531	1.9525	17
145	1.8770	1.8876	10
336	1.8520	1.8523	12
343	1.7809	1.7817	40
0111	1.7618	1.7621	30
3110	1.6924	1.6924	20
517	1.6612	1.6612	08
0112	1.6208	1.6206	09
509	1.5235	1.5235	11

Fig. 1. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of Tl_2TeO_4 with frequency (f) at room temperature.Fig. 2. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of Tl_2TeO_4 with temperature at 10 kHz.

permittivity of the sample, and ϵ_0 = dielectric permittivity in free space. In $\sigma_{ac} V s \cdot T^{-1}$ ($^{\circ}K$) plot is shown in Fig. 3(A) and 3(B) for higher and lower temperature ranges 30 $^{\circ}C$ to 394 $^{\circ}C$ and -70 $^{\circ}C$ to 25 $^{\circ}C$, respectively. The anomaly in the plot of Fig. 3(A) was obtained at the temperature 282 $^{\circ}C$ which is slightly higher, but corresponds to second phase transition temperature. Above 315 $^{\circ}C$ space charge polarization can easily be seen in this figure. An anomaly in σ_{ac} (Fig. 3(B)) is observed near the first transition temperature ($T_1 = T_c$). In σ_{ac} decreases linearly with T^{-1} in temperature range of 30 $^{\circ}C$ to 118 $^{\circ}C$ (Fig. 3(A)). It follows, therefore, that in this region the activation energy (E_a) remains almost constant (0.21 eV). In the temperature range of 118 $^{\circ}C$ to 282 $^{\circ}C$, the non-linear decrease of $\ln\sigma$ with inverse of temperature and the slope of the curve slowly increasing with decreasing T^{-1} indicating the gradual march of the electrical property of the material towards the ferroelectric phase with the activation energy increasing with the increase of temperature. The calculated values of E_a near 227 $^{\circ}C$ and 357 $^{\circ}C$ were 0.52 and 0.63 eV respectively. As the calculation

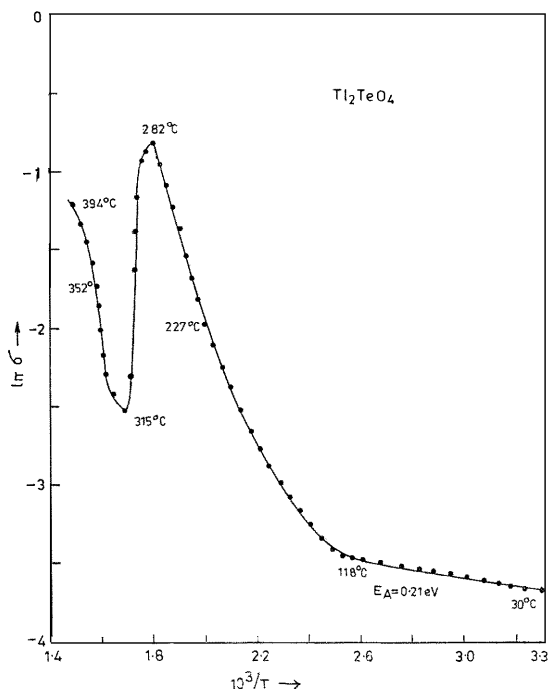


Fig. 3A. Variation of ac conductivity ($\ln\sigma$) of Tl_2TeO_4 with inverse of absolute temperature ($1/T$) from (30 $^{\circ}C$ to 394 $^{\circ}C$) at 10 kHz.

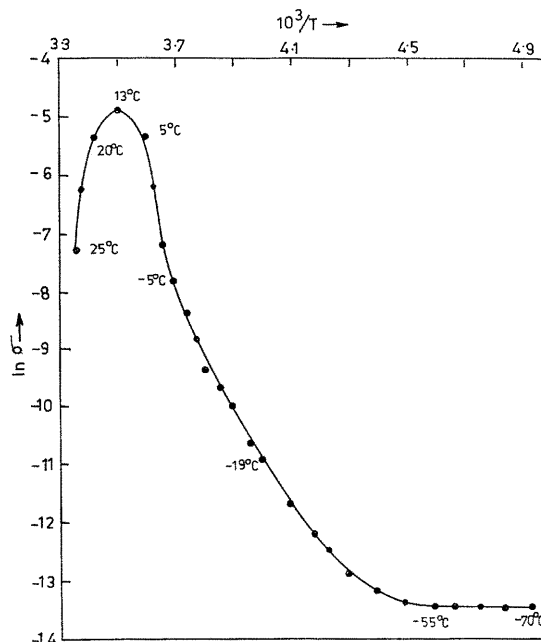


Fig. 3B. Variation of ac conductivity ($\ln\sigma$) of Tl_2TeO_4 with inverse of absolute temperature ($1/T$) from (-70 $^{\circ}$ to 25 $^{\circ}C$) at 10 kHz.

of E_a at low temperature is not important, we have not calculated it from Fig. 3(B).

At room temperature variation of dc resistivity with biasing field (V/cm) is shown in Fig. 4 where $\ln\rho_{dc}$ has been plotted against the biasing electric field. It is observed that the resistivity of the material decreases with increasing biasing field as reported and explained earlier in other ferroelectric compounds [6,10].

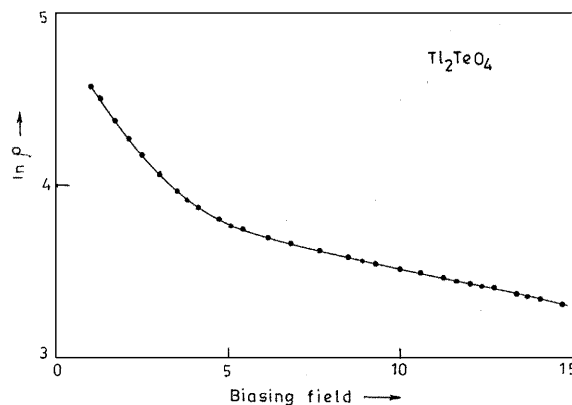


Fig. 4. Variation of dc resistivity ($\ln\rho$) of Tl_2TeO_4 with applied electric field at room temperature.

Temperature dependence of dc resistivity (ρ_{dc}) of the material at constant biasing (10 V/cm) fields is shown in Fig. 5. It is interesting to note that at higher temperatures (above 145°C), ρ_{dc} decreases with the increase of temperature. This may be due to more supply of thermal energy to the material leading to the creation of more and more free electrons. Between 95°C to 130°C, ρ_{dc} of the material does not vary by more than 2%. This indicates that a very few thermally generated free electrons are created in this range of temperature. In the low temperature range (below 110°C), ρ_{dc} decreases as the temperature decreases. Similar temperature dependence property of ρ_{dc} was observed in the Rb_2TeO_4 compound. In the low temperature regions both Ti_2TeO_4 and Rb_2TeO_4 exhibit sharp increase in conductivity with rise in temperature. The calculated values of E_a in the high temperature region (Fig. 5) was about 0.5 eV.

Finally, it is concluded that Ti_2TeO_4 has orthorhombic structure at room temperature with successive

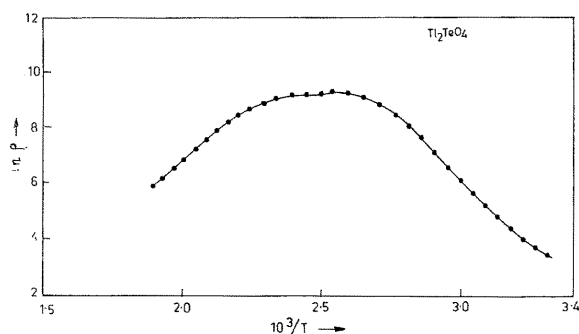


Fig. 5. Variation of dc resistivity ($\ln \sigma$) of Ti_2TeO_4 with inverse of absolute temperature ($1/T$).

phase transitions on cooling from elevated temperature. The first transition probably belongs to a ferroelectric to incommensurate change, the second to a change from incommensurate to normal ferroelectric phase, and in this phase the material has an increasing conductivity with decrease in temperature.

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