

Dielectric Properties of Light Rare-earth Titanates

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Abstract:

This research paper reports the measurement of Dielectric Constant (K') and Dielectric loss (K'') of light rare-earth titanates ($RTiO_3$) in the temperature range of 350-1100K. The compounds of $RTiO_3$ have been prepared by solid state reaction technique and characterised by XRD pattern. The Dielectric constant of all the titanates have much faster increase at higher temperature. The dielectric loss also shows a faster increase above certain critical temperature. The faster increase of K' and K'' at higher temperature is due to space charge effect of thermally generated charge carriers.

Keywords: XRD pattern, Dielectric constant, Dielectric loss

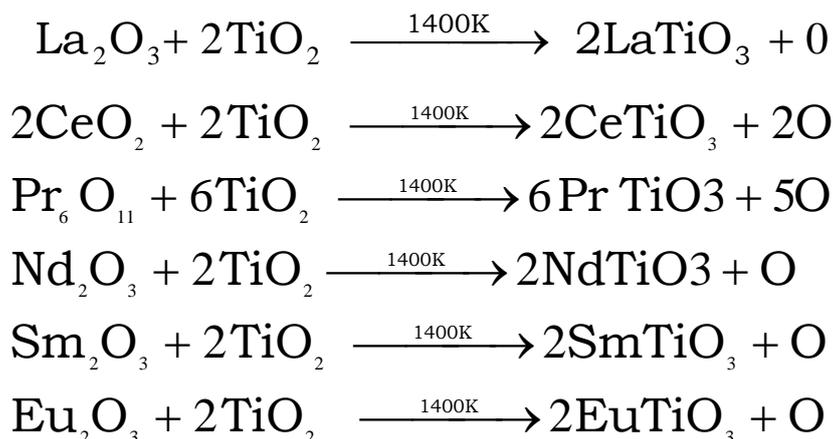
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1. Introduction :

The study of rare-earth compounds has been of increasing interest because of their unique physical properties [1-3]. The light rare-earth titanates $RTiO_3$ (where R stands for La, Ce, Pr, Nd, Sm and Eu) are typical perovskite compounds with a distorted cubic or orthorhombic unit cell at room temperature with four formula units per unit cell [4]. These have been quite few studies [5,6] regarding the electrical conductivity on few compounds of this series but so far no through investigation has been done in view of the dielectric behavior of light rare-earth titanates. This lack of data prompted us to study their dielectric properties.

2. Material preparation and characterization

The starting materials for the preparation of light rare-earth titanates were their common oxides namely La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 and Eu_2O_3 (of 99.99% purity from Fluka A.G., Switzerland) and TiO_2 (of 99.99% purity from Bonds, India). The stoichiometric amounts of respective oxide and TiO_2 were taken to mix thoroughly. After mixing these materials were pressed and fired at 1400K for 50 hours with one intermediate grinding. The compound formation takes place with following solid state reactions.



The weight loss corresponding to loss of oxygen on the right hand side of the above reaction was observed in all cases.

To confirm the complete formation of the prepared compounds, XRD pattern were obtained for each material. Using CuK_α radiation with $\lambda = 0.15418$ nm. From XRD pattern the value of interplaner spacing d_{hkl} have been obtained using relation.

$$d_{\text{hkl}} = \frac{0.15418}{2 \sin \theta} \text{ (nm)} \quad (1)$$

From d_{hkl} values, structure of the prepared compounds have been resolved using standard procedure [7].

The prepared compound was pressed at a pressure of more than $6 \times 10^8 \text{ N m}^{-2}$ to form pellets of circular cross-section (Area $\sim 0.90 \text{ cm}^2$ and thickness $b \sim 0.35$ cm). The pellet was then sintered in air for 24 hours at about 1000K. The mounting of pellet was done between the rigid electrodes of a sample holder after coating with silver.

3. Measurement of Dielectric Constant (K') and Dielectric Loss (K'')

The measurement of capacitance (C) and quality factor (Q) of pressed and sintered pellets of the studied titanates have been done at different temperature using two electrode method. The loaded sample holder was then put in a furnace. The capacitance and Q factor of the sample have been measured using Autocompute LCR-Q meter (APLAB 4910, India). The temperature of the sample inside the furnace was raised by a rectangular furnace which automatically records the temperature with chromal-alumel thermocuple fitted inside it. The dielectric constant (K') and dielectric loss (K'') of the material have been determined using the following formula

$$K' = \frac{tC}{A \epsilon_0} \tag{2}$$

and $K'' = K'/Q \tag{3}$

where t and A are the thickness and face-area of the pellet respectively and ϵ_0 is the permittivity of the vacuum.

4. Result and discussion

The variation of $\log K'$ is shown in figs. 1 to 6 for La, Ce, Pr, Nd, Sm and Eu titanates respectively. It is seen from these figures that the light rare-earth titanates have relatively high dielectric constant from 16 to 190 for all but La and Ce at 400K have exceptionally high dielectric constant of about 1585 at 400K. Since dielectric constant (K') seems to have almost no temperature dependence these values may be taken as the room temperature values of the materials.

We have measured the dielectric constant of all the light rare-earth titanates at frequency 1 KHz as a function of temperature. The value of dielectric constant of all the studied titanates at temperature 400K, 600K, 800K and 1000K at the frequency 1 KHz are given in Table1

TABLE 1

The dielectric constant (k') for the studied titanates at different temperatures measured at 1 khz

RTiO ₃ with R =	Dielectric constant at			
	400K	600K	800K	1000K
La	1585	1660	1738	3981
Ce	1584	1621	1905	2512
Pr	190	199	1.10x10 ⁴	6.31x10 ⁴
Nd	69	72	251	1000
Sm	100	103	91	158
Eu	16	17	23	48

It is evident from the Table 1 that –

- (i) the dielectric constant (K') decreases as we go down in the series upto Nd but after that it has a trend of increase
- (ii) the highest dielectric constant at 400K is that of lanthinum titanate
- (iii) the dielectric constant has a very slow increase with temperature at least upto 600K.

The limit of constancy of K' goes upto 900K for La, 975 for Ce, 710 for Pr, 675 for Nd, 625 for Sm and 765 for Eu. The titanates of La, Ce, Pr and Nd are iso-structural and the decrease of dielectric constant down the series seems to be due to the decrease in ionic bonding. Sm and Eu titanates have slight different structure and thereby a smaller value of dielectric constant. This systematic trend of K' variation reveals that polarization mechanism in all these titanates is same. A relatively larger value of K' in case of La appears due to the presence of impurities which forms some kind of donor centres and have larger polarizability. The dielectric constant has a very slow increase at lower temperature. Generally for any solid, the contribution to K' is made by the following factors :

- (i) the electronic polarizability of constituent
- (ii) atomic (or ionic) polarizability of the lattice
- (iii) orientational polarizability of dipoles (if any)
- (iv) space charge polarizability of thermally generated charge carriers. This arise when some or group of charges are held somewhere in the solid
- (v) interfacial polarization due to air gap between electrodes and material surface.

All the studied titanates have very large value of energy band gap ($E_g > 3$ eV). Hence there is no chance for the existence of thermally generated charge carriers at lower side of temperature ($T < 800$ K). The lower value of K' below 600K indicates that free charge carriers generated from impurities is also small. The slow increase of K' for all indicate that the number of thermally generated charge carriers below 600K are small. This rules out the possibility of strong space charge polarizability. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizabilities seems to compensate the slight decrease of polarizability due to decrease in the number of ions per unit volume following the lattice expansion with temperature. However, it must be noticed that the increase of K' with T is very slow in comparison to the variation one expects for ionic solids or even for the oxides of light rare-earth elements [8]. This indicates that either thermal expansion of these materials is very small or they have some other kind of polarization mechanism.

It is seen from Figs. 1 to 6 that dielectric constant of all these materials have much faster increase at higher temperature. The dielectric loss also shows a faster increase above certain critical temperature. It appears that the higher increase in K'' at higher temperature is due to the space-charge polarization of thermally generated charge carriers. In Table 2 we have listed that temperature (T''_k) at

which break is observed in K'' and temperature (T_1) at which break is observed in $\log\sigma$ vs T^{-1} plot [9]. Both the temperature are comparable. Thus it appears that thermally generated charge carriers play a significant role at higher temperature.

TABLE 2

Break temperatures obtained from dielectric loss (t''_k) and electrical conductivity (t_1) studies of the studied titanates

Titanates of	La	Ce	Pr	Nd	Sm	Eu
T''_K	690	650	710	675	712	760
T_1	694	694	671	671	714	769

It is well known that dielectric loss (K'') arises due to combined effect of mobile charge carriers, dipoles, defects and localized or bound charges. The total dielectric loss (K'') is related to a.c. conductivity (σ_{ac}) of the material by the relation [10,11]

$$K'' = \frac{\sigma_{ac}}{w \epsilon_0} \tag{6}$$

using above relation we have evaluated as well as experimentally measured values of K'' are given in Table 3.

TABLE 3

Dielectric loss (k'') as measured experimentally and calculated from a.c. electrical conductivity for the studied titanates

RTiO ₃ with R =	Dielectric loss at 500K		Dielectric loss at 800K	
	K''_{exp}	K''_{cal}	K''_{exp}	K''_{cal}
La	82	80	766	766
Ce	100	101	1.27×10^3	1.27×10^3
Pr	402	402	6.38×10^3	6.38×10^3
Nd	20	18	478	478
Sm	35	35	200	201
Eu	9	8	20	18

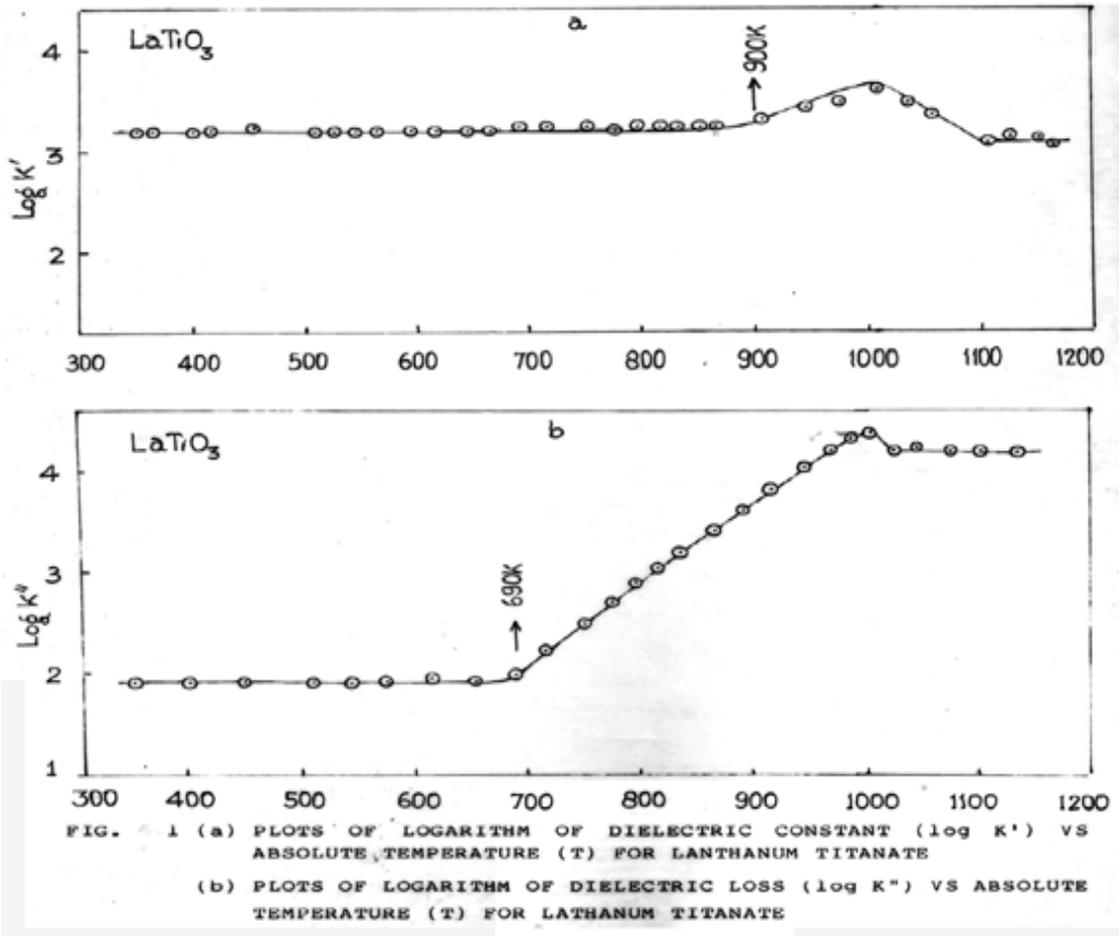
It is seen from this table that there is a fair agreement between these values. Therefore we draw following conclusion

1. The studied titanates have relatively high value of dielectric constant and low value of dielectric loss around 400K.

2. The dielectric constant and loss have very slow increase upto a temperature T_1 K. However above T_1 this increase becomes much more faster. The value of T_1 is different for different titanates.
3. The highest value of K' (~1660) occurs for La and lowest value ($K' = 16$) for Eu titanates upto $T = T_1$.
4. The reason for faster increase of K' and K'' at higher temperature is due to space charge effect of thermally generated charge carriers.

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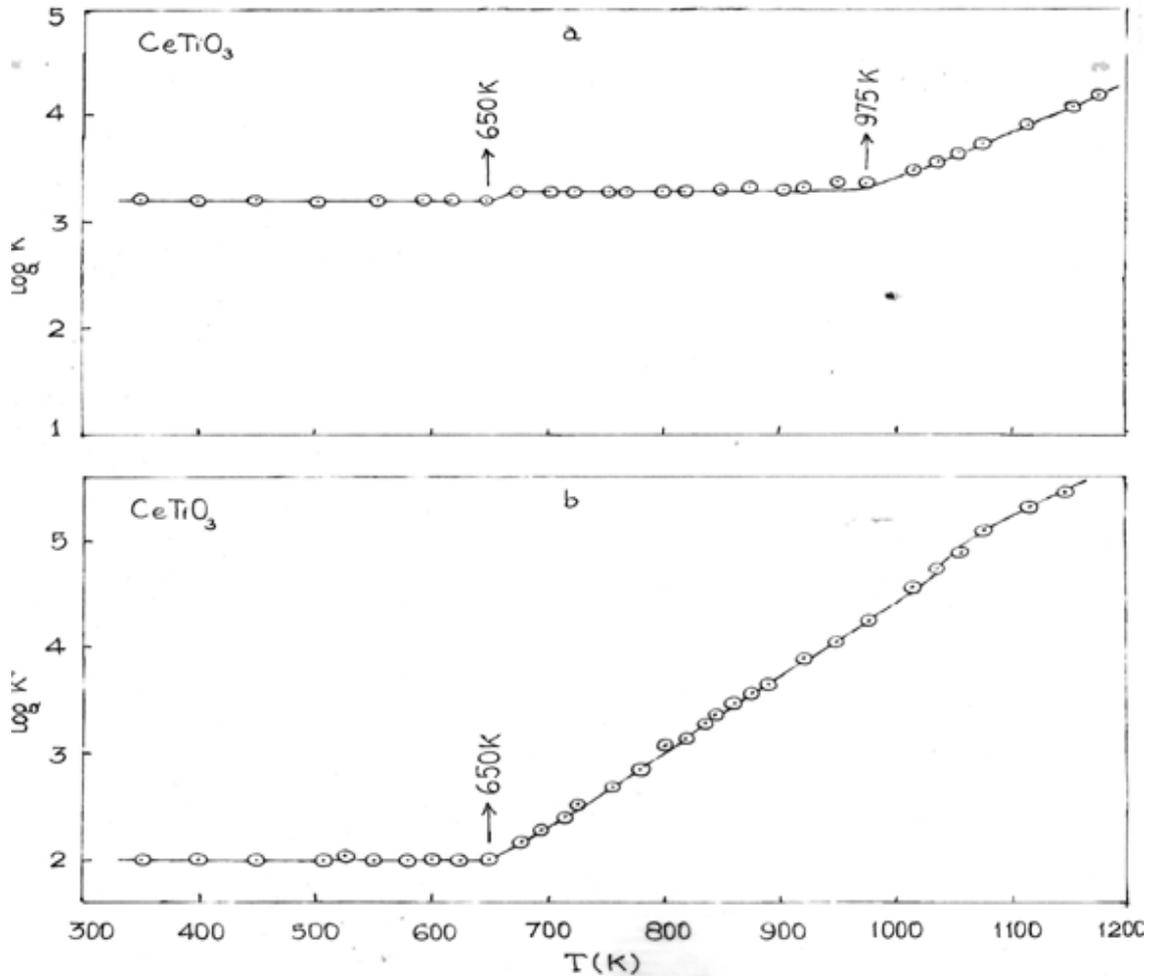


FIG. 2 (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT ($\log K'$) VS ABSOLUTE TEMPERATURE (T) FOR CERIUM TITANATE
 (b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS ($\log K''$) VS ABSOLUTE TEMPERATURE (T) FOR CERIUM TITANATE

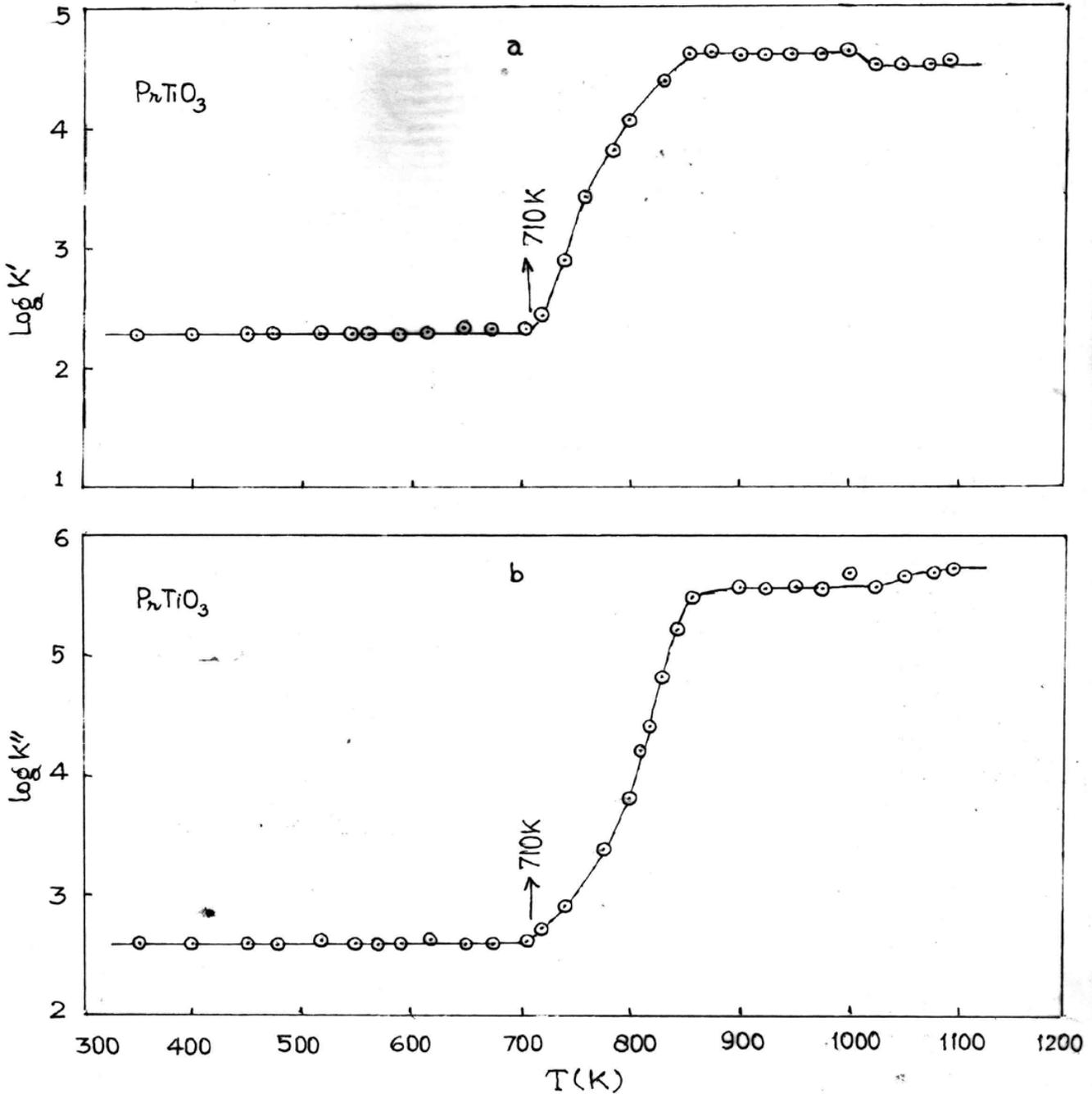


FIG. 3 (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT ($\log K'$) VS ABSOLUTE TEMPERATURE (T) FOR PRASEODYMIUM TITANATE
 (b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS ($\log K''$) VS ABSOLUTE TEMPERATURE (T) FOR PRASEODYMIUM TITANATE

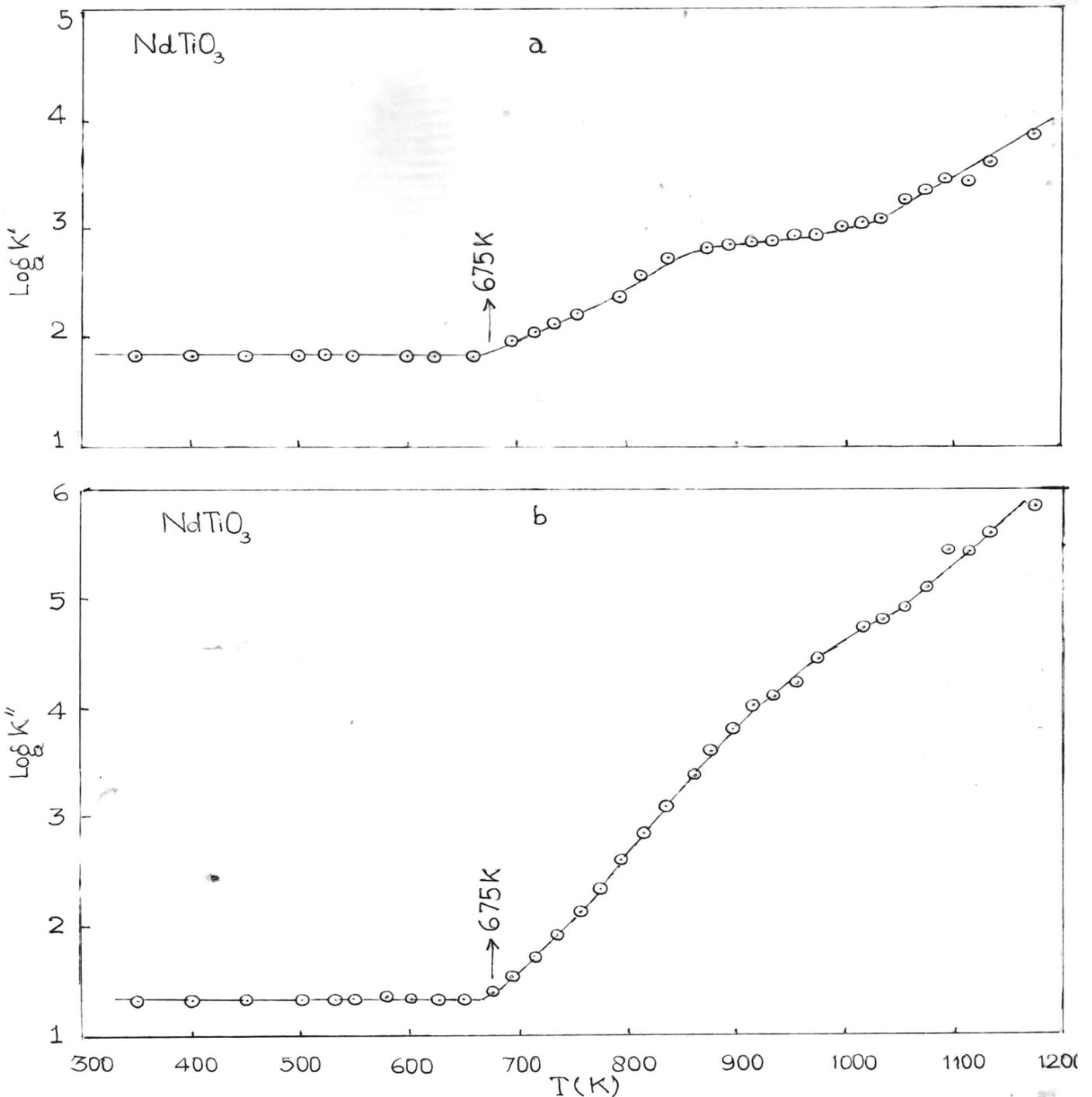


FIG. 4 (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT ($\log K'$) VS ABSOLUTE TEMPERATURE (T) FOR NEODYMIUM TITANATE
 (b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS ($\log K''$) VS ABSOLUTE TEMPERATURE (T) FOR NEODYMIUM TITANATE

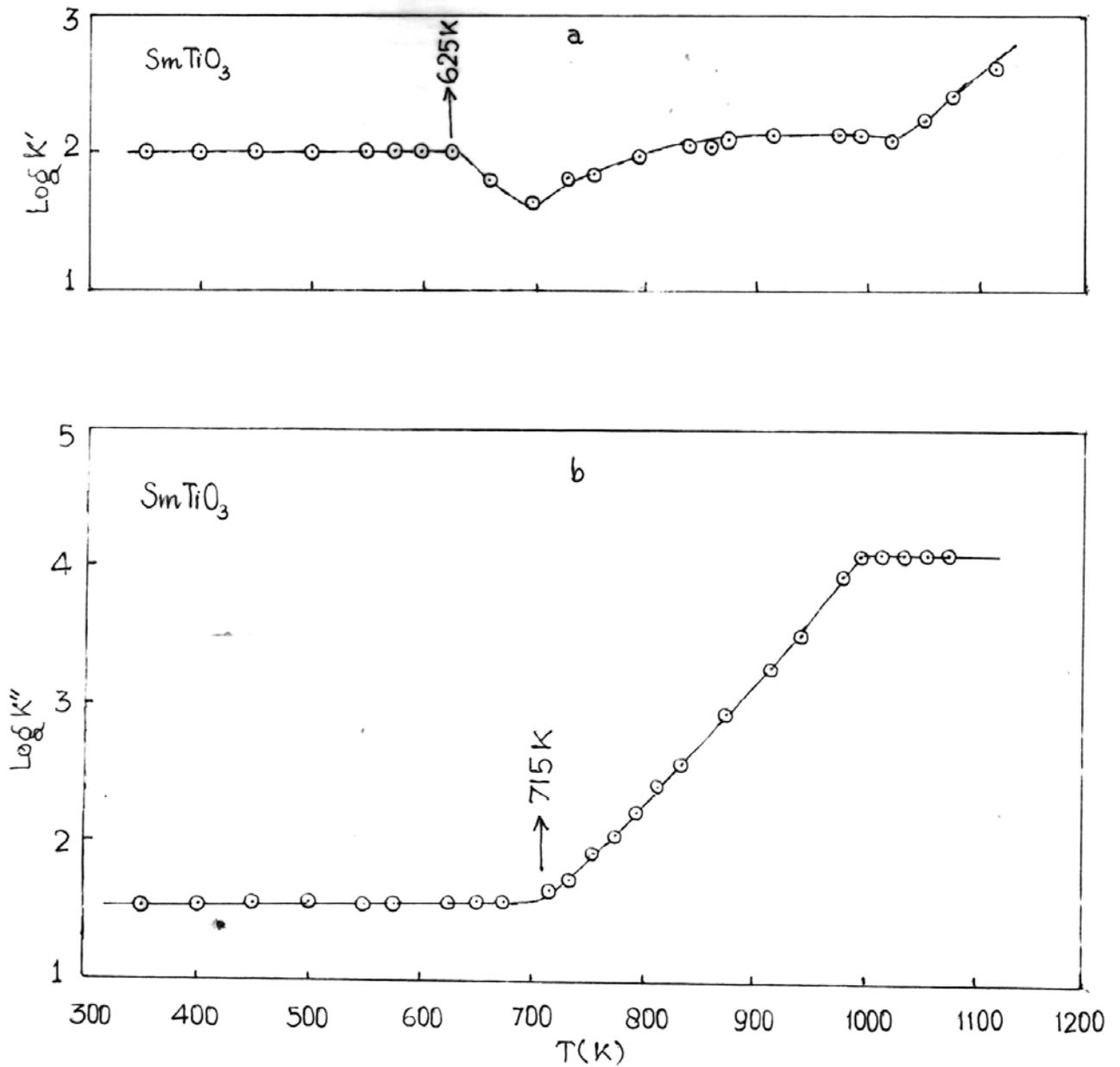


FIG. 5 (a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT ($\log K'$) VS ABSOLUTE TEMPERATURE (T) FOR LANTHANUM TITANATE
 (b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS ($\log K''$) VS ABSOLUTE TEMPERATURE (T) FOR SAMARIUM TITANATE

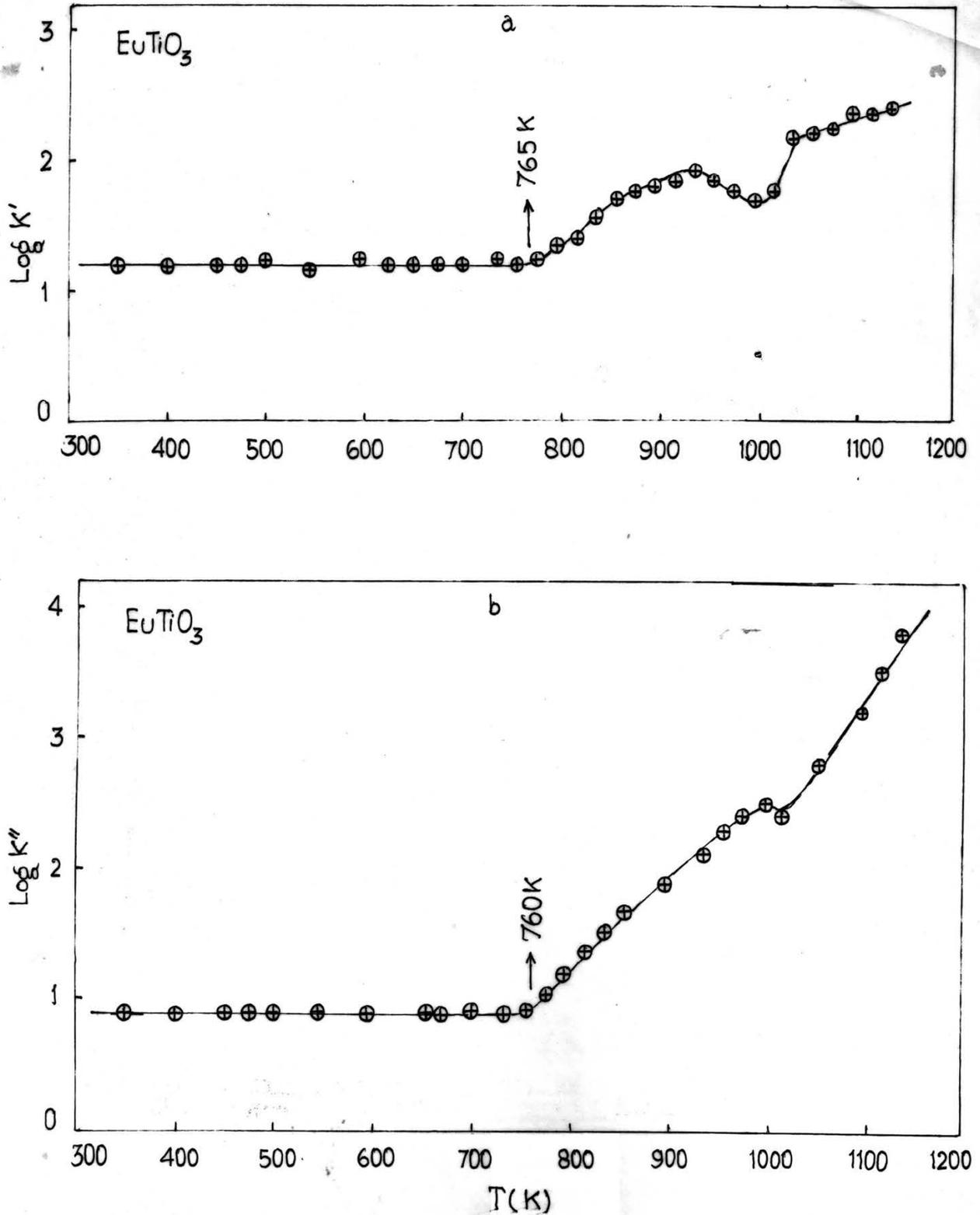


FIG 6.6(a) PLOTS OF LOGARITHM OF DIELECTRIC CONSTANT (log K') VS ABSOLUTE TEMPERATURE (T) FOR EUROPIUM TITANATE
 (b) PLOTS OF LOGARITHM OF DIELECTRIC LOSS (log K'') VS ABSOLUTE TEMPERATURE (T) FOR EUROPIUM TITANATE