

# Structural and Dielectric Behavior of $\text{TiNbXO}_6$ ( $X = \text{W}, \text{Mo}$ ) Ceramics

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Polycrystalline samples of  $\text{TiNbXO}_6$  ( $X = \text{W}, \text{Mo}$ ) were prepared by a high-temperature solid-state reaction technique. Room temperature X-ray diffraction (XRD) studies confirmed the formation of single-phase compounds with an orthorhombic structure. Variation of dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) with frequency (1–1000 kHz) and temperature (room temperature to 600 K) showed that  $\text{TiNbWO}_6$  had a ferroelectric-like dielectric anomaly at  $330 \pm 5$  K whereas  $\text{TiNbMoO}_6$  did not exhibit any such anomaly in the said temperature range. The sharp fall of dc resistivity ( $10^6$  to  $10^3 \Omega\text{m}$ ) with rise in temperature showed the superionic nature of the compounds in the high-temperature region. © 1998 Academic Press

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## INTRODUCTION

The tungstenate and molybdenate niobates of thallium (i.e.,  $\text{TiNbWO}_6$  and  $\text{TiNbMoO}_6$ ) are members of a structural family of general formula  $\text{ABXO}_6$ , where  $A =$  alkali ion,  $B = \text{Nb}$  and  $\text{Ta}$ , and  $X = \text{W}$  and  $\text{Mo}$ . The available literature on the family (1–3) shows that  $\text{TiNbWO}_6$  has an order–disorder type of ferroelectric phase transition with superionic character in the high-temperature (paraelectric) phase. Studies of dielectric, optical, and thermal properties of the  $\text{TiNbWO}_6$  crystal have been carried out in the microwave (i.e., megahertz to gigahertz) range. In view of the interesting and unusual superionic behavior of ferroelectric compounds and no systematic investigation of any other members of the  $\text{ABXO}_6$  family, we have carried out extensive studies of the structural, dielectric, thermal, and other properties of both members of the  $\text{TiNbXO}_6$  ( $X = \text{W}, \text{Mo}$ ) family. In this paper, we report our preliminary structural, detailed dielectric, and electrical behaviors of  $\text{TiNbWO}_6$  (TNW) and  $\text{TiNbMoO}_6$  (TNM) ceramics.

## EXPERIMENTAL

The polycrystalline samples of TNW and TNM were prepared using high-purity ingredients [ $\text{Ti}_2\text{CO}_3$  (99%,

Johnson Matthey Chemicals Ltd., England),  $\text{Nb}_2\text{O}_5$  (99%, BARC, India),  $\text{WO}_3$  (99%, John Baker Inc., U.S.A.), and  $\text{MoO}_3$  (99%, Loba Chemie Pvt. Ltd., India)] in the desired stoichiometry. All precursor powders were mixed thoroughly in an agate mortar for 2 h. The mixed oxides were calcined at 773 K in air for 10 h in alumina crucibles. The process of grinding and calcination was repeated several times to get homogeneous and single-phase compounds. Finally, the calcination was completed at 1113 and 1033 K for TNW and TNM, respectively. The calcined powders were used to make pellets of diameter  $\sim 10$  mm and thickness  $\sim 1$ –2 mm at an isostatic pressure of  $6 \times 10^7$  kg/m<sup>2</sup> using a hydraulic press. Poly(vinyl alcohol) (PVA) was used as binder, which reduces the brittleness of the pellets. The organic binder was burnt out during sintering (in air) at 1263 K (for TNW) and 1133 K (for TNM) for 5 h. The sintered pellets were polished with fine emery paper to make both of the faces flat and parallel. The polished pellets were then electroded with high-purity, air-drying silver paste for the electrical measurements. For preliminary structural study, X-ray powder diffractograms of the compounds were recorded at room temperature with a Rigaku (Miniflex, Japan) X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) over a wide range of Bragg angle ( $10^\circ \leq 2\theta \leq 70^\circ$ ) at a scanning rate  $2^\circ/\text{min}$ .

The dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) of the samples were measured as a function of frequency (1–1000 kHz) at room temperature (RT) and also as a function of temperature (RT to 600 K) at 10, 100, and 1000 kHz using a GR 1620 AP capacitance measuring assembly and an HP 4342A Q-meter with a laboratory-made three-terminal sample holder. Polarization measurement was carried with a modified Sawyer–Tower circuit developed by us. The dc resistivity was measured as a function of applied electric field (1.5–9 kV/m) and temperature (RT to 600 K) with the help of a Keithley 617 programmable electrometer.

## RESULTS AND DISCUSSION

The sharp and single peaks of the XRD patterns of both of the samples, which were different from those of the

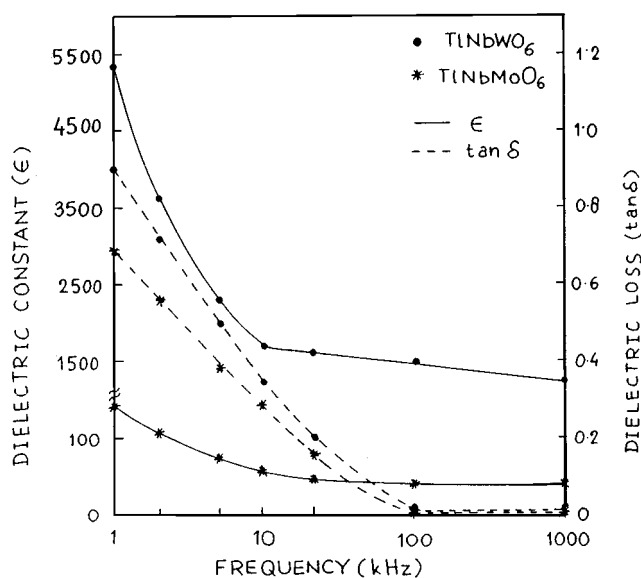
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**TABLE 1**  
**Comparison of Some Observed [o] and Calculated [c]**  
 **$d$ -Values of Some Reflections of  $\text{TiNbWO}_6$  and  $\text{TiNbMoO}_6$**   
**Ceramics at Room Temperature**

$\text{TiNbWO}_6$		$\text{TiNbMoO}_6$	
$hkl$	$d(\text{\AA})$	$hkl$	$d(\text{\AA})$
011	[o] 6.0259 (17) <sup>a</sup> [c] 6.0259	200	[o] 5.1405 (6) [c] 5.1405
020	[o] 3.6776 (29) [c] 3.6776	201	[o] 4.7450 (6) [c] 4.7450
121	[o] 3.1372 (100) [c] 3.1372	220	[o] 3.7777 (14) [c] 3.7777
202	[o] 3.0029 (40) [c] 3.0060	031	[o] 3.5617 (31) [c] 3.5559
312	[o] 2.1199 (4) [c] 2.1214	131	[o] 3.3634 (59) [c] 3.3606
321	[o] 1.9976 (17) [c] 1.9980	023	[o] 3.3143 (100) [c] 3.3082
040	[o] 1.8379 (19) [c] 1.8388	222	[o] 3.2204 (69) [c] 3.2215
141	[o] 1.7586 (6) [c] 1.7584	004	[o] 3.0841 (23) [c] 3.0840
413	[o] 1.5839 (7) [c] 1.5856	231	[o] 2.9308 (26) [c] 2.9244
422	[o] 1.5655 (9) [c] 1.5657	312	[o] 2.8938 (26) [c] 2.8929
503	[o] 1.3525 (5) [c] 1.3524	114	[o] 2.8533 (11) [c] 2.8553
		204	[o] 2.6443 (9) [c] 2.6446
		042	[o] 2.5391 (9) [c] 2.5384
		340	[o] 2.1634 (22) [c] 2.1614
		243	[o] 2.1034 (9) [c] 2.1040
		016	[o] 2.0209 (8) [c] 2.0218
		521	[o] 1.9047 (12) [c] 1.9058
		145	[o] 1.8224 (12) [c] 1.8177
		107	[o] 1.7368 (11) [c] 1.7369

<sup>a</sup>Relative intensities are given in parentheses.

constituents, suggested the formation of single-phase compounds. All of the peaks were indexed and cell parameters were determined in different crystal systems and cell configurations using the standard software "POWD," with observed  $d$ -values of strong-, medium-, and low-intensity peaks widely spread over the  $2\theta$  range. Finally, an orthorhombic unit cell was selected for which  $\sum\Delta d = \sum(d_{\text{obs}} - d_{\text{cal}})$  was found to be minimum. The cell parameters were refined by a least-squares method, which were  $a = 7.3301 \text{\AA}$ ,  $b = 7.3552 \text{\AA}$ , and  $c = 10.5089 \text{\AA}$  for TNW and  $a = 10.2810 \text{\AA}$ ,



**FIG. 1.** Variation of dielectric constant ( $\epsilon$ ) and loss ( $\tan\delta$ ) of TNW and TNM with frequency at room temperature.

$b = 11.1406 \text{\AA}$ , and  $c = 12.3358 \text{\AA}$  for TNM (with estimated errors of  $10^{-4} \text{\AA}$ ). The reported tetragonal cell of TNW (1, 2) was very close to our selected orthorhombic cell. Table 1 shows good agreement between observed and calculated  $d$ -values of TNW and TNM, which supports the correctness of the selection of the crystal system and its cell parameters. However, it was not possible to determine the space group of the compounds with the limited number of reflections.

The frequency dependence of the dielectric parameters (i.e.,  $\epsilon$  and  $\tan\delta$ ) of TNW and TNM at room temperature is shown in Fig. 1. The dielectric constant of both of the compounds decreases rapidly up to 10 kHz but beyond that it becomes almost constant. A similar type of variation is also observed in the dielectric loss of both of the compounds. It decreases very rapidly up to 100 kHz and after that it remains almost constant. This type of variation of  $\epsilon$  and  $\tan\delta$  with frequency is a feature of semiconducting dielectric materials with transport properties.

**TABLE 2**  
**Comparison of Some Dielectric Parameters of  $\text{TiNbWO}_6$  and  $\text{TiNbMoO}_6$  at Different Frequencies**

Parameter	$\text{TiNbWO}_6$			$\text{TiNbMoO}_6$		
	10 kHz	100 kHz	1000 kHz	10 kHz	100 kHz	1000 kHz
$\epsilon_{\text{RT}}$	1707	1516	1214	56	46	37
$\tan\delta_{\text{RT}}$	0.34	0.0206	0.0156	0.30	0.01	0.0056
Ferroelectric-like anomaly, $T_c$ (if any) (K)	340	333	333			
$\epsilon_{T_c}$	3391	1658	1601			
$\tan\delta_{T_c}$	0.826	0.0219	0.0199			

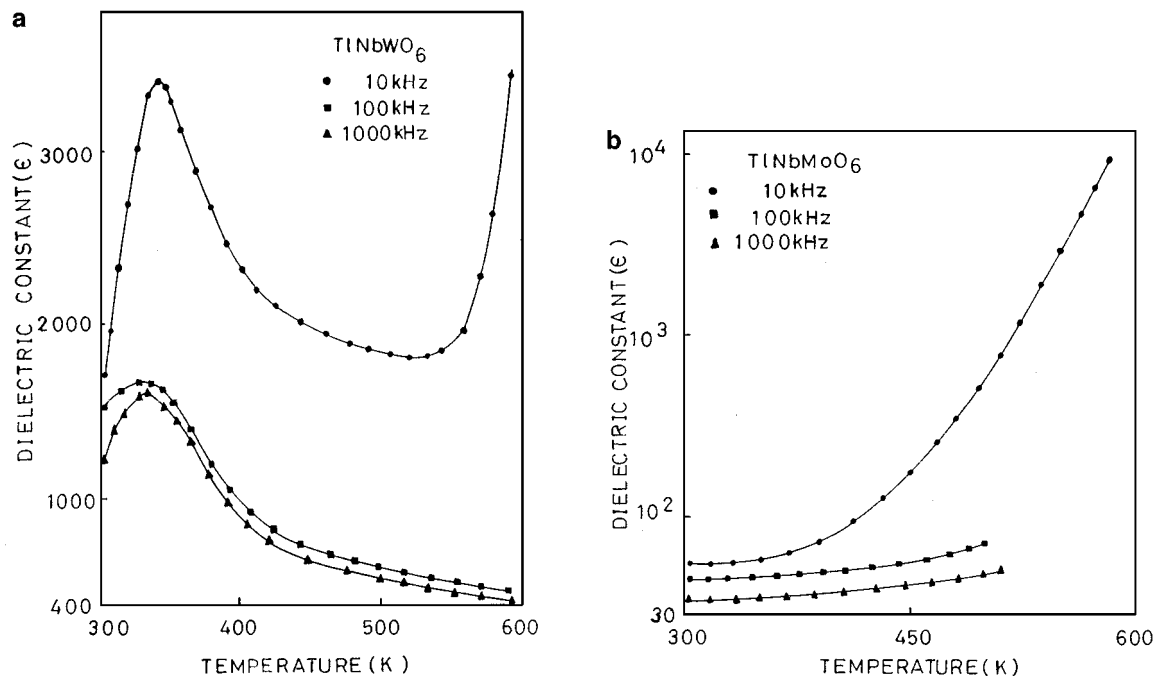


FIG. 2. Variation of dielectric constant ( $\epsilon$ ) of (a) TNW and (b) TNM with temperature at different frequencies.

Figures 2a and 2b show the temperature variation of  $\epsilon$  of TNW and TNM at 10, 100, and 1000 kHz. In TNW (Fig. 2a) a ferroelectric-like dielectric anomaly was observed at  $330 \pm 5$  K, which is found to be very close to the reported value at 330 K of its single-crystal counterpart (1–3). It is found that at 10 kHz,  $\epsilon$  of TNW starts increasing very rapidly at

temperatures above 500 K, which is not found at the other two frequencies. Such a rapid increasing trend in the high-temperature and low-frequency region was observed in our measurements of other members of the family in their ceramic form (5–7). The dielectric constant of TNM (Fig. 2b) varies very slowly with temperature at 100 and 1000 kHz,

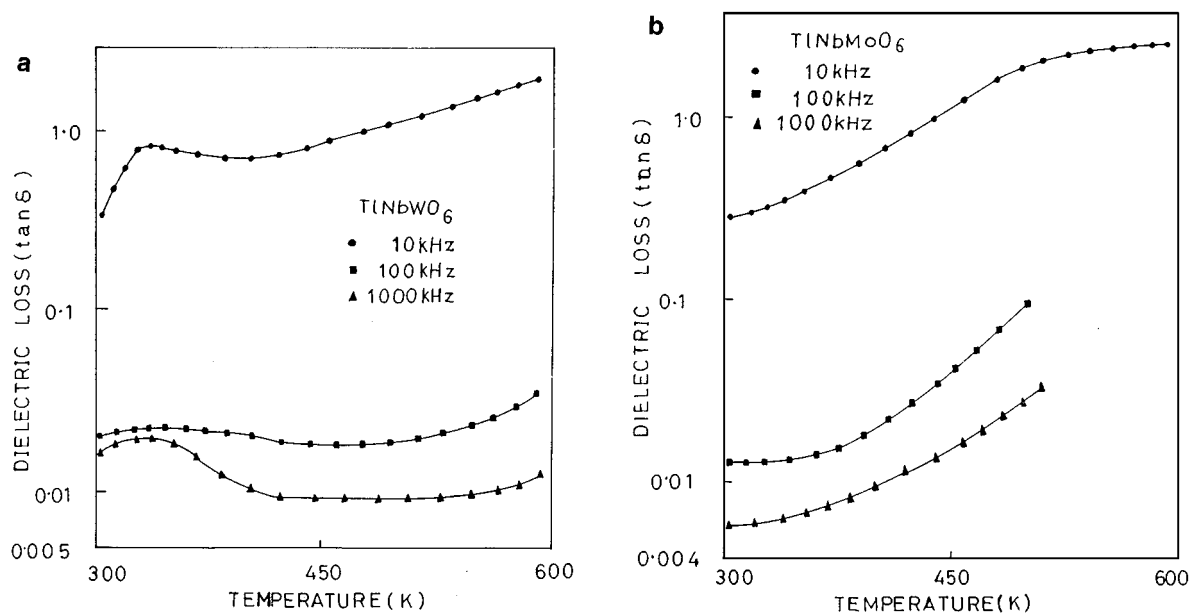


FIG. 3. Variation of dielectric loss ( $\tan \delta$ ) of (a) TNW and (b) TNM with temperature at different frequencies.

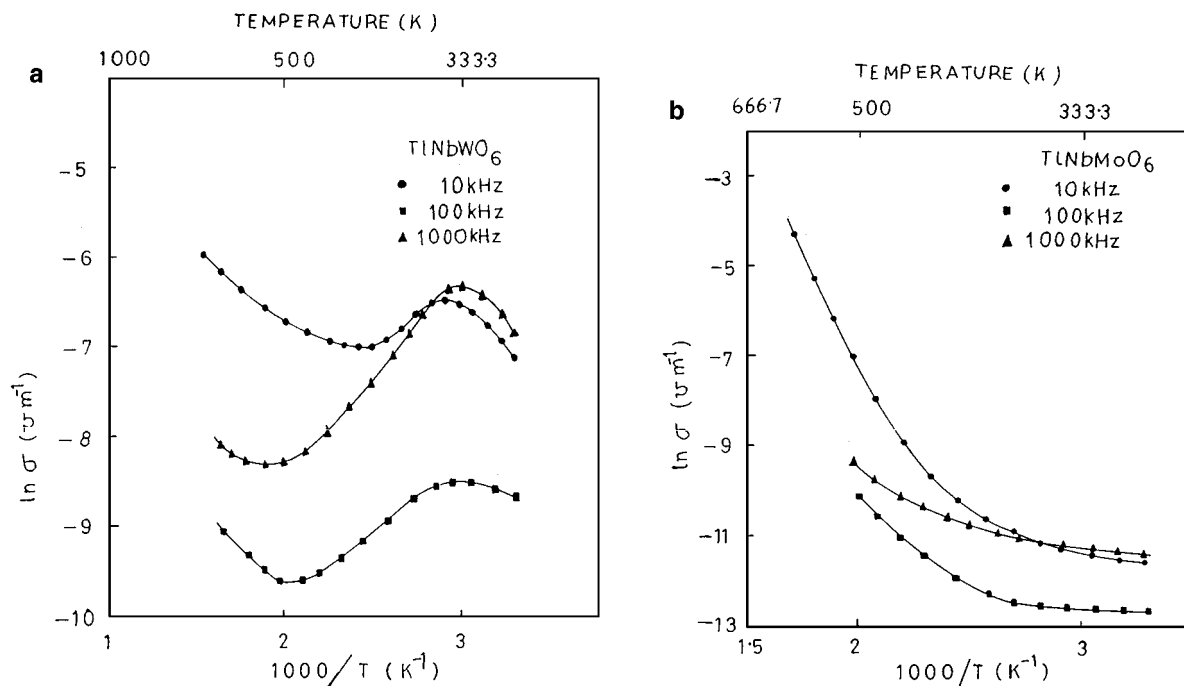


FIG. 4. Variation of ac electrical conductivity ( $\ln \sigma$ ) of (a) TNW and (b) TNM with the inverse of absolute temperature ( $1/T$ ) at different frequencies.

whereas at 10 kHz it increases rapidly at temperatures above 400 K. TNM does not exhibit any dielectric anomaly in the studied temperature range. The dielectric constant of TNW is greater than that of its isomorphous TNM compound. The rapid increase in  $\epsilon$  at high temperature and low frequencies in both of the compounds can be explained by the superionic nature of them in the said temperature region due to motion of cations, i.e.,  $\text{Ti}^+$ ,  $\text{Nb}^{5+}$ ,  $\text{W}^{6+}$ , and  $\text{Mo}^{6+}$  ions in the oxygen-octahedral skeleton (3,4). Table 2 gives some dielectric data of TNW and TNM.

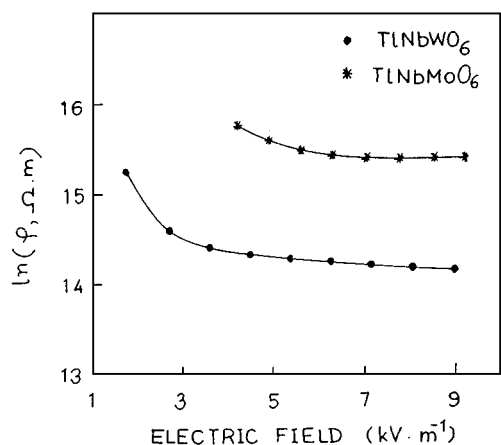


FIG. 5. Variation of dc resistivity ( $\ln \rho$ ) of TNW and TNM with applied electric field at room temperature.

Figures 3a and 3b show the variation of  $\tan \delta$  of TNW and TNM with temperature. The dielectric loss of both compounds starts increasing with rise in temperature and varies as shown in the figures.

The ac conductivity ( $\sigma$ ) of TNW and TNM was calculated using the formula  $\sigma = \omega \epsilon \epsilon_0 \tan \delta$ , where  $\omega$  = angular frequency,  $\epsilon_0$  = vacuum permittivity. Figures 4a and 4b show the variation of  $\ln \sigma$  of TNW and TNM with the inverse of absolute temperature ( $1/T$ ) at 10, 100, and 1000 kHz. The anomaly in ac conductivity of TNW (Fig. 4a) occurs exactly at the same temperature corresponding to the ferroelectric-like dielectric anomaly, which indicates a phase transition in the compound. In spite of this anomaly in dielectric constant (Fig. 2a) of TNW, no proper hysteresis loop has been observed in these high dielectric loss ceramic samples. Attempts are being made again to modify the Sawyer-Tower circuit (8) for this sample.

TABLE 3  
Some Electrical Parameters of  $\text{TiNbWO}_6$  and  $\text{TiNbMoO}_6$  Ceramics

	$\rho(\Omega\text{m})$		$t_{\text{ion}}$				
	300 K	600 K	305 K	400 K	473 K	573 K	673 K
$\text{TiNbWO}_6$	$2.4 \times 10^6$	$17.1 \times 10^3$	0.01	0.06	0.11	0.39	0.41
$\text{TiNbMoO}_6$	$8.0 \times 10^6$	$1.3 \times 10^3$	0.02	0.10	0.18	0.77	0.78

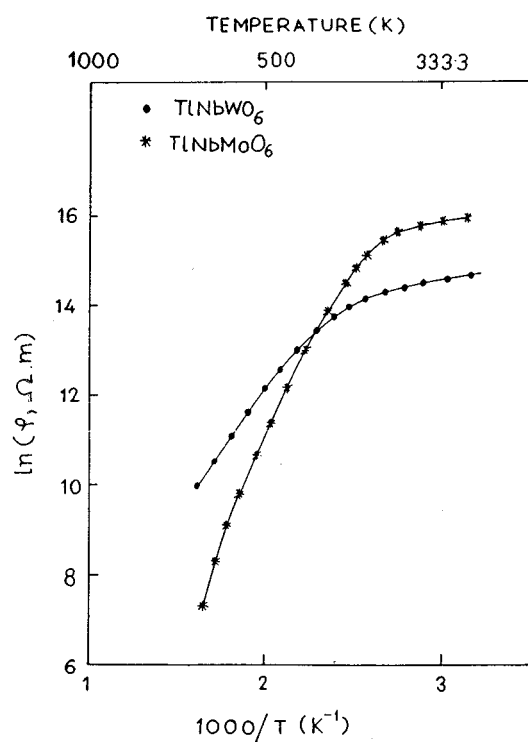


FIG. 6. Variation of dc resistivity ( $\ln \rho$ ) of TNW and TNM with the inverse of absolute temperature ( $1/T$ ) at constant electric field.

Figure 5 gives the variation of dc resistivity ( $\ln \rho$ ) with applied electric field at room temperature. The resistivity decreases slowly with increasing electric field, which may be due to a number of causes: formation of space charge in the dielectric, change in the shape of moisture in the pores of the dielectric under the action of an applied electric field, influence of contacts with electrodes, etc. (9).

Figure 6 shows temperature variation of dc resistivity at a constant electric field of 8.9 and 7.1 kV/m for TNW and TNM, respectively. It is found that the resistivity of these compounds is  $10^6 \Omega\text{m}$  at RT, which decreases rapidly to  $10^3 \Omega\text{m}$  at 600 K (Table 3). The resistivity of TNM decreases more rapidly than that of TNW. Other members of the family (5-7) also show similar variation with electric field and temperature.

The transference number ( $t$ ) is a quantitative measure of the extent of ionic/electronic contribution to the total conductivity. The ionic and electronic transference numbers are defined as

$$t_{\text{ion}} = \sigma_{\text{ion}}/\sigma_{\text{T}} = I_{\text{ion}}/I_{\text{T}},$$

and

$$t_{\text{e}} = \sigma_{\text{e}}/\sigma_{\text{T}} = I_{\text{e}}/I_{\text{T}}$$

$$t_{\text{ion}} + t_{\text{e}} = 1,$$

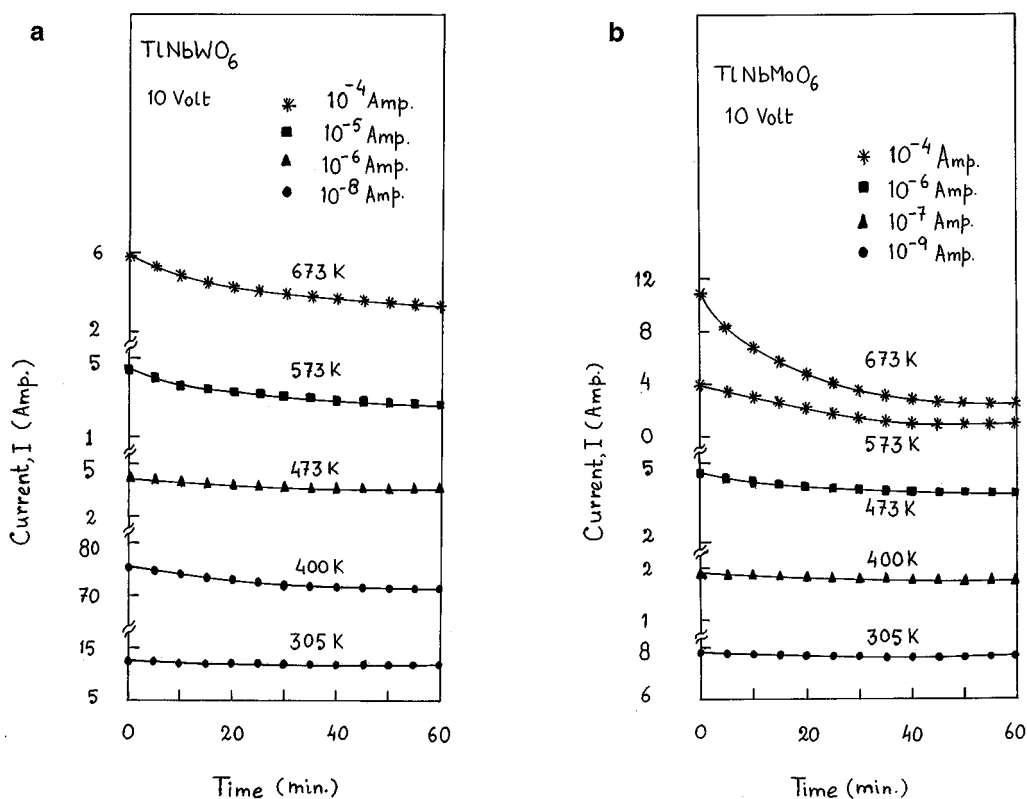


FIG. 7. Variation of current ( $I$ ) in (a) TNW and (b) TNM with time at different temperatures.

where  $I_{\text{ion}}$ ,  $I_e$ , and  $I_T$  are the ionic, electronic, and total current, respectively. The instantaneous value of current at a particular temperature gives the value of  $\sigma_T$  and the final stabilized current gives the total  $\sigma_e$  (10). Figures 7a and 7b give the variation of current through the sample with time at a constant source voltage of 10 V at different constant temperatures. It is found that  $t_{\text{ion}}$  increases very slowly up to 473 K in both compounds; after that, it starts increasing. This increasing trend exists up to 573 K and a very small variation is observed in its value at higher temperatures (Table 3). TNM has a much higher value of ionic transference number compared to that of TNW, indicating that it is a better ionic conductor. The existence of this property of TNM is also indirectly supported by a relatively sharper fall of its dc resistivity compared to that of TNW in the same temperature range.

### CONCLUSION

It can be concluded that TNW ceramics have a ferroelectric-like dielectric anomaly at  $330 \pm 5$  K whereas its

isomorphous compound TNM does not have any such anomaly in the studied temperature range. Both compounds show a superionic nature in the high-temperature region.

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