Structural, Dielectric and Electrical Conducting Behaviour of TlTaXO$_6$ [X= W, Mo] Ceramics

Dr. Tanika Kar

Department of Physics, Kharagpur College, West Bengal, India

e-mail : tanikakar @yahoo.in

Abstract – **The polycrystalline samples of TlTaXO$_6$ (X = W, Mo) compounds were synthesised by solid-state reaction technique. The formation of the compounds was checked by X-ray diffraction (XRD) technique. The compounds have cubic crystal structure at room temperature. Studies of dielectric properties (ε, tanδ) as function of frequency (10 k - 1 MHz) and temperature (300 - 600 K) reveal that the compounds do not have any dielectric anomaly in the said frequency and temperature range. Detailed studies of electrical properties (i.e., ac and dc conductivity, transference number, etc.) as function of various parameters, e.g., frequency, dc electric field, time and temperature, are carried out.**

Keywords – **Ceramics, Electrical properties, Ionic conduction, Transference number**

I.INTRODUCTION

Ceramics are commonly known for their insulating properties. But in practice, they exhibit a wide range of electrical conductivities, competing metals (highest electronic conductivity) and liquid electrolytes (highest ionic conductivity). Ceramic materials find applications in fuel cells, solid-state batteries and gas sensors because of their high ionic conductivities. The physical rigidity and inertness of ceramic makes it useful where a liquid electrolyte would be impractical. There are different types of skeleton structures which facilitate fast ion conduction. Among all the three-dimensional skeleton structures, pyrochlores offer interesting possibilities to act as fast ion conductors. The cubic pyrochlores have a general formula A$_2$B$_2$X$_6$Y where A is large cation, B is a small cation octahedrally coordinated by six X ions and Y is O, OH, F, H$_2$O. The B$_2$X$_6$ sub-array forms a rigid skeleton of corner – shared octahedra [1]. These octahedra are arranged in a tetrahedral array according to a diamond-type net and a system of open channel is observed. It is the presence of these channels which makes pyrochlores potentially useful. In normal pyrochlores, the channels contain an array of stoichiometry (A$_2$Y)$_n$ unit. The chemical bond between the rigid framework and the array may be more or less weak according to the chemical composition, but is critical in determining the chemical and physical properties. In fact, because of the weakness of that interaction, atoms A and Y may be partly or completely missing giving rise to 'defect' pyrochlores. 'Defect' pyrochlores have a B$_2$X$_6$ network similar to regular pyrochlores, but with vacancies introduced in the A$_2$Y array. Thus these compounds are generally formulated as □AB$_2$X$_6$□ or □$_2$B$_2$X$_6$A (□: vacancy) depending on the size of A cation. These are the most interesting ones making fast ion conduction possible for having structural disorder. Studies on structural, dielectric and electrical conducting properties of some members of defect pyrochlore family having general formula ABXO$_6$ [A= Li, Na, K, Cs, Tl; B = Nb, Ta; X = W, Mo] were already reported [2 – 9]. In this article, structural and detailed dielectric and electrical conducting properties of polycrystalline TlTaXO$_6$ (X = W, Mo) compounds are reported.

II. MATERIALS & METHODS

The proposed compounds were prepared from the pure carbonates and oxides: Tl$_2$CO$_3$ (99%, Jhonson Matthey Chemicals Ltd., England), Nb$_2$O$_5$ (99%, BARC, India), Ta$_2$O$_5$ (99%, M/s E. Merck, Germany), WO$_3$ (99%, M/s John Baker Inc., USA) and MoO$_3$ (99%, M/s Loba Chemie Pvt, Ltd., India). Conventional high-temperature solid-state reaction technique was used to synthesise the compounds. The stoichiometrically weighed constituents for a particular composition were thoroughly mixed in agate mortar for 2 hours. The mixed powders were then calcined in alumina crucible at 773 K for 15 hours in air. The initially calcined powders were ground once again and recalcined at some higher temperatures in the same atmosphere. This practice was repeated several times till the formation of the compounds. The completion of reaction was checked by X-ray diffraction technique (XRD). The XRD pattern of calcined powder was obtained by using X-ray powder diffractometer (Rigaku Miniflex, Japan) with CuK$_\alpha$ radiation (λ= 1.5418 Å) in the Bragg angle range 20º - 70º at a scanning rate of 2º min^{-1}.

The fine homogeneous recalcined powders were cold pressed into cylindrical pellets (discs) at a pressure $\sim 5 \times 10^6$ Pa. An organic solution (Polyvinyl Alcohol – PVA) was used as binder to reduce the brittleness of the pellets. These pellets were sintered for 6 hours in air. The organic binder was burnt out during high temperature sintering. The diameter of the green samples was reduced by 0.5% after sintering. The thickness of the pellets was 1-3 mm. The samples were cooled down to room temperature by rapid cooling process. The final calcination temperature and time, sintering temperature and time and cell parameter of $TlTaXO_6$ (X = W, Mo) compounds along with their isomorphous compounds $TlNbXO_6$ (X = W, Mo) have been given in Table I. The sintered pellets were polished with fine emery paper to make both the surfaces flat and parallel. The pellets were electroded with high purity silver paste for electrical measurements. Some researchers [10, 18] had reported that the electrode material did not affect the dielectric and electrical properties of the compounds. The dielectric parameters (ε, $\tan\delta$) were measured as a function of frequency (10^3 - 10^6 Hz) and temperature (100 – 500 K) using GR1620AP capacitance measuring assembly and HP 4342A Q-meter along with laboratory-made three-terminal sample holder and heating arrangements. The dc conductivity of all the compounds were measured as function of applied dc electric field (10 – 110 V/cm) and temperature (300 – 673K) using KEITHLEY 617 Programmable Electrometer along with laboratory-made sample holder, heating arrangements and automatic temperature controller (Aplab, Model 9601). In order to find out the nature of charge carrier and their contribution in conduction mechanism, ionic transference number (t_{ion}) was calculated using the formula $t_{ion} = (\sigma_{ion}/\sigma_T) = (I_{ion}/I_T)$ at five different temperatures, viz. 300, 400, 473, 573 and 673 K respectively. The source voltage was kept constant of 10 Volts. The temperature variation of measured ac conductivity, $\sigma_m(\omega)$, was obtained at two frequencies, viz., 10^5 and 10^6 Hz. All these measurements were carried out using HP 4342 A Q-meter, laboratory-made sample holder and necessary heating arrangements. As most of the members of the defect pyrochlore family have a tendency to get contaminated by moisture, special care was taken to avoid the problem. All the samples were kept at 400K for 12 h before each experiment. In order to prevent rehydration of the samples during experiments silica gel was kept inside the sample holder.

TABLE I
Some preparational and dimensional data of the proposed compounds

Compound Studied	Abbr. Name	Calcination Temp.(K) [Time(hr.)]	Sintering Temp.(K) [Time (hr.)]	Cell Parameter (Å)
$TlNbWO_6$	TNW	1113 [15]	1263 [06]	10.3905
$TlTaWO_6$	TTW	1323 [15]	1373 [06]	10.2617
$TlNbMoO_6$	TNM	1033 [15]	1133 [06]	10.4891
$TlTaMoO_6$	TTM	793 [15]	853 [06]	10.9989

III. RESULTS & DISCUSSION

A. STRUCTURAL STUDTY

All the peaks in the XRD patterns of both the compounds were indexed and cell parameters were determined in different crystal systems and cell configurations using the standard computer program 'PowdMult' with observed d-values of strong-, medium- and low-intensity peaks. Finally, a cubic unit cell was selected for which $\Sigma\Delta d = \Sigma(d_{obs} \sim d_{cal})$ was found to be minimum. The obtained cell parameter of TTW is slightly smaller (0.95%) than the reported one [12]. According to Grins et al., the cell parameter along with other physical properties depends upon the method of preparation of the compounds [18]. No such comparison is possible for TTM compounds.

B. DIELECTRIC STUDY

The dielectric parameters (ε, $\tan\delta$) were measured as a function of temperature (100 – 500 K) at frequencies 10^4, 10^5 and 10^6 Hz respectively. TTW and TTM do not have any dielectric anomaly in the studied frequency and temperature range. The dielectric constant in these compounds starts increasing with temperature. The rate of increase is more rapid in 10^4 Hz than in other two frequencies, viz., 10^5 and 10^6 Hz. In most the compounds rapid increasing trend in the values of ε is observed at temperatures ≥ 450 K. This type of behaviour of the compounds can be explained by their conducting nature at high temperatures. A characteristic feature of a material to become fast ion conductor / sold electrolyte is the complexity / disordering of its crystallographic structure [11]. The disordering of the cation sublattices consists of a shift of a cation from a site to one of the interstices available. Although the disordering of the sublattice as result of the movement of the cations from sites to interstices does not lead by itself to the appearance of carriers (excess carriers and their vacancies),

it does facilitate substantially their formation. The reason is that the disorder is accompanied by an increase of ε and this weakens the coulomb interaction between the cation that departed to another unit cell and the vacancy that left behind. The increase of ε because of the transition of cations from sites to interstices is due to the fact that each such transition produces an equivalent dipole in the crystal whose positive charge is in the interstice and the negative charge in the site. The dipole orientation is practically arbitrary and it can orient itself with external electric field. Therefore there is an increase in the dipole moment of the system. The departure of cation to the interstice increases greatly the polarisability of the unit cell, since the length of the equivalent dipole is very large – of the order of lattice constant. The increase in the number of equivalent dipoles with rising temperature should be due to purely statistical causes, even if one disregards the interaction between them. Their number must then increases continuously with temperature and a transition from a state with low ε (ordered cation sublattice) into a state with high ε (disordered cation sublattice) occur. Therefore, a very high value of ε leads to increase in the number of carriers which in turn increase the conductivity of the compound. Some dielectric data of $TlTaXO_6$ (X = W, Mo) compounds along with their isomorphous compounds $TlNbXO_6$ (X = W, Mo) have been given in Table II.

The tangent loss of all the compounds increases with temperature. Though the tanδ values are smaller at 10^5 and 10^6 Hz compared to those at 10^4 Hz, in many compounds it could not be measured above 500K at these two frequencies. In these cases, tanδ becomes high enough and exceeds the limit of the Q-meter. High values of tanδ at temperatures $\geq$ 450 K can be explained by the highly conducting nature of the compounds in the above region. Addition of thermal energy increases the movement of cations in the main skeleton of the compounds – resulting in the increase of tanδ.

TABLE II

Some dielectric data of the proposed compounds

Compound	Frequency (Hz)	ε at 300 K	tanδ at 300 K	Dielectric Anomaly (K)	ε at 500 K	tanδ at 500 K
TNW	10^4	1800	0.35	335	3500	2.0
	10^5	1500	0.02	333	500	0.035
	10^6	1400	0.016	333	410	0.011
TTW	10^4	31.5	0.02	-	820	3.0
	10^5	31.2	0.0084	-	55	0.09
	10^6	31	0.0076	-	45	0.03
TNM	10^4	57	0.3	-	12000	3.0
	10^5	46	0.012	-	100	0.20
	10^6	37	0.0056	-	92	0.10
TTM	10^4	29.6	0.022	-	10000	4.3
	10^5	29.6	0.006	-	100	0.10
	10^6	29.6	0.0048	-	45	0.016

C. DC CONDUCTIVITY

The total dc conductivity (electronic + ionic), $(\sigma_{dc})_{TOTAL}$ values of $TlBXO_6$ [B = Nb, Ta; X = W, Mo] compounds at different temperatures are given in Table III. The conductivity increases with increasing temperature. The amount of increase is different in different compounds as temperature increases from 373 K to 673 K.

TABLE III

Comparison of $(\sigma_{dc})_{TOTAL}$ [(ohm.cm)$^{-1}$] of the studied compounds at different temperatures

Compound	300 K	573 K	673 K
TNW	1.92×10^{-8}	9.08×10^{-6}	6.46×10^{-5}
TTW	1.31×10^{-11}	5.30×10^{-7}	2.80×10^{-6}
TNM	1.02×10^{-10}	1.78×10^{-6}	1.85×10^{-5}
TTM	1.03×10^{-11}	1.85×10^{-6}	7.80×10^{-5}

The activation energy, E_A, was calculated using the well known Arrhenius relation: $\sigma = \sigma_o \exp(-E_A/K_BT)$ [$K_B \rightarrow$ Boltzmann constant] in high temperature ($\geq$ 500 K) region. The values of E_A are given in Table IV. The nature of octahedral framework (e.g. size of the bottlenecks) plays an important role in determining the activation energy of a compound [13, 14]. The values of E_A obtained in the present study are in good agreement with the reported ones [12 - 14]. In order to find out the nature of charge carrier and their contribution in conduction mechanism, ionic transference number (t_{ion}) was calculated at five different temperatures, viz. 300, 400, 473, 573 and 673 K respectively. The source voltage was kept constant of 10 Volts. As the temperature increases, the current through the compounds increases due to increase in conductivity. It is observed that in all the samples t_{ion} has very small value at 300, 400 and 473 K (Table IV). In this temperature region (i.e., 300 - 473 K), electrons/holes are the main contributors in conduction process though the value of t_{ion} increases slowly. Beyond this region, t_{ion} increases. The value attained by t_{ion} at 573 K remains almost constant at 673 K also. At high temperatures ($\geq$ 573 K), TNM is a good ionic conductor ($t_{ion} \geq 0.7$) while TNW, TTW and TTM are not.
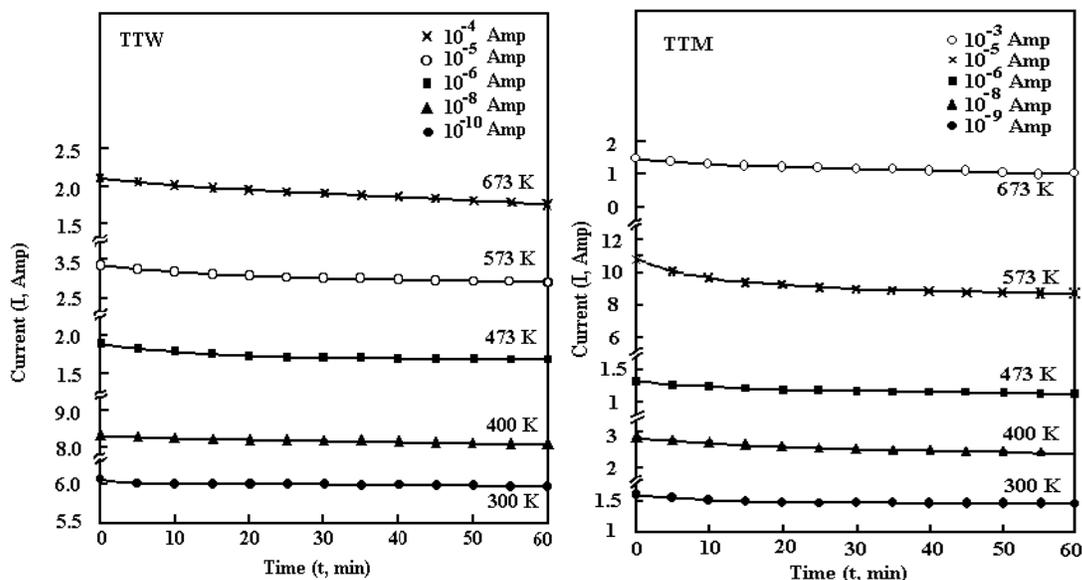

Fig. 1. Variation of dc current [I] through specimens of TTW and TTM with time at different temperatures.

According to Sleight et al. [15] and Castro et al. [12], ionic conductivity depends on polarisability of cations involved in conduction process. However, another determinant factor, which offsets the former one, is the size of the channel through which conduction takes place. According to the models of Huberman et al. [16] and Rice et al. [17], in pure ionic conductors an abrupt or gradual increase in the mobile ion density takes place with increase in temperature causing high values of conductivity. Ionic conduction is not so prominent in TNW, TTW and TTM in the studied temperature range. A few data are available on some tungstate compounds in literature [12 - 14], but no such data are available for molybdate compounds. It is also reported that ionic conductivity depends on various factors including synthesis technique, cell parameters, etc. [18]. Absence of detailed experimental data on the proposed compounds makes any comparison impossible.

TABLE IV

Comparison of t_{ion} and E_A of the studied compounds

Compound	t_{ion}					E_A (eV)
	300 K	400 K	473 K	573 K	673 K	
TNW	0.01	0.06	0.11	0.39	0.41	0.55
TTW	0.01	0.02	0.08	0.13	0.14	0.67
TNM	0.02	0.10	0.18	0.77	0.78	0.77
TTM	0.06	0.12	0.15	0.31	0.33	0.86

D.   AC CONDUCTIVITY

In order to use a material most effectively for solid electrolyte applications, it has to be characterised as fully as possible. Measurement of the response when a sinusoidal potential difference is applied across a sample is a useful method for electrical characterisation. A great deal can be learnt from frequency and temperature dependence of the resulting impedance. In an ideal insulator, there are no free charges and ac conductivity is related to only to the bound charges or charges hopping between well defined sites, without contributing anything to long range motion or dc conductivity. However, in real materials, there are also some free charges, which give rise to dc conductivity without contributing anything to dielectric polarisation. Hence, the measured ac conductivity, $\sigma_m(\omega)$, will have the contribution from both ac and dc conduction. Study of alternating current conductivity has become the most widely used method for investigating the ionic conductivity of electrolytes. In case of mixed ionic-electronic conductors, however, the ac technique yields only the total conductivity and dc measurements are normally required to identify the contributions of different carriers to the total conductivity.

The temperature variation of measured ac conductivity, $\sigma_m(\omega)$, was obtained at two frequencies, viz., 10^5 and 10^6 Hz. It is found that the conductivity increases with frequency. As expected, the values of $\sigma_m(\omega)$ of all the compounds are greater than that of their dc conductivity in the temperature range 300 - 500 K. Table V and VI give the comparison of the values of ac and dc conductivity of TlBXO$_6$ [B = Nb, Ta; X = W, Mo] compounds at 300 and 500 K . Further comparison above 500 K is not possible because in most of the cases the conductivity of the compounds becomes so high that it exceeds the limit of the Q-meter. It is found that in all the compounds, the rate of increase of $\sigma_m(\omega)$ with increasing temperature is much slower than $(\sigma_{dc})_{TOTAL}$.
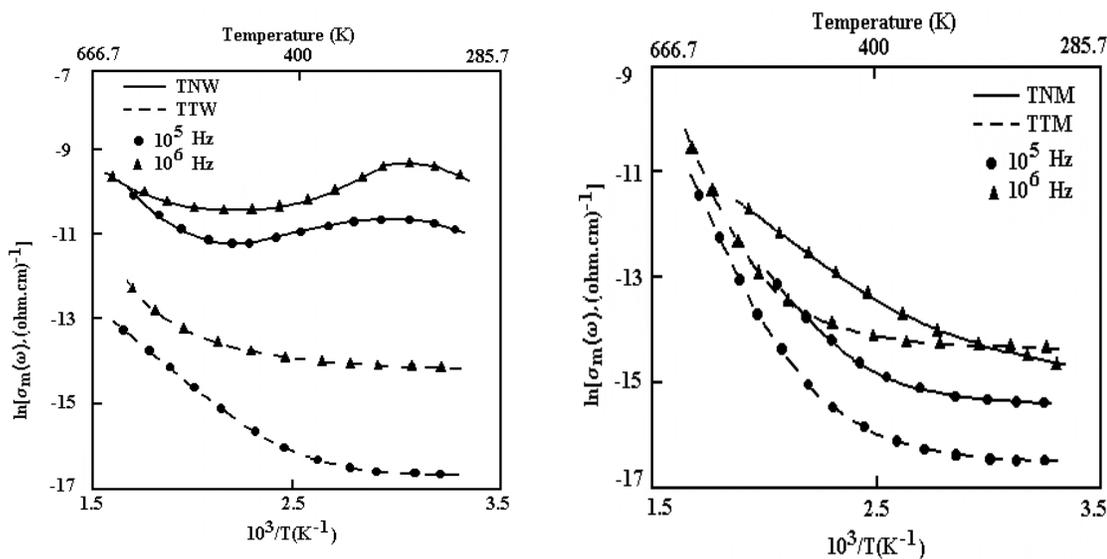

Fig.2. Variation of measured ac conductivity [$\sigma_m(\omega)$] of TlBXO$_6$ [B = Nb, Ta; X = W, Mo] compounds with temperature at 10^5 and 10^6 Hz.

TABLE V

Comparison of $\sigma_m(\omega)$ and $(\sigma_{dc})_{TOTAL}$ [(ohm.cm)$^{-1}$] at 300 K

Compound	$\sigma_m(\omega)$		$(\sigma_{dc})_{TOTAL}$
	10^5 Hz	10^6 Hz	
TNW	2.04×10^{-5}	7.49×10^{-5}	1.92×10^{-8}
TTW	6.18×10^{-8}	8.32×10^{-7}	1.31×10^{-11}
TNM	2.05×10^{-7}	4.13×10^{-7}	1.02×10^{-10}
TTM	6.81×10^{-8}	5.57×10^{-7}	1.03×10^{-11}

TABLE VI

Comparison of $\sigma_m(\omega)$ and $(\sigma_{dc})_{TOTAL}$ [(ohm.cm)$^{-1}$] at 500 K

Compound	$\sigma_m(\omega)$		$(\sigma_{dc})_{TOTAL}$
	10^5 Hz	10^6 Hz	
TNW	1.62×10^{-5}	3.29×10^{-5}	1.74×10^{-6}
TTW	4.56×10^{-7}	1.64×10^{-6}	7.62×10^{-8}
TNM	2.50×10^{-6}	6.79×10^{-6}	2.24×10^{-7}
TTM	9.19×10^{-7}	2.26×10^{-6}	1.46×10^{-7}

V. CONCLUSION

TlTaWO$_6$ and TlTaMoO$_6$ have cubic crystal structure at room temperature ($\sim$ 300 K). Both the compounds do not have any dielectric anomaly in the studied frequency (10^3 -10^6 Hz) and the temperature (100 – 500 K) range. Ionic conduction is not so prominent in the compounds in the temperature range (300 – 673 K).

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