Metal Insulator Transition in vacant 3d orbital Quantum Spin Liquid: Tb$_2$Ti$_2$O$_7$

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Abstract

Tb$_2$Ti$_2$O$_7$: The cubic pyrochlore - Quantum spin liquid reveals a sharp metal to insulator transition (MIT) at 600 K, due to the empty 3$d$ orbitals of Ti$^{4+}$ along with the interactions of O$^{2-}$ and Tb$^{3+}$ ions. Electric modulus plot, Nyquist plot and variations in relaxation time confirm the transition which is of second order. A broad change in magnetic moment, evident from the first-order derivative graph of M vs T without any magnetic phase transition is a behaviour typical in this family of compounds. Heat capacity measurements and their mechanism were discussed which supports MIT observed in Tb$_2$Ti$_2$O$_7$, a phenomenon which is seldom observed in an empty $d$ orbital pyrochlores.
**Introduction**

A little frustration in the spin of a material gives remarkable properties also making its physics more interesting. This is true in geometrically frustrated materials which have unusual phenomena like random alignment of spins, interaction with neighbouring atoms, corner sharing tetrahedra and many more [1-4]. The term ‘geometrical frustrated’ refers, the spin of individual ions are well ordered but absence of individual interaction due to its competing magnetic behaviour of neighbour ions. Among all frustrated compounds, a large number of elements crystallize in the form $A_2B_2O_7$, where $A$ is a rare earth trivalent ion and $B$ is a non-magnetic transition metal ion ($A$ = Tb, Y, Dy, Ho, Gd, Er and $B$ = Mo, Ti, Sn, Ir, Ru, Os, Mn) with eight-fold and six-fold oxygen co-ordination respectively [5,6]. This class of compounds form two interpenetrating lattice network of corner sharing tetrahedra of $A$ and $B$ which makes them thermal and chemically inert [7].

In a short review of $A_2B_2O_7$ pyrochlore compounds - Cd$_2$Re$_2$O$_7$ is the first superconductor in series of oxides, evident from heat capacity measurements revealing a clear second and first order phase transition with change in their electrical resistivity at 200 K and 120 K. Consequently, Pr$_2$Ru$_2$O$_7$, heat capacity also shows a $\lambda$-type divergence at 162 K, which is due to antiferromagnetic ordering of Ru$^{4+}$ ion in the B-sites[8,9]. Even in the last decade, Hg$_2$Ru$_2$O$_7$ shows a metal to insulator transition (MIT) at 108 K, from the work Wilhelm Klein, et al.[10]. In general, for most of a pyrochlore compound A-site ion is responsible for low temperature magnetic properties and B-site ion is responsible for electrical transition in the high temperature regime.

Pyrochlore oxides having a $4d$ or $5d$ transition metal ion in the B-site are usually on the consociate with MIT with the ground state magnetic properties of the A-site ion. MIT in pyrochlore family is relatively due to electron-electron correlation of B-site ions which play an important role in electrical and magnetic transitions. For example, A$_2$Ir$_2$O$_7$ ($A$ = Nd, Sm and Eu) were found to exhibit metallic behaviour at low temperature regime, while A’$\prime$Ir$_2$O$_7$ (A’$\prime$ = Gd, Tb, Dy) exhibits semiconducting behaviour. This type of electrical property is due to hybridisation of $t_{2g}$ band of Ir$^{4+}$ with A-site ions [11-13]. Nd$_2$Ir$_2$O$_7$, Sm$_2$Ir$_2$O$_7$, Eu$_2$Ir$_2$O$_7$ have sharp MIT at 36, 117 and 120 K respectively [11]. Similarly Cd$_2$Os$_2$O$_7$[14], Pr$_2$Mo$_2$O$_7$ are also associated with electrical transition in the low temperature regime. Except Cd$_2$Os$_2$O$_7$, where MIT is peculiarly associate with magnetic ordering and second order phase transition confirmed from heat capacity measurement [14].
Among all the pyrochlore family \(A_2\text{Ti}_2\text{O}_7\) is exceptional because the compound do not show any sign of electrical transition due to the vacant 3\(d\) orbital of Ti. By comparing Ti\(^{4+}\) ion with rest of the B-site electronic configuration in Ru\(^{4+}\),Ir\(^{4+}\),Os\(^{4+}\),Mo\(^{4+}\), Ti\(^{4+}\) has vacant \(d\) \((3d^0)\) configuration [2]. Hence interesting electrical properties can be expected in the Ti based pyrochlore oxides.

\(\text{Tb}_2\text{Ti}_2\text{O}_7\) is novel candidate because of the (i) absence of long range ordering even down to 200 mK (ii) absence of superconducting behaviour unlike \(\text{Cd}_2\text{Re}_2\text{O}_7\) (iii) strong magnetic anisotropy along [111] axis and (iv) due to co-operative Paramagnetism which is contrary to the long range spin order, a property of spin ice and spin glass [15]. The level of magnetic frustration in a magnetic system is called as frustration index \((f)\) defined as the ratio of Curie Weiss temperature \((\theta_{cw})\) to critical temperature \((T_c)\). For \(\text{Tb}_2\text{Ti}_2\text{O}_7\) \(f\)-index is calculated as 157 where \(\theta_{cw}=3000 \text{ K}\) and \(T_c=19 \text{ K}\), which indicates high frustration [16]. Also, \(\text{Tb}_2\text{Ti}_2\text{O}_7\) is not associated with any structural transition upto 600 K, suggesting that this compound is a perfect pyrochlore lattice. This is proved by S.W.Han.et.al through the neutron powder diffraction (NPD) studies.

The effect of \(d\)-electron (B site) in this compound is unexplored, due to the non-degenerate ground state of Tb\(^{3+}\) similar to Ti\(^{4+}\) in \(\text{Ho}_2\text{Ti}_2\text{O}_7\). Pyrochlore irridates like \(\text{R}_2\text{Ir}_2\text{O}_7\), where \(R=\text{Y, Ho, Tb, Dy, Gd, Sm, Eu, Nd, Yb}\), show the lanthanide effect due to Ir electron density from \(f\) and \(d\) orbitals which play an important role in magnetic and electrical transitions. But the major contribution will be due to \(f\)-electron, neglecting the \(d\) electron density [10,11,17]. But in \(\text{Tb}_2\text{Ti}_2\text{O}_7\), Ti consists of \(d\)-electron density. Therefore, absence of \(f\)-orbital electron leads to investigate the property of vacant \(d\)-electron, in detail [17].

This article provides first information on

- the formation of \(\text{Tb}_2\text{Ti}_2\text{O}_7\) phase at a relatively low synthesis temperature, prepared by high energy ball milling and subsequent sintering
- Metal insulator transition in Ti based pyrochlore at 600 K supported by magnetic and heat capacity measurements.

**Experimental**

Preparation of phase pure pyrochlore oxides is difficult due to the formation of oxygen deficient secondary oxide phase’s at higher temperatures. Usually pyrochlore oxides are prepared by solid state method by firing corresponding rare-earth oxides and transition metal
oxides in stoichiometry in the temperature range of 1350 °C [7,8,18] for several days with intermediate grinding (takes more than 5 days).

In the present study, polycrystalline Tb$_2$Ti$_2$O$_7$ was prepared by high energy ball milling of the precursors, Tb$_4$O$_7$ and TiO$_2$ in stoichiometry, and subsequent firing at 950°C (1223 K) in an alumina crucible only for 5 h. The prepared sample was subjected to X-Ray diffraction (XRD) study, at room temperature, using Cu-K$_\alpha$ radiation (λ=1.5406Å) with 2θ ranging from 10° to 70° with a scan rate of 0.02 steps per second. The electronic state of Tb and Ti was determined through X-ray Photoelectron spectroscopy. The temperature dependent magnetisation measurement was performed from 19 K to 800 K at a constant field of 1000 G. To understand the electrical property of the sample, temperature dependent impedance spectroscopy (SOLATRON 1260 impedance analyser) measurements were performed.

**Results and discussion**

Figure 1 shows the characteristics reflections (JCPDS file no. 41-0363) of the cubic pyrochlore Tb$_2$Ti$_2$O$_7$ with the space group $Fd-3m$. The lattice parameters determined, $a = b = c = 10.1504(2)$ Å are in agreement with the reported values[7]. The XPS spectra is shown in figure 2. The survey spectrum in figure 2.a shows the binding energy peaks corresponding to Tb, Ti and O. The peak obtained for Ti (fig 2.b) is deconvoluted and the corresponding binding energies obtained are 464 and 458 eV. It is well known that the peak at 464 and 458 eV correspond to Ti$^{4+}$ oxidation states $2P_{1/2}$ and $2P_{3/2}$ respectively [19]. Fig 2.c shows spectrum of Tb $3d_{5/2}$ and $3d_{3/2}$ corresponding to 1278.1 and 1241.6 eV respectively. High resolution XPS spectrum of Tb, in fig 2.d, shows the peak corresponding to 150 eV due to the $4d$ electron [20]. Therefore, comparison of the XPS binding energy with standard data, confirms Tb, Ti in 3+ and 4+ oxidation states, without any oxygen deficiency.

The dc magnetic susceptibility measurement is carried out at a constant magnetic field of 1000 G. Figure 3 show the inverse susceptibility as a function of temperature. The data is fitted using Curie-Weiss law where the parameters were adopted from Gingras et al., as, $C = 23.0$ emu K mol$^{-1}$, $\theta_{CW} = -18.9$ K and the effective Bohr magnetron (Peff) is calculated using electronic configuration($^{7}F_6$) of Tb$^{3+}$ ion as 9.7μ$_{B}$ per Tb$^{3+}$ ion [2]. This confirms that the Curie Weiss law describes the experimental data till 50 K as reported by Gingras et al., and the negative Curie temperature indicates the interaction as anti-ferromagnetic in nature. Therefore dc susceptibility reinforce the magnetic phase purity of the prepared Tb$_2$Ti$_2$O$_7$ sample.
The prepared sample is subjected to impedance analysis in the frequency range of 10 MHz to 1 Hz, from which the resistivity is obtained by fitting $z'$ vs $z''$ (real part vs imaginary part of impedance) and is shown in fig 4 as a function of temperature. The resistivity plot confirms that Tb$_2$Ti$_2$O$_7$ exhibits a metal to insulator transition (MIT) around 600 K ($T_{MIT} = 600$ K). The magnitude of the resistivity changes from MΩm to kΩm. Fig. 5 shows the $z''$ vs log f, which shows suppression in the peak at MIT and shift towards high frequency regime. The inset in Fig. 5, shows unity in $\tau$ (relaxation time) before MIT, thereafter decreasing by 1/100th of order after the transition.

Similar kind of a transition is also exhibited by Nd$_2$Ir$_2$O$_7$ and Sm$_2$Ir$_2$O$_7$, associated with MIT in the range of 50 to 150 K, which is due to hybridisation of 5$d$ electron of Ir$^{4+}$ [11]. Even molybdenum pyrochlore (A$_2$Mo$_2$O$_7$) series also shows sharp transition at low temperatures [2], due to Mo$^{4+}$ interaction with oxygen and A-rare earth ion. Even in the last decade, a new pyrochlore compound – Hg$_2$Ru$_2$O$_7$ is reported to exhibit a MIT with magnetic transition [10]. Even single crystal works on pyrochlore compounds also confirm MIT with electrical and magnetic transitions in Sm$_2$Mo$_2$O$_7$-δ, Gd$_2$Mo$_2$O$_7$-δ, Ho$_2$Mo$_2$O$_7$-δ [2,3,5].

The observed MIT in Tb$_2$Ti$_2$O$_7$ is due to vacant 3$d$ orbital of Ti$^{4+}$ ion. As a result of hybridisation of 3$d$ orbital with 2$p$ orbital of oxygen ions, there is a relative increase in the electron density of Ti$^{4+}$ (3$d$) as a result of which the bandgap of the material decreases. The valence electron of Tb is transferred to the O ion of 2$p$ band without any significant hybridization due to the variation in their energy levels. On the other point of view, B cation is in six fold coordination with oxygen due to which $d$-state of B cation (empty $d$-state of Ti$^{4+}$ ion) show a significant covalent interaction with 2$p$ state ion. Therefore, transfer of electrons from 2$p$ orbital of O to vacant 3$d$ orbital of Ti$^{4+}$ ion which has relatively closer energy levels are responsible for the metallic nature. $\rho(T)$ for Tb$_2$Ti$_2$O$_7$ shows a metallic behaviour at $T > T_{MIT}$, which is confirmed by calculating the temperature co-efficient. The MIT in Tb$_2$Ti$_2$O$_7$ is the only observation in the high temperature regime, whereas all other compounds exhibit MIT in the low temperature regime as discussed in the previous sections.

The structural stability of this compound is already verified by Han et.al using neutron powder diffraction and X-ray absorption fine structure and confirm that Tb$_2$Ti$_2$O$_7$ is not associated with any structural transitions between 4.5 to 600 K [7]. Hence the metal to insulator transition in Tb$_2$Ti$_2$O$_7$ is not associated with any structural distortion. Curie-Weiss temperature $\theta$ amounts to the range of -3000 (33) K which could be attributed to a very strong anti-
ferromagnetic interaction in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \). By assuming the MIT as Neel temperature, ratio of \( T_{\text{MIT}} : \theta \sim 0.2 \), indicates a high degree of magnetic frustration - a common feature in pyrochlore systems. By comparing the \( T_{\text{MIT}} : \theta \) with other compounds like \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) \( (T_{\text{MIT}} : \theta \sim 0.6) \) it is found that the magnitude is one third, which shows \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) system is more frustrated compared to other compounds [10].

However MIT is one of the common properties exhibited by iridates pyrochlore family. But the major difference in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) is, the MIT temperature is around 600 K. This is the first metal to insulator transition report for Ti based pyrochlore family. Even though \( \text{A}_2\text{Ir}_2\text{O}_7 \) and \( \text{A}_2\text{Mo}_2\text{O}_7 \) exhibits series of metal insulating/semiconducting transitions in the low temperature regime, no reports are available for the high temperature regime in spin glass, spin ice and spin liquid materials.

Figure 6 shows the electric modulus (imaginary) spectra as a function of applied frequency. The plot shows a decrease in magnitude till 703 K above which there is a clear shift in the peak towards higher frequency beyond MIT which is relatively due to the consequence of \( \text{Ti}^{4+} 3d \) orbital. Figure 7 shows temperature dependent dc-susceptibility from 500 K to 800 K. Even though there is no structural phase transition, two major conclusions can be drawn from it (i) At 600 K there is a small difference in magnetic moment, which is clearly shown in the inset as a first derivative of magnetic moment - this may be due to the increase in the number of free electrons in 3\( d \) orbital and (ii) above 700 K, the peak is broad, diffused and consistent with the peak shift obtained in \( M'' \) vs log \( f \) plot as shown in figure 6.

Fig 8 shows heat capacity measurements of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \), which shows a broad hump at MIT. The peak at 600 K, which is relatively due to electrical transition, confirm increase in the \( d \)-electrons of \( \text{Ti}^{4+} \) ions. Similarly \( \text{Cd}_2\text{Re}_2\text{O}_7 \) shows two transitions at 119 K and 200 K due to the reduction of density of states (DOS) [8,21]. The specific heat capacity plot reasserts the electrical and magnetic transitions obtained in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) due to increase in d-electron density, with respect to temperature. Figure 9 shows a schematic representation of electron transfer mechanism between the 3\( d \) orbital of Ti and 2\( p \) orbital of oxygen. The orbital 3\( d_{x^2-y^2} \) and 3\( d_{z^2} \) of Ti will not participate in hybridisation due to the difference in their energy levels with Oxygen 2\( p \).

In summary, we have synthesized a cubic pyrochlore quantum spin liquid \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) by solid state reaction at relatively low phase formation temperature and found a metal to insulator transition (electrical resistivity) at 600 K. Nyquist plot, relaxation time and electric modulus
plots (real and imaginary) also confirm MIT. DC magnetic susceptibility and heat capacity measurements also confirm the MIT and the plots are also continuous and exhibit no thermal hysteresis at the transition temperature ($T_{\text{MIT}}$) - which indicates the second order phase transition. The MIT in Tb$_2$Ti$_2$O$_7$ is a consequence of $d$-orbital unlike other pyrochlore oxides. This is the first report on Ti- based pyrochlore oxides which shows MIT which is driven by empty 3$d$ orbital of Ti$^{4+}$. This study opens up new avenues for further research in Ti based pyrochlore oxides.

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Figure captions:

Figure 1: Room temperature X-ray diffraction pattern 950° C sintered for 5 hour. Insert picture shows the formation of tetrahedra with Tb atom in centre.

Figure 2: XPS spectra of the prepared sample. (a) survey spectrum of Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} (b) binding energy spectrum of Ti\textsubscript{2}p\textsubscript{3/2} (c) and (d) binding energy spectrum of Tb- 3d\textsubscript{5/2} and 4d.

Figure 3: DC susceptibility for Tb\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} temperature dependence on the inverse molar susceptibility versus temperature obtained at constant magnetic field of 1000 Oe.

Figure 4: Variation of resistivity versus temperature from 400 K to 800 K. insert plot shows an extended region from 500 K to 650 K in which metal to semiconducting like transition is clear.

Figure 5: Imaginary spectrum (Z") as a function of applied frequency, insert plot shows the difference in relaxation time before and after transitions.

Figure 6: Electric modulus spectrum vs log (f) the plot shows the shift in their peak and responding region after transition temperature.

Figure 7: Temperature dependent dc-susceptibility, insert plot shows the first derivative with notable change in emu/g at 600 K.

Figure 8: Heat capacity measurement carried out at 450 – 800 K.

Figure 9: 3d orbital interaction (Ti) and 2p orbital (O) possible interactions.
