Concurrence of ferroelectric, dielectric and magnetic behaviour in Tb$_2$Ti$_2$O$_7$ pyrochlore

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We report the ferroelectric property in Tb$_2$Ti$_2$O$_7$ pyrochlore, prepared by a two-step solid-state reaction method. A concave P-E (polarisation vs electric field) loop observed from 382 K confirms ferroelectricity, below which the loop remains as pointed or banana-shaped. Dielectric plots clearly show an anomaly at 383 K and the magnetic data reveals a deviation from 380 K supporting the observed ferroelectric ordering. The origin of ferroelectricity in Tb$_2$Ti$_2$O$_7$ is discussed which is due to the structural distortion in TiO$_6$ octahedron.
Pyrochlores are compounds that have been extensively investigated over the decades due to their fascinating spin liquid, spin ice, superconducting, metal to insulator, and magnetoresistance properties. They have the general formula of A₂B₂O₇ (A₂B₂O₆O') where A is a trivalent rare-earth ion like Tb³⁺, Ho³⁺, Gd³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and B is a tetravalent transition metal ion like Ti⁴⁺, V⁴⁺, Mn⁴⁺, Ir⁴⁺, Mo⁴⁺, Nb⁴⁺. The A-site ion is coordinated with eight oxygen ions which can be represented as AO(6)O'(2) and B site ion is coordinated with six oxygen by forming BO₆ octahedra. It is also interesting to note that all the six B-O bonds and six A-O(6) and other two A-O(2) are equidistant. A-O' bond length is greater than A-O, because of the spatial repulsion of other six oxygen with A ion. Most of the pyrochlores crystallise in the Fd-3m space group with the crystallographic site of A³⁺ ion in the position of 16d {1/2 1/2 1/2}, B⁴⁺ ion in 16c {0 0 0}, O(1) in 48f {x 1/8 1/8} and O(2) in 8b {3/8 3/8 3/8}. The only variable is O(1) in 48f x site, with x = 0.375 for a perfect cube and x = 0.3125 for a perfect octahedron about 16d. The value of x also decides the angle of octahedron - for ideal it should be 90° but ranges between 81° to 100°.

Tb₂Ti₂O₇ is one among the pyrochlores where A and B site are occupied by Tb³⁺ and Ti⁴⁺ ions, respectively, with cubic structure (space group: Fd-3m). This compound continuously attracts physicists because of its intriguing properties like cooperative paramagnetism, absence of superconductivity, glassy behaviour, and absence of lattice defect or deformation. S. W. Han et al., in 2004 verified the structural property of Tb₂Ti₂O₇ using Neutron Powder Diffraction (NPD) in the temperature range of 4.5 to 600 K and the following points were concluded from it:

- It is not associated with any structural phase transition
- It forms a perfect pyrochlore lattice without any anionic disorder
- The lattice constant (a) is found to increase considerably with temperature
- For O(1) 48f {x 1/8 1/8} - x decreases with temperature

Ferroelectric (FE) materials exhibit polarisation as a function of the applied electric field. Some of the pyrochlores also exhibit FE phenomenon. In 1952 W.R. Cook et al., first reported ferroelectricity in Cd₂Nb₂O₇ pyrochlore which was followed by reports in other pyrochlores such as Ho₂Ti₂O₇, Bi₂Ti₂O₇, Eu₂Ti₂O₇, Dy₂Ru₂O₇, RbBiNb₂O₇. Table I (supplementary) shows some of the pyrochlores with structure details and coexisting properties with FE. It is interesting to note that if A site is occupied by a magnetically activated ion and if the compound shows FE property as a function of temperature (ferroelectric transition temperature), then magnetic measurements at ferroelectric transition temperature will show an
anomaly as in Ho$_2$Ti$_2$O$_7$. If the A site has a non-magnetic ion and shows an FE as function of temperature, a dielectric anomaly will be seen as in Bi$_2$Ti$_2$O$_7$. Among them, Ti-based pyrochlores (Ho$_2$Ti$_2$O$_7$ and Bi$_2$Ti$_2$O$_7$) attracts our interest because, despite having cubic structure and centrosymmetry, they show FE property which is unusual. The study we report here is motivated mainly by two papers (i) Structural properties of the geometrically frustrated pyrochlore Tb$_2$Ti$_2$O$_7$ by S.W. Han et al.,$^8$ and (ii) Coexistence of magnetic and ferroelectric behaviours of pyrochlore Ho$_2$Ti$_2$O$_7$ by X.W. Dong et al.,$^{10}$

We attempt to seek FE property in Tb$_2$Ti$_2$O$_7$. This compound is not associated with any magnetic phase transition from 20 to 800 K. This leads to the confirmation if Tb$_2$Ti$_2$O$_7$ shows any sign of FE it should also mediate the dielectric property. We report the ferroelectric property in Tb$_2$Ti$_2$O$_7$ from polarisation versus electric field above 382 K, and the dielectric and magnetic measurements also show an anomaly around 383 K evincing FE probably due to a distortion in TiO$_6$ octahedron at T > 382 K. As far as we know there are no experimental reports of ferroelectricity in Tb$_2$Ti$_2$O$_7$.

Polycrystalline Tb$_2$Ti$_2$O$_7$ was synthesized by firing the high energy ball milled powder composition of Tb$_4$O$_7$ and TiO$_2$, as discussed elsewhere, and the crystalline nature was verified using X-Ray diffraction.$^{15}$ For ferroelectric measurement a pellet of 8 mm diameter and 1 mm thickness sintered at 500 °C for 5h (to remove moisture) had been used. A thin layer of high quality silver paste was coated on both sides of the pellet and the polarization versus electric field measurements was done at 20 Hz using Marine high-end PE loop ferroelectric test system 20PE-1 kHz-1N. The dielectric property had been studied using a two probe set up with platinum electrodes sandwiching a pellet of 8 mm diameter and 0.95 mm thickness (also sintered at 500 °C for 5 h to remove the moisture content in it) and connected to the Solatron 1260-impedance analyser. The magnetisation measurement was performed in a Lakeshore 7410 Model Vibrating sample magnetometer.

Figure 1 (a to f) shows the polarisation vs electric field loop (PE) in the temperature range of 301 K to 382 K. The plot till 371 K appears to be pointed or banana type of a loop.$^{16}$ The maximum polarisation value is also nearly the same in the range of 1.5µC/cm$^2$ to 1.4µC/cm$^2$ at 6 kV/cm and the ferroelectric property is absent in the prepared Tb$_2$Ti$_2$O$_7$ pyrochlore till 371 K. The plot 1.f shows the PE loop taken at 382 K. The loop appears to be concave and the maximum polarisation value decreases evincing the ferroelectric behaviour from 382 K. The PE loop from 391 K to 412 K (figure 2) also clearly shows the hysteresis
behaviour confirming the ferroelectric nature. The maximum polarisation decreases from 0.85 \( \mu \text{C/cm}^2 \) to 0.28 \( \mu \text{C/cm}^2 \) in the temperature range of 382 K to 412 K. Also, the magnitude of polarization observed in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) is comparable with \( \text{Ho}_2\text{Ti}_2\text{O}_7 \).\(^{10}\) It is to be noted that temperature-dependent FE property is reported in some of the pyrochlores like \( \text{Bi}_2\text{Ti}_2\text{O}_7 \) (at 308 K),\(^{17-18}\) \( \text{Ho}_2\text{Ti}_2\text{O}_7 \) (at 60 K),\(^{10}\) and \( \text{Cd}_2\text{Nb}_2\text{O}_7 \) (at 77 K).\(^9\)

Figure 3(a) shows the real part of the dielectric constant (\( \varepsilon' \)) of \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) from 303 K to 440 K. The \( \varepsilon' \) at room temperature is observed as 40.8 which is in agreement with the reported value\(^{19}\). The real part of dielectric constant decreases as the temperature increases and remains constant from 383 K – which is a sign of FE in the prepared sample. To confirm the behaviour, \( 1/\varepsilon' \) vs \( \log f \) is plotted that will reveal the transition clearly as a function of temperature (fig 3.b). A dielectric anomaly seen at 383 K is the sign of ferroelectricity. Figure 3 (c) and (d) shows the imaginary part of impedance (\( Z'' \)) and the inverse electric modulus (\( M'' \)) vs \( f \). \( Z'' \) plot
(Fig 3.c) attains a maximum value at 383 K and starts decreasing beyond this temperature, and $1/M''$ plot confirms the observed FE.

Figure 2: PE-Loop from 391 K to 412 K confirming ferroelectric property in Tb$_2$Ti$_2$O$_7$ above 382 K.

Figure 3: (a) Real part of dielectric constant ($\varepsilon'$) as a function of temperature from 303 K to 433 K at 1000 Hz for Tb$_2$Ti$_2$O$_7$, (b) $1/\varepsilon'$ to compare the response of material at 383 K, and the plot shows a significant increase at 383. Inset shows a maximum peak between 1kHz to 10 kHz (C). Imaginary part of impedance ($Z''$) shows a maximum value at 383 K beyond which a decreasing trend is seen and (d) Imaginary part of electric modulus ($1/M''$) vs frequency at various temperature shows a dielectric anomaly, and a ferroelectric loop is observed.
The magnetic moment as a function of temperature shows a deviation from 380 K (figure 4.a) which supports the possible ferroelectric nature of Tb$_2$Ti$_2$O$_7$, the origin of which is discussed based on the crystallographic features. As discussed in the beginning, even a small shift in the ideal position of O (1) - 48f – {x 1/8 1/8} will result in the distortion of octahedron altering the bond angle of O$^2$-Ti$^{4+}$-O$^2$. In other words, symmetry breaking without any structural phase transition$^{10}$ drives the material to the ferroelectric state. The above statement is also true in the case of other pyrochlores that are driven to the FE state.$^{8,20}$ The variation in the coordinate(s) of O(1) - 48f – {x 1/8 1/8} had been reported by S.W. Han et al., for Tb$_2$Ti$_2$O$_7$ where x decreases with increase in temperature.

Therefore, beyond 382 K the alteration in x of O(1) is significant, contributing to the distortion and the net polarization. Figure 4.b shows the ideal TiO$_6$ octahedra in Tb$_2$Ti$_2$O$_7$. It can be viewed easily that even a small shift in O (1) can drive the material into the ferroelectric phase as reported in the compounds Ho$_2$Ti$_2$O$_7$, Bi$_2$Ti$_2$O$_7$, Eu$_2$Ti$_2$O$_7$.$^{10,12,17-18}$ Ferroelectricity in Bi$_2$Ti$_2$O$_7$ at 308 K (35 °C) is also due to structural distortion in TiO$_6$ octahedron.$^{18}$ But, the ferroelectric ordering is observed at a comparatively lower temperature due to the presence of lone pair in Bi$^{3+}$ cation that easily distorts the TiO$_6$ octahedra and leading to the ferroelectric state at a lower temperature (compared with Tb$_2$Ti$_2$O$_7$ at 382 K). Absence of lone pair electron...
in Tb$^{3+}$ makes the compound to be ferroelectric at a much higher temperature (than Bi$_2$Ti$_2$O$_7$). However, in addition to the structural distortion, any other possible reason for ferroelectric property in Ti-based pyrochlores need to be understood.

In summary, the letter detailing the ferroelectric property in cubic Tb$_2$Ti$_2$O$_7$ from 382 K is affirmed due to the structural distortion in TiO$_6$ octahedron. The dielectric constant, imaginary part of the impedance and electric modulus shows a variation around 382 K, supported by the deviation in the magnetic moment from 380 K. The coexistence of ferroelectricity with dielectric and magnetic property is thus established, beyond 382 K.

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**Data availability statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflict of interest**

The authors declare, there is no conflict of interest.
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Supplementary:

Table 1: Shows some of the pyrochlores which exhibit Ferro electricity and coexisting properties, with their space group and symmetry indicated.

| Pyrochlore Compound | Structure  | Space Group | Symmetry | Coexisting property with FE | Ref. |
|---------------------|-----------|-------------|----------|-----------------------------|------|
| Ho$_2$Ti$_2$O$_7$    | Cubic     | Fd-3m       | Centro   | Magnetic                     | 1    |
| Bi$_2$Ti$_2$O$_7$    | Cubic     | Fd-3m       | Centro   | Magnetic                     | 2-4  |
| Eu$_2$Ti$_2$O$_7$    | Cubic     | Fd-3m       | Centro   | Electric                     | 5    |
| Dy$_2$Ru$_2$O$_7$    | Cubic     | Fd-3m       | Centro   | Magnetic                     | 6    |
| Cd$_2$Nb$_2$O$_7$    | Cubic     | Fd-3m       | Centro   | Dielectric / Electric        | 7    |
| RbBiNb$_2$O$_7$      | Orthorhombic | P2$_1$am | Non-centro | Dielectric / Electric | 8    |

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