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Low temperature neutron diffraction studies on $Bi_4Ti_3O_{12}$

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Abstract

The detailed crystal structure of $Bi_4Ti_3O_{12}$ obtained by the Rietveld refinement of the powder neutron diffraction data in the temperature range of 300–15 K is being reported. At ambient temperature $Bi_4Ti_3O_{12}$ has an orthorhombic structure (Space Group: B2cb) with unit cell parameters: $a = 5.4432(5)$ Å, $b = 5.4099(5)$ Å, $c = 32.821(2)$ Å, and $V = 966.5(1)$ Å^3. The low temperature neutron diffraction studies revealed the retention of the orthorhombic structure without any significant change in the atoms arrangement. A marginal decrease in the unit cell parameters is observed with the lowering of the temperature.
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1. Introduction

Crystalline materials of Aurivillius [1] type structure have been studies owing to their interesting ferroelectrics [2] and fast ion conduction Abraham et al. [3] properties. The Aurivillius type layered compounds can be represented by the general formula $[M_2O_2]^{+2}[A_{m-1}B_mO_{3m+1}]^{2-}$, where M is generally Bi^{3+}. The crystal structure of such compounds is built by the intergrowth of fluorite-type layers and perovskite type layers [1,4]. The perovskite-type layer is formed with A and B cations and the thickness of this slab is governed by the integer *m*. Thus, the $m = 1$, 2, 3, etc. indicate the one, two and three layer perovskite layers. The selection of the A and B cation is mainly based on the nature and ionic radii requirement of the perovskite lattice. The perovskite slab is formed with the corner sharing of the BO_6 octahedra and the interstices are occupied by the A type cations. The fluorite-type layer is formed by the Bi and O atoms, and Bi have square pyramidal polyhedra with lone pair of the Bi^{3+} as an apex. The presently studied compound bismuth titanate ($Bi_4Ti_3O_{12}$) is a three layers Aurivillius compound, i.e., $m = 3$, and the composition can be written as $(Bi_2O_2)(Bi_2Ti_3O_{10})$ [5].

Bismuth titanate ($Bi_4Ti_3O_{12}$) bears a special interest in the Aurivillius family of compounds due to its ferroelectric properties, which has switching application with low leakage and fatigue and high remnant polarization [6,7]. Due to these properties this materials is a promising candidate for nonvolatile memory and dynamic memory of computers. This compound shows ferroelectric to paraelectric phase transition at about 675 °C [5,8]. There are several structural studies at room temperature and higher temperature available in the literature explaining the crystal structure of both ferro- and paraelectric phase [5,8,9,10]. The early powder XRD studies on $Bi_4Ti_3O_{12}$ indicated an orthorhombic lattice with space group Fmmm [1]. Later the detailed crystal structure of ferroelectric phase of $Bi_4Ti_3O_{12}$ showed the similar orthorhombic lattice but the space group is changed to B2cb [8,9]. Further, the crystal structure was re-determined by [10,11] with a monoclinic (Pc) lattice. However, the monoclinic distortion in the lattice is reported to be too small to differentiate these two lattice types. Kim and Jeon [12] studied this compound by combined neutron and X-ray diffraction of the polycrystalline sample and supported the monoclinic lattice. Besides, there are few reports dealing with structure below ambient temperature [13–15]. A possible existence of low temperature phase was earlier indicated from dielectric anomalies [13]. Recently, the change

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in crystal structure at low temperature has been observed by variable temperature Raman spectroscopy [15]. But, no detailed natures of crystallographic transformations are available in literature.

All the available structural studies on $Bi_4Ti_3O_{12}$ are carried out at either ambient or high temperatures. To the best of our knowledge, no diffraction data are available below ambient temperature. In the present study our intention was to look for the low temperature crystal structure.

2. Experimental

The titled compound was prepared by heating a homogeneous mixture of appropriate amounts of pre-dried Bi_2O_3 and TiO_2 at 750 °C for 12 h in a platinum boat. The product obtained was reground and pelletized and the pellet was further heated at 850 °C for another 12 h. The product obtained was characterized by powder XRD for its phase purity. The powder XRD data was collected using a Philips PW1710 model diffractometer in the two theta range 10–70°, with Ni filtered Cu Kα radiation. The observed diffraction data agree well with reported powder data JCPDS 35-795. Further the crystal structure was verified by the Rietveld refinement of the powder neutron diffraction data. For the neutron diffraction studies, the sample was packed in a vanadium can (8 mm diameter and 5 cm height) and diffraction data were recorded using 1.249 Å wavelength, with an array of five linear PSD based powder diffractometer at 100 MW Dhruva Research Reactor at BARC, Mumbai. Low temperature diffraction data were collected using an APD make closed cycle helium refrigerator. The diffraction data were analyzed by Rietveld refinements of the observed data using the Fullprof-2K software package [16].

3. Results and discussion

The Rietveld refinement of the observed powder neutron diffraction data was initiated with the starting model based on the orthorhombic (B2cb) data reported by [9]. This space group shows an excellent fit to our diffraction data. The profile was fitted with Pseudo-Voigt profile function. The profile refinement was started with scale and background parameters followed by the unit cell parameters. The typical half-width parameters, mixing parameter and preferred orientation parameter were also refined. After getting a proper match in the profile model, the positional parameters and overall thermal parameters were refined. The goodness of the refinements was observed by the residuals (*R*-values). The typical observed and calculated neutron diffraction patterns at 300 K are shown in Fig. 1. The refined unit cell parameters and the residuals of refinement are given in Table 1. The observed refined positional coordinates do not show any significant difference from the earlier reported values [9]. The low temperature diffraction data were similarly analyzed using the observed ambient temperature structural model. The observed and calculated neutron diffraction patterns at the lowest studied temperature (15 K) are identical to Fig. 1. The refined unit cell parameters at different temperatures are collected in Table 1. A three-dimensional representation of the $Bi_4Ti_3O_{12}$ unit cell is shown in Fig. 2.

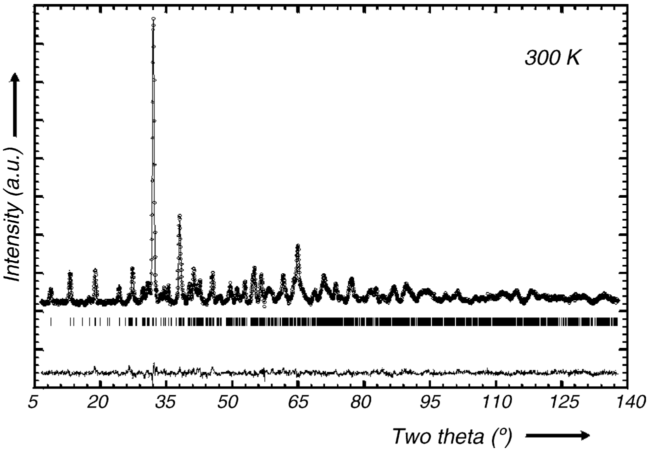

Fig. 1. Experimental (○) and calculated (continuous line) neutron diffraction pattern of $Bi_4Ti_3O_{12}$ at 300 K. The difference profile is given at the bottom. The Bragg positions are indicated by the vertical marker below the observed pattern.

As it was mentioned in the introduction section, the crystal structure of the $Bi_4Ti_3O_{12}$ is made by stacking of layers of

Table 1
Typical crystallographic and refinement parameters of $Bi_4Ti_3O_{12}$ at various temperatures

	300 K	150 K	75 K	15 K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	B2cb	B2cb	B2cb	B2cb
a (Å)	5.4432(5)	5.4393(6)	5.4363(4)	5.4354(4)
b (Å)	5.4099(5)	5.4035(6)	5.4012(4)	5.4004(4)
c (Å)	32.821(2)	32.772(3)	32.756(2)	32.743(2)
V (Å^3)	965.51(1)	963.2(2)	961.8(1)	961.1(1)
Neutron wavelength (Å)	1.249	1.249	1.249	1.249
2θ Range (°)	6.61–138.00	6.61–138.00	6.61–138.00	6.61–138.00
Number of variables parameters	46	46	46	46
R_p%	5.21	7.78	5.62	5.85
R_{wp}%	6.66	9.90	7.17	7.44
R_e%	3.94	3.89	3.91	3.93
R_{Bragg}%	5.24	6.55	5.65	5.94
χ^2	2.85	6.39	3.37	3.58

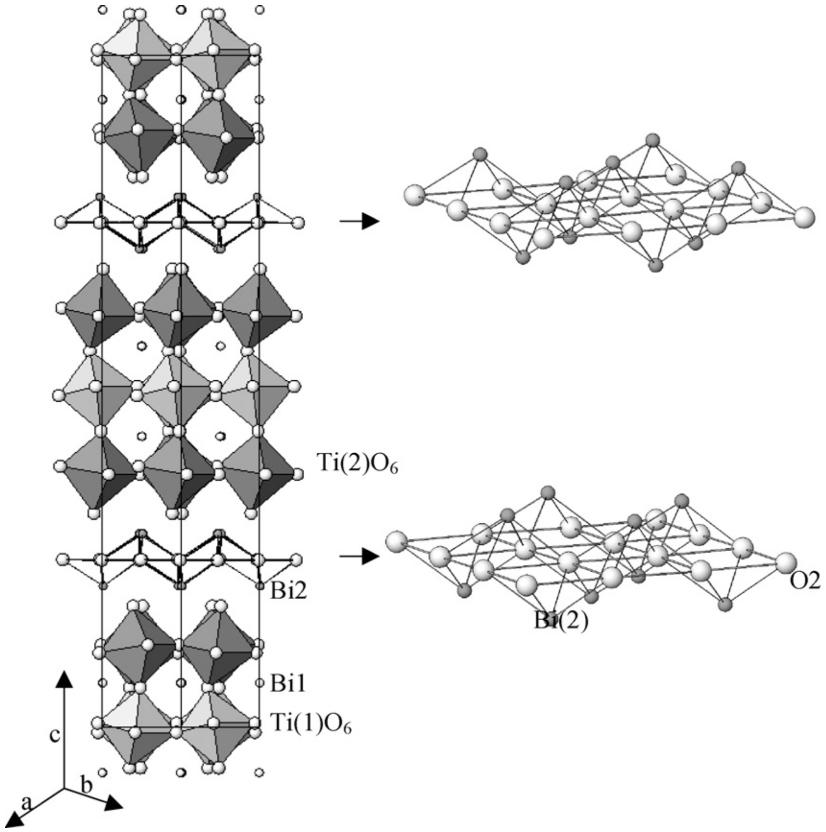

Fig. 2. Typical three-dimensional representation of $Bi_4Ti_3O_{12}$ lattice, viewed along the ⟨1 1 0⟩ direction (inset: two layers of Bi_2O_2 are zoomed).

$Bi(2)_2O_2$ and $Bi(1)_2Ti(1)Ti(2)_2O_{10}$ units. The Bi_2O_2 layers bears a close resemblance to the fluorite-type lattice with Bi^{3+} eight coordinated polyhedra. These Bi(2) atoms have four nearest oxygen atoms forming an approximately square pyramidal configuration and have other four oxygen atoms (from the perovskite units) are at relatively longer distances completing the eight coordination polyhedra, which balance the charge on the Bi^{3+} ion. Other bismuth atoms Bi(1) occupy the interstitial of the perovskite cage and have highly distorted 12 coordinated polyhedra. The crystallographically distinct Ti atoms (Ti(1) and Ti(2)) have octahedral coordination. Out of these two Ti atoms, Ti(2) has a highly distorted polyhedra with bond lengths ranging from 1.70 to 2.35 Å. The distortion of this octahedral unit is related to the off axis displacement of the Bi(2) atoms. It needs to be mentioned here the displacement of the Bi(2)to be related to the ferroelectric transition in the $Bi_4Ti_3O_{12}$. The $Ti(2)O_6$ unit and $Ti(1)O_6$ are tilted significantly leading to a highly distorted interstitial site for the Bi(1) atoms as shown in Fig. 2.

A comparison of crystal structures at various temperature shows that the unit cell parameters gradually decrease as the temperature is lowered. The typical unit cell volume of $Bi_4Ti_3O_{12}$ lattice decreases from 965.5 to 961.1 $Å^3$ as the temperature is lowered from 300 to 15 K. The analysis of various inter-atomic distances in $Bi_4Ti_3O_{12}$ unit cell at various temperatures shows no significant change with temperature. It may be mentioned here that the two Ti atoms have octahedral coordination $Ti(1)O_6$ and $Ti(2)O_6$. Along *c*-axis these two octahedra are connected via O3 atoms and along *a*- or *b*-axis the $Ti(1)O_6$ and $Ti(1)O_6$ are connected via O1 atoms whereas the $Ti(2)O_6$ and $Ti(2)O_6$ octahedra are linked through the O5 and O6 atoms. It was mentioned earlier that the $Ti(2)O_6$ octahedra are significantly distorted and have an off center shift of the Ti(2) atom in the octahedral environments of oxygen atoms. The O4 atom of $Ti(2)O_6$ polyhedra link to the Bi_2O_2 fluorite layer. The Bi_2O_2 layers have Bi with up and down square pyramid type configurations, which share their edges of the planar oxygen atoms along *a* and *b*-axes. The charge balance to this Bi atoms is further provided by the O4 atoms of the $Ti(2)O_6$ octahedra. The high temperature diffraction studies on $Bi_4Ti_3O_{12}$ show the decrease in *z*-coordinate of Bi(2) atoms as well appreciable increase in Ti–O–Ti bond angles with increase in temperature [9]. However, the present low temperature study shows no significant shift in position coordinates of various atoms. Besides, there is no discontinuity in any of the unit cell parameters with change in temperature. Thus, this factor cannot explain the change in unit cell parameters observed with the variation of temperature. The increase in tilt of the octahedra is the possible reason in the decrease in the unit cell parameters with temperature. However, there is a slight decrease in various Ti–O–Ti bond angles with the decrease in temperature. The typical Ti(1)–O(1)–Ti(1) bond angle decreases from 164.0(7) to 160.2(6)° as the temperature decreased from 300 to 15 K. Similarly, an appreciable decrease in Ti(1)–O(3)–Ti(2) bond angle is observed from 156.0(7) to 155.0(6)° as the temperature is changed from 300 to 15 K.

This indicates that there is an increase in tilt in the TiO_6 octahedra. Besides, no appreciable changes in any other structural parameters are observed.

The comparison of various residuals of the refinements shows an appreciably higher value for the refinements of the data collected at 150 °C compared to other temperatures. This may be either due to the fluctuation in the unit cell near this temperature, as observed in the earlier studies [13–15]. But, no other indication for any structural transformation was observed in the present neutron diffraction study.

4. Conclusions

From the refinements of crystal structure of $Bi_4Ti_3O_{12}$ in the temperature range of 300–15 K, it was found that the orthorhombic lattice is retained down to 15 K. The unit cell parameters show a marginal decrease with decrease in temperature. There is no significant change in the arrangement of various atoms in the lattice at lower temperature. Also, we did not observe any discontinuity/anomaly at lower temperatures as observed in earlier spectroscopic studies.

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