Chapter 6

Growth and characterization of sodium bismuth double tungstate crystal

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Single crystals of NaBi(WO$_4$)$_2$ (NBW) are of current interest for detection of ultra high energy radiation and charged particles in the TeV energy range as encountered in accelerators like Large Hadron Collider (LHC), CERN and as efficient laser host and high gain Raman shifter when doped with rare earth ions [43,44]. It is one of the promising materials, which can be used as a Cherenkov detector for luminosity and calorimetric measurements under a high charge background that is encountered in the LHC, CERN [4, 222]. The applicability for radiation detection arises due to its high stopping power, insensitivity towards background charge and high yield for Cerenkov photons. Lead tungstate is being used as a scintillation detector in the electromagnetic calorimetry in these accelerators [223–225]. The application is based on the measurement of light emitted out from the crystal in response to the incidence of high energy radiation/charged particle. This can happen either (i) instantaneously (scintillation/Cherenkov) or (ii) delayed (phosphorescence/afterglow) or (iii) much later only on thermal (TSL) or optical (OSL) stimulation. Relative proportion of these three components depends upon the band structure of the lattice which invariably gets modified by the impurities and/or defects. Such modifications cause coloration in the crystal which is called radiation damage i.e. deterioration in the light yield which may or may not be reversible. Radiation hardness i.e. the highest value of exposures which do not affect the transmission properties happens to be one of the most important aspects for a scintillation/cherenkov detector.

The procedure for obtaining high quality NBW single crystal suitable for such high energy applications has been worked out, which also appeared on the cover page of “Crystal research and technology, 45, (2010)” journal. Effect of growth and annealing conditions on the nature of color center formation was investigated. Band structure calculations have also carried out to
determine the optical properties that can be expected if the lattice was perfect. Each of these aspects is described in the following section.

6.1 Crystal growth

6.1.1 Effect of starting charge

NBW crystals of large dimensions exhibiting high optical homogeneity, low lattice absorption, steep absorption edge and high radiation hardness required for detector application can be grown by the Czochralski technique [112-114], though growth by the Bridgman technique has also been reported [115]. Continuous lowering of crystallization temperature and tapering of diameter are the major difficulties encountered during the Czochralski growth of NBW [114]. Chemical analyses of deposits found in the growth chamber during the melt growth are reported to have presence of sodium tungstates as the majority component [116, 117]. Some of the experiments adopted to compensate for these losses were (a) use of Bi deficient charge for crystal growth and utilizing only two third of it in each experiment [114], (b) doping with trivalent ions of lesser electro negativity [116] and (c) using a charge prepared by three layer method, followed by re-crystallization [117]. While dependence of some of the optical properties and radiation hardness on crystal composition have been studied [118, 226], post growth residual charge has never been analyzed.

Polycrystalline charge for the NBW crystal growth was synthesized by raising the temperature of a stoichiometric mixture of 99.99% pure constituent oxides viz. Na₂CO₃, Bi₂O₃ and WO₃ (1:1:4 molar ratio) rapidly to ~950 °C so as to melt it within 4 h followed by soaking for the next 4 h. The crystal thus grown (henceforth referred as crystal “A”) was found to have markedly different appearance in different regions as can be seen in Fig. 6.1. The upper portion of ~30 mm length
has a good transparency, middle being somewhat translucent and the lowermost region used to
be totally opaque. The plot in this figure shows that the onset of transparency degradation in the
crystal is also accompanied by a downward drift in heater power and this decrease became much
faster from the same position where the ingot had an opaque appearance. When the upper
transparent portion of the crystal was separated out and used as a starting charge, the resulting
crystal (henceforth referred as crystal “B”) was found to have a high transparency till the bottom,
as shown in Fig. 6.2. These crystals were grown with uniform diameter and light yellow
coloration. The plot in Fig. 6.2 shows that this crystal grew at a constant power in most of the
cylindrical region, followed by a slight increase in the power requirement in the lower portion,
which is understandably due to increased heat losses from the increasing ingot length.

![Image of crystal growth and heater power changes](image)

**Fig 6.1:** Photograph and changes in controlling heater power with increase in length during
growth of NaBi(WO$_4$)$_2$ crystal from sintered charge (Total power: 50 kW).

The residual charge of ~ 1 mm height left after the growth of crystal B was also found to be
transparent. In one of the experiments, about four hours after the growth of type B crystal, the
heater power was switched off. The crystal did not develop any crack during cooling or crystal
processing. On the other hand crystals of type A used to crack readily and separate out from the lower opaque region during handling.

![Photograph and changes in controlling heater power with increase in length during growth of NaBi(WO4)2 crystal grown from re-crystallized charge (Total power: 50 kW).]

**Fig. 6.2:** Photograph and changes in controlling heater power with increase in length during growth of NaBi(WO4)2 crystal grown from re-crystallized charge (Total power: 50 kW).

### 6.1.2 X-ray diffraction analysis

The XRD patterns recorded for a transparent portion of crystal A and the residual charge are shown as plots ‘a’ and ‘b’ respectively in Fig. 6.3. While plot ‘a’ matches well with JCPDF data of the NBW phase, [227] plot ‘b’ had larger number of diffraction peaks in addition to that of NBW. Most of these peaks could not be identified with any of the phases reported in Na2O-Bi2O3-WO3 system, barring a few that matched with the JCPDF data of the Na2WO4 phase [228].

The data of plot ‘b’ was analyzed through a crystal structure refinement program available with the Rigaku system after omitting the peaks identified for NBW and Na2WO4 phases. These remaining set of peaks could be fitted into a single phase material of tetragonal structure with space group I41/a and lattice constant values as a: 11.501 Å and c: 11.367 Å. These crystal structure parameters were found to closely match to those reported for Na5Y(WO4)4 phase [229].
Since Y and Bi both are trivalent ions, the molecular formula of this new phase which is isostructural to Na$_5$Y(WO$_4$)$_4$ is contemplated to be Na$_5$Bi(WO$_4$)$_4$. XRD pattern of the synthesized Na$_5$Bi(WO$_4$)$_4$ phase shown in plot ‘c’ of the same Fig. is found to have close matching with initially unidentified peaks of the post growth residual charge given in plot ‘b’ of the same Fig.

While the XRD pattern recorded for the translucent portion of crystal “A” was found to be similar to that shown in plot ‘a’ of Fig. 6.3, the presence of some additional diffraction peaks was noted in the opaque region. The XRD pattern recorded for powdered samples of crystal B as shown in Fig.6.4 could be fitted into a tetragonal structure with lattice parameters $a = 5.28110$ Å, $c = 11.50808$ Å, $Z = 2$ and I4$_1$/a space group. The pattern generated from the Rietveld refinement, also given in the same figure, is seen to have good matching with the experimental data ($\chi^2: 1.13$). The values of residual factors Rp and wRp were 3.78% and 4.70% respectively. Position coordinates thus calculated from the refinement are listed in Table 1. Here Na$^+/Bi^{3+}$ cations are coordinated by eight oxygen atoms and W$^{6+}$ and O$^{2-}$ form coordinated WO$_4^{2-}$ tetrahedral anionic
complexes. The bond lengths and bond angles between atoms, as calculated in the atomic basis of the NBW crystal are given in Tables 2 and 3 respectively. The separation between W and O atoms is found to be the shortest bond length (1.7534 Å) in the crystal. The bond angles (i.e. O-W-O) subtended by two of the O atoms attached to a single W atom is found to be different (105.312° and 116.889°), though their bond lengths were the same. However this was not constrained in the calculation.

![X-ray powder diffraction pattern of NaBi(WO₄)₂ crystal.](image)

**Table 6.1:** Crystallographic data for NaBi(WO₄)₂ crystal as refined by Rietveld analysis.

<table>
<thead>
<tr>
<th>Ion</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occupancy</th>
</tr>
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<tbody>
<tr>
<td>Na⁺</td>
<td>0</td>
<td>0.25</td>
<td>0.625</td>
<td>0.50</td>
</tr>
<tr>
<td>Bi³⁺</td>
<td>0</td>
<td>0.25</td>
<td>0.625</td>
<td>0.50</td>
</tr>
<tr>
<td>W⁶⁺</td>
<td>0</td>
<td>0.25</td>
<td>0.125</td>
<td>1.00</td>
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<tr>
<td>O²⁻</td>
<td>0.1507</td>
<td>0.0086</td>
<td>0.2106</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 6.2: Bond lengths in the atomic basis of NaBi(WO₄)₂ crystal

<table>
<thead>
<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>Distance (Å)</th>
<th>Number of bonds</th>
</tr>
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<tbody>
<tr>
<td>Na</td>
<td>Na</td>
<td>3.90514 (4)</td>
<td>4</td>
</tr>
<tr>
<td>Na</td>
<td>O</td>
<td>2.47064 (2)</td>
<td>4</td>
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<tr>
<td>Na</td>
<td>O</td>
<td>2.49496(3)</td>
<td>4</td>
</tr>
<tr>
<td>W</td>
<td>O</td>
<td>1.75342 (1)</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 6.3: Inter bond angles in the atomic basis of NaBi(WO₄)₂ crystal

<table>
<thead>
<tr>
<th>Angle (θ)</th>
<th>Number of angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>O – Na – O</td>
<td>97.069</td>
</tr>
<tr>
<td>O – Na – O</td>
<td>138.928</td>
</tr>
<tr>
<td>O – W – O</td>
<td>105.312</td>
</tr>
<tr>
<td>O – W – O</td>
<td>116.889</td>
</tr>
<tr>
<td>Na – O – W</td>
<td>130.732</td>
</tr>
</tbody>
</table>

6.1.3 Differential thermal analysis

DTA plots for samples taken from transparent portions of crystal A and given in Fig. 6.5 show the presence of single sharp endothermic and exothermic peaks at 930 and 928 °C during heating and cooling cycles respectively, indicating a congruent melting composition. While similar DTA plots were obtained for the translucent portion of the crystal B, the opaque portion exhibited more number of low temperature peaks, besides overall decrease in melting and solidification temperatures. The DTA plot recorded for the residual charge and given in Fig. 6.6 shows the occurrence of an endothermic processes in the temperature range of 700 – 850 °C, in addition to
the presence of well defined sharp endothermic peaks at 918, 864, 640 and 590 °C during the heating cycle. This indicates the presence of multiple phases in residual charge in addition to the NBW phase whose melting is observed at a lower temperature of 918 °C due to compositional deviations. The DTA pattern of synthesized Na5Bi(WO4)4 phase shown in Fig. 6.7 is found to consist of endothermic peaks at 590, 637 and 643 °C which are observed for post growth residual charge also.

![Fig. 6.5 DTA plots](image)

![Fig. 6.6 DTA pattern](image)

![Fig. 6.7 DTA pattern](image)

**6.1.4 Discussion**

Above observations on DTA measurements and crystal appearance show that those regions of crystal ingot which were crystallized at lower temperatures, exhibit poor transmission characteristics. This indicates the presence of low melting phases in the opaque portion of crystal and post growth residual charge. In the following we examine whether these phases are formed due to thermal decomposition of NBW or during material synthesis itself. Former possibility is
ruled out from the observation that the DTA pattern of NBW (Fig. 6.5) remained the same even after several heating and cooling cycles. Successful growth of the crystal B from a re-crystallized charge is another example indicating thermal stability of the NBW melt. The formation of these foreign phases can therefore be explained in terms of involvement of two step reactions between the constituents in a homogeneous stoichiometric mixture that was used during the initial synthesis of the NBW phase. In the first stage sodium tungstate is formed due to a high reactivity between Na₂CO₃ and WO₃. It may be noted that these two compounds can readily combine in almost all proportions to form a series of sodium tungstate compounds at molar ratios of 1:1, 1:2, 1:4, 1:6 viz. Na₂WO₄, Na₂W₂O₇, Na₂W₄O₁₃, and Na₂W₆O₁₉ besides some nonstoichiometric compositions [230]. Majority of these compounds melt in the temperature range of 600–750°C and exhibit significant evaporative losses at higher temperatures. The NBW phase is thought to be forming in the second stage, as a consequence of a reaction between sodium tungstate and Bi₂O₃. While the vapor pressures of all the three constituents (Na₂CO₃, WO₃ and Bi₂O₃) are low at 950°C, the evaporative losses of sodium tungstates become significant whenever the temperature of the mixture is raised above 700 °C. Since the amount of evaporative losses depends on both the temperature and duration, the deviation from the stoichiometry is expected to be the same in either of the two methods adopted for the material synthesis i.e. sintering at 750°C, where duration is long or rapid melting at 950 °C where the temperature is higher. We indeed did not find any difference in crystallization behavior in the two cases. Enrichment of the residual melt with Na₂CO₃ and Bi₂O₃ is expected from the report that the average composition of condensation product above NBW is in molar ratio of 1: 3.33 for Na₂O and WO₃ [116]. The presence of low melting phases viz. Na₅Bi (WO₄)₄, Na₂WO₄ and traces of Bi₂O₃ in the NBW melt therefore is thought to be responsible for the observed decrease in crystallization
temperature and formation of opaque region in crystal A. Impairment of crystal quality due to the presence of foreign phase(s) is a commonly encountered problem in complex oxides, which is caused due to inhomogeneous mixing and dissimilar vapor pressure of the constituents. Control of crystal stoichiometry involves appropriately compensating either of the two species or segregating out the excess phase [75, 231]. Single crystal growth of ternary oxides like NBW is however more complex due to the presence of large number of components formed at different stages of material synthesis and melt growth.

6.2 Investigations related to radiation hardness

6.2.1 Radiation hardness

Deterioration in the performance is the most common problem with radiation detectors. Material testing is therefore carried out by separately exposing it to similar radiation fields before putting the detector into the accelerator. Monitoring the changes in transparency after exposing the material to a $\gamma$ ray source is one of the simplest methods for testing radiation hardness. Transparency recovery with time, temperature or annealing is another aspect defining the suitability of the detector and its possible use in such major experiments. The reported value of radiation hardness of the NBW compares with present generation detectors viz. PbWO$_4$ ($10^7$ rad) [124] and lead glasses based Cherenkov detectors ($10^3 – 10^4$ rad) [232]. A $^{60}$Co gamma-ray source having dose rate of 2 Gy/s was used for the present study. The transmission spectra of the samples were recorded after subjecting them to exposure of $10^5$ and $10^6$ Gy. The transmission spectra recorded for both A and B crystal samples, after the gamma irradiation to $10^5$ and $10^6$ Gy are shown in Fig. 6.8. A comparison of the quantitative values of transparencies of these two crystals shows the value of lower wavelength cutoff ($\lambda_{\text{cutoff}}$) for crystal B as 355 nm which is significantly lower, as compared to 375 nm observed for crystals A. It is seen that a dose of $10^5$
Gy degrades the transmission of crystal A by about 10% while B crystal show a negligibly small (1-2%) degradation. This suggests a low defect density in the B crystals apart from a light coloration. A dose of $10^6$ Gy decreases the transmission of both crystals; however, degradation in the transmission of the B crystal was still significantly smaller than that of A. The radiation hardness exhibited by crystals B was found comparable to that reported by B.I. Zadneprovski et al [116]. The similar effect of starting charge composition on the radiation hardness of PWO crystals has been reported by Sabharwal et al. [231].

Fig. 6.8: Transmission spectra of crystal “A” & “B”, (a) before irradiation and after exposure to (b) $10^5$ Gy and (c) $10^6$ Gy.

For the study of radiation induced color/defect centers, the induced absorption of the crystals after a dose of $10^6$ Gy was considered and calculated using a formula as given below:

$$
\mu_{irr} = \frac{1}{d} \ln \left( \frac{T_0}{T} \right)
$$

(1)
Here, ‘d’ is the thickness of the crystal disk in cm, $T_0$ and $T$ are the transmittance before and after irradiation, respectively. A plot of induced absorption coefficient for a crystal “A” as shown in Fig. 6.9 agrees well with the one reported by B.I. Zadneprovski et al [116]. The results were same in case of crystal B except the lower value of induced absorption. From the graph it is clear that the induced absorption curve is the sum of several absorption peaks distributed over different wavelengths. The curve could be fitted in five individual Gaussian peaks centered at 3.1, 2.8, 2.6, 2 and 1.7 eV as shown in Fig. 6.9. A similar type of fitting was reported by Q. Zhang et al for a PbWO4 (PWO) crystal where peaks at nearly similar energies were obtained [233].

Fig. 6.9: Induced absorption spectrum of crystal A recorded within an hour of irradiation, (-o-) experimental data, (····) deconvoluted individual peaks and the envelop curve (solid line) [Exposure: $10^6$ Gy].
Fig. 6.10: Decay of radiation induced absorption intensity at 445 nm (2.8 eV) with time (results of fitting are shown in table – 6.4).

![Graph showing decay of radiation induced absorption intensity with time](image)

Table 6.4

<table>
<thead>
<tr>
<th>Component</th>
<th>Life time (hr)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ1</td>
<td>2000</td>
<td>62</td>
</tr>
<tr>
<td>τ2</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>τ3</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

Fig. 6.11: Induced absorption spectrum of crystal A recorded after 10 days of irradiation, (-○-) experimental data, (•••) deconvoluted individual peaks and the envelop curve (solid line) [Exposure: 10⁶ Gy].

![Graph showing induced absorption spectrum of crystal A](image)
The decay of the radiation induced absorption intensity with time is given in Fig. 6.10. The curve fitting was done considering three decay components and the relevant data are given in Table-6.4. An average life time was found out to be nearly 50 days that shows the formation of a relatively deep trap in the NBW. A full induced absorption spectrum recorded after 10 days of irradiation is shown in Fig. 6.11. When this spectrum is compared with that shown in Fig. 6.9, it is clear that different color centers have different decay rates. TSL glow curve of crystal “A” recorded for a dose of $10^6$ Gy is shown in Fig. 6.12. The glow curve is very broad and appeared to be consisting of more than one peaks. By using an initial rise method this glow curve gives an average activation energy of $\sim 0.9$ eV which is also consistent with the average decay time at room temperatures.

The recovery time of transmission at room temperatures is reported to be around 10-15 days for PWO [234], whereas for NBW it is about 50 days. This finding is consistent with the observation
that the TL glow peak of NBW is at ~105°C while that for the PWO the main glow peak is at ~50°C [124, 235]. Further, it may be suggested that the trap/color centers in the NBW crystals formed by the irradiation are relatively deep compared to those in the PWO crystals. In order to find out the role of oxygen in the defect formation and its relation to the radiation induced defect centers, effects of annealing under air and vacuum were analyzed.

6.2.2 Effect of annealing
The induced absorption spectra of the annealed samples in air and vacuum are given in Fig. 6.13 (a) and (b) respectively. These plots were also fitted with a similar procedure followed for the radiation induced absorptions. A clear difference in the intensity of induced absorption peaks due to oxygen and vacuum annealing could be seen in the fitted curves are also shown in the same figures. The resemblance of induced absorption curve due to oxygen annealing and irradiation is very clear from Fig. 6.9 and Fig. 6.13 (a). However, our results do not agree with those reported by Hongsheng Shi et al who showed that the irradiation induced absorption matches well with the vacuum annealing induced absorption [119].

6.2.3 Discussion
The similarities in absorption bands formed on crystal annealing (Fig. 6.13) and irradiation (Fig. 6.9) (except for a slight difference in the relative intensities) indicates that the nature of defects in the two cases should also be similar. On annealing the sample in oxygen ambient at high temperatures the possibility of formation of interstitial oxygen becomes high but the creation of oxygen vacancies also cannot be completely ruled out. Chen Teng et al had also suggested that at high temperatures oxygen vacancies are created even in the presence of oxygen ambient [28].
Fig. 6.13: Induced absorption for crystal A after annealing in (a) oxygen, (b) vacuum, (●●●) experimental data, (⋯⋯) deconvoluted individual peaks and the envelop curve (solid line).

Thus the absorption band in this case (oxygen annealing) is thought to arise due to the formation of both types of centers, interstitial oxygen as well as oxygen vacancies. An observed low defect density in crystal B, as seen in figure 6.8, appears to be due to a controlled stoichiometry. On the other hand differential evaporative losses of constituent oxides may be responsible for the large number of defects in crystal A. The defects related to oxygen dominated due to the presence of large number of oxygen in the unit cell (a unit cell of NBW contains 2-Na, 2-Bi, 4-W, 16-O) and a low atomic weight makes it easy to be displaced (by gamma rays). Thus the presence of intrinsic oxygen defects makes crystal “A” prone to radiation damages. During the irradiation gamma-rays may displace an oxygen atom from its position in the form of either $O^0$ leaving behind an F center or $O^-$ leaving behind an $F^+$ center. These liberated oxygen atoms may find an interstitial position to form $O^0$ or $O^-$ center. Considering the two different positions for each $O^0$ and $O^-$, four centers would be formed that together with F and $F^+$ will have a total of six centres. Experimentally we obtained five distinct peaks and the sixth peak might have remained unresolved due to poor signal-to-noise ratio and broader peak at higher wavelengths. Chen Teng
et al have calculated the band structure for the PWO that has interstitial oxygen at two different positions in the $\text{WO}_4^{2-}$ tetrahedral and showed the formation of a band in the forbidden gap. This theory may hold well in the case of NBW too, because both have similar crystal structures and tetrahedral tungstate group. To see the similarities in electronic band structure of both materials, first principles calculations were carried for NBW crystal and described in following section.

6.3 Calculations of electronic and optical properties

The LAPW/DFT calculations are based on cells constructed by placing Na on one cation site and Bi on the other in the unit cell of NaBi($\text{WO}_4$)$_2$ and assuming that these two ions are too far apart to interact directly due to the large size of the ($\text{WO}_4$)$_2^{-}$ anionic units. In order to verify this assumption, internal coordinates of the cell were relaxed within the local density approximation (LDA). The Na, Bi and W atoms are located at the symmetry points and hence the forces on them are zero. Only the O atoms have forces. We have minimized the forces on the O atoms to less than 1 mRy/au. The optimized positions of the O atoms are $(0.0092, 0.1574, 0.2086)$ compared to the experimental positions $(0.0086, 0.1507, 0.2106)$. As can be seen the optimized positions are not much different from the positions obtained from the XRD results. It is noted that the relaxation has a little effect on the electronic structure, and that the bond lengths remain close to their experimental values. Further, because of very similar Shannon radii of Bi$^{3+}$ (1.31 Å) and Na$^+$ (1.32 Å) the average Na-O bond length of 2.51 Å is found to be close to the average Bi-O bond length of 2.45 Å. Also, both Na$^+$ and Bi$^{3+}$ ions remain in the center of their 8-fold coordinate sites and in particular Bi$^{3+}$ does not become off-centred.
The muffin tin radii for Na, Bi, W and O were taken as 2.32, 2.32, 1.79 and 1.59 bohr, respectively. The zone sampling was done using a set of approximately 500 uniformly spaced \( k \) points in the irreducible Brillouin zone (IBZ) during self consistent iterations.

The band structure of NBW calculated using GGA, given in Fig.6.14, shows that, while the valence band maximum is located at symmetry point N, the conduction band minima is in \( \Delta \) direction away from the centre of Brillouin zone (BZ). This result gives an indirect gap of 3.1 eV for GGA and the value obtained from LDA is 3.0 eV. The band gap was also calculated experimentally by plotting absorption coefficient and energy \( \alpha = A_k (E-E_g)^n \) near the absorption edge which shows a linear response for \( n=2 \), as seen in Fig.6.15. The extrapolation of this plot gives an effective band gap value of about 3.3 eV and indicates existence of an indirect band gap. These results show that DFT calculations underestimate band gaps. The underestimate for GGA is smaller as compared to LDA. Fig.6.16 shows the partial density of states (PDOS) calculated for various elements in the NBW. The valence band (VB) is mainly formed by non-bonding states of the oxygen \( p \) orbitals, with very little contribution coming from tungsten \( d \) orbitals. The conduction band (CB) is mainly formed from the W \( d \) states with a similar amount of contributions coming from \( p \) states of bismuth and oxygen. While strong hybridization is evident in DOS, the hybridized \( \sigma \) bonding combinations of O \( p \) and W \( t_{2g} \) are at the bottom of the O \( p \) manifold. There was no observable contribution from the Na, except for a very small value at rather high energy \( \sim 10 \) eV above the CB. Thus the band gap in NBW is of charge transfer character involving the \((\text{WO}_4)^{2-}\) units similar to the other tungstates [93].
Fig. 6.14: Band structure of NBW as calculated from GGA.

Fig. 6.15: Plot of $\alpha^2$ vs energy near absorption edge ( $\alpha$: absorption coefficient (cm$^{-1}$)).

Fig. 6.16: Density of states of NBW as calculated from GGA.
It would be interesting to compare the DOS for the NBW with other similar compounds. Our study shows that the PDOS of Na has a very small contribution and is located at high energy of \(\sim 10\) eV above CB and therefore it does not influence the electronic structure. Consequently almost the entire CB in the NBW is primarily composed of W 5d or states and VB from O 2p states as in most of the other Scheelite crystals having a structural formula ABO\(_4\) \([A= Ca \text{ or Pb and B=} \text{ W or Mo}]\) \([93, 94]\). In CaMoO\(_4\) and CaWO\(_4\) both the CB and VB band extreme are located at the \(\Gamma\) point and thus these are direct band gap crystals, but PbMoO\(_4\) and PbWO\(_4\) are indirect band gap materials where the valence band maxima is located away from the \(\Gamma\) point \([93]\). In case of NBW crystals, it was found to be located at N point of the Brillouin zone. The width of the valence band in the NBW crystal is found to be approximately \(5\) eV. While the Bi 6s states form a narrow band at \(4\) eV below the bottom of this value is just \(1\) eV for Pb 6s states in the lead based materials. The unoccupied Bi 6p states hybridized with W 5d states throughout the CB are reminiscent of the Pb 6p states in lead tungstate/molybdate. Substantial contributions from W 5d states in the lower part of the O p derived VB also contains, reflecting strong W-O hybridization, which in turn reflects the high valence state of W. Due to striking similarities between NBW and other Scheelites like PWO, its electronic structure can also be explained from a ligand field model.

The imaginary and real parts of the dielectric constant \(\varepsilon(\omega)\) calculated with a spectral broadening of \(0.1\) eV are shown in Figs. 6.17a and 6.17b respectively. The presence of tetragonal symmetry implies that there exist two components of the dielectric tensor, \(\varepsilon_{zz}(\omega)\) and \(\varepsilon_{xx}(\omega)\) relating to the electric field being parallel and perpendicular to the optics axis (c-axis) respectively. Here prominent peaks located at \(5.8\) and \(7.8\) eV are observed in both directions for \(\text{Im } \varepsilon(\omega)\). These peaks correspond to transitions between O p states in the VB and W d states in the CB. These,
however, could not be assigned to a single interband transition, because many direct transitions corresponding to these energy regions and originating from different parts of the BZ may be found in the band structure. An additional peak at 4.2 eV seen only in $\varepsilon_{xx}(\omega)$ arises due to transitions from topmost VB to bottom most CB in the N-Γ-P direction where these bands are parallel involving transition between O p states to W d states. This additional peak is observed in other Scheelites like PWO and CWO where it appears at a slightly higher energy of 4.3 eV [37, 95].

Fig. 6.17 Energy dependence calculated for optical properties of NaBi(WO4)2 crystal: (a) imaginary part of dielectric function $\text{Im} \varepsilon(\omega)$, (b) real part of dielectric function $\text{Re} \varepsilon(\omega)$, (c) refractive index $n(\omega)$ and (d) reflectivity $R(\omega)$. 
The values of static optical dielectric constant $\varepsilon_\infty = \text{Re} \varepsilon(0)$, as calculated from the spectral dependence of dielectric constant $\text{Re} \varepsilon(\omega)$ and given in Fig. 6.17b are found to be 4.5 and 4.9 along and perpendicular to the optic axis respectively giving a uniaxial anisotropy of 0.4. Figs. 6.17c and 6.17d show the energy dependences calculated for the refractive indices and reflectivity along and perpendicular to the optic axis. From the energy dependence of refractive indices $n(\omega)$, plotted in Fig. 6.17c, the values of $n(\omega)$ in the directions parallel ($n_e$) and perpendicular ($n_o$) to the optic axis are found to be 2.36 and 2.50 respectively at 2.76 eV (450nm). These results show that NBW is a negative crystal exhibiting a birefringence ($\Delta n$) of 0.14. Anomalous value of $n_o$ at 4.2 eV and the corresponding peak in $n_{xx}$ is not of any physical consequence, as birefringence has relevance in the transmission region alone i.e. for energies below the band gap. The value of ordinary refractive index as 2.36 is in good agreement with the experimental value of 2.4 reported elsewhere [112, 113, and 116]. Fig. 6.17d shows that the reflectivity spectrum consisting of four distinct peaks in the low energy range from 4 to 6.5 eV besides a sharp decrease in value around 10 eV and a broad band of lower intensity in 11-20 eV region. The fine structure of the spectrum is seen to have anisotropy in the two crystallographic directions. While the zz component is found to have a doublet at 4.8 and 4.9 eV, single distinct peak at 4.2 eV and a doublet at 5.5 and 5.8 eV is observed for the xx component. Reflectivity maxima observed for both the directions at lower energies can be attributed to interband transitions involving charge transfer from both Bi 6s and O 2p states to W 5d states. The doublet structures could be due to the crystal field splitting of Bi 6p levels in CB and/or different values of VB in different point of the BZ. A reflectivity minimum at approximately 11 eV indicates the occurrence of a collective plasma resonance. The depth of plasma minimum is determined by
imaginary part of the dielectric function at plasma resonance, which is representative of the
degree of overlap between inter-band absorption regions.

The structure of reflectivity spectra for NBW crystals in the energy region between 6 and 11
eV, which arises due to interband transitions, is also similar to that reported for PWO crystals.
The only major difference between the two materials is that the excitonic peaks in NBW are
relatively less prominent as compared to PWO. It is seen that the sharp excitonic peak observed
at 4.2 eV in the xx component for the NBW, is similar to the peak observed at 4.3 eV in the
PWO crystal only when E || a [37, 95]. The reflectivity decreases gradually above 11 eV in the
case of NBW while in PWO crystals it happens above 9 eV. Structures observed at higher
energies are due to Bi$^{3+}$ core levels, similar to Pb$^{2+}$ core levels.

6.4 Conclusion
Undoped NBW crystals exhibiting $\lambda_{\text{cutoff}}$ of 355 nm have been successfully grown. The lowering
of crystallization temperature and shift in optical absorption edge of NBW crystal were found to
arise due to the formation of Na$_5$Bi(WO$_4$)$_4$ and Na$_2$WO$_4$ foreign phases in the melt and
associated compositional changes in crystal ingots. The detection of these phases became
feasible only because we could grow the crystals with a nearly flat interface that facilitated
pulling of almost the entire charge. Though these phases would have formed in the initial stages
of the material synthesis itself, they could not be clearly identified by the XRD until the
concentration in the melt was sufficiently high. Control of crystal stoichiometry involves
appropriately compensating either for evaporative species or segregating out impurity phase.
Single crystal growth of ternary oxides like NBW is however more complex due to the presence
of large number of components formed at different stages of material synthesis and melt growth.
The methodology of adding an excess component as adopted in PMO did not work. The method of segregation however was successful in the present case, because the low melting impurity phases were last to crystallize during CZ growth.

The analysis of induced absorption spectra of irradiated and annealed samples showed presence of peaks around 3.1, 2.8, 2.6, 2 and 1.7 eV which could be related to different type of defect centers. The transparency of crystals exposed to 106 Gy γ-rays took about 50 days for complete recovery at room temperature. Color centres formed due to the irradiation are similar to those formed during annealing of the NBW crystals under oxygen ambient. Color centers formed in the NBW are similar to those in the PWO but the trap depth in the case of NBW is larger and hence color centers are relatively stable in NBW which is undesirable. The defect density after irradiation was observed smaller in crystal B which was grown from a recrystalized charge. This was due to a controlled stoichiometry while differential evaporative losses of constituent oxides may be responsible for the large number of defects in crystal A. Therefore the crystals grown from recrystalized charge were found to be more suitable for application as detectors.

The electronic and optical properties of NBW and other Scheelite crystals, particularly PWO are found to have striking similarities as the 3s states of Na in NBW lie fairly above the bottom of the conduction band. Our calculations show a strong hybridization of W d and O p orbitals giving rise to relatively broad bands which are similar to other Scheelite tungstates.