Investigations on single crystal growth of Nd:NaY(WO$_4$)$_2$ from stoichiometric charge

The growth of Nd:NYW single crystal was first reported in 1993 by HE Yizong [1]. The crystal growth was carried out by a top seeded solution growth method. In this experiment, during the heating of polycrystalline Nd:NYW material some unexpected behavior was observed which could not be explained on the basis of available phase diagram of the Na$_2$WO$_4$ - Y$_2$(WO$_4$)$_3$ system. The powder X-ray diffraction measurements were carried out on the as-grown crystal and the data obtained were presented. The Nd:NYW crystal rod of dimensions 2.5 mm d× 5 mm l was pumped by xenon flash-lamp and pulsed emission was first obtained at wavelength 1.06 µm with a threshold lower than 1 J [2].

In 1999 Alexander A. Kaminskii obtained Nd: NYW crystals using the Czochralski method and its spectroscopic, laser and $\chi^{(3)}$ nonlinear optical properties were studied [3]. After this work, several researchers have reported growth of various rare-earth ion doped NYW using the Czochralski method. Some of them, Zh. X. Cheng in 2001 [4] and Jiandong Fan in 2008 [5] have observed the stoichiometric variation of the NYW melt during the growth of the crystal. Subsequently, along with the stoichiometric variations of the melt during the growth, presence of inclusions and cracking of the crystal during and after the growth and in subsequent handling are reported as the major problems associated with the growth of the crystals [6]. These problems with their possible causes are yet to be understood thoroughly. Therefore it is important to have detailed analysis of these problems with their possible causes.

This chapter deals with the investigations on the single crystal growth of Nd: NYW from a stoichiometric charge using the Czochralski technique. The growth experiments were carried out on undoped and Nd doped NYW. The X-ray diffraction and differential thermal analysis measurements were performed to characterize the as-grown crystals as well as the residual charge remained in crucible after completion of the growth process. The effect of variations in synthesized charges, oriented seeds, growth environments and growth parameters on the growth of crystal is discussed. The thermal expansion measurements were carried out on the as-grown crystal samples containing different amounts of inclusions and the results are presented. The role
of impurity phases in the Nd:NYW lattice during the growth is discussed on the basis of obtained results. The mechanism by which the presence of inclusions results in cracking of the crystal is also discussed.

4.1 Single crystal growth of Nd:NYW

Recent years have witnessed considerable research on the melt growth of Nd:NYW crystals. Though the Czochralski technique is applicable for the growth of these crystals due to their congruently melting nature, the preparation of starting charge happens to be one of the most critical factors for a successful crystal growth. Single crystal growth experiments were carried out initially on the undoped NYW from a stoichiometric charge employing the Czochralski technique and after optimizing the growth parameters Nd doped crystals were grown and the occurrence of compositional changes in the crystal and melt has been studied. The melting temperature and phases present in different parts of the crystal ingot, residual charge and depositions found in the growth chamber were analyzed using differential thermal analysis and X-ray diffraction techniques.

4.1.1 Starting charge preparation

The stoichiometric polycrystalline NYW material to be used for the growth of single crystals were synthesized by different methods as given below.

1] Sintering

In this case the stoichiometric NYW composition was prepared by a solid state reaction as given in Eq.4.1.

\[
Na_2WO_4 + Y_2(WO_4)_3 \rightarrow 2NaY(WO_4)_2
\]  

(4.1)

Initially both the constituent oxides (all 99.99% pure) taken in a composition corresponding to 50 mole % of Na$_2$WO$_4$ and 50 mole % of Y$_2$(WO$_4$)$_3$ were mixed. The mixture obtained was ground thoroughly in a mortar-pestle to fine powder. The resultant material was pressed to form pallets. These pallets taken in a platinum crucible were heated rapidly at a rate of 200°C/h up to
800°C and kept for 24 h in air and cooled to room temperatures at the same rate. The resultant material obtained was again crushed to fine powder and same heat-treatment was repeated two times to ensure the formation of a single phase NYW compound.

2) Rapid heating

In this case, initially both the constituent oxides (all 99.99% pure) taken in the composition corresponding to 50 mole % of Na₂WO₄ and 50 mole % of Y₂(WO₄)₃ were mixed using a mortar-pestle to fine powder. The resultant material was taken in a platinum crucible of dimensions 50 mm d × 50 mm l and kept inside an induction furnace (Cyberstar Model-Oxypuller) and heated at the rate of 300 - 450 °C/h up to 1210°C to complete melting. Prior to the growth of the crystal the melt was held at this temperature for a few hours to attain a thermal equilibrium.

3) Chunks of previously grown crystals

In these experiments, the starting charge consisted of previously grown NYW crystals that were free from any visible defects. The crucible containing the crystal chunks was heated at a rate 200 - 250 °C/h up to 1210°C to complete melting of the crystal chunks prior to the growth of the crystal. The melt was held at this temperature for a few hours to attain a thermal equilibrium in the melt.

4.1.2 Crystal growth

Single Crystal growth experiments were carried out employing the Czochralski technique using an automatic diameter controlled crystal puller (Cyber star Model-Oxypuller). For a typical growth experiment 100 g of the polycrystalline stoichiometric NYW material was used. In separate growth experiments the starting charge was prepared either by sintering the constituents oxides at 800 °C, constituent oxides rapidly heated to the melting point or from the chunks of previously grown crystals as described above. Starting charge obtained was filled in a platinum crucible of dimensions 50 mm d × 50 mm l. The crucible was kept inside an induction furnace,
heated rapidly and held at 1210°C for a few hours to homogenize the melt and attain thermal equilibrium prior to the crystal growth.

**Table 4.1. Single crystal growth of NYW carried out by Czochralski technique employing stoichiometric starting charge.**

<table>
<thead>
<tr>
<th>Growth Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
</tr>
<tr>
<td>Crucible</td>
</tr>
<tr>
<td>Rotation rate</td>
</tr>
<tr>
<td>Pulling speed</td>
</tr>
<tr>
<td>Seed</td>
</tr>
<tr>
<td>Temperature gradient</td>
</tr>
<tr>
<td>Atmosphere</td>
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</table>

Ceramic after-heaters were used in the growth geometry to tailor the axial thermal gradient. Different growth station set-ups were used in separate growth experiments to obtain desirable temperature gradients and growth conditions. The pulling and rotation rates of the seed used throughout the experiments were 1-2 mm/h and 10-25 rpm, respectively. The details of the different growth experiments are given in Table 4.1. The growth experiments were carried out in different atmosphere such as free air, argon and oxygen. Initially some undoped crystals of NYW were grown and after optimizing the growth parameters Nd doped NYW crystals were also grown. In the NYW matrix, the rare-earth ion (Y^{3+}) can be partly or completely replaced by other rare-earth ion (Nd^{3+}). The doping concentration of Nd was kept as 4 at. %. After successful completion of the growth process crystals 15 mm in diameter and 40 mm length were obtained.
The grown crystals were transparent, however found to have cracks along with presence of inclusions inside the bulk. The grown crystals were carefully cut into different pieces of same thickness and used for further characterizations.

4.1.3 Problems associated with growth of the crystal

The results of investigations on the Czochralski growth of the undoped and Nd doped NYW crystals have shown that the presence of inclusion, crystal cracking, color variation of the grown crystal, growth instability and stoichiometric variations of the melt during the growth are some of the main problems that warrant further investigations. Some of the as-grown crystals are shown in Fig. 4.1. Undoped NYW crystals show light green coloration, while Nd-doped NYW crystals are blue in appearance.

![Figure 4.1: As-grown crystals of (a) NYW and (b) Nd:NYW.](image)

Many a times the grown crystals were observed to develop cracks during the cooling down to room temperatures. This problem could not be overcome simply by the application of lower cooling rates. Consequently, attempts were made to minimize thermal stresses by carrying out growth under the application of very small axial temperature gradients of ~15 °C/cm. Under the situation, the crystal-melt interface became highly unstable and the crystals were found to get detached during the seeding stage itself. On the other hand, the growth was seen to progress
smoothly under a high temperature gradient of ~150 °C/cm. In this case, no cracking of the crystal was observed till the growth was in progress, however, the ingots were observed to develop cracks upon detaching from the melt at the end of a growth experiment. In order to avoid the problems of unstable growth and cracking, the growth was also experimented at intermediate axial temperature gradients of ~75 and 50 °C/cm and along different crystallographic directions i.e. <100>, <101> and <001> but the results were similar.

The growth instability at a low gradient of ~15 °C/cm caused large changes in the error signal of the automatic diameter control circuit leading to unscheduled termination of the growth at early stages. The error signal corresponds to a difference between the mass growth rates computed from pre-set crystal growth parameters (diameter, shoulder, pull rate etc.) and actually observed in practice. In order to rule out any possibility of improper synthesis of the polycrystalline starting charge prepared from the constituent powders being responsible for the observed instability, crystal growth was also carried out using clear and transparent chunks obtained from the previously grown crystals. Here again the problem of growth instability was found to exist. The growth was also carried out by using a left over charge from a previous growth run that was supplemented with a requisite amount of crystalline chunks, however the same problem prevailed. Sometimes a thin layer of a pale colored material was found to appear in the left over charge after the completion of a growth run. The tail end of the crystal ingot also exhibited coloration that was different from the cylindrical region.

Various problems observed during the growth runs are described briefly in the following.

1) Inclusions

The careful observation of an as-grown crystal shows that the bulk of the crystals contain inclusions. Different crystals grown in different atmosphere and from differently synthesized charges have shown presence of inclusions. Various growth parameters such as pulling and rotation rates, different temperature gradients (15 – 150 °C/cm) utilized during the growth experiments could not help to avoid the inclusions.
2] Crystal cracking

Cracking took place throughout the crystal and no specific pattern was observed as shown in Fig. 4.1. Most of the time cracking was observed in the region of the crystal where inclusions were present inside the bulk of the crystal. The use of different temperature gradients, different cooling rates and different growth station geometries during the growth experiments could not avoid the cracking of grown crystals.

3] Color variation

A careful visual inspection of the grown crystals shows a variation in the color along the length of the crystal i.e. from top to bottom of the crystal. Also, as described above the presence of inclusions and cracking have been observed throughout the crystal which significantly affected the transparency of the grown crystals.

4] Growth instability

Although the different growth experiments were carried out in different atmosphere and with different growth parameters, most of the time during the growth the crystal-melt interface was found unstable and growth could not proceed smoothly. The problem was more severe when the growth was carried out under a low temperature gradient (15-75 °C/cm). Because of the instability of the crystal-melt interface, sometimes the crystal got detached from the melt and growth was stopped.

5] Control of growing processes and conditions

Despite growth experiments carried out using an automatic diameter controlled crystal puller the control over the growth process was a measure problem. Consequently the control of shape and size of the growing crystal was a major concern during the growth and it was difficult to grow large size crystals.
6] Presence of impurity phases

Sometimes a pale colored material was found inside the crucible along with the residual charge after the completion of a growth experiment. A similar type of material was found attached to the bottom of an as-grown crystal. Also after completion of a growth process large amounts of deposition of materials were found on the walls of the growth chamber.

4.2 Stoichiometric deviations

Use of differently synthesized charges, different temperature gradients, different crystal pulling rates (1-2 mm/h) and rotation (10-25 rpm) rates did not solve the problems associated with the growth of the crystal from stoichiometric charges. With a view to understand these problems further, we have carried out investigation on the occurrences of compositional changes in crystal and melt. The melting temperature and phases present in different parts of the crystal ingot, residual charge and depositions found in the growth chamber were analyzed using DTA and XRD techniques.

4.2.1 Impurity phases

Along with the problems associated with the growth of the crystal as described above a pale color material was found deposited at the crystal bottom. A similar material was also found in the crucible after the completion of a growth experiment along with the residual charge. The material was carefully separated and grinded thoroughly in a mortar-pestle to fine powder and used for XRD and DTA measurements.

i) X-ray diffraction measurement

X-ray diffraction pattern of the pale colored material powder obtained was recorded using a Rigaku-RINT-2000 diffractometer equipped with a Cu-Kα source. The step size was 0.01° and the scanning speed was 2°/min speed. The pattern obtained is depicted in Fig. 4.2.

The pattern matches well with the Na$_2$W$_2$O$_7$ and Na$_5$Y(WO$_4$)$_4$ phases given in the JCPDS file [7,8]. Hence the material is a mixture of both Na$_2$W$_2$O$_7$ and Na$_5$Y(WO$_4$)$_4$ phases. The origin of
the presence of impurity phases in the melt of stoichiometric NYW composition was explained in the previous chapter with the help of binary phase diagrams of Na$_2$WO$_4$-Y$_2$(WO$_4$)$_3$ and Na$_2$O.WO$_3$-WO$_3$ where the Na$_2$W$_2$O$_7$ and Na$_5$Y(WO$_4$)$_4$ phases are found as impurities along with the intended NYW phase [1,9].

![Powder XRD pattern](image)

*Figure 4.2: Powder XRD pattern of the pale colored material found inside the platinum crucible along with residual charge after completion of the growth process.*

**ii) Differential thermal analysis measurement**

In order to study the thermal behavior of the material at elevated temperatures the material used in the XRD measurement is utilized for DTA measurements. About 50 mg stoichiometric powder was taken in a platinum crucible in a thermal analyzer (SETRAM model 92). The sample was heated at a rate of 10°C/min to 900°C, held there for a few seconds and then cooled to room temperature at the same rate. The DTA plots were recorded during heating as well as cooling cycles. The plots obtained are shown in Fig. 4.3. The atmosphere provided was air and the blank crucible was used as the reference.

The phase diagram of Na$_2$O.WO$_3$-WO$_3$ system reveals that Na$_2$W$_2$O$_7$ compound melts congruently while Na$_2$WO$_4$-Y$_2$(WO$_4$)$_3$ system shows Na$_5$Y(WO$_4$)$_4$ melts incongruently. The results of XRD measurements carried out on the sample used for DTA measurements shows that the sample is a mixture of both Na$_2$W$_2$O$_7$ and Na$_5$Y(WO$_4$)$_4$ phases. This may result in lowering
of the melting point of the individual phase as the phase present may not be in a pure form. The DTA plots in Fig.4.3 for the pale colored material show three endotherms during the heating cycle as well as three exotherms during the cooling cycle. The endotherm observed at 723°C can be attributed to the congruent melting of the Na\(_2\)W\(_2\)O\(_7\) phase while those observed at 799°C and 837°C can be attributed to the incongruent melting of Na\(_5\)Y(WO\(_4\))\(_4\). Similarly the three exotherms observed at 624°C, 744°C and 751°C during the cooling can be attributed to the crystallization of the respective phases.

![DTA plots](image)

**Figure 4.3:** DTA plots of pale colored material obtained during (a) heating and (b) cooling cycle.

In order to confirm this result, we synthesized the polycrystalline Na\(_2\)W\(_2\)O\(_7\) material by a solid state route and its thermal behavior was studied with the help of DTA measurements. The composition corresponding to Na\(_2\)W\(_2\)O\(_7\) was prepared by mixing both the constituents, Na\(_2\)CO\(_3\) and WO\(_3\) (all 99.99% pure) in the desired ratio as given in Eq.(4.2).

\[ \text{Na}_2\text{CO}_3 + 2\text{WO}_3 \rightarrow \text{Na}_2\text{W}_2\text{O}_7 + \text{CO}_2 \uparrow \]  

(4.2)

The mixture obtained was grinded thoroughly in a mortar-pestle to a fine powder. The resultant material was used to form the pallets that were kept in a platinum crucible and heated rapidly at a
rate of 200 °C/h up to 600°C. The product Na₂W₂O₇, was cooled to room temperatures at the same rate after soaking at 600°C for 24 h in air. The resultant material was utilized for the DTA measurements using a platinum crucible of dimensions 5 mm d × 5 mm l. The crucible was kept in a thermal analyzer (SETRAM model 92) for heating. The plots during heating and cooling cycles were recorded as described earlier for the pale colored material. The plots obtained are shown in Fig. 4.4.

![DTA plot](image)

**Figure 4.4:** DTA plots of synthesized stoichiometric Na₂W₂O₇ material obtained during (a) heating and (b) cooling cycle.

The DTA plots show an endotherm during the heating cycle as well as an exotherm in the cooling cycle. The endotherm observed at 729 °C can be attributed to the congruent melting of the Na₂W₂O₇ phase. Similarly the exotherm observed at 638 °C during cooling can be attributed to the crystallization of the Na₂W₂O₇ phase. The DTA plot for the pale colored material also shows similar endotherm and exotherm but at relatively lower temperatures. Hence the presence of Na₂W₂O₇ phase in the pale colored material is confirmed.
4.2.2 Crystal and residual charge

The grown crystals were carefully cut into different pieces of same thicknesses. The crystal pieces obtained from different parts of the crystal and the residual charge remained in the platinum crucible after completion of the growth process were characterized using XRD and DTA techniques.

i) X-ray diffraction measurement

![XRD pattern](image)

**Figure 4.5:** *XRD pattern of the powder obtained from NYW crystal grown by Czochralski technique employing stoichiometric starting charge.*

X-ray diffraction pattern of the powder obtained from the top and bottom parts of the as-grown crystal and the residual charge were recorded using a Rigaku-RINT-2000 diffractometer equipped with a Cu-Kα source with a step size of 0.01° at 2°/min speed. The pattern obtained for different parts of the crystal are found similar and shown in Fig. 4.5. The pattern matches well with the JCPDS file for the NYW [10]. The pattern obtained for the residual charge is found similar to the pattern shown in Fig. 4.2. Along with NYW phase, it also shows the presence of Na₃Y(WO₄)₄ and Na₂W₂O₇ phases.
ii) Differential thermal analysis measurement

Fig. 4.6 shows the DTA patterns of top and bottom parts of a 40 mm long NYW crystal ingot and that of the residual charge. While the melting temperatures of the two regions of the ingot were found to be 1216°C and 1212°C respectively, an additional endotherm at 725°C was also observed in the bottom region.

![DTA plots](image)

**Figure 4.6:** DTA plots of (a) Top part and (b) Bottom part of the as-grown NYW crystal grown by Czochralski technique employing stoichiometric starting charge; (c) residual charge remained in the platinum crucible after completion of the growth process.

The residual charge was found to melt at yet lower temperature of 1190°C with the emergence of three additional endotherms in the range from 580°C to 700°C. This indicates a continuous drift in the composition during the crystal growth. These compositional changes can be explained in
terms of a partial decomposition of the NYW melt that results in the drifting composition caused due to dissimilar distribution coefficients of the decomposed constituents.

The cracking in oxide crystals may arise due to several reasons but whatever be the mechanism its ultimate effect is to produce strain in excess of the breaking strain of the crystal. The results of high temperature XRD experiments described in the previous chapter show that the cracking in the NYW crystal could not be due to any structural phase transition. The application of differently oriented seeds, stringent control on starting material preparation and low axial temperature gradient could not overcome the problem. However, under the application of low axial gradient the growth becomes highly unstable. The cause of instability has been traced to a partial decomposition of the melt.

In the previous chapter, results of DTA studies of polycrystalline NYW material showed that the degree of super-cooling in the NYW is small and was a function of the melt stoichiometry. Further, the results of DTA measurements carried out on the different parts of the crystal ingots and residual charge reveal a continuous drift in the melt composition with progressing crystal growth. As a consequence, the difference between the melting and solidification temperatures becomes small. A small difference in the melting and solidification temperatures and inefficient conduction of the heat of crystallization at the growing interface can result in the partial re-melting of the grown crystal. The growth and partial melting regimes operating concurrently make the growth unstable. When the growth is effected under the application of a high axial temperature gradient, the heat of crystallization is efficiently conducted away that prevents shift between the melting and solidification regimes. The changes occurring in the melt stoichiometry during the growth could not be exclusively related to the synthesis of starting charge because due care was taken in its preparation. To eliminate weighing errors, the constituent powders were first individually heated at 800°C to drive away any moisture or other volatile components present. A stoichiometric mixture of the constituent powders taken in a covered crucible was rapidly raised to the melting temperature thus avoiding any significant selective loss of the constituents due to the difference in their vapor pressures at elevated temperatures. In spite of these precautions, the compositional variations in the ingots were revealed by the DTA measurements. Besides, this was also the case when transparent polycrystalline chunks were
used for the growth. In the DTA plot of the bottom part of the crystal shown in Fig.4.6, the presence of an endotherm at 725°C is observed. It is to be noted that a signature of this endotherm is also seen in the DTA plots recorded for the pale colored material and synthesized Na$_2$W$_2$O$_7$ material, indicating the presence of impurity phases in the grown crystal.

The formation of this phase should be a continuous process since its concentration is found to increase along the crystal length. A significant amount of the Na$_2$W$_2$O$_7$ impurity phase is evident from the presence of an endotherm recorded during heating of the bottom part of the crystal. A partial decomposition of the melt is consistent with the observation of Na$_2$W$_2$O$_7$ phase formation even when transparent crystalline chunks of NYW were used for the growth. It may be noted that in several cases (Czochralski growth of PbWO$_4$ crystal), where the stoichiometric deviations in the starting powder material could not be fully controlled but a pure crystal and melt are highly stable with time at the elevated temperatures, the growth of pure phase crystals can be successfully accomplished by the application of clear crystal chunks obtained from the previous growth runs [11]. Indeed, this is not found to be the case with the NYW thus suggesting the partial decomposition of the melt at elevated temperatures.

The use of an orientated seed crystal to overcome the problem of cracking has been suggested in the literature, however, no unanimity regarding the growth direction is found. However, recently for some materials a highly detrimental role of non-stoichiometry in promoting cracking has been shown [12-19]. This also is found to be the case with the NYW where stoichiometric deviations arise due to the formation of impurity phases with a partial decomposition of the melt. The concentration of impurity phases with lower melting temperatures increases in the melt and consequently in the grown crystal with the progressing growth.

4.3 Effect of inclusions in Nd:NYW crystals

Along with the stoichiometric deviation of the melt, presence of inclusions and cracking of the crystal are the major problems associated with the growth of Nd:NYW crystals. The cracking of crystals is always associated with the presence of inclusions. In order to understand these problems with their possible causes a number of crystal growth experiments were carried out on the Nd:NYW and crystals were characterized using Thermo Mechanical Analyzer (TMA) and
differential thermal analysis (DTA). On the basis of obtained results possible reasons for cracking of the Nd:NYW crystals are discussed.

4.3.1 Crystal growth

A number of single crystal growth experiments were carried out on the Nd:NYW using the Czochralski technique employing differently synthesized starting charges, different axial temperature gradients (15-150°C/cm), seeds of different orientations and different pulling and rotations rates.

![A typical as-grown Nd:NYW crystal grown by Czochralski technique employing stoichiometric starting charge.](image)

Figure 4.7: A typical as-grown Nd:NYW crystal grown by Czochralski technique employing stoichiometric starting charge.

Growth attempts were made on the software controlled and fully automated crystal puller. Most of the times crystals up to 15 mm diameter and 40 mm length were pulled out successfully. However during the after-growth cooling the crystals cracked in the temperature range 600-800°C. In the subsequent growth experiments the cooling rate was lowered to 15-20°C/h but the cracking of the crystals could not be avoided. Most of the time cracking took place in the same temperature range. Photograph of a typical as-grown crystal is shown in Fig. 4.7.

A careful observations of the cracked crystals revealed that the cracking took place throughout the bulk without any specific pattern. Different cracked pieces of the as-grown
crystals always found to have different amounts of inclusions present inside the bulk. These pieces were observed carefully and three samples containing different amounts of inclusions were chosen for further characterizations as shown in Fig 4.8.

**Figure 4.8:** Samples of Nd:NYW crystal with (a) transparent (the mark at left side is developed during after-growth handling), (b) less inclusions and (c) heavy inclusions.
All the crystal pieces from as-grown cracked crystals were cut and polished. These were chosen based on the visual inspection such that first sample was completely transparent without inclusions, second had relatively fewer inclusions inside the bulk and third with heavy inclusions. For these samples growth was carried out along the crystallographic c-axis and all the samples were cut perpendicular to the growth direction.

**4.3.2 Structural analysis**

X-ray diffraction patterns of the powder obtained from the three samples (viz. transparent, with fewer inclusions and heavy inclusions) were recorded using a Rigaku-RINT-2000 diffractometer equipped with a Cu-Kα source. The step size and scan speed kept during the measurements were 0.01° and 2°/min, respectively.

![XRD pattern](image)

**Figure 4.9: Powder XRD pattern of the transparent part of an as-grown Nd:NYW crystal.**

Fig.4.9 shows the powder X-ray diffraction pattern obtained from the transparent part of the as-grown crystal. The XRD measurements carried out on the remaining two samples were found to
be similar. The pattern matches well with the NYW phase given in the JCPDS file and hence confirmed the formation of the NYW single phase [10].

4.3.3 Optical characterization

The absorption was recorded for all the three samples using a Jasco V-670 spectrophotometer in the range of 200-1100 nm. The absorption spectra recorded for the three samples show ten prominent peaks corresponding to transitions from the ground state $^4I_{9/2}$ of Nd$^{3+}$ to higher levels. Fig. 4.10 show the plot for absorbance calculated and regenerated for the broad peak occurring at 806 nm for the three samples. This peak is found to match with the wavelength of commercially available diode lasers.

![Absorbance peak at 806 nm](image)

**Figure 4.10**: Absorbance peak at 806 nm for the samples (a) transparent, (b) with less inclusions and (c) with heavy inclusions.

A crystal slice of 5 mm thickness was found to exhibit an absorbance value of 2.1 and FWHM of 16 nm for a doping concentration of 4%. A nominal difference in values of absorbance and FWHM of the three samples is observed which can be attributed to the presence of inclusions.
4.3.4 Thermal expansion measurement

Thermal expansion measurements on these samples were carried out in the temperature range 50-800°C employing a SETARAM make SETSYS Evolution Thermo Mechanical Analyzer (TMA). A constant heating rate of 10°C/min was employed in all measurements. Fig. 4.11 shows the thermal expansion (ΔL/L) curves along the c-direction for the three samples viz. transparent without inclusions, containing fewer inclusions and heavy inclusions, respectively.

![Thermal expansion curves](image)

**Figure 4.11:** Strain (ΔL/L) measured for the samples (a) transparent, (b) with less inclusions and (c) with heavy inclusions.

It is observed that for each sample the expansion occurred is linear in nature. This is consistent with an earlier reported result [20]. It was also found that the thermal expansion increases with the amount of inclusions present in the sample and this effect becomes more pronounced at higher temperatures. Fig. 4.12 shows average linear thermal expansion coefficient α for the three samples.
Figure 4.12: Average $\alpha$ measured for the samples (a) transparent, (b) with less inclusions and (c) with heavy inclusions.

Table 4.2: Average thermal expansion coefficient ($\alpha$) for different samples.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$\alpha \times 10^{-6} /{}^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent</td>
<td>11.31</td>
</tr>
<tr>
<td>With Less Inclusions</td>
<td>12.50</td>
</tr>
<tr>
<td>With heavy Inclusions</td>
<td>12.68</td>
</tr>
</tbody>
</table>
It is observed that $\alpha$ is less for the transparent sample compared to the other two samples containing inclusions. For comparison the average value of $\alpha$ for all the samples at a particular temperature is given in Table 4.2.

4.3.5 Differential thermal analysis

The DTA measurements were carried out on the same samples using a thermal analyzer (SETRAM model 92). For this purpose, about 30 mg of the finely grounded powder was taken in a platinum crucible of dimensions 5 mm $d \times 5$ mm $l$. The samples were heated at a rate of 10°C/min up to 1220°C, held there for a few seconds and then cooled down to room temperatures at the same rate. Air was used as ambient and blank crucible was used as the reference. As the melting of materials is, in general, an endothermic process, the peak obtained in the DTA plot that corresponds to the melting is called an endotherm.

![Figure 4.13: The melting endotherm for the samples (a) Transparent, (b) with less inclusions and (c) with heavy inclusions.](image-url)
The DTA plots obtained for the samples used in thermal expansion measurements show an endotherm for each sample in the temperature range 1180-1220°C during the heating cycle as shown in Fig. 4.13. The plot corresponding to the transparent sample shows a sharp endotherm at 1210°C which can be attributed to the congruent melting of the sample. Similarly for the second sample containing less inclusion the endotherm is observed at 1206°C. This endotherm was observed to be broader and less symmetric compared to that of the transparent sample. The melting point is also lowered compared to the transparent sample. The plot corresponding to the sample containing heavy inclusions shows two nearby endotherms at 1206°C and 1202°C respectively. The broadness of this more asymmetric endotherm was found to be increased significantly.

The single crystal growth experiments on the Nd:NYW were carried out employing differently synthesized charges, different temperature gradients and differently oriented seed but problem of crystal cracking could not be avoided even after lowering of the minimum possible cooling rate. The use of different growth parameters such as pulling and rotation rates of the seed, the after growth annealing of the grown crystal for several hours at elevated temperatures to relieve the strain produced during the growth could not yield crack-free crystals. No specific pattern in cracking was observed and it took place throughout the crystal. However the careful observation of the cut pieces of as-grown crystals revealed that the different pieces are having different amount of inclusions. This suggested that the cracking of the crystal has some relation with the inclusion present in the crystal with different amounts which, consequently result in generating the excess strain beyond the breaking strain of the crystal [21]. Hence, it is inevitably important to understand the mechanism by which presence of inclusions results in cracking of the crystal to get crack-free crystals. Therefore a study of the thermal behavior of cracked Nd:NYW crystals having different amounts of inclusions was important. As shown by the results of TMA measurements the difference in the strain (ΔL/L) produced below 500°C for all the three samples are nominal. But as the temperature increases further the difference also increases and found to be significantly larger in the temperature range of 600-800°C. For the transparent sample containing no inclusions the strain produced is always smaller than that produced in samples containing inclusions in the temperature range 400-800°C. The difference increases at
any point in the temperature range 400-800°C as the temperature increases. Further, the strain produced in the crystal at a given temperature is proportional to the amount of inclusion present in the crystal. Therefore, if the crystal has inclusions present inside the bulk at different regions with different amounts, the crystal will experience additional inhomogeneous strain at elevated temperatures. Also the linear thermal expansion coefficient (α) measured up to 800°C for all the three samples shows different values at any given temperature. For the samples containing inclusions this value is always greater than that of the transparent sample without inclusions. This implies that the inclusions are having a large linear thermal expansion coefficient than that of the pure Nd:NYW phase. This mismatch between the thermal expansions caused by pure Nd:NYW phase and that of the inclusions may increase the strain in the crystal. If this strain exceeds the breaking strain of the material the crystal may suffer crack.

During growth experiments of the Nd:NYW crystals, most of the times it was observed that the crystal growth took place without cracking. But during the post-growth cooling to room temperature the grown crystals suffer cracking in the temperature range 600-800°C, where the difference in the strain produced in samples containing different amount of inclusions was large. DTA results show that the thermal behavior of the material changes as the amount of inclusion present in the crystal increases. Sharp and symmetric melting endotherm for the transparent sample suggests a congruent melting of the material. The endotherm corresponding to the sample containing less inclusions is broadened with a lowering of the melting point while for samples containing heavy inclusions the melting took place in two stages resulting in a more broader and asymmetric endotherm. The lowering of the melting point with increased amount of inclusions indicates the presence of impurity phases in the sample with lower melting points than that of the Nd:NYW phase. The incorporation of these impurity phases in the Nd:NYW lattice results in strain due to a difference in the physical properties. Therefore during the post-growth cooling of the grown crystals these impurity phases may undergo some exothermic phase transformations due to their crystallizations at lower temperatures than that of the Nd:NYW phase. Consequently the crystal may not be able to sustain the higher stresses exerted by the production of heat of solidification in the interior of the crystal. This also explains the fact that the growth of crystals
took place without cracking but after some time during the post-growth cooling to room temperatures the grown crystals suffer cracking.

The origin of the impurity phases as inclusions in the Nd:NYW crystal has been explained in the previous chapter with the help of a binary phase diagrams of Na$_2$WO$_4$-Y$_2$(WO$_4$)$_3$ and Na$_2$O.WO$_3$-WO$_3$ where the Na$_2$W$_2$O$_7$ and Na$_5$Y(WO$_4$)$_4$ phases are found as impurities along with the desired NYW phase [22]. These phases melt and crystallize in the same temperature range where cracking of the Nd:NYW crystal took place. Here also during the growth experiments after the completion of the growth process such phases are observed in the residual charge along with the Nd:NYW phase. The thermal behavior of the NYW at elevated temperatures gets affected significantly due to the presence of such impurity phases. Since the impurity phases are likely to be distributed throughout the bulk, the cracking in the NYW crystal does not follow a particular pattern.

4.4 Conclusions

Czochralski growth experiments carried out on the Nd:NYW crystals show that crystal cracking and presence of inclusions are the main problems associated with the growth of crystals. The origin of both the problems is traced to the formation of impurity phases in the melt. The formation of impurity phases has been observed to take place irrespective of the case whether a starting charge is synthesized from the constituent powders or transparent crystalline chunks obtained from previously grown crystal ingots are used. The results of thermal expansion and DTA measurements carried out on samples containing different amounts of inclusions show that the presence of inclusions affects the thermal behavior of Nd:NYW crystal significantly. The incorporation of the impurity phases in the Nd:NYW lattice during the growth results in excessive strain leading to cracking of the crystal. To grow crack-free, good quality crystals, the formation of these impurity phases in Nd:NYW crystal needs be suppressed.
References

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