

## CHAPTER 7

### GROWTH OF NEODYMIUM ACTIVATED STOICHIOMETRIC BORATE CRYSTALS

#### 7.1. STOICHIOMETRIC LASER MATERIAL

Stoichiometric laser materials—commonly known as self activated laser materials—are pure chemical compounds capable of emitting coherent light in the undiluted state as opposed to conventional laser materials, where the active ions or molecules are dispersed in a host. Specific search for such compounds started in 1971 and resulted to several successful and a number of promising materials suitable for miniature lasers. The first room temperature stoichiometric observation of stimulated emission for such crystals was first made by Varsanyi [77] using highly efficient laser pump, which excites stimulated emission from  $1\ \mu\text{m}$  size  $\text{PrCl}_3$  and  $\text{PrBr}_3$  crystals. Successively several promising neodymium ion activated phosphate and Borate stoichiometric laser crystals have been developed. An extensive review has been made by Danielmeyer [78] on stoichiometric laser materials. A chapter has been devoted by Kaminskii [74] for the self activated materials and their spectral properties.

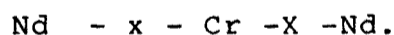
The stoichiometric laser materials have certain merits over conventional laser materials. In the case of activated or conventional laser materials several limitations are being imposed by the host material over activator ions, such as size, charge and co-ordination of impurity which are determined by the capacity of the host

materials. Stoichiometric laser materials are not subject to such restrictions. It allows within certain limits to combine a priori desirable activator ion with desirable host materials and to form compounds. Secondly, in self activated crystals the minimum spacings between the adjacent atoms are fixed by the structure of the molecules. This is a major advantage of the stoichiometric laser crystals; because all interactions between activator ions usually increase with decrease of separation. In the activated laser crystals doping normally results to a statistical distribution of spacings between active ions; a statistical fraction of small spacings leads to detrimental interactions.

Concentration quenching of luminescence of laser active ions is one of the major problems in laser Crystal Physics. In the case of Nd:YAG, the fluorescence life time decreases through pairwise interaction with the increase in Nd concentration. The smallest useful average Nd separation was found to be approximately 15 Å. In the same way the initial studies of Schawlow et al [177] on ruby system revealed that there exists strong exchange coupling of Cr<sup>3+</sup> pairs for doping levels greater than  $4 \times 10^{19} / \text{cm}^3$ . From this result it was deduced that the minimum possible average spacing between Cr ions was in the vicinity of 30 Å. However, in the case of stoichiometric laser crystals, the quenching is caused by impurities as well as by the cross relaxation between activator ions. Impurity quenching in most cases is a phonon assisted transfer of an excitation to an adjacent trap which quenches the fluorescence very well if it has closely spaced levels to the ground state facilitating phonon relaxation. Hence impurities are the major problem in

stoichiometric laser materials. Neodymium is notorious for its ability to self quench. The worst path is via the  $4I_{15/2}$  (manifold) which is often exactly at the mean energy between the  $4F_{3/2}$  states and the ground states  $4I_{9/2}$ . It is very fortunate that the successful stoichiometric laser crystals such as phosphates and borates exhibit anomalous weak concentration quenching of the luminescence from the  $4F_{3/2}$  metastable state, though the  $Nd^{3+}$  ion concentration is about 30 times higher than the conventional lasers. Several detailed studies have been made to understand the nature of weak concentration quenching phenomenon [178-180]. It was observed that the neodymium ions occupy only regular lattice sites which are well shielded from one another, thus minimizing Nd-Nd cross relaxation in spite of the high Nd concentration. It is quite evident that the most extensively used activator ion in laser crystal is trivalent neodymium. It acts as a laser active ion in as much as 130 laser host materials. In the case of stoichiometric laser materials neodymium activated materials are found more promising than any other active ions.

In the year 1971, the idea occurred to synthesize a stoichiometric crystals with Nd and Cr in which the arrangement would be



$Cr^{3+}$  has broad absorption bands, could in principle, transfer its excitation over the short spacing (-X-) efficiently to  $Nd^{3+}$ . The trivalent neodymium has narrow emission line width which could result in low threshold. The

separation between trivalent neodymium ions would be larger than  $5 \text{ \AA}$  so that wave function overlap would be avoided. Since the compound should be a non metal one, X should not be a metal.

i.e.  $X = O, B, C, N, S, P, F, Si$

Cl, Br, and I were excluded because they tend to yield hygroscopic crystals. Weber [ 181] attempted from left to right for X. The first crystalline output was neodymium pentaphosphate with the arrangement of Nd-O-P-O-Nd and the composition  $NdP_5O_{14}$ . Successive attempts made by several researchers yielded variety of new stoichiometric compounds. Among the available stoichiometric materials, promising compounds and their important laser properties have been presented in Table 7.1.

Table 7.1 Promising stoichiometric crystals with their important laser parameters in  $1.064 \mu\text{m}$  wave length

Crystal	Life time $\mu\text{s}$	Cross-section $\text{cm}^2$	Gain $G = \exp( N )$
$NdP_5O_{14}$	120	$2 \times 10^{-19}$	1.088
$Nd LiP_4O_{12}$	120	$3.2 \times 10^{-19}$	1.158
$Nd Al_3(BO_3)_4$	20	$10 \times 10^{-19}$	1.754

Apart from the above mentioned compounds several other phosphate compounds like  $\text{MNdP}_4\text{O}_{12}$  ( $\text{M}=\text{Na}, \text{K}$ ) [182],  $\text{K}_3\text{Nd}(\text{PO}_4)_2$  [183], molybdates [184] and tungstate compounds [185, 186] have been synthesized and characterised for their properties.

Though neodymium is extensively used as activator ions in the stoichiometric laser compounds because of their excellent spectral properties compounds with other laser active ions are also attempted. For example  $\text{ErAl}_2\text{O}_3$  has been grown and studied by Prokhovov et al [187]. Kaminiskii et al [188] have studied stimulated emission of various compounds containing high concentration of  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$  ions.

## 7.2 GROWTH OF NEODYMIUM ALUMINIUM BORATE CRYSTALS FROM FLUX

Neodymium aluminium borate (NAB) is one of the best stoichiometric laser crystals exhibiting weak concentration quenching of luminescence, highest emission cross-section and low optical pump threshold. The combination of laser active ions and small quenching allow effective miniaturization of laser. Miniature laser will be useful whenever, size, weight and materials have to be considered. Continuous wave laser action in NAB crystals ranging from 136 to 340  $\mu\text{m}$  in length ((i.e.) the distance between the lasing facets not the length of the rod) with threshold power ranging from 0.55 to 1.9mW have been demonstrated by Chinn and Hong [183].

Growth of NAB crystals was first reported by Ballman in the year 1962. NAB which has the chemical formula  $\text{NdAl}_3(\text{BO}_3)_4$ , melts incongruently and hence, it can be

grown only by high temperature solution growth method. Hong and Dwight [185] have grown NAB crystals from molten solution of potassium sulphate and molybdic anhydride in the 1:3 molar ratio. The NAB crystals obtained were with hexagonal morphology. Later on in the year 1975 Chinn and Hong [183] have successfully grown NAB crystals by using  $\text{BaO}-2\text{B}_2\text{O}_3$  flux system.  $\text{PbO}-\text{PbF}_2$  flux was used by Lutz et al [189] with 50% excess of  $\text{B}_2\text{O}_3$  for the growth of epitaxial layers of NAB on the  $\text{Gd}_{0.59}\text{La}_{0.41}\text{Al}_3(\text{BO}_3)_4$  substrate. Though NAB crystals have been crystallized from several flux systems the size of the crystal is too small for a detailed investigation of luminescence and generation characteristics. Increase of crystal size may be achieved by adopting any kind of seeded technique or by suitably changing the growth parameters. Another approach to the size limitation problem is to find out more suitable flux either by improving the present flux or attempting to find out altogether a new flux system. In the present chapter the author reports the growth attempts made for NAB crystals from barium-lead and molybdate based flux systems and their characterization.

#### 7.2.1. Growth of NAB crystals from $\text{BaO}-\text{B}_2\text{O}_3$ flux

Solubility of NAB crystal in  $\text{BaO}-2\text{B}_2\text{O}_3$  flux has been studied extensively by Timechenko et al [190]. They have found that  $\text{BaO}-2\text{B}_2\text{O}_3$  system with eutectic mixture melts completely at 1373K, whereas in the case of eutectic mixture with  $\text{BaO}-\text{B}_2\text{O}_3$  did not melt at 1453K. Hence, the author prefers the use of  $\text{BaO}-2\text{B}_2\text{O}_3$  flux system. From the experience gained for the growth of YAG from  $\text{BaO}/\text{B}_2\text{O}_3/\text{BaF}_2$  flux system by using alumina crucibles, it has been decided to use the alumina crucibles for the growth of

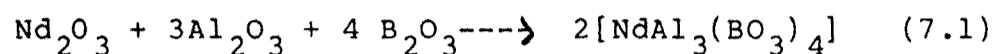
NAB crystals from  $\text{BaO}-2\text{B}_2\text{O}_3$ . The alumina crucibles used by the author for the growth of NAB crystals are shown in Figure 7.3.

Initial growth run was made with the typical composition of starting material as given below:

Neodymium oxide	:	8	gms
Aluminium oxide	:	7.5	gms
Barium Oxide	:	7.5	gms
Boron tri-oxide	:	15.0	gms

These starting materials were mixed thoroughly and then charged in a thermally recrystallised alumina crucible of 25ml capacity. Usually the crucibles were charged more than one time to have more melt content. The crucible was placed inside a uniform hot zone silicon carbide furnace. The furnace temperature was increased at the rate of 50K/hr upto 1500K and kept at this temperature for 24 hours, to ensure complete homogenization. This period is commonly referred to as soaking period. While heating it was observed that the ingredients turned into pink in colour and start melting at 1288K. After the soak period was over, the furnace was cooled at the rate of 2K/hr till it reaches 1263K. Later on cooling was performed by adopting the cooling rate of 5K/hr, 10K/hr and 50K/hr till the furnace reached 1173K, 973K and finally to room temperature respectively. The crucible was placed inside a hot nitric acid to leach the flux. Several tiny NAB crystals have been collected from the crucible after four days of leaching. The obtained pink coloured crystals exhibited hexagonal rod shaped morphology as reported earlier [84]. NAB crystal obtained from the growth run(I) is shown in Figure 7.1.

The formation of NAB may be represented by the chemical equation as



Excess of boron tri-oxide added in the growth composition will serve as a solvent. This behaviour of a solute component acting as a solvent is not a rare occurrence in the solution growth

In the second growth run two crucibles of 20ml capacity have been used. In this attempt the solvent composition has been increased. The actual compositions used in the second growth run are given in Table 7.2.

	Crucible A	Crucible B
Neodymium	5.330 gm	4.580 gm
Aluminium oxide	5.000 gm	4.280 gm
Barium Oxide	5.740 gm	5.950 gm
Boron tri-oxide	11.480 gm	11.800 gm

The ingredients were mixed thoroughly and loaded in two crucibles respectively. Growth parameters such as soak temperature, soak period and heating and cooling programmes were followed same as in the first growth run. After cooling the furnace to the room temperature it was found that pink colour material was deposited over the outer wall of the crucible B, which might be due to the capillary rise phenomena of the solution. Though we have obtained



NAB crystals from both the crucibles. A and B, the crucible B yield better size of the crystal than that of the crystals obtained from other crucible and that obtained from first growth run. It was observed that the crystals are very delicate and break into several pieces while handling. NAB crystals obtained from crucible B is shown in Figure 7.2. and 7.4.

#### 7.2.2. Growth of NAB from Lead Based Flux System

Third growth run was made by using lead oxide-lead fluoride-boron trioxide flux system. Experience gained from the growth of YAG crystals using lead based flux system suggests that the alumina crucible cannot be used for this flux. Hence, a platinum crucible of 20 ml capacity has been used for the present attempt. The composition used in the attempt is as follows.

Neodymium oxide	:	2.290 gms
Aluminium oxide	:	2.140 gms
Lead oxide	:	5.300 gms
Lead fluoride	:	6.745 gms
Lead di-oxide	:	0.280 gms

The lead di-oxide ( $Pb_2O$ ) has been added in small concentration to reduce the possibility of lead oxide to become lead, which may result in crucible failure. The furnace was heated at the rate of 100K/hr to 1473K. Soaking period has been given as 12 hours, and then the furnace was cooled at the rate of 2K/hr till it reached 1223K. Later on 25K/hr and 50K/hr cooling rates were adopted to cool the furnace to 973K and to room temperature respectively. A clear, transparent pink colour solid material was formed in the crucible instead of crystals with solidified flux.

### 7.2.3. Growth of NAB from molybdate flux

The oxides of  $V_2O_5$ ,  $MoO_3$ , and  $W_3O_3$  have good solvent properties but are highly volatile. Hence, the alkali vanadates, molybdates and tungstates are generally preferred. The high valency state of vanadium, molybdenum and tungsten prevents significant incorporation. Bonner [122] has suggested a molybdate based flux system for the synthesis of garnets. Several rare earth orthoborates have been synthesised from potassium sulphate and molybdenum tri-oxide flux. The same technique was found unsuccessful in an attempt to prepare  $NdAl_3(BO_3)_4$ . Hong and Dwight [185] have grown NAB crystals by synthesising a solvent separately. They have mixed potassium sulphate and molybdic anhydride in 1:3 molar ratio fired at 873K for few hours and then quenched to room temperature. The quenched material was used as flux for the growth of NAB. Watts [191] has grown  $HoAl_3(BO_3)_4$  crystals using an improved flux system as  $K_2SO_4 - MoO_3 - B_2O_3$ . The same flux system was attempted by the author for the growth NAB crystals, but failed to get crystals. Hence, the author attempted to use a new  $NaMoO_3 - NaF - B_2O_3$  flux system for the growth of NAB crystals. The composition used is given below:

Neodymium oxide	:	4.500 gms
Aluminum oxide	:	3.950 gms
Boron tri-oxide	:	3.350 gms
Sodium Molybdate	:	18.150 gms
Sodium fluoride	:	0.500 gms

The above ingredients were mixed and loaded in a 40ml alumina crucible. This crucible was covered with a lid, so as to reduce the rate of evaporation. The furnace was heated upto 1455K and then kept at this temperature



FIG. 7.1

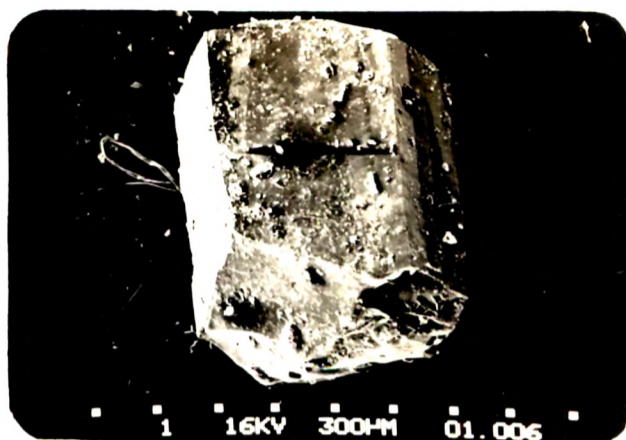


FIG. 7.2



FIG. 7.3



FIG. 7.4

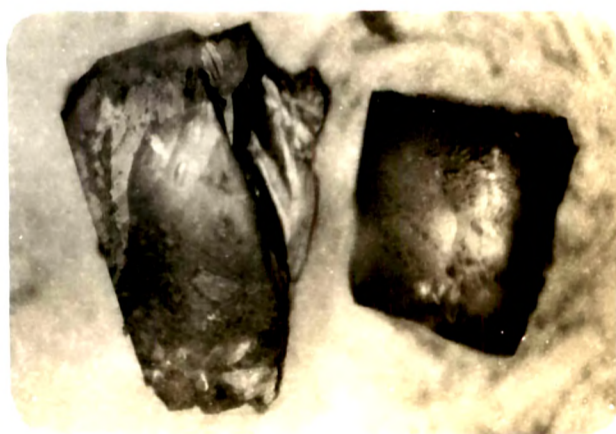


FIG. 7.5

for 12 hours. Then the furnace was cooled at the rate of 2K/hr until it reached 1236K. Later on 10K/hr and 25K/hr cooling rates have been adopted to cool the furnace to 873K and room temperature respectively. It was observed that the flux vapour had deposited on the inner muffle walls as a thick layer. It has been found that water is good solvent for this flux. After leaching the flux with hot water, NAB crystals were collected. Large number of tiny crystals obtained in this run might be due to uncontrolled evaporation of the solvent. Figure 7.5 shows crystals obtained from Molybdate base flux.

### 7.3. CHARACTERIZATION

Grown NAB crystals have been characterised for their purity, structural and optical absorption.

#### 7.3.1. Electron Probe Micro Analysis (EPMA)

It has been observed that among the crystals obtained in the first growth run, few of them are dark red in colour. These crystals were subjected to the electron probe micro analysis for their purity, which indicates the presence of barium ion in large concentration. From this result we can conclude that in the growth of NAB crystals the solvent barium oxide forms complexes also.

#### 7.3.2. Structure of NAB crystals

Structure of the stoichiometric laser material is one of the important factors determining the laser efficiency. In the stoichiometric laser material minimum spacings between the laser active ions are fixed, by the structure of the molecule. In general all interactions between activator ions increase with decrease of separation.

Structural analysis of NAB crystals by the earlier workers suggested that it composed of two isolated  $(\text{BO}_3)$  triangles, one perpendicular, the other nearly so to the C axis. The  $\text{Al}^{3+}$  and  $\text{Nd}^{3+}$  ions occupy oxygen octahedra and trigonal prisms respectively. The concentration of quenching of  $\text{NdAl}_3(\text{BO}_3)_4$  is reduced by the isolation of Nd trigonal prisms. Latter on Hong and Cinn [178] made a correlation between the radiative life time in various laser crystals and local site symmetry. They have ascertained that NAB crystal belongs to R32 point group. Later on it has been reported that the NAB crystallizes into two monoclinic space group C2/2 and C2. Further it has been added that the symmetry group of NAB is either monoclinic or rhombohedral depending on the growth conditions.

#### 7.3.3. Optical absorption spectrum

Absorption spectrum of the neodymium aluminium borate crystals grown from the first growth run has been recorded using a double beam U-V, visible, near IR, model U3400-Hitachi spectrophotometer. The spectrum was recorded in the range from 300 to 900 nm. The absorption spectrometer automatically selects the scan speed and the slit width. The spectrum recorded is presented in Figure 7.6.

#### 7.4. SUMMARY AND CONCLUSION

Neodymium Aluminium Borate crystals have been grown by using thermally recrystallised alumina crucibles from

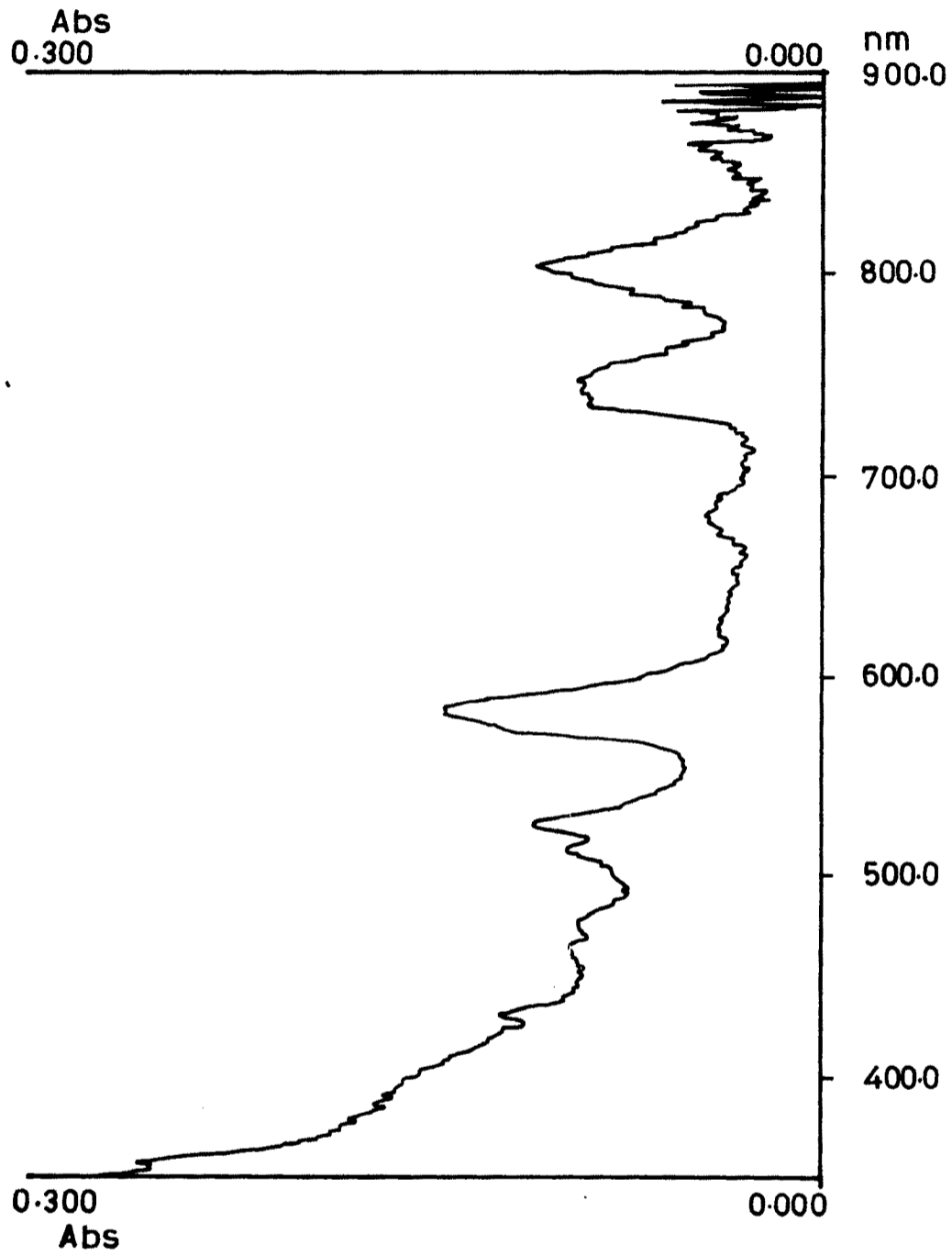


Fig. 7.6

OPTICAL ABSORPTION SPECTRUM RECORDED FOR NAB  
CRYSTALS

BaO-B<sub>2</sub>O<sub>3</sub> and NaMoO<sub>4</sub>-NaF-B<sub>2</sub>O<sub>3</sub> flux systems. However, an attempt to grow NAB crystals from PbO-PbF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> results in pink coloured transparent glassy material. The optical absorption spectrum indicates this material has absorption bands at 580, 730 and 800 nm.