CHAPTER 5

STUDIES ON MACROSPIRALS AND HOLLOW MORPHOLOGY PRESENT IN FLUX GROWN YAG CRYSTALS

5.1. INTRODUCTION

The presence of growth spiral has been established over wide variety of crystals grown by different techniques [47-49]. Frank [46] proposed a growth theory stating that the dislocation having a screw component acts as continuous source of layers on the surface of the crystal, which removes the need for surface nucleation. But often spirals and growth features which are observed experimentally are not of unit cell dimensions; but may be built of 100-1000 unit cells. These spirals with large step height are termed as macrospirals or giant spirals. Presence of macrospirals on large number of materials grown by different techniques has been reported. In flux grown barium molybdate single crystals, Arora et al [140] observed the macrospirals. Cook et al [50] reported the presence of polygonised macrospirals on flux grown barium zinc ferrite.

Hollow and hopper morphologies have been observed quite often in a large variety of materials grown from different techniques. Buckley [16] in his monograph has given information on some hollow crystals of $KClO_3$ from solution. Hydrothermal crystallization of selenium also yielded small hollow needles. A series of studies on hollow ice crystals has been made [141, 142]. It is evident from the literature that hollow and hopper morphologies are existing in different forms like hexagonal prisms, rods, whiskers and pyramidal. Simov [143] has attempted to present an extensive review on morphology and kinetics involved in the formation of hollow crystals of II-VI compounds.

Though the literature available is large, a vivid theory of formation of macrospiral, hollow and hopper morphology are still lacking. Their existence however attracts the researchers by a number of specific questions related mostly to the growth mechanism. In the present chapter author reports the presence of macrospirals and hollow crystals in YAG grown from $BaO/BaF_2/B_2O_3$ and $PbO/PbF_2/B_2O_3$ flux systems respectively and attempts to give a possible formation mechanism relating the growth conditions.

5.2. CRYSTAL GROWTH AND NATURE OF THE MACROSPIRAL OBSERVED

Stoichiometric amount of yttrium oxide and aluminium was added with a mixture of 0.41 BaO - 0.41 B_2O_3 -0.18 BaF_2. After mixing the solute and solvent systems thoroughly, the ingredients were taken in a 40ml platinum crucible and kept inside a uniform hot zone silicon carbide furnace. The furnace temperature was raised to 1573K and kept at this temperature for 24 hours, to ensure complete homogeneity. The furnace was cooled at the rate of 2K/hr till it reached 1548K and then 5K/hr and 200K/hr colling rates were adopted to cool the furnace to 1273K and room temperature respectively. Grown YAG crystals were removed by dissolving the flux in hot concentrated nitric acid for two weeks. Large number of tiny crystals were collected from the crucible and examined with an a optical microscope. It was observed that most of the crystals obtained are with regular facets. HOwever, about 5% of them developed as platelets. Examination of these platelet crystals with optical and scanning electron microscope reveals the presence of centrally basin like depression spirals on the flat faces. Some of the observed spirals have been presented in figures 5.1-5.4. It was also observed that the other side of the flat face exhibits regular facets. Further examination of the depressed spiral illustrates that the centre of the spiral is in rhombus shape, which is shown in figure 5.5. It was observed that the inner walls of the depression are covered with uneven roughness and step like character (Fig. 5.5 and 5.6). It was also observed that in between two successive steps few more lines are visible and also the edges are not vertical. Fig. 5.7 shows such typical steps exisiting in the macrospiral. The spiral which appears with rhombus shape at the centre is hexagonal at the edges.

5.3. GROWTH OF YAG HOLLOW CRYSTALS

A few hollow YAG crystals were present along with well faceted crystals obtained from $PbO/PbF_2/B_2O_3$ flux system. The typical composition used in this grown run is as follows:

Yttrium oxide	12.408 gms
Aluminium oxide	11.640 "
Lead oxide	42.408 "
Lead di-oxide	2.232 '
Lead fluoride	53.960 "
Boron tri-oxide	4.880 "

The above ingredients were mixed thoroughly and then loaded in a 50 ml platinum crucible. The crucible was placed in a uniform hot zone silicon carbide furnace. Then

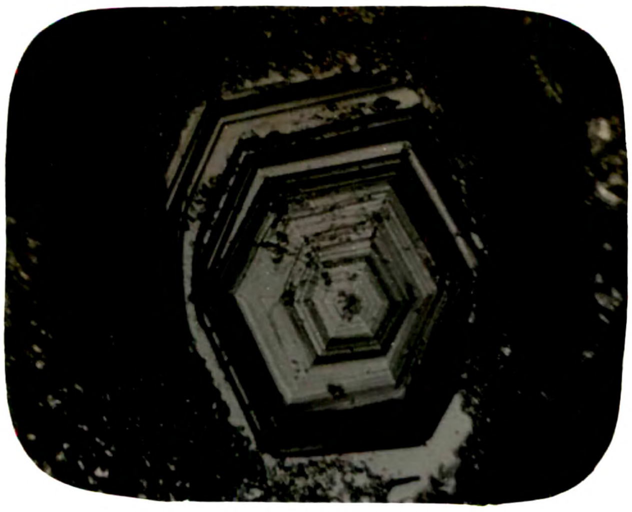

FIG. 5·1

FIG. 5·2

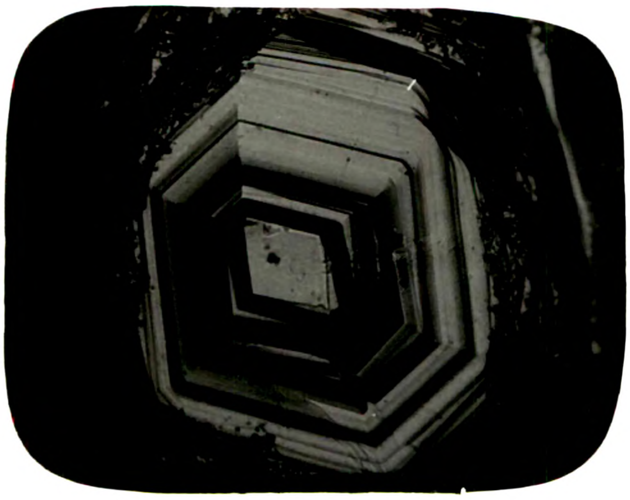

FIG. 5·3

FIG. 5·4

FIG. 5·5

FIG. 5·6

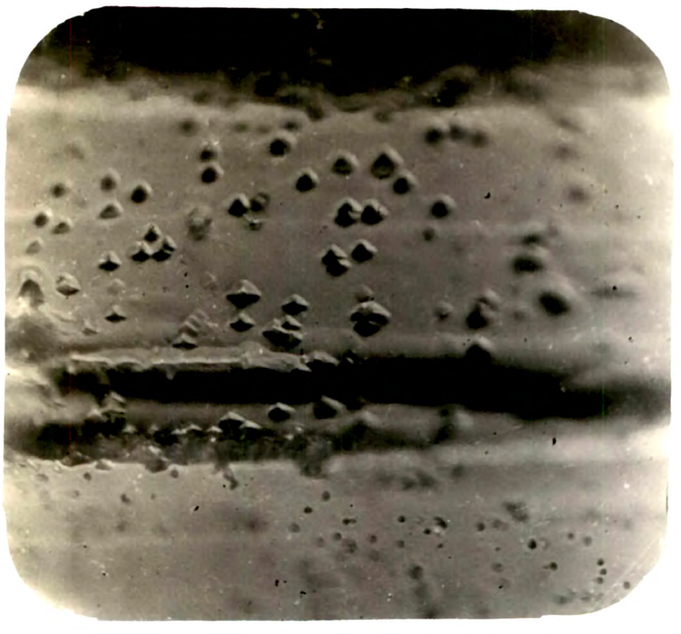

FIG. 5·7

FIG. 5·8

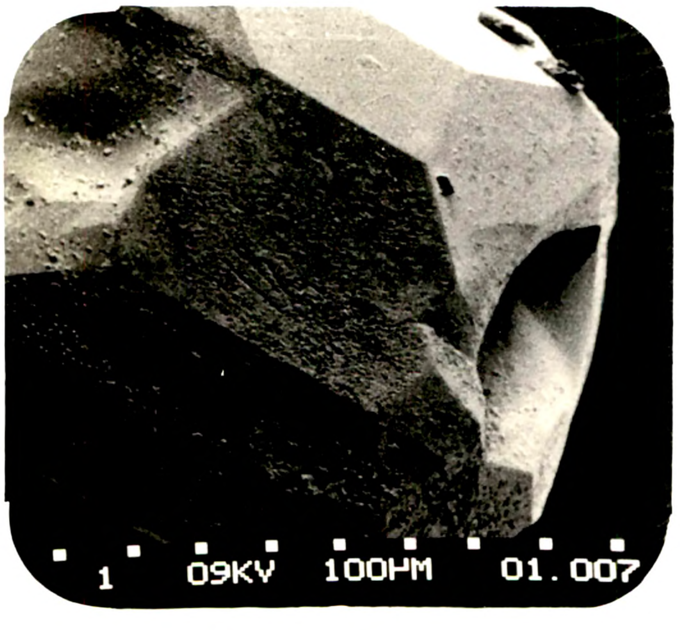

FIG. 5·9

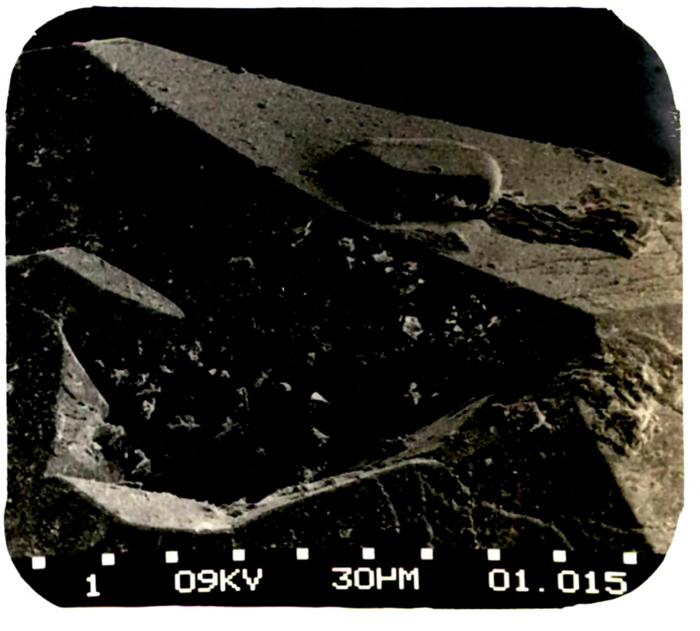

FIG. 5·10

the furnace was heated at the rate of 100K/hour to 1573K and kept at this temperature for 12 hours as soaking period. Then the furnace was cooled at the rate of 1K/hour till it reached 1513K. There was a power failure for 30 minutes and hence the furnace temperature dropped down to 1263K. After resumption of power the furnace was again heated at the rate of 50K/hour till it reached 1515K. The temperature of the furnace was held constant for 4 hours. Then a cooling rate of 2K/hour was adopted till the furnace reached to 1323K. Cooling rates of 5K/hr and 50K/hr were adopted to cool the furnace to 1123K and room temperature respectively. Grown YAG crystals were removed after leaching the flux by using hot concentrated nitric acid. It has been found that most of the crystals developed with regular facets and some of them are hollow crystals. Observed hollow YAG crystals are shown in figs. 5.9 and 5.10.

5.4. DISCUSSION

Several hypotheses have been proposed and discussed by the earlier workers to explain the formation of macro-spiral and hollow morphology; by considering several parameters such as growth conditions, defects nature, presence of impurity etc., Woods [144]. Chandrasekaraiah and Krishna [145] observed that hollow crystals were mostly grown from higher supersaturation, which is also observed in ice crystals [146]. This was supported by Lendvay and Kovacs [147] after observing the two dimensional nucleation on the surface of the crystals. In the case of YAG crystals grown by the author also the absence of growth hillock may be considered as an evidence for the growth at higher supersaturation. It has been observed that in most of the hollow crystals the outer faces are smooth, while the inner are uneven with macrosteps. The crystals grown by Sharma and Malhotra [148], Paorici [149] and

Dreeben [150] are hollow prismatic rods. However it has been observed that at the bottom of the hollow crystals either a spiral growth structure is present or a consistent column grows at the top of which a spiral appears. In some crystals clusters are observed at the bottom of the hollow crystals. Chandrasekaraiah and Krishna [145] established that in a hopper crystal the angle of the hollow cone is 12° to 20°, further it has been observed that the inner and outer faces are carrying a step like character.

According to Frank a growth spiral should originate from a single screw dislocation. To confirm this the obtained crystal was etched with hot phosphoric acid (85%) for five minutes. It was found that the etch pits appeared all over the surface without specific etch pit at the centre of the spiral (Figure 5.7). It has been discovered that dislocation etch pits are present on the upper surface of periphery of the hollow crystals which was attributed to the thermal stress induced by the difference between the speeds of cooling of the inner and outer surface of the crystal.

Lang [151] suggested a theory stating that a bluff could be the cause of macrospiral formation. He explained that the spirals are simply manifestation of lamellar growth and that a screw dislocation need not be involved. Hence we conclude that the Frank's growth spiral could not be related with the formation of macrospiral.

Amelinckx [152] reasoned out the formation of macrospirals as due to wobbling of the centre of spirals at hellicoidal screw dislocations.

In low temperature solution growth it has been predicted by Buckley [16] that the face on which a crystal rests on the bottom is deprived of material and ceases to grow. Just around its resting face, a trace of material is able to percolate in and cause a slight rising of the crystal, and the continuation of this peripheral growth gives this depression. Cook et al [50] observed that the depression spirals appeared over the surface of the crystals which grow while floating on the nutrient flux. In the present case the crystals obtained are all not platelets. Most of them developed regular facets and about 5% of the crystals only exhibit flat platelet faces. These platelet crystals exhibit regular facet on the other side. Hence, it is concluded that the crystals which nucleated at the bottom of the crucible walls and on the surface of the solution due to evaporation might be developing macrospirals.

Buckley [16] claimed that impurities could be the reason for the structure and it was supported by several researchers. But Paorici [149] obtained hollow crystals of CdS with and without impurities. Hence, he concluded that the impurities were important though not necessarily an essential factor. Due to high supersaturation the probability of two-dimensional nucleation is increased and a second source of step arises. Lefever et al [138] observed several growth steps which were concave from the point of origin on the surface of flux grown garnet crystals. It is suggested that the concave shape of the step is an indication for high supersaturation at the corners of the faces than the edges. Similar layer were observed by Chase [153] on In_2O_3 crystals and Quon et al [154] on YIG crystals. Whatever may the real cause of these spirals; the higher step height or macro step is due to the bunching of steps or advancing growth layers. Elwell and Neate [155] observed triangular layers on ferrite crystals.

5.5.1. Suggested formation mechanism.

The author views that the formation mechanism of these depressed macrospirals can be sequenced as follows.

i) Nucleation at the wall of the crucible and at the surface of the solution.

ii) Development of flat face due to insufficient solute transport

iii) Layer by layer growth, nucleating at the edges and corners and tending towards the centre of the face

iv) Bunching of steps

v) Formation of hollow or hopper morphology.

There is a greater possibility for a heteogeneous nucleation to occur at the walls of the container. It is also probable that the nucleation occurs at the surface of the solution, because of relative higher supersaturation at the surface due to solvent evaporation. The flat face might have developed at the side which rests on the walls of the crucible and on the side which is exposed to the atmosphere. The insufficient solute transport might have initiated the lateral growth, thus resulting in the flat face. Further growth on this flat face is mainly due to the layer by layer growth mechanism caused by the nucleation at the edges and corners of the faces. The presence of growth steps and non existence of growth hillocks are evidences for the layer by layer growth mechanism. Attolini et al [156] discussed that in layer by layer growth it is more probable for nucleation to occur at the edges than at the centre of the face, because of relative higher supersaturation at the edges than at the centre of the faces. If growth occurs by a mechanism of layer spreading from corners and edges, it is very probable that the inclusions will be formed at the face centres of the crystal where the supersaturation is low. This has been confirmed by the work of Carlson [157] on aqueous solution growth and Lefever [138] on YIG from flux. A detailed description of the mechanism is given by Chernov [158] in his review work.

A step will develop whenever densely packed atomic sheets make a small angle with the crystal surface. Growth is occurring predominantly by attachment of atoms at the sheets or in other words, growth is mainly due to propagation of these steps. These movements of atomic sheets or steps are getting bunched together forming a macrostep or a giant step with large step height. In this way steps developed at the edges and corners might have proceeded towards the centre. Various models were previously discussed by early workers to explain the movement of steps and crowding or bunching phenomena.

Except for the observations of Torgeson and Jackson [160] all the microspirals observed are partly or completely polygonized. Extensive theoretical works are being carried out by several researchers to explain the polygonization of the macrospirals. Hartman [4] has pointed out that the strongest periodic bond chain (pbc) corresponds to the direction of longest elongation on the growth fronts, since they have lowest density of kinks.

Author agrees with the view that the difference in the step velocity causes the bunching or crowding of steps. The difference in step velocity is due to various factors like faster growth along the preferential direction, presence of foreign atoms, which some time block the advencement of steps and thus resulting in the polygonization and bunching of steps.

The first step will nucleate at the edges and might have proceeded towards the centre. Before the fist step reaches the centre a second step might have nucleated over the first step and also move towards the centre with relatively higher velocity than the first step velocity. Hence the second step may catch the previous step before the first step reaches the centre. In this way bunching or crowding of steps could have occurred.

After the formation of macrospiral or spiral with large step height, if the crystal is allowed to grow further in the higher supersaturted condition the hollow or hopper morphology will develop.

5.5. VALIDITY OF THE SUGGESTED FORMATION MECHANISM

Though the literature available on the macrospiral and hollow morphology is enormous the contradictory reports presented by various researchers make the task of presenting a more satisfactory hypthesis difficult. The suggested formation mechanism may not be able to expalin several phenomena such as the hollow crystals developed in the interiror of the solution, the hollow morphology exhibiting more than one facet and the reason for the formation of hollow and hopper morphologies etc.,

5.6. SUMMARY AND CONCLUSION

The author has observed macrospirals and crystals with hollow morphology among the YAG crystls grown by using barium and lead based flux systems respectively. From the literature it is evident that a large number of materials grown from different techniques have yielded crystals with macrospiral on the surface, hollow and hopper morphologies. Though these features are frequently observed a vivid theory is still lacking. Formation mechanism of macrospiral and hollow morphology in the solution grown crystals by considering the growth conditions used are presented. The author views that the growth at higher supersaturation is the main driving force fot the formation of macrospirals. The author presents a sequence as i) nucleation at the walls or surface of the solution ii) development of flat face iii) further growth on the flat face by two dimensional layers iv) bunching of steps resulting to macrospiral v) development of hollow morphology. The author has also discussed the validity of the suggested formation mechanism.