

# Improvement of Crystalline Perfection Leading to Enhanced Physical Properties in Technologically Important Crystals by Various Novel in Situ/Post Growth Processing Methods

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**Abstract:** *Enhancement of crystalline perfection in variety of technologically important crystals was successfully achieved by adopting various novel in situ growth and post growth processing methods including dopants and additives. The enhanced crystalline perfection was assessed by high-resolution XRD (HRXRD). The influence of crystalline perfection on various physical properties was studied. The following in situ or post growth processing methods to improve the quality are described: (i) Post growth annealing and electrical poling in LN crystals, (ii) Poling and reduction in potassium niobate (KN) crystals (iii) Maintenance of proper solid-liquid interface shape (convex/flat/ concave) by controlling the seed rotation in Nd-doped GGG (Nd:GGG), (vi) Liquid crystal additive to Benzophenone, (v) Doping of L-threonine (LT) in KDP crystals, (vi) Effect of necking on LiF crystals, and (vii) Effect of double wall crucible design in benzimidazole single crystals grown by the VBT.*

**Keywords:** Situ growth, post growth, HRXRD, BBO.

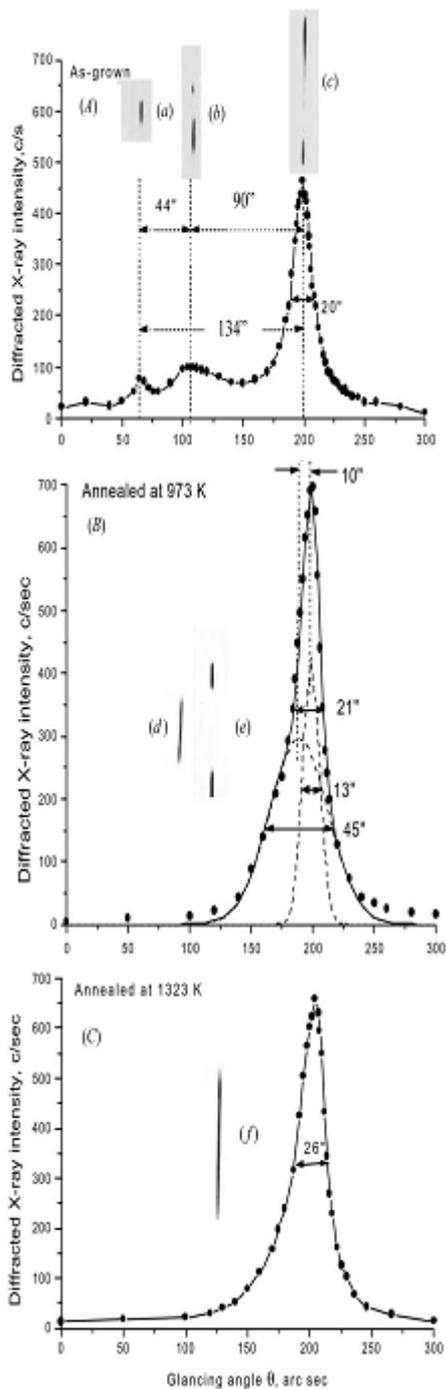
## 1. Introduction

Many important technologies like microelectronics, optoelectronics, communication, computers, photonics, lasers, information science, nuclear science, photovoltaics etc. need well characterized bulk single crystals. The strategic bulk single crystals like silicon, germanium,  $\beta$  barium borate (BBO), lithium iodate ( $\text{LiIO}_3$ ), KN, KDP, LN, Nd:GGG etc. are being routinely grown by different crystal growth methods like Czochralski (CZ), Vertical Bridgman Technique (VBT), solution growth etc. Because of the stringent properties of modern devices based on single crystals, continuous efforts are going on to improve the crystalline quality. Enhancement in the crystalline quality by various novel processing methods during and after growth is possible. Necking<sup>1</sup>, controlling of solid/liquid interface in CZ method<sup>2</sup>, incorporating of dopants<sup>3</sup> or co-dopants<sup>4</sup>, additives<sup>5</sup> and/or introducing after growth processing steps like annealing<sup>6</sup>, reduction<sup>7</sup>, poling<sup>8</sup> etc. are a few examples of such methods. In the recent past with the help of collaborators we have grown and characterized variety of bulk size single crystals like LiF<sup>1</sup>, LN<sup>6</sup>, KN<sup>7</sup>, Nd:GGG<sup>2</sup>, benzophenone<sup>5</sup>, benzimidazole<sup>9</sup>, LT-doped KDP<sup>3</sup>, etc by incorporating such novel processing methods during and after the crystal growth process, which are described briefly in this article.

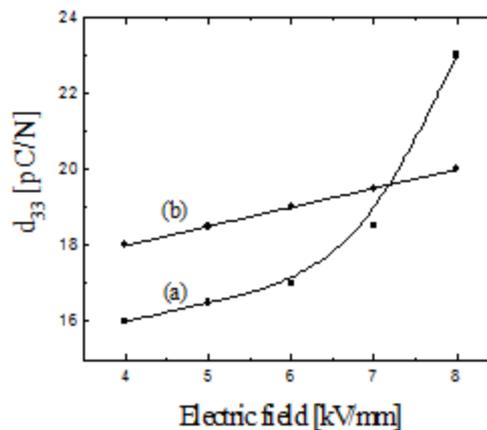
## 2. Experimental, Results and Discussion

### 2.1 Enhancement of crystalline perfection followed by enhanced piezoelectric response due to post growth annealing and subsequent poling in $\text{LiNbO}_3$ Crystals

LN crystals in general grow with cracks and structural grain boundaries as the grown crystal undergoes structural phase transition associated with volume changes. In such crystals annealing was found to be a best method to improve their crystalline perfection as seen in Fig.1<sup>6</sup>. The additional peaks in curve (A) along with the corresponding section topographs depict the very low angle boundaries which are slowly disappeared due to annealing at high temperatures [Curves (B) and (C)]. To verify the effect of annealing on the physical properties, piezoelectric constant ( $d_{33}$ ) was measured at different poling intensities for the chosen specimen at the as grown state and after annealing at a most effective temperature ( $A_T$ ) 1373 K<sup>8</sup>. Fig. 2(a) shows the  $d_{33}$  versus electric field for the annealed specimen at 1373 K where the crystalline perfection was found to increased well<sup>8</sup>. As seen in the figure, poling leads to considerable enhancement in piezoelectric constant  $d_{33}$ . Particularly at 8 kV/mm field,  $d_{33}$  value reached to 23 pC/N, which is much higher than that reported (16.2 pC/N) in the literature. Curve (b) in Fig. 2 shows the  $d_{33}$  versus electric field plot for an un-annealed specimen. By comparing curves (a) and (b), it is evident that though the  $d_{33}$  values at lower fields in case of annealed sample are low (due to misorientation of ferroelectric domains at elevated temperature of 1373 K), the  $d_{33}$  value at higher fields ( $>7.25$  kV/mm) is much higher. From these observations, one can conclude that annealing has a strong effect not only in improving the crystalline perfection as observed from the HRXRD measurements but also in enhancing the piezoelectric response. Considerable enhancement of optical transparency was also observed due to annealing<sup>6</sup>.



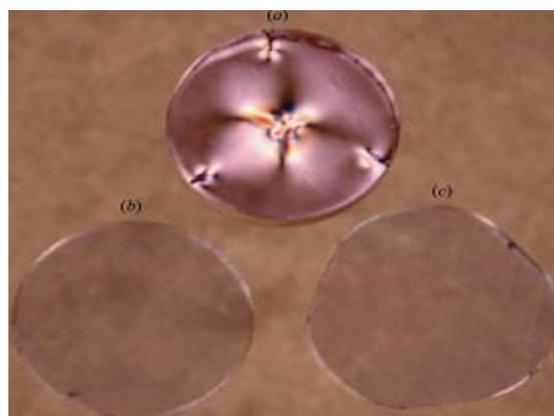
**Figure 1:** Diffraction curves recorded for (006) diffracting planes of the Fe-doped LiNbO<sub>3</sub> single crystal: (A) as-grown, and annealed at (B) 973 K and (C) 1323 K. The insets (a)–(f) are the section topographs recorded at the peak positions.



**Figure 2:** Piezoelectric charge constant  $d_{33}$  versus poling field. Curves (a) and (b) are respectively, for annealed (at 1373 K) and un-annealed specimen.

### 2.2 Effect of crystal/melt interface shapes (convex/flat/concave) on crystalline perfection and optical homogeneity in Nd:GGG

Nd:GGG crystals grown with different crystal/melt interface shapes (convex/flat/concave) by varying seed rotation rate using Czochralski technique were studied for their optical homogeneity and crystalline perfection by optical polarization microscopy (OPM) and high-resolution X-ray diffractometry (HRXRD) respectively<sup>2</sup>. It was found that there is a remarkable effect of seed rotation which decides the shape of the crystal/melt interface on the optical homogeneity and crystalline perfection. Crystals were grown with different seed rotation rates and found experimentally that as the rotation rate increases, the crystal/melt interface changes from convex to flat. If the rate further increases the interface becomes concave. With steep convex interface (for low rotation rates), certain facets are concentrated at the small central portion due to segregation of oxygen leading to optical inhomogeneity [Fig.3(a)], and as the rate increases, these facets slowly move outward and lead to improve the optical homogeneity [Figs.3(a) & (b)] and crystalline perfection<sup>2</sup>.



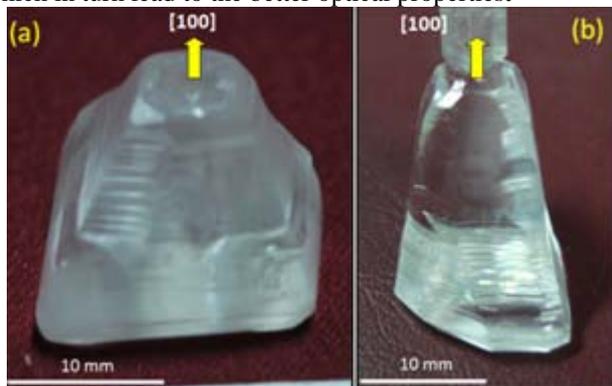
**Figure 3:** Cross-section views of Nd-doped GGG crystals as seen under polarized light. Crystals were grown with different solid/liquid interface shapes: (a) steep convex (b) flat and (c) slight concave.

As it has uniform properties, this kind of crystal can be used

in the form of slab as active medium for high power solid-state laser such as heat capacity solid-state laser (HCSSL).

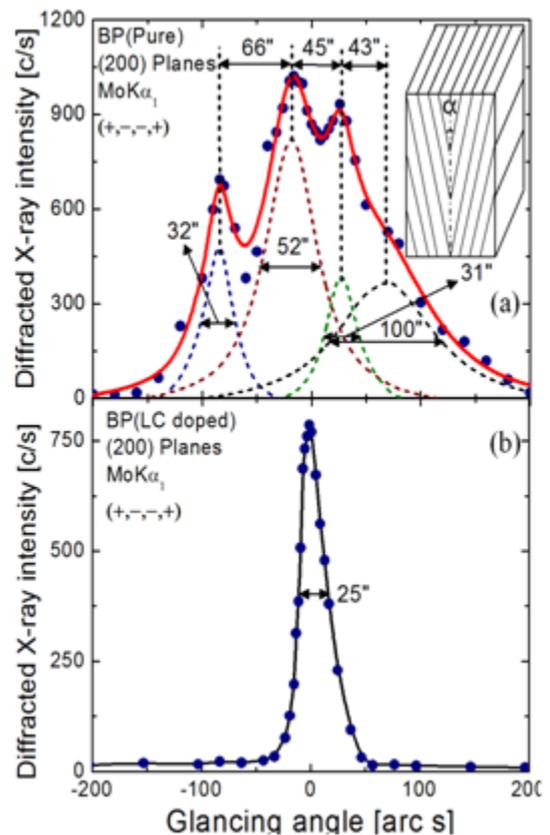
### 2.3 Effect of liquid crystal (LC) additive in Benzophenone (BP) single crystals grown by CZ method

The remarkable enhancement of crystalline perfection of BP crystals (Fig.4) grown by CZ method in the presence of LC as additive in the molten charge has been investigated<sup>5</sup>, which in turn lead to the better optical properties.



**Figure 4:** The (a) and (b) are the photographs of pure and LC doped BP single crystals respectively. The yellow colour upward arrows indicate the growth direction of crystals which is [100].

High resolution X-ray diffractometry (HRXRD) analysis demonstrates that the structural grain boundaries persisting in pure crystals could be eliminated (Fig.5) when the crystal was grown with LC doping (which acted as additive only as it was not entered in the crystalline matrix). The high alignment capability of LC was realized for the first time to enhance the quality of BP bulk single crystals. The LC doped crystal exhibited higher optical transparency over its entire transparency region. The optical polarizing behavior of the doped BP crystal was also found to be improved<sup>5</sup>.

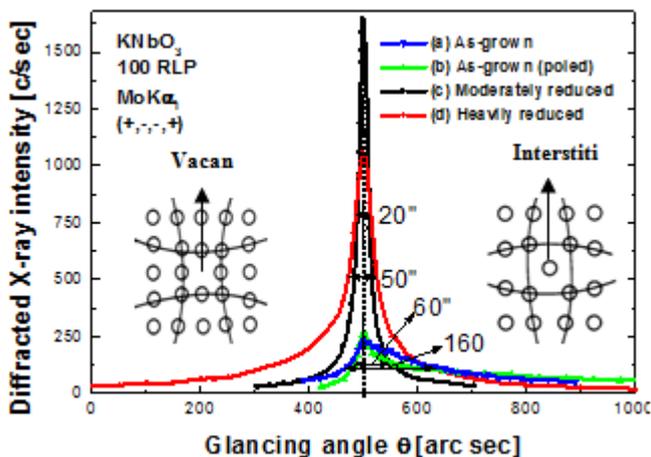


**Figure 5:** High resolution X-ray diffraction rocking curves for (200) diffraction planes of (a) pure and (b) LC doped Benzophenone single crystals. The inset indicates the schematic for a structural grain boundary.

### 2.4 Effect of poling and reduction in Rh-doped $\text{KNbO}_3$

As-grown and reduced Rh doped (1500 ppm)  $\text{KNbO}_3$  (KN) single crystals grown by top seeded high temperature solution method have been characterized<sup>7</sup>. The reduction of the grown crystals at different levels was carried out under a mixture of CO and  $\text{CO}_2$  gases as the crystals were grown with excess oxygen. The effect of reduction and poling on crystalline perfection was studied by HRXRD using an in-house developed Multicrystal X-ray diffractometer. The diffraction curves of as-grown, electrically poled, medium reduced and highly reduced single crystal specimens have remarkable differences. The studies by HRXRD reveals that: (i) Poling has some influence on the improvement of crystalline perfection, (ii) reduction has a great influence on the crystalline perfection; at moderate reduction the crystal becomes very perfect and when the reduction is very high the crystal quality slightly decreased but better than unreduced samples. Asymmetry of the diffraction curves with respect to the peak position reveals that as grown specimens contain high concentration of both vacancies and self interstitials. Due to poling, the concentration of self interstitial defects is reduced to some extent. When the specimen is reduced moderately, the scattered intensity on both the sides of the peak is greatly reduced showing that the concentration of both vacancies and interstitials is reduced to a great extent due to reduction. This clearly indicates that due to reduction of excess oxygen in the crystal, the crystalline perfection is

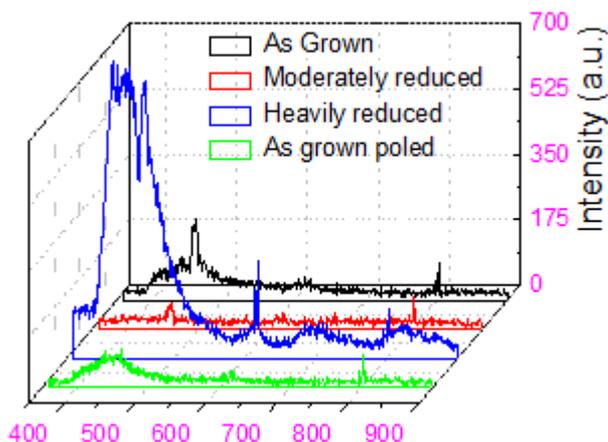
enhanced significantly. However, at heavy reduction, vacancy defects have been increased to a significant extent. The measured Raman scattering, dielectric and photoluminescence (Fig.7) studies also show interesting features with excellent correlation with respect to the crystalline perfection influenced by the process of reduction and poling<sup>7</sup>.



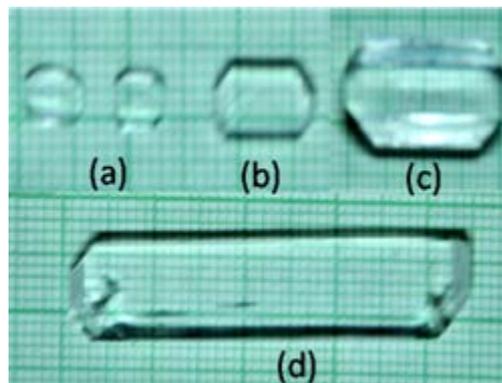
**Figure 6:** High resolution rocking curves: (a), (b), (c) and (d) are respectively for as grown, moderately reduced, heavily reduced and as grown poled specimens, recorded for (100) planes in symmetrical Bragg diffraction geometry. Insets indicate the strained lattice around the vacancy and interstitial defects.

### 2.5 Effect of L-threonine (LT) doping in KDP crystals

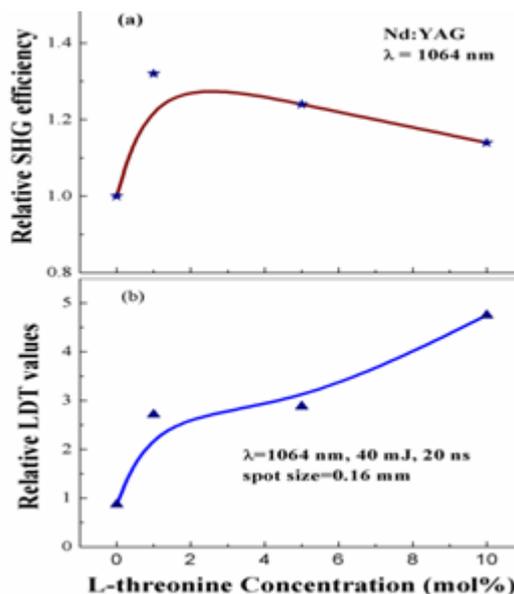
Effect of LT doping on crystalline perfection, second harmonic generation (SHG) efficiency, optical transparency and laser damage threshold (LDT) in potassium dihydrogen phosphate (KDP) crystals grown by slow evaporation solution technique (SEST) has been investigated<sup>3</sup>. The (100) Planes of KDP terminate with K sites, so LT molecules easily interact with these planes due to COO group and lead to the enhancement in crystalline perfection as well as growth rate (Fig.8).



**Figure 7:** Photo luminescence spectra for the as grown, moderately reduced, heavily reduced and as grown poled specimens confirming the fact that heavily reduced sample has good number of vacancy defects in tune with the HRXRD results .



**Figure 8:** SEST grown (a) undoped, (b) 1.0, (c) 5.0 and (d) 10 mol% LT doped KDP single crystals



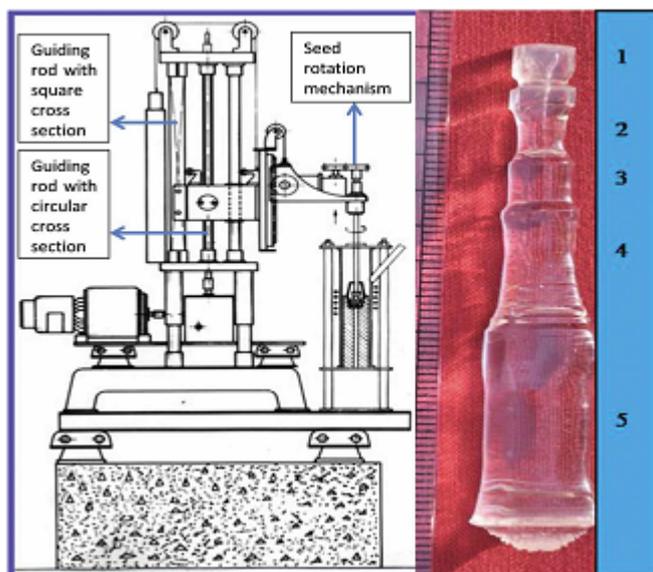
**Figure 9:** Relative (a) SHG efficiency and (b) laser damage threshold of KDP crystals with different doping concentrations of LT.

HRXRD curves indicate that crystalline perfection has been improved to a great extent at low concentrations with a maximum perfection at 1 mol% doping. At higher concentrations (5 to 10 mol%), it is slightly reduced due to excess incorporation of dopants at the interstitial sites of the crystalline matrix. The enhanced crystalline perfection significantly increases the optical transparency of crystals. Due to high transparency, the moderately doped crystals exhibit highly elevated second harmonic generation (SHG) efficiency [Fig 9(a)]. All doped crystals possess high resistance for the laser induced damage threshold, due to the lesser probability of trapping of laser photons [Fig.9(b)].

### 2.6 Effect of necking on LiF crystals

A bulk single crystal of lithium fluoride (LiF) was grown using an in-house developed Czochralski crystal puller [Fig.10]<sup>1</sup>. The effect of necking on crystalline perfection, which in turn was found to influence the optical and dielectric properties, was studied<sup>1</sup>. The necking was performed at two places at different growth lengths (regions#1 and 2). The required diameter control was achieved by slight temperature variations. The crystalline

perfection of the grown crystal was assessed along the length of the boule using high-resolution X-ray diffraction (HRXRD), and it was found that the grain boundaries that were present in the seed crystal were stopped gradually from propagating into the bulk crystal by necking. The UV-vis transparency of the crystal region having best crystalline perfection (region#4) was found to be higher. Photoluminescence (PL) spectra revealed that a crystal region (region#5) that was found to contain vacancy (point) defects by HRXRD yielded the maximum PL intensity because of color centers at the vacancies. The dielectric properties were also studied over a wide range of frequency.

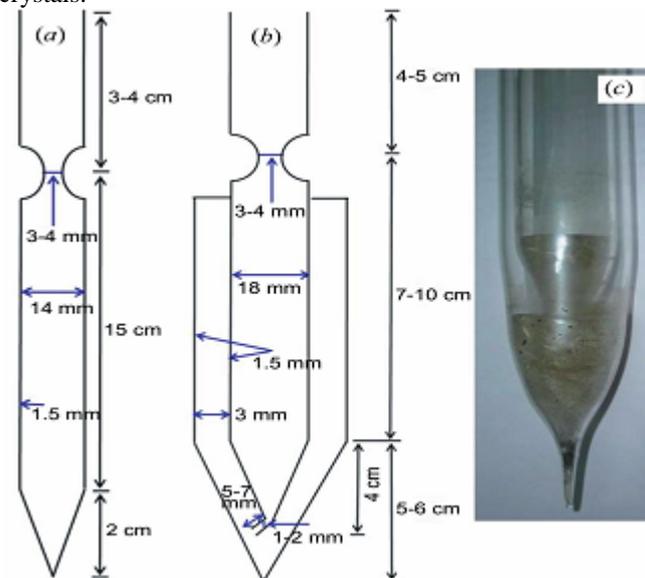


**Figure 10:** Schematic of the home-made Czochralski crystal puller and (b) grown LiF single crystal

### 2.7 Effect of double wall crucible design on benzimidazole single crystals grown by the VBT

Benzimidazole, a potential nonlinear organic crystal was found to grow by the standard VBT melt method. However, due its low melting point and softness being an organic material these crystals grows with grain boundaries<sup>10</sup>. Recently we have tried to grow these with a double walled VBT ampoule and found that the crystalline quality is much better than that grown with single wall ampoule by the same method<sup>9</sup>. The modified VBT ampoule has double-wall with a slope and a narrow open portion at the end of the inner wall. The designed single- and double-walled ampoules are shown in Figs. 11(a) and 1(b). In both ampoules, there is a 3–4 mm opening at the top through which the charge can be filled. The ampoules were made of high-quality glass of thickness 1.5 mm. The inner diameters of the single- and double-walled ampoules are about 14 and 18 mm, respectively. The angle at the bottom of the conically shaped inner wall is about 30 deg, the conical length is 5–7 mm and the double-wall thickness in the conical region is about 1–2 mm. This design helps in restricting spurious nucleations that may be entering from the outer wall and allows only one nucleation to initialize the growth. The conical end of the outer wall normally encourages the initiation of fine nucleation. The double-wall ampoule helps us to avoid thermal fluctuation during and

after growth, and the vacuum inside the growth ampoule also acts as a thermal insulator to ensure good quality single crystals as observed by HRXRD. The improved crystalline perfection was found enhance the optical properties. This study reveals that the present VBT growth method with a double-wall ampoule is effective for growing good quality single crystals of BMZ-like low-melting-point organic crystals.



**Figure 11:** Schematics of the ampoules: (a) single wall and (b) double wall. (c) A double-wall-grown BMZ single crystal within the ampoule.

### 3 Conclusions

Depending upon the nature of the material and the growth technique one can adopt various in situ/after growth processing methods to improve the crystalline perfection of the bulk single crystals and thereby one can improve the device characteristic parameters needed for the advanced technological applications.

### 4 Acknowledgements

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