Journal of
Applied Crystallography
ISSN 0021-8898

Received 6 August 2012
Accepted 10 December 2012

Effect of crucible design on crystalline perfection and the enhanced optical properties of benzimidazole single crystals grown by the vertical Bridgman technique

B. Riscob,[a,b] N. Vijayan,[a] Mohd Shakir,[b] M. A. Wahab[b] and G. Bhagavannarayana[a]*

[a]National Physical Laboratory, Council of Scientific and Industrial Research, Dr K. S. Krishnan Road, New Delhi, 110 012, India, and [b]Department of Physics, Crystal Growth and X-ray Diffraction Laboratory, Jamia Millia Islamia, New Delhi, 110 025, India. Correspondence e-mail: bhagavan@mail.nplindia.ernet.in

Good quality benzimidazole (BMZ) single crystals were successfully grown by the vertical Bridgman technique (VBT). The unavoidable thermal-induced structural grain boundaries formed in the normal VBT growth of these crystals with low melting point were controlled by using a double-wall ampoule. The grown single crystals were subjected to high-resolution X-ray diffraction to assess their crystallinity. The enhancement of optical properties due to the improvement in crystalline perfection is also reported.

1. Introduction

Benzimidazole (BMZ) is a typical organic material having good nonlinear optical properties (three times second harmonic generation efficiency) in comparison with the standard nonlinear optical material, *viz.* potassium dihydrogen phosphate (KDP). BMZ has been grown by a variety of methods (Vijayan, Ramesh Babu *et al.*, 2004; Vijayan *et al.*, 2007; Vijayan, Balamurugan *et al.*, 2004). These studies reveal that the vertical Bridgman technique (VBT) is one of the best methods to grow large size BMZ crystals, but the quality of the grown crystal is very poor, with many structural grain boundaries in comparison to crystals grown by other methods (Vijayan, Bhagavannarayana, Ramesh Babu *et al.*, 2006; Vijayan *et al.*, 2007). This lack of quality arises because of the very sensitive nature of BMZ (it is a low-melting-point and soft organic material, yet it does not decompose at its melting point, which makes it suitable for crystal growth by the melt method) for even minor thermal gradients along the growth ampoule. The present note mainly deals with the improvement of crystalline quality achieved by use of a special ampoule design and the enhancement of optical properties thereby.

2. Experimental

2.1. Ampoule design for crystal growth

In this report, we present a method of growth to achieve good quality benzimidazole single crystals by using a double-wall ampoule 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. 1(*a*) and 1(*b*). In both ampoules, there is a 3–4 mm opening at the top through which they 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°, 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.

2.2. Growth of BMZ single crystals by VBT

The commercially available BMZ powder [purchased from CDH Chemicals (P) Ltd] was zone purified before it was charged into a well cleaned ampoule, which was then evacuated to $\sim 10^{-6}$ Torr (1 Torr = 133 Pa) and sealed carefully. In the present experiment, a specially designed single-zone furnace was used for the growth of BMZ single crystals. The ampoule was translated from the hot zone to the cold

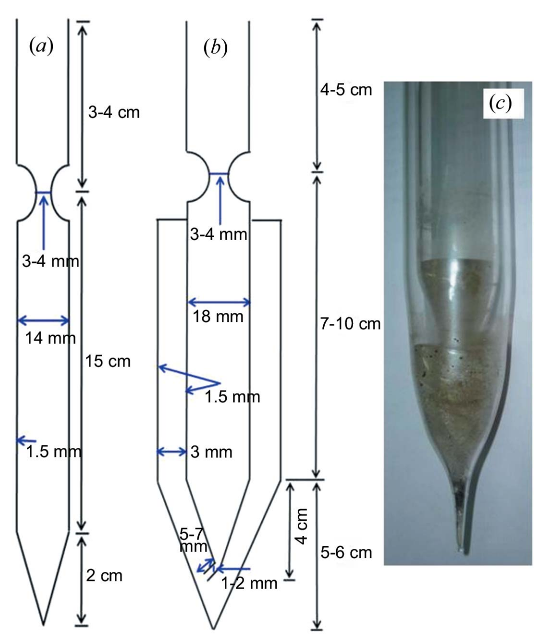

Figure 1
Schematics of the ampoules: (*a*) single wall and (*b*) double wall. (*c*) A double-wall-grown BMZ single crystal within the ampoule.

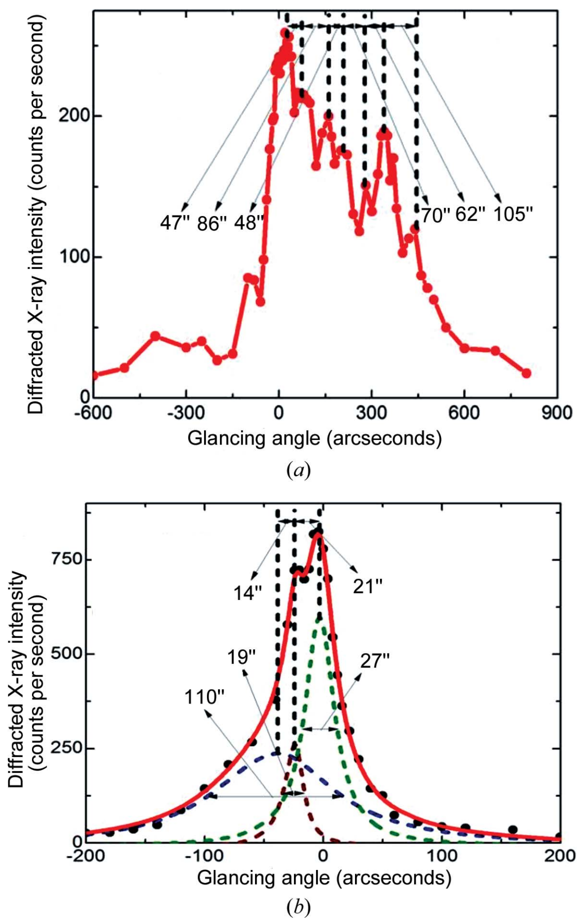

Figure 2
Diffraction curves recorded in symmetrical Bragg geometry for (*a*) single-wall- and (*b*) double-wall-grown BMZ single crystals using (200) diffracting planes.

zone with a precise translation movement (T. E. Brown Barrington & Co). The ampoule translation speed in the present experiment was kept at 1 mm h^{-1}. Transparent single crystals were harvested using the single- and double-walled ampoules in a time span of 10 d. A typical double-wall-grown crystal is shown in Fig. 1(*c*).

2.3. Characterization techniques

The powdered sample of BMZ was analyzed with a Bruker D8 ADVANCE powder X-ray diffractometer. A multi-crystal X-ray diffractometer developed at the National Physical Laboratory (NPL) (Lal & Bhagavannarayana, 1989) was used to evaluate the crystalline perfection of the grown specimen. The optical improvement has been assessed by using UV–Vis and photoluminescence spectrometers.

3. Results and discussion

The lattice parameters obtained from the powder X-ray diffractometry for the grown crystals are a = 13.502 (1), b = 6.811 (1), c = 6.946 (1) Å with the space group $Pna2_1$.

Fig. 2(*a*) shows a typical diffraction curve (DC) recorded for a BMZ specimen grown with the single-walled ampoule for the (200) diffracting planes using Mo $K\alpha_1$ radiation in symmetrical Bragg geometry. As seen in the figure, the DC contains multiple peaks, as observed in earlier studies (Vijayan, Bhagavannarayana, Balamurugan *et al.*, 2006), in an angular range of ~15′. There are six main peaks whose half-widths are in the range of a few minutes, having angular separations ranging from 47 to 105″ as shown in the figure. These multi-peaks indicate that the specimen contains many very low (tilt angle $\alpha \leq 1'$; α may be defined as the misorientation angle between the two crystalline regions on either side of the structural grain boundary) and low-angle ($\alpha > 1'$ but less than a degree) structural grain boundaries. It may be mentioned here that this type of low-angle boundary (Bhagavannarayana *et al.*, 2005) could be found because of the high resolution of the diffractometer. The thermal gradient within the crystal boule along the vertical length of the crucible may be responsible for the thermal stress, which is released later and causes multiple low-angle sub-grain boundaries to form.

Fig. 2(*b*) shows the high-resolution DC recorded for a VBT crystal grown within the inner wall of the double-walled ampoule. The experimental conditions are identical to those of Fig. 2(*a*). The solid line (convoluted curve) is well fitted by the experimental points represented by dots. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 14 and 21″ away from the central peak. These two additional peaks correspond to two very low angle boundaries whose tilt angles are 14 and 21″ from their adjoining regions. The FWHM of the main peak and the low-angle boundaries are, respectively, 27, 19 and 110″. The broad and lower intensity peak with an FWHM of 110″ shows that this particular grain boundary contains mosaic blocks. However, the lower number of peaks and the low angular range of the diffraction curve (~400″) in comparison with that of Fig. 2(*a*) reveals that the crystalline perfection of the crystal grown in the double-walled ampoule is much better than that grown in the single-walled ampoule. This observation is also valid when we compare the crystalline perfection of the earlier investigated single-wall VBT-grown BMZ crystals (Vijayan, Bhagavannarayana, Ramesh Babu *et al.*, 2006).

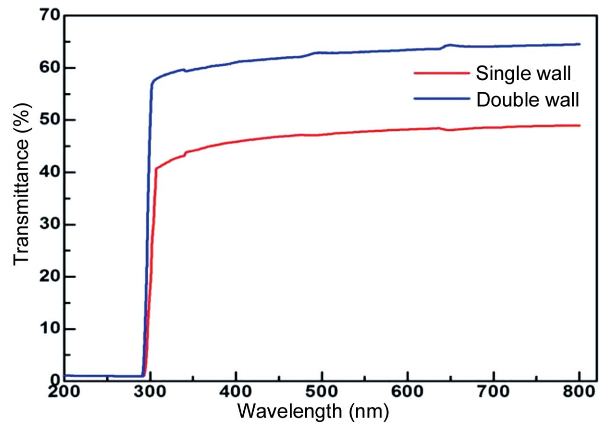

Figure 3
UV-Vis spectra of single-wall- and double-wall-grown BMZ single crystals.

Fig. 3 shows the UV-Vis transmittance spectra of the single- and double-walled crucible-grown VBT crystals; one can see the enhanced transmittance in the specimen grown with the double-walled crucible due to improved crystalline perfection as observed by high-resolution X-ray diffraction and also supported by the improved photoluminescence spectra.

4. Conclusions

The improved crystalline perfection and optical properties of the double-wall-grown crystal suggests 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.

BR acknowledges the Council of Scientific and Industrial Research for the award of a senior research fellowship [31/1/(384)/2012-EMR-I].

References

Bhagavannarayana, G., Ananthamurthy, R. V., Budakoti, G. C., Kumar, B. & Bartwal, K. S. (2005). *J. Appl. Cryst.* **38**, 768–771.
Lal, K. & Bhagavannarayana, G. (1989). *J. Appl. Cryst.* **22**, 209–215.
Vijayan, N., Balamurugan, N., Ramesh Babu, R., Gopalakrishnan, R., Ramasamy, P. & Harrison, W. (2004). *J. Cryst. Growth*, **267**, 218–222.
Vijayan, N., Bhagavannarayana, G., Balamurugan, N., Ramesh Babu, R., Maurya, K., Gopalakrishnan, R. & Ramasamy, P. (2006). *J. Cryst. Growth*, **293**, 318–323.
Vijayan, N., Bhagavannarayana, G., Ramesh Babu, R., Gopalakrishnan, R., Maurya, K. K. & Ramasamy, P. (2006). *Cryst. Growth Des.* **41**, 784–789.
Vijayan, N., Nagarajan, K., Alex, M. Z., Slawin, Shashidharan Nair, C. K. & Bhagavannarayana, G. (2007). *Cryst. Growth Des.* **7**, 445–448.
Vijayan, N., Ramesh Babu, R., Gopalakrishnan, R., Ramasamy, P. & Harrison, W. (2004). *J. Cryst. Growth*, **262**, 490–498.