CHAPTER 6

GROWTH OF $<1\ 0\ 0>$ DIRECTED ADP CRYSTAL
AND ITS CHARACTERIZATION

6.1 INTRODUCTION

The very high-energy Nd-glass lasers used for inertial confinement fusion research need large plates of nonlinear crystals for electro-optic switches and frequency converters (Yoreo et al. 2002, Zaitseva et al. 2002). The approximately 40x40 cm$^2$ aperture of lasers under construction in the US and France, require single crystal boules with linear dimensions in the 50–100 cm range (Li et al. 2005). In recent years, an appreciable attention is given to grow crystals from solutions with high quality and faster growth rates (Zaitseva and Carman 2001). Various techniques have been developed and modifications were carried out in the growth experiments to promote the crystal quality (Balamurugan and Ramasamy 2006, Zaitseva et al. 1999).

One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality (Yokotani et al. 1986). Naturally in ADP and KDP crystals growth, the metallic cations present in the crystals especially ones with high valency were considered to strongly affect the growth habit and optical properties of the crystals. The most dangerous impurities are trivalent metals Cr$^{3+}$, Fe$^{3+}$ and Al$^{3+}$, which make also important habit distortions (Alexandru and Antohe 2003). An impurity can suppress, enhance or stop the growth of crystal completely. It usually acts on certain
crystallographic faces. The effects depend on the impurity concentration, supersaturation, temperature, and pH of the solution (Seif et al 2004).

Even after repeated recrystallization, the presence of small amount of those kinds of impurities in the solution suppresses the crystal quality and growth rate. In order to overcome the problem some dopants are added to suppress the effect of metal ion impurities on ADP and KDP crystals, for example EDTA or KCl reduces the effect of metal ion impurities and enhance the metastable zone width and increases the growth rate of the crystals. The addition of such kind of dopants does not remove the impurities present in the solution, it just reacts with the metal ions and is making complexes. By making complex, the ions become bigger in size and it is not possible to enter into the growing crystal (Podder 2002). It is nowadays taken for granted that interfacial segregation influences a good many crystalline material properties, such as growth, corrosion, creep or diffusion (Benlamari et al 2006).

A growing crystal segregates the unwanted impurities as much as possible, however in SR method growth the growing crystal segregates the unwanted impurities and the segregated impurities are accumulated just above the crystal. After 1 or 2 cm of growth the concentrations of the impurities become higher. The presence of the impurities reduces the growth rate and quality of the crystals. In order to overcome the problem we have recrystallized the raw material several times and the defects caused by the impurities have been reduced. Many of our results assure that the quality of the SR method grown crystal is higher than the conventional method grown crystals (Senthil Pandian et al 2008, Ezhil Vizhi et al 2007). Even though we got such results, we thought that the recrystallization is not only the way to reduce the impurities and providing another way to take the segregated impurities away from the crystal can give good improvement in unidirectional ADP and KDP growth. In this connection, in SR method, a way has been
found to drive the impurities away from the crystal by making slots spread over the ampoule.

Recently many papers give the conclusion that the SR method grown crystals have higher crystalline perfection than conventional method grown crystals. Previous chapters reported the growth of pure ADP and the effect of ammonium malate, L-Lysine monohydrochloride, oxalic acid and Dl-malic acid on ADP single crystals in which the ammonium malate doped ADP crystals show higher crystalline perfection and growth rate. However, the pure ADP along its <1 0 0> orientation is not elaborately discussed. Also the prismatic (100) type faces are much more sensitive to Me$^{3+}$ impurities than the pyramidal (101) faces (Alexandru and Antohe 2003). So, in <1 0 0> directional crystal growth, it is very necessary to take the segregated impurities away from the crystal.

Keeping this in mind, ADP single crystals have been grown along its <1 0 0> direction by (i) SR method and (ii) SR method with slotted ampoule. The grown crystals were characterized by UV visible spectroscopy, high-resolution X-ray diffractometer, dielectric, piezoelectric and laser damage threshold studies. The results obtained are reported herein and discussed. The comparative results of the SR method grown crystal as against the conventional method grown crystal are also presented.

### 6.2 GROWTH OF <1 0 0> DIRECTED ADP SINGLE CRYSTAL BY SR METHOD

Saturated solution of ADP was prepared and the conventional slow solvent evaporation technique was conducted at room temperature in order to collect the seed crystal. Based on the quality of the grown crystals a suitable seed crystal having a size of 30x30x3 mm$^3$ was selected for single crystal growth with <1 0 0> orientation. The orientation is indicated in the
Figure 6.1. To control the spurious nucleation, care has been taken while preparing the growth vessel and the solution. The chosen \(<1\ 0\ 0>\) direction of the seed crystal was mounted in the bottom of the ampoule without polishing the surface. The growth vessel was porously sealed and placed in a dust free chamber. The growth was initiated with a suitable temperature provided by the ring heater at the top region of the saturated solution under equilibrium condition. The effective zone width of the solution and the maximum temperature of the ring heater determine the effective evaporation rate of the solvent for a given diameter of the ampoule thereby the degree of supersaturation. The placement of ring heater at the top of the growth solution also controls the spurious nucleation near the surface region of the solution during the entire growth period. Under optimized condition highly transparent crystal growth was seen. The growth rate was approximately 1 mm/day. After 50 days of the growth 40x40x50 mm\(^3\) size good quality transparent crystal was harvested. The grown crystal is shown in the Figure 6.2 (a). Using the same material ingredients, crystal of size 40x35x50 mm\(^3\) grown by the conventional method is shown in the Figure 6.2 (b). The cut and polished SR method grown crystal is shown in the figure 6.3.
Figure 6.2  Grown ADP single crystals by (a) SR method and (b) conventional method
6.3 CONVENTIONAL METHOD CRYSTAL AS AGAINST THE SR METHOD CRYSTAL

The optical transmission spectra are shown in figure 6.4. It is observed from the figure that both the crystals have sufficient transparency and the ADP crystal grown from SR method has 10% higher transparency than the crystal grown from conventional method in the entire visible and near IR region. The result shows that the SR method grown crystal has higher quality than the conventional method grown crystal. Obtained results are in good agreement with the reported values (Balamurugan and Ramasamy 2008).
Figure 6.4 UV-Vis-NIR spectra of the grown crystals

Figure 6.5 shows the dielectric constant of SR method grown and conventional method grown ADP crystals as a function of temperature. It is observed from the figure that dielectric constant increases with increase in temperature. From the Figure 6.5, it is noted that dielectric constant is higher in SR method grown ADP crystal than the crystal grown by conventional method. In order to get the reproducibility the above experiment was repeated several times and the same results were obtained for all the crystals. The reproducibility was observed clearly.

Dielectric loss obtained in the present study for SR method grown ADP crystal and conventional method grown ADP crystal are shown in the Figure 6.6. Dielectric loss increases with increase in temperature for the crystal grown by both the methods at 1 kHz. It is seen in the Figure 6.6 that low dielectric loss is obtained for SR method grown ADP crystal compared to the crystal grown by conventional method. Thus it is known that, if the grown crystal contains minimum defects the values of dielectric loss will be less.
Figure 6.7 shows the relation between the hardness and load. The hardness of ammonium dihydrogen phosphate increases with increase of load for both of the crystals. The cracks were formed in the conventional method grown crystal at 100 g. But no cracks were observed up to 100 g in the crystal grown by SR method. This again confirms that the mechanical property of the SR method grown ADP single crystal is also better than the crystal grown by conventional method. Hardness is the resistance offered by a solid to the movement of dislocation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. Higher hardness value for SR method grown crystal indicates that greater stress is required to produce dislocations thus confirming greater crystalline perfection. Similar results were reported in KDP crystal (Balamurugan and Ramasamy 2008).

![Dielectric constant vs Temperature](image)

**Figure 6.5** Plot for dielectric constant and temperature
Figure 6.6 Plot for dielectric loss and temperature

It is known from the above three results that the crystalline perfection of the SR method grown ADP crystal is higher. The higher crystalline perfection indicates that the dislocation is very low in SR method grown crystal. The generations of the dislocations are strongly correlated with the formation of the inclusion of the crystals. Depending on the shape of the seed crystal inclusion may arise. If the important habit faces do not bound the seed, the facet of these will be formed in the early stages of growth. The area between these facets develops terraces parallel to the habit faces. In these areas solvent is easily trapped into the crystal. It is also observed that dislocations can originate from the growth sector boundaries (Bhat 1985). In SR method, as the growth is only on morphology defined facet the dislocations of the above causes are avoided.
Figure 6.7 Plot for Vickers microhardness

Bulk single crystals of ADP have been grown successfully by conventional method and also by SR method. Higher transparency and higher hardness values have been achieved in SR method grown crystal compared to the crystal grown by conventional method. Dielectric measurements reveal that dielectric constant is high and dielectric loss is low in SR grown crystal compared to the crystal grown by conventional method. In order to enhance the crystalline perfection of the <1 0 0> ADP single crystal, a modification has been done and it is discussed in the coming sections.

6.4 GROWTH OF <1 0 0> DIRECTED ADP WITH SLOTTED AMPOULE

6.4.1 Crystal Growth

The commercially available ADP was used for growth, after two times of recrystallization. Saturated solution of ADP (1500 ml) was prepared
at 33 °C. SR method setups were arranged to grow unidirectional ADP crystals. Suitable seed crystals of size 20 mm in diameter and 5 mm in thickness were selected for single crystal growth of <1 0 0> face. To control the spurious nucleation, care has been taken while preparing the growth vessels and the solutions. The chosen <1 0 0> plane of the seed crystal was mounted in the bottom of the ampoule without polishing the surface. The solution was prepared at 33 °C and it was overheated to 35 °C for a few hours and again reduced to 33 °C. The solution was filtered using Whatman filter paper. Filtered solution was carefully transferred into the growth vessel. The growth vessel was porously sealed and placed in a dust free chamber. The growth was initiated with a suitable temperature provided by the ring heater at the top region of the saturated solution under identical condition. The applied temperature at the top of the ampoule was 38 °C and at the bottom 33 °C. The ring heater at the top of the growth solution controls the spurious nucleation near the surface region of the solution during the entire growth period. Under optimized condition, after 10 days transparent crystal growth was seen. The growth rate was approximately 1 mm/day for the given ampoule of diameter 45 mm. After 50 days of the growth a good quality crystal of size 35 mm in diameter and 40 mm in length was harvested. Similarly, in the same time, in another SR method setup, in order to drive away the impurities present in the solution many identical slots were made in the ampoule with equal distance above the seed mounting pad.

A crystal when it is growing segregates the impurities and all the segregated impurities are staying near to the growing crystal and there is no way to go away from the region in the normal SR method experimental assembly. When the concentration of the segregated impurities increases the quality of the crystal will become bad. It is well known that the matter diffuses from regions of high concentration to regions of low concentration. The slots made in the ampoule allow diffusion of impurities from the high concentration to the low concentration medium, that is the impurities present
near the crystal diffused to the outer ampoule and several slots were made to continue this process through out the crystal growth process. The slots are in rectangular shape and 6 mm in length and 2 mm in breadth. The diagram of the ampoule with slots is shown in the Figure 6.8.

It is expected that the impurities segregated by the growing crystal diffuse away from the crystal vicinity to the outer ampoule thus avoiding the defects in the crystal and other deleterious effects of the impurities. Similar seed crystal of size 20 mm in diameter and 2 mm in thickness was selected for single crystal growth of \(<100\) face, and it was mounted carefully in the slotted ampoule. The ampoule is placed into another big ampoule. Saturated solution of ADP (900 ml) was used for growth. The solution was prepared at 33 °C and it was overheated to 35 °C for few hours and again reduced to 33 °C. The solution was filtered using Whatman filter paper. Filtered solution was carefully transferred into the growth vessel. Both the inner and outer ampoules are now filled with the solution. It is arranged such that the inner ampoule is just taller than the outer ampoule because, the inner ampoule is covered with porously sealed cover and allowed for controlled evaporation and the outer ampoule is covered fully and no evaporation is allowed. The ring heaters placed on the top and bottom of the outer ampoule are providing necessary temperatures. Similar temperatures were applied and after 10 days, under optimized condition highly transparent crystal growth was seen.

The growth rate was approximately 1.5 mm/day for the given ampoule of diameter 45 mm. The growth setup and grown crystal with slotted ampoule is shown in the Figure 6.8. After 40 days of the growth a good quality crystal of size 40 mm in diameter and 45 mm in length was harvested. The grown crystals are shown in the Figure 6.9. Ammonium dihydrogen phosphate used in the present study was bought from M/S. Merck (GR grade), India and the deionized water got from Millipore water purification unit. The resistivity of the used deionized water is 18.2 MΩ cm.
Figure 6.8 Slotted ampoule diagram
Figure 6.9  Crystal grown by (a) SR method and (b) SR method with slotted ampoule
6.4.2 Growth Rate

The main limitation in growth of large crystals by traditional techniques is growth rates of only 0.5 - 1 mm/day typical for low-temperature solution growth. Slow growth leads to growth cycles for long period (Zaitseva and Carman 2001). The difficulties in providing reliable equipment, the high risk of failure, and defect formation during such long periods result in low yield and high cost of the final crystals. These reasons stimulated development of new techniques to accelerate the growth without sacrificing optical quality of large crystals.

In the slow evaporation method using the same materials ingredients the achieved growth rate along slow face was less than 0.5mm/day and in the case of SR method it was 1 mm per day whereas in SR method with slotted ampoule it was 1.5 mm per day. This indicates that, as said by Zaitseva and Carman (2001) increasing the chemical purity by segregating the impurities to outer ampoule resulted in raising the growth rate of the crystal.

6.5 CHARACTERIZATION

6.5.1 UV-Vis-NIR Studies

Optical transmission spectra were recorded for the crystals in various places in the wavelength region from 200 to 1100 nm using Perkin-Elmer Lambda 35 UV-Vis spectrometer. It is given in the Figure 6.10. It is observed from the figure that the ADP with slotted ampoule shows more than 80% of transmittance. In order to confirm the reproducibility, several times the beam was passed through the various regions of the crystal and the same results were observed. The conventional method grown ADP has 52 % transmittance and SR method grown ADP without slots has transmittance of about 60% in the entire visible region. In conventional and SR methods, the used crystal samples were of thickness 2 mm only, whereas in the case of SR
method with slotted ampoule the used crystal was as grown and thickness was 35 mm. The large transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications. Usually the addition of organic materials significantly increases the transparency of parent crystals. Srinivasan et al (1998) have shown 70% of transparency of pure ADP in the visible region. L-arginine monohydrochloride and L-alanine increase the transparency of ADP crystals (Dhanaraj et al 2008). L-glutamic acid, L-histidine and L-valine increase the transparency of KDP crystals (Kumaresan et al 2008). ADP and KDP crystals grown from deuterium show more than 80% of transparency in the entire visible region (Li 2005, Genbo 2002). The ADP crystal grown by slotted ampoule also shows approximately same transparency and indicates that the crystal has higher crystalline perfection and is suitable for device fabrications. The above results indicate that the impurities segregated during crystal growth diffused to the outer ampoule and resulted in the increase of transmittance of the grown crystals.

Figure 6.10 UV-Vis-NIR spectra of the grown ADP crystals with and without slots in the ampoule
6.5.2 HRXRD Analysis

Figure 6.11 (a) shows the high-resolution diffraction curve (DC) recorded for a typical $<1\ 0\ 0>$ directed ADP crystal grown by SR method specimen using (200) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoK$\alpha_1$ radiation. The DC of the specimen contains a single peak and shows that it is free from structural grain boundaries. The FWHM is 38 arc s. It is interesting to see the asymmetry of the DC with respect to the peak position denoted by the dotted line at zero position. For a particular angular deviation ($\Delta \theta$) of glancing angle with respect to the peak position, the scattered intensity is much more in the negative direction in comparison to that of the positive direction. This feature clearly indicates that the crystal contains predominantly vacancy type of defects rather than interstitial defects. This can be well understood by the fact that due to vacancy defects or voids in the crystalline matrix, the lattice around these defects undergoes tensile stress and the lattice parameter $d$ (interplanar spacing) increases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly lower Bragg angles ($\theta_B$) as $d$ and $\sin \theta_B$ are inversely proportional to each other in the Bragg equation ($2d \sin \theta_B = n\lambda$; $n$ and $\lambda$ being the order of reflection and wavelength respectively which are fixed). Fast growth rates of the crystals sometimes lead to this type of vacancy defects. However, these point defects with much lesser density as in the present case (if the concentration is high, the FWHM would be much higher and often lead to structural grain boundaries) hardly give any effect in the performance of the devices made by such crystals.

Figure 6.11 (b) shows the high-resolution diffraction curve (DC) recorded for SR method with slotted ampoule grown ADP single crystal for (200) diffracting planes. As seen in the figure the DC is quite sharp without any satellite peaks. The full width at half maximum (FWHM) of the diffraction curves is 10 arc s, which is quite low and close to that expected from the plane wave theory of dynamical X-ray diffraction (Betterman and Cole 1964). The
single sharp diffraction curve with very low FWHM and perfect symmetry with respect to the peak position indicates that the crystalline perfection is quite good. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries (Bhagavannarayana et al 2005). Its perfection is slightly better than that grown by conventional method (Bhagavannarayana et al 2008).

Figure 6.11 HRXRD curves of (a) SR method grown crystal (b) SR method with slotted ampoule grown crystal
In the chapter 5, it is reported that the FWHM of Dl-malic acid doped ADP grown by SR method shows 17 arc s. Similarly in KDP growth the obtained FWHM is 20 arc s. Even the <0 0 1> direction grown crystal contains the interstitial type of defects (Balamurugan et al 2009), whereas in the present case it is eliminated. The FWHM of <1 0 0> directed ADP grown in the ordinary ampoule is very large compared to this and it confirms that the prismatic sector inhibits more trivalent ions. Subsequently ammonium malate doped ADP grown by slow cooling along with seed rotation technique, given in chapter 2, shows 5.5 arc s FWHM, but in the present case, though the value is slightly higher, the achieved growth rate is more along the specific orientation. Comparing the results it is known that the crystal grown by slotted ampoule has higher crystalline perfection.

6.5.3 Dielectric Studies

Using Agilent 4284-A LCR meter, the capacitances of the crystals were measured for frequencies 100, 1 k, 100 k and 1 MHz at various temperatures. The extended portions of the crystals were removed completely and the crystals were ground to proper thickness and polished. A sample of dimension 9x9x2 mm$^3$ having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. Figures 6.12 (a) shows the temperature dependence of dielectric constant of the ADP crystals at frequency 100 Hz. It is observed from the figure that the dielectric constant increases with increase in temperature up to 140 °C. This shows there is no phase transition between the measured temperature ranges. This is normal dielectric behaviour of an antiferroelectric ADP crystal (Lines and Glass 1977). The same behaviour was observed for all the frequencies (not shown in the figure). The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies. At low frequencies, all
these polarizations are active. The space charge polarization is generally active at low frequencies and high temperature. It is seen from the figure that the dielectric constant is higher in ADP crystal grown by slotted ampoule than the other crystals at the measured frequencies.

The dielectric loss of the grown crystals for various temperatures at the frequency was measured. It is observed that the dielectric loss increases with increase in temperature for the crystals grown by all of the methods. Figure 6.12 (b) shows the dielectric loss of the grown crystals at 100 Hz. It is also observed from the figure that dielectric loss is low for slotted ampoule grown ADP crystal than the conventional and ordinary ampoule grown crystal. The low values of dielectric loss indicate that the grown crystal contains minimum defects.

6.5.4 Piezoelectric Studies

The piezoelectric studies were made using piezometer system. A precision force generator applied a calibrated force (0.25N) which generated a charge on the piezoelectric material under test. The output was measured directly from oscilloscope which gives the $d_{33}$ coefficient in units of pC/N. Without poling the crystal the piezoelectric measurement was carried out for the grown crystals. A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied. The piezoelectric property is related to the polarity of the material. The obtained piezoelectric coefficient ($d_{33}$) value for conventional method grown pure ADP is 0.12 pC/N, SR method grown $<1 0 0>$ directed ADP is 0.30 pC/N and for slotted ampoule $<1 0 0>$ directed ADP is 0.45 pC/N. Approximately four times higher $d_{33}$ value has been obtained for the slotted ampoule grown ADP crystal compared to conventional method grown pure ADP. Higher crystalline perfection may be the reason for the same.
Figure 6.12  Temperature dependence of (a) dielectric constant (b) dielectric loss at 100 kHz
6.5.5 Laser Damage Threshold Studies

Like other optical materials used in Laser technology, NLO crystals are susceptible to optically induced catastrophic damage. Optical damage in non-metals (dielectrics) may severely affect the performance of high power laser systems as well as the efficiency of optical systems based on nonlinear process and has therefore been subjected to extensive research for some 30 years. From this viewpoint, we carried out laser damage threshold measurements on the grown crystals using an actively Q-switched diode array side pumped Nd:YAG laser. The pulse width and the repetition rate of the laser pulses were 7 ns and 10 Hz, respectively, at 1064 nm radiation. For this measurement, a beam was focused onto the sample with 8 cm focal length lens. The beam spot size on the sample was 70 μm.

Figure 6.13: Cracks obtained in the crystal during laser damage threshold studies (a,b) SR method grown crystal (c) SR-method with slotted ampoule grown crystal
Two similar ADP samples (one was SR method without slot and the other one was SR method with slot) were prepared for laser damage threshold studies. The beam was passed along the <1 0 0> direction for both crystals. Initially 30 mJ was applied on the surface of the crystal and within a few seconds a crack was seen. In the same crystal the experiment was repeated second time with 15 mJ of energy and after 23 s damage was seen in the second place. In the case of SR method grown crystal with slotted ampoule, initially 25 mJ was applied and upto 60 s no crack was seen and the experiment was repeated for 30 mJ and after 20 s a small dot was seen on the surface and finally a crack was seen when applying 34 mJ for 10 s. The observed cracks are shown in the Figure 6.13. The calculated damage threshold for the crystal grown by slotted ampoule is 125 Gw-cm\(^{-2}\) and for the crystal without slotted ampoule it is 53.79 Gw-cm\(^{-2}\). The laser damage threshold of ADP crystal grown with slotted ampoule is higher than the crystal grown without slots in the ampoule. Sankaranarayanan and Ramasamy also showed that the damage threshold for the SR method grown benzophenone is higher than the conventional grown crystal (Sankaranarayanan and Ramasamy et al 2005). The higher crystalline perfection of SR method (with slotted ampoule) grown crystal may be responsible for larger laser damage threshold. Nishida et al (1988) used KDP samples with few dislocations in which the organic impurities seemed to play a main role in causing bulk laser damage. Newkirk et al (1983) showed no direct relation between the dislocation in KDP crystals and the damage threshold.

### 6.6 CONCLUSIONS

The slots made in the ampoule segregated the impurities present inside the solution and improved the quality of crystal. High quality ADP crystal was grown of size 45 mm in length and 40 mm in diameter with higher growth rate. The slotted ampoule grown crystal is found mechanically harder
and with higher optical transmission than the other crystals. The crystal shows higher piezoelectric charge coefficient and higher crystalline perfection because of having better optical quality. The laser damage threshold is directly related to the impurities present in the crystal and the measured higher laser damage threshold indicates the suitability of the crystal for device fabrications. SR method with this modification will be useful to grow high quality crystals with relatively higher growth rate in desired orientation.