Optical bandgap modification in unidirectionally grown pure and doped potassium dihydrogen phosphate

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Abstract: Potassium dihydrogen phosphate (KDP) is an excellent nonlinear optical material that has many potential applications, such as laser frequency conversion, Q-switches, Pockels cells, 3-D optical data storage devices, etc. Doping enhances various optical parameters of KDP. Unidirectionally grown crystals are always a matter of interest for the researchers and industry due to their specific applications. In the present study KDP crystals are grown in a direction and their modification of optical properties with doping with aspartic acid, succinic acid, glycine, and L-alanine were investigated. The grown samples were tested for temperature stability using TGA/DTA analysis.

Keywords: Potassium dihydrogen phosphate, Unidirectional growth, Tauc Plot, Optical bandgap, Absorbance.

1. INTRODUCTION

The progress in crystal growth techniques helped researchers to grow crystals of various dimensions based on the requirement for specific applications. Potassium dihydrogen phosphate KH_2PO_4(KDP) is an excellent nonlinear optic and electro-optic material. It is one of the crystals that can be grown to large size. But the unidirectional growth and variations in its optical parameters are not investigated much. The present study attempt to grow the KDP crystals in one direction and to modify their properties by doping with various dopants such as aspartic acid, glycine and L-Alanine and succinic acid.

2. EXPERIMENTAL

2.1 Materials used for synthesis

Potassium dihydrogen phosphate, Aspartic acid, Glycine, L-Alanine, De ionized water

2.2 Equipment

We used a crystallizer which is suitable for slow cooling solution growth. It is a double walled chamber fitted with vertically opposite quarts windows and rotatable seed holder which can be mechanically lifted up as the crystal grows to restrict the growth in a single direction as in the case of a Czochralski Crystal puller. So, it is a miniature combination of Czochralski crystal puller with slow cooling solution growth.



Figure 1: The Crystallizer

The growth of the crystal can be monitored using a laser shadowgraph arrangement that set up along with the crystallizer. The temperature of the supersaturated solution can be reduced from 50 ^{o}C to 20 ^{0}C with the help of a PID based temperature controller.

2.3 Material Synthesis

Supersaturated solution is prepared by dissolving analar grade KDP in de ionized water and filtering and dissolving again to eliminate micro clusters or any dust particles. Supersaturated solution is transferred to the crystallizer and the saturation temperature is determined by inserting a seed and monitoring using shadowgraph. It is then set for the slow cooling growth by programming the temperature controller to cool from the saturation temperature to 20 ^{o}C. By monitoring using shadowgraph and operating the crystal puller, the seed is slowly pulled up so as to restrict the growth happens only along the axis of pulling. There should be a match between the cooling rate and the pulling rate for getting best results. The pulling motor speed is adjusted accordingly. Doped samples are also prepared using the same method. The grown crystals are shown in figure 2.

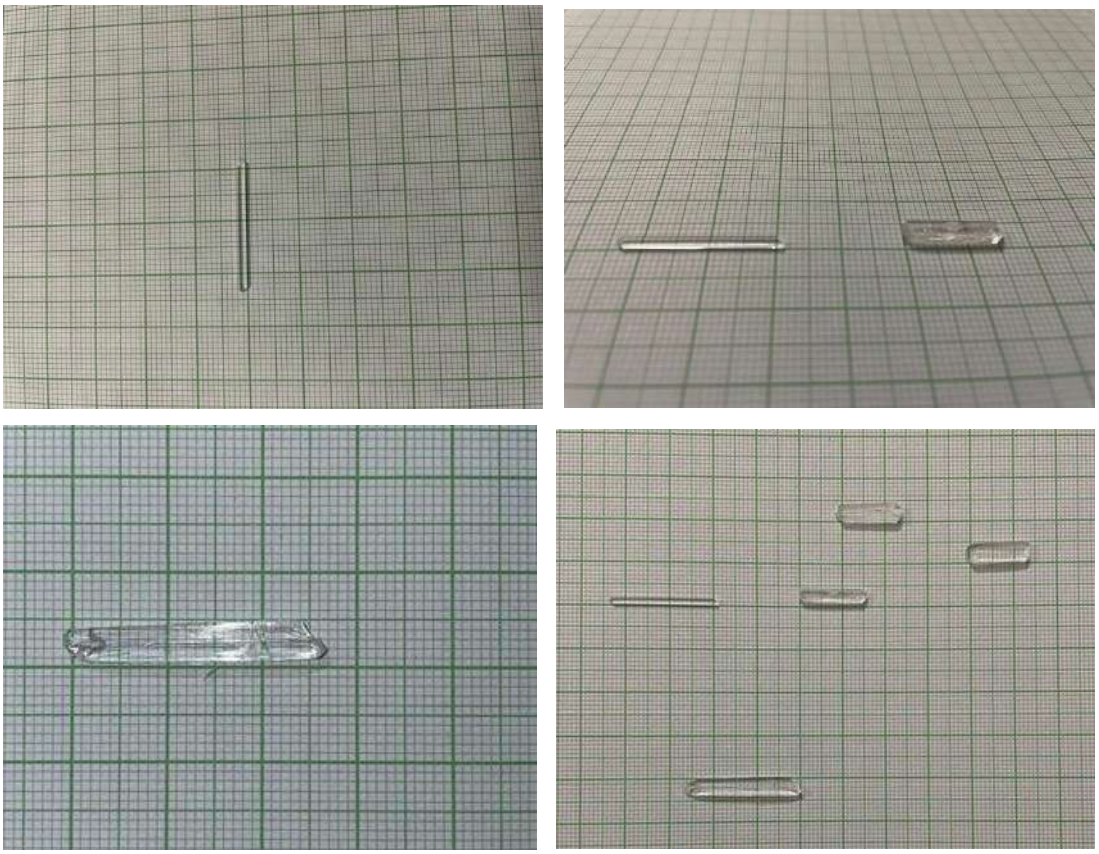


Figure 2: The grown crystals

3. CHARACTERIZATION

3.1 Optical bandgap

The optical bandgap of the grown samples was determined from Tauc Plot using the absorbance data obtained from UV-Vis-NIR spectroscopy. The absorbance data obtained is shown in the table 1. The Tauc plot is shown in Figure 3. The thermal stability of the grown samples is determined by TGA/DTA analysis and is shown in Figure 3. The doped samples are found to be equally stable to thermal variations, in comparison with the pure sample.

Sample	Bandgap eV
Pure	5.36984
AKDP	5.58443
LA-KDP	4.48953
GKDP	4.89067
SA-KDP	5.19061

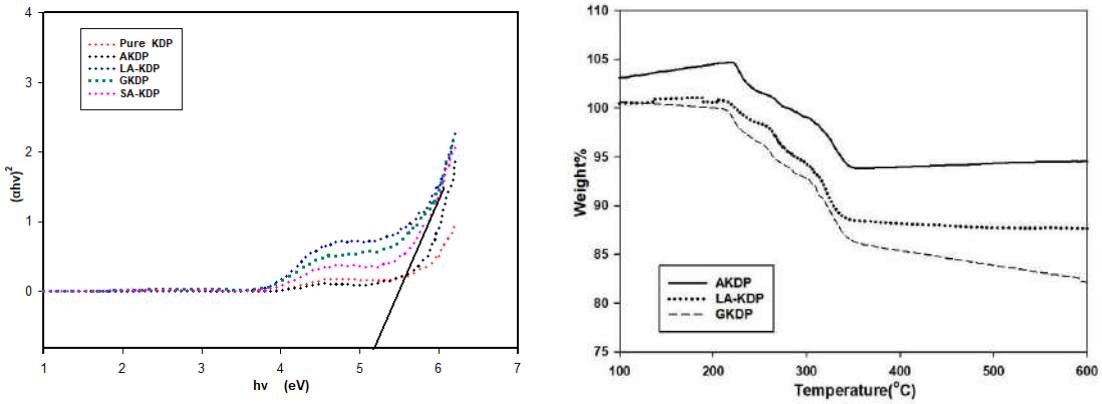


Figure 3: (i) Tauc Plot (ii) TGA

4. RESULTS AND DISCUSSION

Unidirectional single crystals of pure and doped KDP were grown from supersaturated solution using slow cooling solution growth technique. It is shown that the band gap is modified by doping. The bandgap of samples like LA-KDP, GKDP and SA-KDP decreased to 5.58443 eV, 4.48953 eV, 4.89067 eV and 5.19061 eV respectively and that of AKDP increased to 5.58443 eV in case of AKDP. The modification in band gap is due to the change in the electronic transition that induced due to doping. Also, the doped samples are equally stable to variations in temperature, in comparison with the pure sample.

5. CONCLUSION

Thermally stable, unidirectional pure and doped crystals of KDP were grown and characterized. The modification in bandgap is an important parameter as it gives a way to modify the crystal to fit for desired applications. Or we can prepare crystal to grow in a direction as well as we can tune the bandgap of the crystals to match the requirement.

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