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Growth and electro-optic studies in mixed $(NH_4)_x K_{1-x}H_2PO_4$ single crystals

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Abstract. Single crystals and mixed crystals of KH_2PO_4 (KDP) and $NH_4H_2PO_4$ (ADP) were grown with different dopant concentrations of $NH_4H_2PO_4$ in KH_2PO_4 in solution by Holden's rotary crystallizer technique. The effect of additives like Borax ($Na_2B_4O_7 \cdot 10H_2O$), seed crystal rotation rate and qualities of the crystals were studied. The half-wave voltages (in longitudinal mode) for KDP mixed with 1% ADP (by weight) were found and hence the unclamped (low frequency) electro-optic coefficients (r_{63}) were calculated for various wavelengths in the visible region of the spectrum. It was noted that the half-wave voltage increases with increase in wavelength and temperature.

Keywords. Electro-optic studies; crystal growth.

1. Introduction

Investigation of the electro-optic properties of crystals is important because these crystals find widespread applications in quantum electronics and opto-electronics. Single crystals of different sizes and ratios along various crystallographic directions are needed to suit the geometry of the electro-optic device in which the crystals are to be used. An attempt was made in the present work to obtain sufficiently thick single crystals for carrying out electro-optic studies. Borax was found to be (Brice 1973) one of the best additives for obtaining sufficiently large size, of KDP and their mixed crystals.

2. Experimental set-up

2.1 *Crystal growth*

Holden's rotary crystallizer technique (Laudise 1970) was employed to grow KDP and the mixed crystals of KDP and ADP (see figure 1). This was used to obtain single crystals either by slow evaporation or by slow cooling techniques. It has a cylindrical glass tank of 3 litres capacity wound with heating tap (about 1 kW), controlled by the contact thermometer and maintaining a saturation temperature of the solution. The crystal holder was a glass rod with a paddle arrangement. The rotor speed was optimized by trial and error for each kind of solution. In mixed crystals of ADP and KDP the optimum speed was between 1 and 30 rpm. The crystals were grown by slow evaporation Holden's rotary crystallizer method at a constant temperature. An optimum temperature of 36°C was used to obtain large sized and optical quality KDP crystals with 1%, 2%, 3%, 4% ADP of dimensions (35 x 10 x 10mm). Higher percentages of ADP in KDP resulted in needles.

Borax was found to be a suitable additive to increase the axial ratios of ADP and KDP crystals. Solubility studies of both ADP and KDP with different percentages of borax in triple distilled water were carried out using a constant temperature water bath as shown in figure 2. This was a fibre reinforced plastic tank holding 30 litres of water and covered by a plastic sheet to hold the contact thermometer, motor (to agitate water) and the heater. The temperature of the solution was controlled by an order of ± 0·1°C. Figures 3 and 4 represent the solubilities of ADP and KDP as a function of temperature in 100 ml of water containing different quantities of borax. It was observed that the pyramidal faces of KDP crystals were contracted and the growth rate along direction perpendicular to [001] increased.

2·2 *Polishing and testing*

Most of the crystals grown had well-defined faces and it was possible to fix the orientation of some crystallographic axis with respect to the faces of the crystals. A slice of the grown crystal was cut (using diamond wheel) perpendicular to long axis, ground using silicon followed by Al_2O_3 powders on soft beeswax lap with light weight lubricating oil. Light input and exit surfaces of

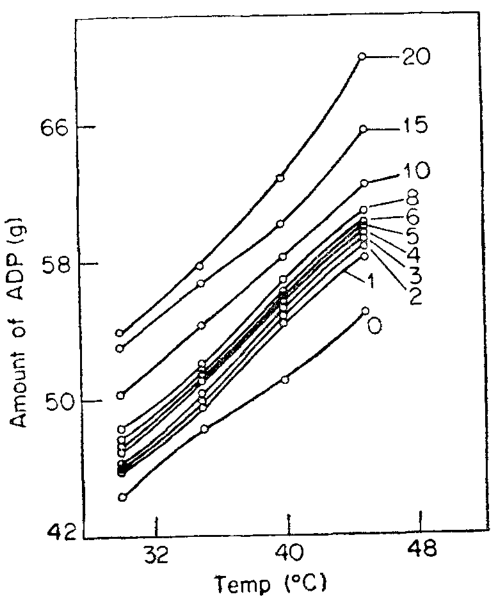

Figure 3. Solubility of ADP in water with borax as a function of temperature.

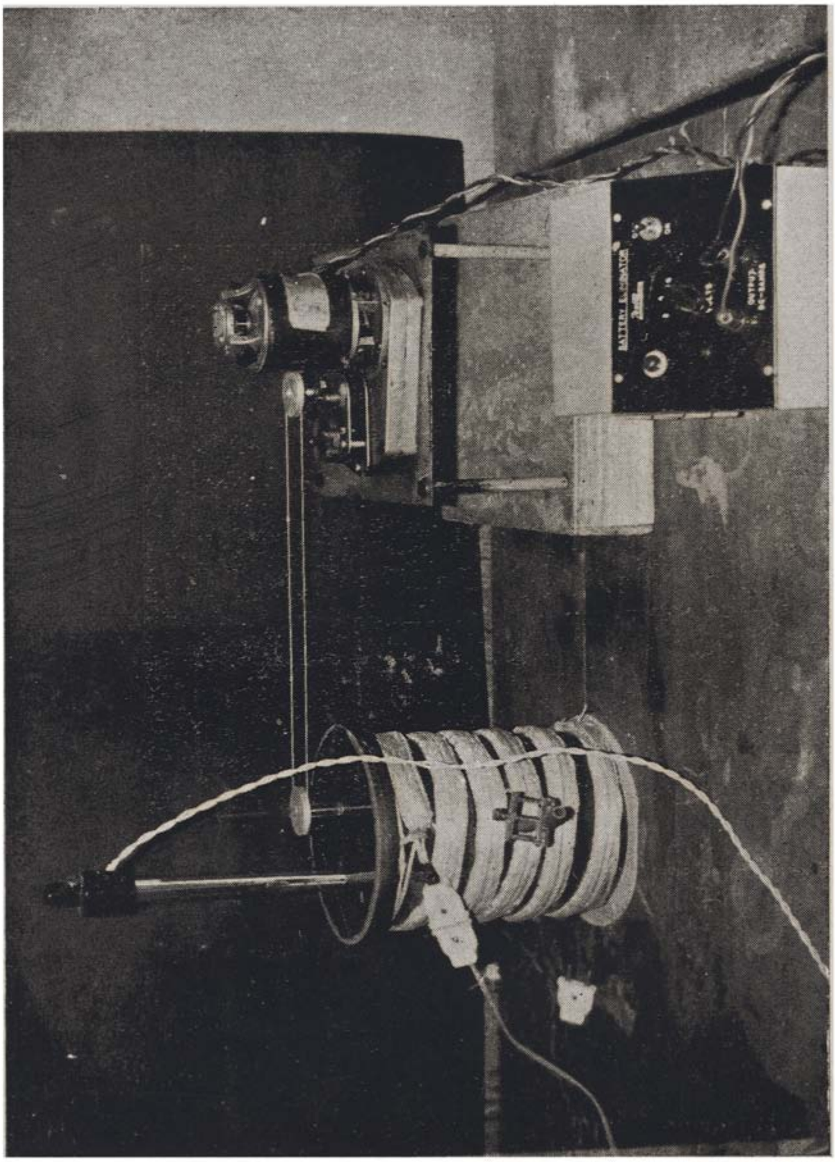

Figure 1. Holden's rotary crystallizer technique for growing crystals in solutions.

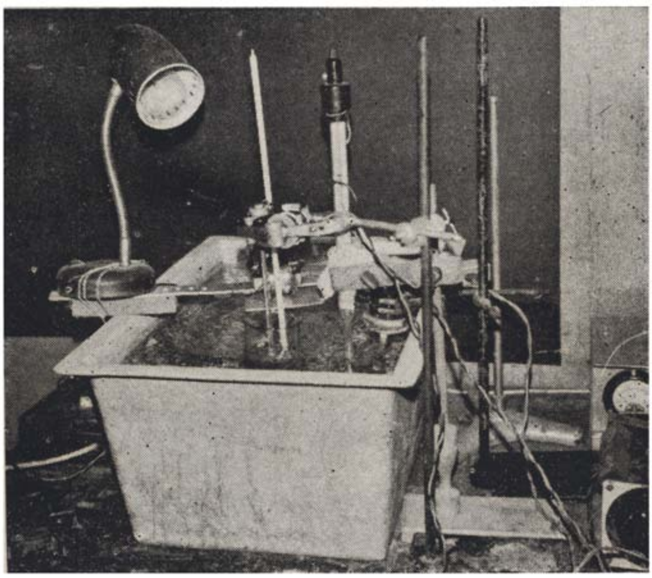

Figure 2. Constant temperature waterbath.

the crystals were polished to an optical finish using a rouge powder spread on a soft leather piece.

The optical finish was examined by reflected images on a nearby light source. A well-polished crystal would show an undistorted clear image of the source. The second test was to allow light from a He-Ne laser to pass through finished surfaces and checked for scattering from the surfaces. The flatness of the crystal was checked by the divergence of the beam on emerging from the crystal. The optical quality of the crystals was also checked by polarographic examination. The regularity and symmetry of the optic figure was used to test the homogeneity of the crystal. The symmetry of the extinction fringes also proved that the crystal was cut perpendicular to the optic axis.

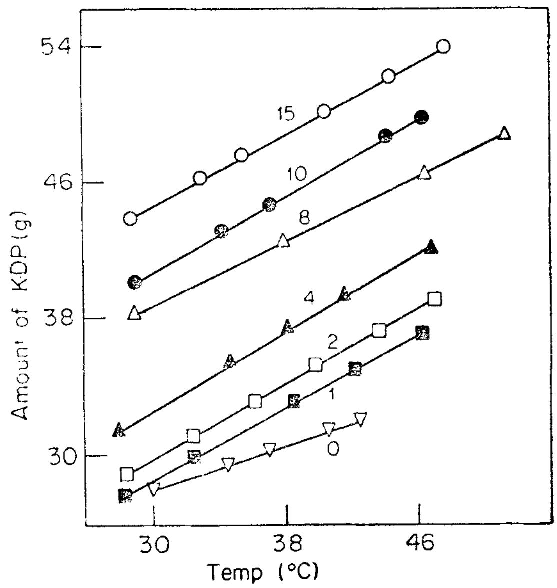

Figure 4. Solubility of KDP in water with borax as a function of temperature.

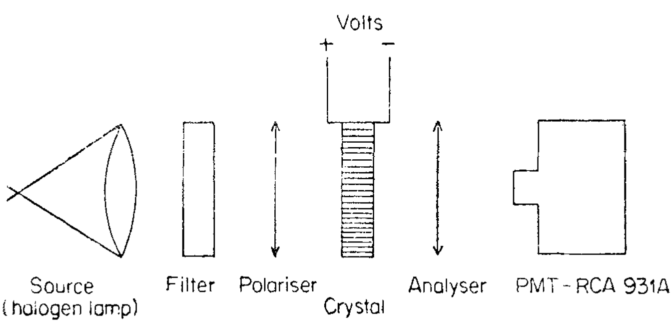

Figure. 5 Experimental set-up (schematic) for measuring electro-optic coefficients.

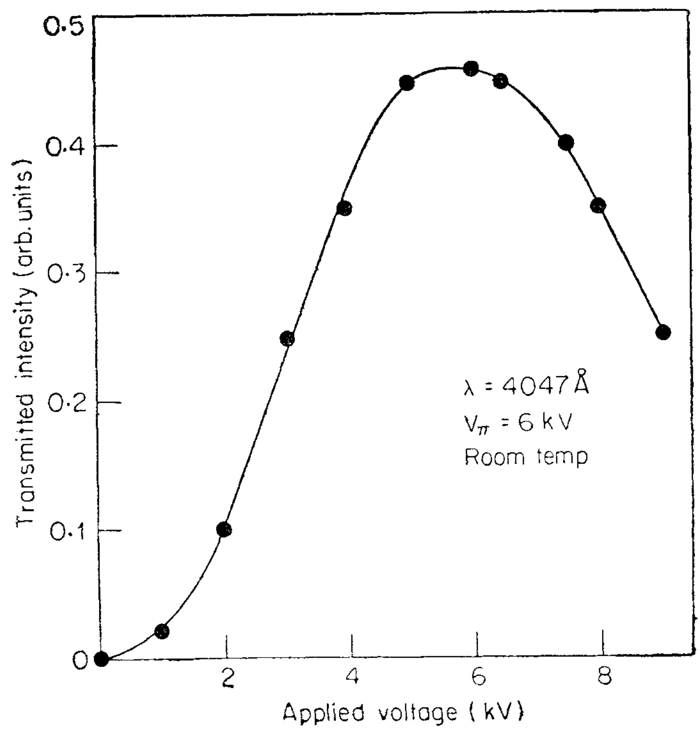

Figure 6. Variation of transmitted intensity with applied DC voltage at room temperature.

2·3 *Half wave voltages and electro-optic coefficients*

Figure 5 shows the longitudinal linear electro-optic set-up for determining the half-wave voltages of crystals (Kaminow 1974). Light from a halogen lamp was filtered by interference filter (4047 Å), polarised and transmitted by a crystal cell (consisting of a crystal with two transparent electrodes attached to the ends of the crystal immersed in silicone oil). The output from the cell is passed through another polarizer (analyzer) and then collected on a photomultiplier tube (RCA 931).

3. Results and discussion

The present paper reports the measurement of half wave voltages for KDP doped with 1% ADP at different wavelengths of light and various temperatures. The solubilities of both KDP and ADP were increased with an increase in borax, presumably due to the neutralization of $Na_2B_4O_7$ and KH_2PO_4 with each other enhancing the mutual solubilities. Figure 6 shows the variation of transmitted intensity of light at 4047 Å as a function of voltage applied and with the analyzer crossed with polarizer at room temperature. Similar curves were

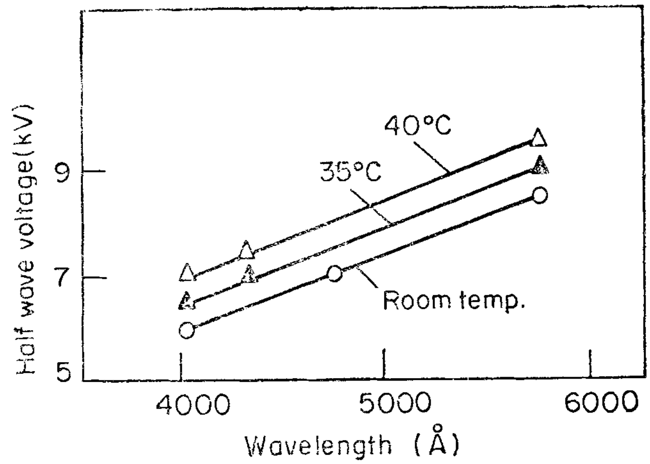

Figure 7. Longitudinal half wave voltage of $(NH_4)_xK_{1-x}H_2PO_4$ crystal as a function of wavelength at room temperature 35°C and 40°C.

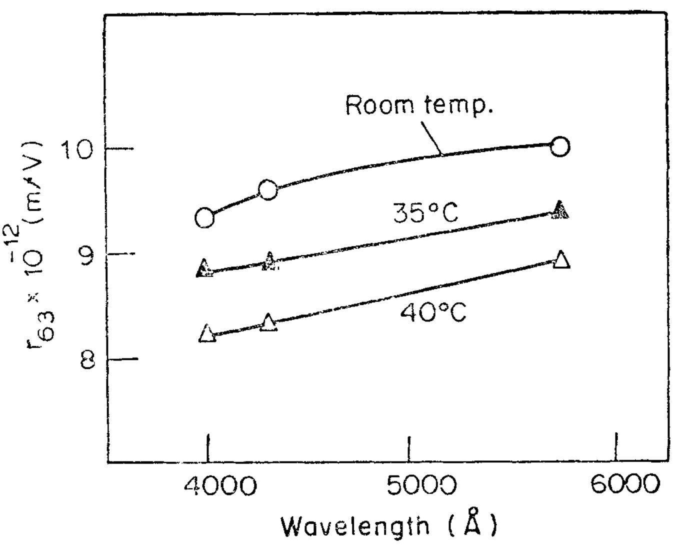

Figure 8. Dispersion of r_{63} as a function of wavelength.

obtained at 4358 and 5770 Å at different temperatures. The voltage corresponding to a maximum of transmitted light or half wave voltage was substituted in the formula $\gamma_{63} = \lambda/2n_o^3 v_\pi$ and the coefficients obtained at different wavelengths. The refractive index data were taken from Milek and Neuberger (1972). Figure 7 shows the variation of half wave voltage with temperature at different wavelengths of light. The trend in the variation of electro-optic coefficient

r_{63} with wavelength for mixed crystals of KDP and ADP reported in the literatature (Milek and Neuberger 1972). Figure 9 shows the variation of r_{63} coefficient as a function of temperature at different wavelengths.

4. Conclusions

The solubilities of both ADP and KDP increase with increasing amount of Borax in triple distilled water. The half wave voltage for KDP mixed with 1% ADP crystals increases with increase in wavelength in the visible region of the spectrum. The half wave voltage increases with increase of temperature and hence the electro-optic coefficients decrease with increase of temperature. The present results show that the electro-optic coefficient for pure KDP agree with published data (Milek and Neuberger 1972) while it is low for doped crystals.

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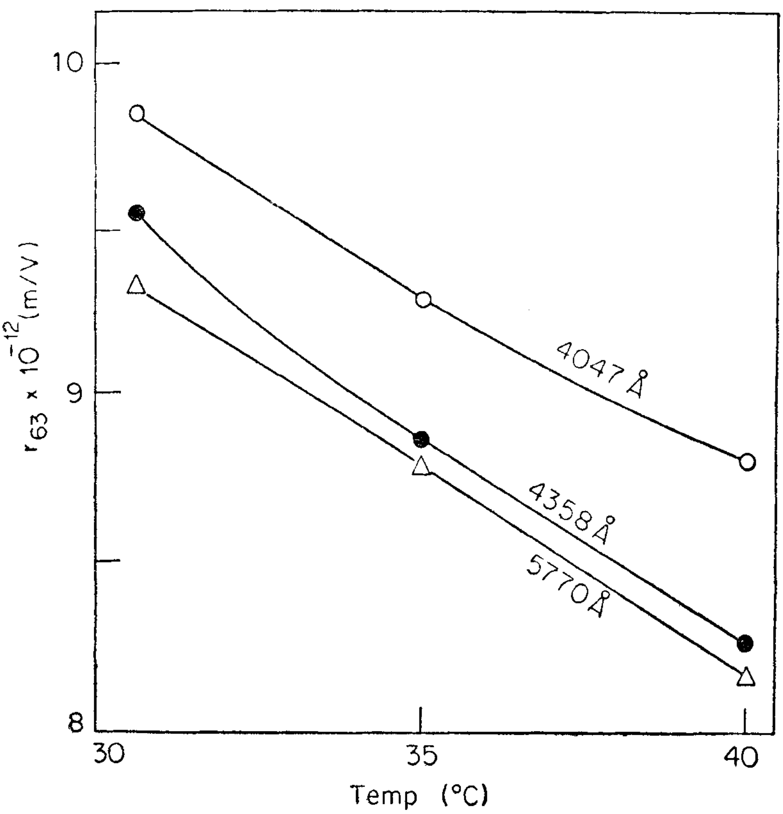

Figure 9. Variation of r_{63} as a function of temperature.

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