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Effect of crystal violet dye on the structural, optical, mechanical and piezoelectric properties of ADP single crystal

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ABSTRACT

Single crystals of pure and crystal violet (CV) dye doped (0.05 mol%) ammonium dihydrogen phosphate (ADP) were grown and characterized. Structural and compositional studies were carried out using XRD, EDAX and FTIR. In UV–vis-NIR measurements, characteristic absorption at 590 nm was observed for CV dye, with increased transmittance, wider optical window and increased band gap from 5.80 eV to 6.0 eV. In photoluminescence studies, CV doping resulted in partial quenching of blue emission at 440 nm. The piezoelectric charge coefficient was also enhanced from 1.82 pC/N to 2.78 pC/N. In micro-hardness studies, CV doped crystals exhibited better mechanical strength. The distribution of hardness number was statistically analyzed using Weibull statistics. The values of transition point, critical load, etc. were evaluated for both the crystals. Raman studies revealed that no structural phase transformations were observed after indentation for both the samples.

1. Introduction

In recent years, an appreciable attention is given by many researches to grow non linear optical (NLO) crystals with high transparency in the broad spectral range (near IR to ultraviolet region). Ammonium dihydrogen phosphate ($NH_4H_2PO_4$; ADP) crystals are widely used for optical switching in modern optoelectronics, optical storage devices, frequency conversion in laser technology and as monochromators for X-ray fluorescence analysis [1,2]. Currently, $NH_4H_2PO_4$ (ADP) and KH_2PO_4 (KDP) are used in various applications in laser fusion system by the virtue of their non linear optical (NLO) property [3–5]. Large plates of NLO crystals are needed for frequency converters and electro-optic switches. A lot of studies had been carried out by researchers on pure ADP and KDP crystals [6–10]. These crystals continue to be an important material for researchers both industrially and academically because of their unique NLO, piezoelectric, electro-optic and antiferroelectric (at low temperature) properties. ADP crystallizes in tetragonal crystal system with I-42d space group and its unit cell parameters are a = b = 7.4979 Å and c = 7.5393 Å [11]. Recently extensive research has been carried out on the growth and characterization of ADP doped with organic and inorganic dopants [12–15]. Large size good quality pure ADP single crystals were grown by Sankaranarayanan-Ramasamy (SR) method [3].

The crystal violet (CV; tris(*p*-(dimethylamino)phenyl)methyl) dye is an organic dye which belongs to an important class of commercial dyes (triphenylmethane; TPM). CV dye has a wide range of applications in medical community (active ingredient in Gram's stain and antibacterial agents) and in the textile industry (sensitizers for photoconductivity) [16–19]. This dye is used as a pH indicator and as an external skin disinfectant in animals and humans [20]. Mostly, organic dye doped sol-gel glasses and polymer matrices are being used as working media for solid state dye laser (SSDL). However, organic dye doped crystals can be an attractive alternative for laser gain media by virtue of their high thermal stability, intrinsic polarization and reduced scattering [21]. Recently numerous works has been done on the development of SSDL in which solid matrix embedded with organic dye is realized in order to achieve lasing action [22,23]. It had already been reported in literature that "organic impurities get easily incorporated into the water soluble inorganic matrices" [21]. As shown in [23–25], a variety of organic dye compounds like Amaranth, sunset yellow, xylenol orange, trypan blue etc can color KDP crystals. Organic dye molecules inclusion into the inorganic lattice makes them a promising material for photonic, optical and spectroscopic applications [26]. In our knowledge, there is no study on crystal violet (CV) dye doped ADP crystals. However, there are plenty of works on pure ADP crystals [6–10]. In the present

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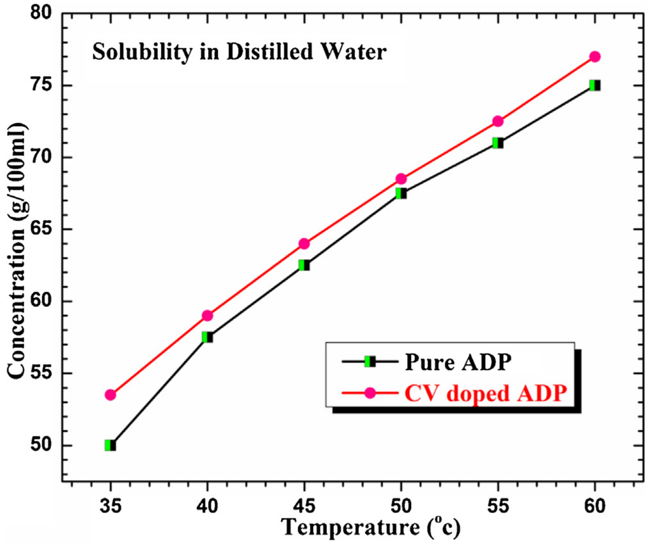

Fig. 1. Solubility curve of pure and CV dye doped ADP.

paper, we aimed at designing the new NLO media by doping ADP with organic dye (crystal violet). Our main intention was to combine chemical flexibility and high optical nonlinearity of organic (crystal violet) dye with optical nonlinearity, excellent transmittance and thermal stability of inorganic ADP matrix so that it can be successfully used as an active laser matrix for SSDL.

The influence of crystal violet dye doping on the structural (powder XRD), spectral (FTIR), optical (UV–vis-NIR, PL), mechanical (Vickers micro-hardness), thermal (TG/DTA) and piezoelectric properties of ADP single crystals are discussed in the paper. For an engineer, it is very important to explore the mechanical response of a material when exposed to certain applied loads. We have studied the micro-hardness property of grown crystals using Vickers micro-hardness testing. In past, the study on variation of measured micro-hardness values using Weibull statistics had been employed for thermal spray coating [27] but, this study had not attracted much attention for crystals. In present work, we statistically analyzed the distribution of micro-hardness values on the (100) plane of both crystals at various indenter loads using Weibull statistical distribution. Normally in literature, the micro-hardness values (at various loads) are reported as average values along with standard deviation. But average and standard deviation alone are not sufficient to understand the mechanical properties of crystal. Thus, we have also reported the values of variation coefficient, Weibull modulus, and correlation coefficient. Also the variation of average indentation depth with the applied indenter load has been discussed. Moreover, the values of critical area, critical volume and transition point between load dependent hardness and load independent (constant) hardness are evaluated for first time for ADP crystals. Finally, CV doped ADP crystals were proven to be beneficial for use in optoelectronic devices, light emitting devices, telecommunication, photonic and spectroscopic applications.

2. Experimental procedure

2.1. Crystal growth and solubility

The commercially available (AR grade; Merck) ammonium dihydrogen phosphate (ADP) salt and Crystal Violet dye were used for crystal growth. A clean beaker was filled with 100 ml of double distilled water and measured quantity of the material was added till saturation for different temperatures. The solubility curves of pure and 0.05 mol% CV doped ADP in the temperature range 36 °C to 60 °C in steps of 5 °C are shown in Fig. 1. The solubility of CV doped ADP got slightly increased as compared to pure ADP. Similar results were observed for CV doped KDP [28].

Saturated solution of pure ADP was obtained by dissolving 50 g of ammonium dihydrogen phosphate in 100 ml of double distilled water at 35 °C. The solution was stirred continuously for 2 days using a magnetic stirrer to get transparent and homogenous solution. Now the solution was filtered using ultra micro-pore filter paper and was kept in a clean beaker. The beaker was covered with a perforated aluminum foil paper and was kept for controlled evaporation at 35 °C in a constant temperature oil bath (±0.1 °C). Large size pure ADP crystals with good transparency were grown after 15 days. For the growth of CV dye doped crystals, 0.05 mol% of CV dye was added as dopant to the solution containing 50 g of ADP salt in 100 ml of double distilled water. The same method as described above was followed to obtain 0.05 mol% CV doped ADP crystals. Good quality CV doped ADP crystals were collected from the solution after a time span of 12 days. Fig. 2 shows the photograph of as grown crystals and also the morphology of ADP single crystal.

2.2. Characterization techniques

Various characterizations studies were carried out on pure and CV dye doped ADP crystals to analyze their structural, optical, mechanical and piezoelectric properties. The X-ray diffraction (XRD) studies were performed at room temperature by Bruker D8 Advanced X-ray diffractometer with Cu Kα (1.5408 Å) radiation. Perkin Elmer FTIR RXI spectrophotometer was used for tracing FTIR spectra for both the samples in the mid infrared range 400–4000 cm^{-1}. The UV vis NIR spectrum of pure and CV doped ADP crystal was examined using Perkin-Elmer Lambda-35 UV–vis spectrometer in the wavelength range 200–1100 nm. The PL spectrum of pure and CV doped ADP crystals were examined by Varian Cary Eclipse fluorescence spectrophotometer. Micro-hardness measurements on pure and dye doped ADP crystals

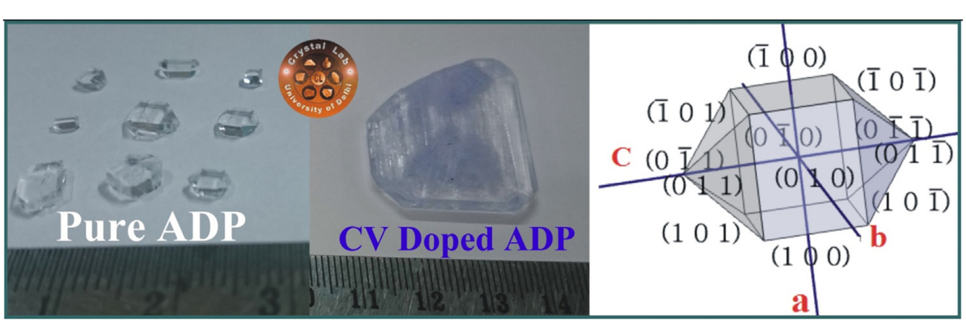

Fig. 2. Photograph of as grown pure and CV dye doped ADP single crystals by slow evaporation technique and morphology of ADP single crystal.