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Characterization of a potential nonlinear optical material: Sodium fluoride additive on ammonium dihydrogen orthophosphate single crystals

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A B S T R A C T

Effects of the additions of sodium fluoride (NaF) on the growth, structural and various optical properties of ammonium dihydrogen orthophosphate (ADP) single crystals grown by a slow evaporation solution growth technique from aqueous solution has been investigated. Crystallinity of the grown crystals was studied by powder X-ray diffraction analysis. Both pure and NaF doped ADP crystals exhibit tetragonal crystal structure. UV–vis–NIR spectral analysis was carried out to study the optical characteristics of the crystals which reveal that the cutoff wavelength for both pure and NaF doped ADP crystal is around 300 nm. From the spectra it can be clearly inferred that the transmittance percentage is increased in the NaF doped crystals. Also there is an absence of characteristic absorption in the region between 340 and 1200 nm, which is a most desirable property of a material for both SHG and other NLO applications. The bonding structure and molecular associations due to chemical reactions were analyzed by FTIR analysis. It also confirms the functional groups present in the grown crystals. Second harmonic generation (SHG) test adopting Kurtz-Perry technique revealed that the second harmonic generation efficiency of NaF doped ADP is 1.3 times that of pure ADP crystal.

1. Introduction

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) is widely used as the second, third, and fourth harmonic generator of Nd:YAG and Nd:YLF lasers. The crystals are widely used for electro-optical applications such as Q-switches for Nd:YAG, Nd:YLF, Ti:sapphire and alexandrite lasers, as well as acousto-optical applications [1–4]. Electronic and photonic materials are the key elements for the scientific growth and technological advances in new millennium. The nonlinear optical (NLO) organic materials have been the subject of extensive theoretical and experimental investigations during the past two decades [5,6]. Nonlinear optical (NLO) single crystals are capable of expanding the available spectral region of laser radiation by the process of frequency conversion [7]. Nonlinear optical crystals can convert laser frequencies to obtain shorter wavelength laser with high beam stability, at a low cost and with compactness. Many NLO crystals include KH_2PO_4 (KDP), $KTiOPO_4$ (KTP), LiB_3O_5 (LBO), β-BaB_2O_4 (BBO), and $CsLiB_6O_{10}$ (CLBO) and so on; have been developed for device applications [8–10]. However, to develop new NLO crystals with large nonlinear optical coefficients and with high mechanical and chemical stabilities, great efforts are being continuously made by researchers working worldwide. Ammonium dihydrogen orthophosphate (ADP) with the molecular formula $NH_4H_2PO_4$ continue to be interesting materials both academically and industrially because it has attracted extensive attention in the investigation of hydrogen bonding behaviors in the crystal and the relationship between crystal structure and their properties and it belongs to the isomorphous series of phosphates and arsenates [11].

Intense attention on ADP is directed due to its wide applications as dielectric, piezoelectric, antiferroelectric, electro-optic and nonlinear optical material [12]. The presence of NH_4^+ ions in ADP leads to an extra hydrogen bond between nitrogen and oxygen [13].

The growth, structural and optical properties of pure and sodium fluoride doped ADP single crystals are studied and reported in this paper.

2. Single crystal growth

Single crystals of pure and 1 mol% sodium fluoride (NaF) doped ADP were grown by solution growth employing slow evaporation

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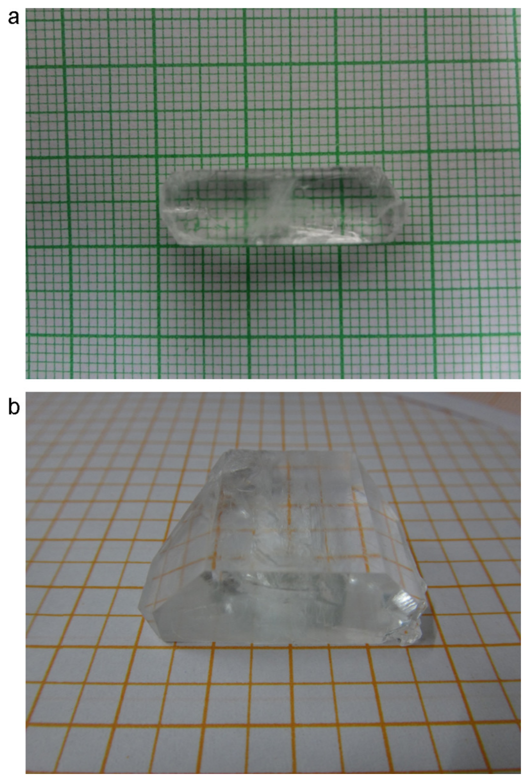

Fig. 1. (a) Photograph of pure ADP single crystal. (b) Photograph of NaF doped ADP single crystal.

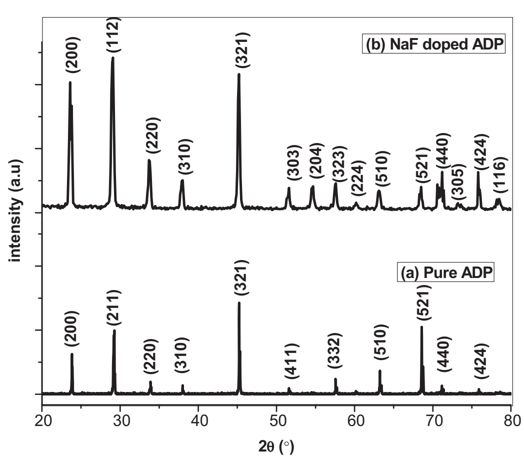

Fig. 2. (a) Powder XRD spectrum of pure ADP crystal. (b) Powder XRD spectrum of NaF doped ADP crystal.

technique using de-ionized water as a solvent at room temperature. Analytical reagent grade (AR) samples of ammonium dihydrogen phosphate and sodium fluoride along with distilled water were used for the growth of single crystals. 1 mol% NaF was added to ADP salt to form a saturated solution. The solution was thoroughly stirred continuously for 6 h for homogenization and then filtered

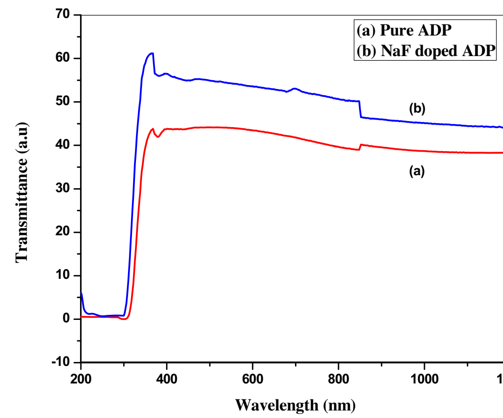

Fig. 3. (a) Transmittance curve of pure ADP crystal. (b) Transmittance curve of NaF doped ADP crystal.

into a borosil beaker using a Whatmann filter paper. The pH of the solution was noted as 4. The beaker containing the solution (200 ml) was closed with a perforated cover and kept in a dust-free atmosphere. Good quality crystals were harvested within a period of 28 days with the dimensions 27 mm × 8 mm × 7 mm for pure ADP and 40 mm × 33 mm × 12 mm for NaF doped ADP crystals. The photographs of pure and 1 mol% NaF doped ADP crystals are shown in Fig. 1(a) and (b), respectively.

3. Results and discussion

3.1. Powder XRD analysis

Powder X-ray diffraction studies were performed on the grown crystals to analyze the crystalline quality and their cell dimensions using Rigaku X-ray diffractometer with CuK_{α} radiation source ($\lambda = 1.540$ Å) in the 2θ range 20–80°. The powder XRD pattern of pure and NaF doped ADP crystals is shown in Fig. 2. Using XRDA and unit cell softwares the peaks were indexed and the lattice parameter values of the grown crystals were calculated and are listed in Table 1. It is confirmed that the grown crystals belong to the scalenohedral class of tetragonal crystal system with the space group $I\bar{4}2d$. The incorporation of dopant (sodium fluoride) in the crystals gives a slight variation in the lattice parameters and the cell volume. It is evident for the incorporation of the dopant, the unit cell volume gets decreased. From the differences observed, it can be inferred that NaF has affected the lattice parameters 'c' more than 'a' and 'b'. X-ray diffraction analysis confirms the presence of impurity in the doped crystals.

3.2. UV–vis–NIR analysis

The purpose of growing pure and NaF doped ADP crystals is to employ them in optical applications. Hence, it is important to study the transmission range of the grown crystals. The optical properties of the materials are important, as they provide information on the electronic band structure, localized state and the type of optical transitions because the absorption

Table 1
Unit cell parameters of pure and NaF doped ADP crystals.

Sample	Lattice parameter		Cell volume (Å^3)	$\alpha = \beta = \gamma$ (°)	Structure
	$a = b$ (Å)	c (Å)			
Pure ADP	7.4909	7.5454	423.4015	90	Tetragonal
NaF doped ADP	7.4893	7.5233	421.9814	90	Tetragonal