Optik 127 (2016) 2419–2423

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Investigations on the effect of transition metals on the growth and characterization of sodium acid phthalate single crystals

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ARTICLE INFO

Article history:
Received 21 May 2015
Accepted 17 November 2015

Keywords:
Nonlinear optics
Alkali crystals
Doping
Single crystal
Characterization

ABSTRACT

Sodium acid phthalate (SAP) $C_8H_5NaO_4$ is one of the efficient semiorganic single crystals employed in second harmonic generation conversion applications. In the present work, optically transparent single crystals of SAP and 1 mol% of transition metals copper (Cu), nickel (Ni) and cadmium (Cd) doped SAP single crystals were grown by slow evaporation solution growth technique at ambient temperature. Powder XRD analysis revealed that all crystals exhibit orthorhombic crystal structure and the crystalline intensity was found to improve due to Cu dopant. The functional groups present in the grown crystal were identified by the FTIR analysis. The UV–vis–NIR study suggests that the crystals are highly transparent in the region 434–1200 nm and % of transmittance is increased by 20% in case of copper doped crystals. Concentration of the transition metals in the grown crystals were quantitatively confirmed from inductively coupled plasma optical emission spectroscopic (ICP–OES) studies. Improvement in second harmonic generation (SHG) efficiency due to transition metal dopants was observed and the thermal stability of pure and doped crystals were analyzed.

1. Introduction

Recent interest in research focuses much on search for highly efficient nonlinear optical (NLO) materials due to their potential applications in data storage devices, laser-based images, optoelectronics, optical communication, optical switches, optical frequency conversion, telecommunication, etc. [1–7]. The desired NLO materials must exhibit large second-order optical nonlinearities, short transparency cut-off and stable physico-chemical performance. Inorganic crystals such as potassium di hydrogen phosphate (KDP), ammonium di hydrogen phosphate (ADP), borate crystals potassium pentaborate (KB5), beta barium borate (BBO), lithium tri borate (LBO), lithium niobate (LN) possess excellent thermal and mechanical stability but their optical response is modest due to the lack of π-electron delocalization. Fast and large optical response over a broad frequency range is the inherent property of organic crystals like L-alanine, L-arginine, L-histidine, etc., due to the presence of delocalized π-electrons between donor (NH_3^+) and acceptor (COO^-) groups but their thermal and mechanical stabilities are low. In order to overcome these difficulties, organic–inorganic hybrid compounds such as zinc tris-thiourea (ZTS), L-arginine phosphate monohydrate (LPA), L-histidine tetra fluoroborate (L-HFB) with flexibility for molecular design, high nonlinearity and also superior thermal and mechanical stabilities have been synthesized and these materials belong to 'semi-organic' group of materials.

Alkali hydrogen phthalate single crystals are such semi-organic crystals with wide applications in long-wave x-ray spectrometers and used as substrate for deposition of thin films. Ammonium acid phthalate, potassium acid phthalate, sodium acid phthalate, rubidium acid phthalate, cesium acid phthalate and thallium acid phthalate are some of the phthalic acid crystals. SAP crystallizes in orthorhombic system with molecular formula $C_8H_5NaO_4$.

Device quality nonlinear optical (NLO) materials can be achieved by modifying various structural and physical properties of SAP by introducing transition metal dopants. It is reported to induce significant changes in structural, thermal, linear and non-linear optical properties in KDP, ADP, KAP, BTZC crystals [8–15]. The aim of the present work is to investigate the effect of transition metals copper, nickel and cadmium doping on the growth and optical properties of SAP single crystals.

2. Experimental details

2.1. Crystal growth

SAP single crystals were grown from aqueous solution by dissolving phthalic acid (Loba Chemie 99%) and sodium hydroxide

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http://dx.doi.org/10.1016/j.ijleo.2015.11.176
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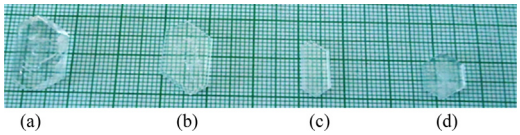

Fig. 1. Photograph of as-grown (a) pure, (b) SAP–Cu, (c) SAP–Ni and (d) SAP–Cd doped SAP single crystals.

(Merck 97%) in equimolar ratio in double distilled water at 40 °C. The solution was stirred for 5 h, filtered and kept for slow evaporation at room temperature. The following chemical reaction was expected to take place between phthalic acid and sodium hydroxide.

$$COOH\text{–}C_6H_4\text{–}COOH + NaOH \rightarrow COOH\text{–}C_6H_4\text{–}COONa + H_2O \quad (1)$$

By successive re-crystallization, purity of the material was improved. Crystal of $20 \times 11 \times 5\,mm^3$ dimension was harvested within 35–40 days. 1 M% of copper (II) chloride dihydrate (Merck, 98%), nickel (II) nitrate hexahydrate (Merck, 98%) and cadmium nitrate tetrahydrate (Merck, 98%) were separately dissolved in the initial growth medium and optically transparent single crystals with the dimensions of $19 \times 10 \times 3\,mm^3$, $15 \times 7 \times 2\,mm^3$, $13 \times 9 \times 3\,mm^3$, respectively, were harvested in 30–35 days and the crystals are referred as SAP–Cu, SAP–Ni and SAP–Cd. The crystals appear to grow preferably along [1 0 0] direction and images of both pure SAP and transition metals doped SAP crystals are given in Fig. 1.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the grown crystals were recorded using Rigaku Mini Flex 2 desktop X-ray diffractometer with Cu*K*α radiation of wavelength 1.5406 Å. FT-IR of solid phase samples were analyzed in Perkin-Elmer RX1. FTIR spectrometer in the range 400–4000 cm^{-1} using KBr pellet technique. UV spectrum was traced with Lambda 35 UV–vis–NIR spectrometer in the wavelength range 190–1100 nm at room temperature. Differential thermal analysis and thermo gravimetric analysis curves were recorded for the grown crystals using a simultaneous thermal analyzer TGA7 (Perkin Elmer), Q500 Hi-Res V20. Composition of transition metals in SAP single crystal was determined by inductively coupled plasma optical emission spectroscopy (ICP–OES) in Perkin Elmer optima 5300 DV spectrometer. Kurtz SHG test was performed to find the NLO property using a *Q*-switched Nd:YAG laser (1064 nm, Quanta ray series with input energy: 4.4 mJ/pulse).

3. Results and discussion

3.1. X-ray diffraction analysis

Powder XRD pattern of SAP, SAP–Cu, SAP–Cd and SAP–Ni crystals are shown in Fig. 2. The XRD patterns revealed good agreement with the standard JCPDS data for SAP (File. No. 32-1895). The lattice parameters *a*, *b*, *c* and unit cell volume (*V*) of the samples were calculated from the following equations for the orthorhombic crystal system.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2)$$

$$V = abc \quad (3)$$

where *d* is the interplanar distance and *h*, *k*, *l* are the Miller indices.

Calculated lattice parameters, unit cell volume and space group are presented in Table 1. Doped patterns contain all the peaks that are found in SAP which confirmed that doping did not affect the phase of the crystal. Variation in peak intensity and slight shift in peak position are observed in all the three cases shown in Table 2, which may be due to the incorporation of dopants in the crystal matrix. The ionic radii of the dopants Cu (73 pm), Ni (69 pm) and Cd (97 pm) are small compared with that of Na (102 pm). Hence the lattice parameter values of transition metal doped crystals increased resulting in increased unit cell volume.

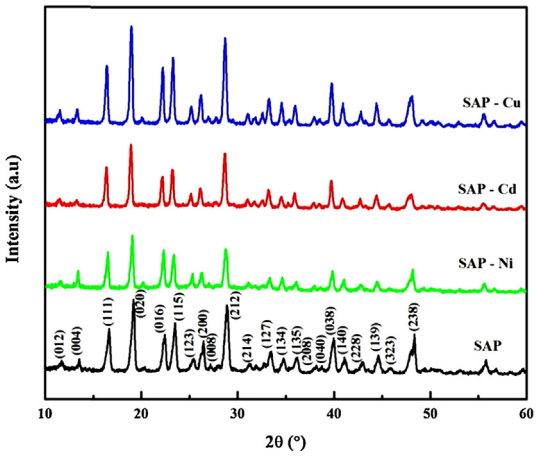

Fig. 2. XRD patterns of pure and transition metals doped SAP crystals.

Table 1
Lattice parameters of pure and transition metals doped SAP crystals.

Sample	Lattice parameters (Å)			Volume (*V*) (Å)^3	Space group
	a	*b*	*c*		
SAP	6.7166	9.2474	26.2146	1628.217	B2ab
SAP–Cu	6.7972	9.3537	26.6070	1691.64	B2ab
SAP–Cd	6.8074	9.3734	26.5673	1696.22	B2ab
SAP–Ni	6.7769	9.3052	26.3311	1660.45	B2ab

3.2. FT-IR analysis

FT-IR spectra of pure and transition metals doped sodium hydrogen phthalate crystals were carried out to observe the characteristic vibrations of carboxylic acid, carboxylate, water molecules and phenyl rings present in the grown crystals. The recorded FT-IR spectra are given in Fig. 3. The C—C stretching in phenyl ring is present at 1347 and 1470 cm^{-1}. Strong band at 1119 cm^{-1} in the spectra corresponds to the C—H in plane bending vibrations of the phenyl ring. Vibrations present at 863 cm^{-1} correspond to the C—H out

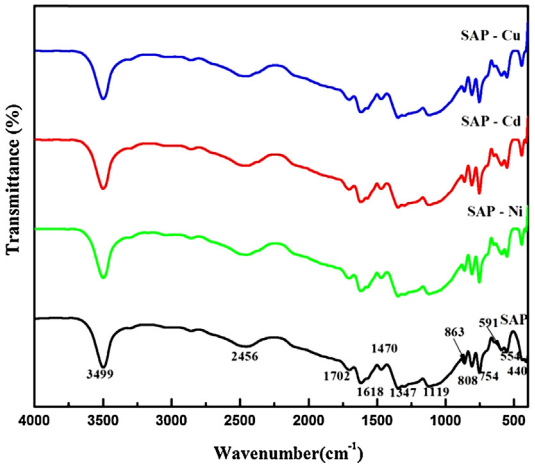

Fig. 3. FT-IR spectra of pure and transition metal doped SAP crystals.