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GROWTH OF K_2CO_3-DOPED KDP CRYSTAL FROM AN AQUEOUS SOLUTION AND AN INVESTIGATION OF ITS PHYSICAL PROPERTIES

RAST KDP KRISTALOV Z DODATKOM K_2CO_3 IZ VODNE RAZTOPINE IN PREISKAVA NJIHOVIH FIZIKALNIH LASTNOSTI

Abrisham Rousta[1], Hamid Rezagholipour Dizaji[2]

[1]Islamic Azad University, Central Tehran branch, Faculty of Basic Sciences, Physics Department, Crystal Growth Laboratory, 2 Rasooli Alley, North Jamalzadeh st., Tehran, Iran
[2]Semnan University, Faculty of Physics, Semnan, Iran
hrgholipour@semnan.ac.ir

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In this present work, KDP and 2M%-K_2CO_3-doped KDP crystals were grown by a slow-evaporation solution technique. The grown crystals were characterized by Fourier Transform Infrared (FT-IR) spectroscopy, X-ray diffractometry (XRD), UV-Vis spectroscopy, and laser damage threshold (LDT) analysis. The presence of the functional groups of the grown crystals was identified from the FT-IR spectra. The XRD tests showed that the grown crystals had a tetragonal structure. A comparison of the optical transmission of the grown crystals revealed that the K_2CO_3-doped KDP crystal had a higher transmission than the pure KDP crystal for the entire UV and visible region.

Keywords: growth from solution, slow-evaporation solution technique, KDP crystal, K_2CO_3 additive

V predstavljenem delu so KDP in z 2M % K_2CO_3 dopirani KDP kristali rasli s tehniko počasnega izhlapevanja tekočine. Dobljeni kristali so bili karakterizirani iz infrardečo spektroskopijo s Fourierjevo transformacijo (FT-IR), z rentgensko difrakcijo (XRD), z UV-Vis spektroskopijo in s pragom poškodbe z laserjem (LDT). Prisotnost funkcionalnih skupin kristalov v rasti je bila določena s FT-IR spektrom. XRD je pokazal, da imajo rastoči kristali tetragonalno zgradbo. Primerjava prepustnosti svetlobe v rastočih kristalih je odkrila, da imajo KDP kristali, dopirani s K_2CO_3, boljšo prepustnost kot pa čisti KDP v celotnem UV in v vidnem področju.

Ključne besede: rast iz raztopine, tehnika počasnega izparevanja raztopine, KDP kristal, dodatek K_2CO_3

1 INTRODUCTION

Potassium dihydrogen phosphate KH_2PO_4 (KDP) is a material that is soluble in water with a positive solubility coefficient. The crystal structure is tetragonal with the lattice parameters $a = b = 0.7448$ nm and $c = 0.6977$ nm. A KDP single crystal is piezoelectric at room temperature, and below 123 K (Curie point) it transforms to the ferroelectric phase and has an orthorhombic structure. This crystal is an excellent electro-optic and nonlinear optical (NLO) material, so it is used in optical modulators such as a second-harmonic generator. In addition, it is characterized by its good UV-visible transmission, high damage threshold, etc. Many attempts have been made to modify its properties, either by changing the growth condition or by adding different impurities.[1–7]

P. V. Dhanaraj et al.[8] showed that the addition of K_2CO_3 could make the KDP solution more stable than with other additives and enhanced the metastable zone width of the KDP solution for all temperatures.[8] They also found that the laser-induced damage threshold of a K_2CO_3-added KDP crystal was higher than that of the pure KDP crystal.

In the present study, pure and 2M%-K_2CO_3-doped KDP crystals were grown from an aqueous solution using the slow-evaporation method at room temperature. The grown crystals were then subjected to various characterization techniques.

2 EXPERIMENTAL PROCEDURE

KDP crystals, pure and with added 2M% K_2CO_3, were grown from an aqueous solution using the slow-evaporation method at room temperature. A saturated solution of KDP was prepared by dissolving an appropriate amount of commercially available KDP powder in double distilled water without any further purification. The solution was then stirred well for two hours using a magnetic stirrer, filtered using Whatmann filter paper and transferred into the growth container for the slow evaporation. In a similar way, a saturated solution of KDP with added 2 M% K_2CO_3 was prepared. Then each container was covered with a perforated cover and kept in a dust-free place. Within two weeks, transparent KDP crystals of both pure (22 mm × 21 mm × 8 mm) and with added 2 M% K_2CO_3 (24 mm × 20 mm × 14 mm) were grown. **Figures 1a** and **1b** show the pure and doped crystals, respectively.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis (XRD)

Both the pure and 2M%-K_2CO_3-added KDP crystals were subjected to powder X-ray diffraction (XRD) analysis using an X-ray diffractometer (Advance Model D8) with high-intensity Cu-K_α radiation (λ = 0.15406 nm). The grown crystals were ground using an agate mortar and pestle in order to determine the crystal phases by XRD. **Figure 2** shows the XRD patterns of the pure and doped KDP single crystals. From the data, both the crystals were found to crystallize in the tetragonal system. Comparing the two patterns, we found no extra peaks due to the doping; hence adding K_2CO_3 to KDP did not affect its crystal structure. The sharp peaks observed in both patterns indicate the good crystallinity of the grown crystals.

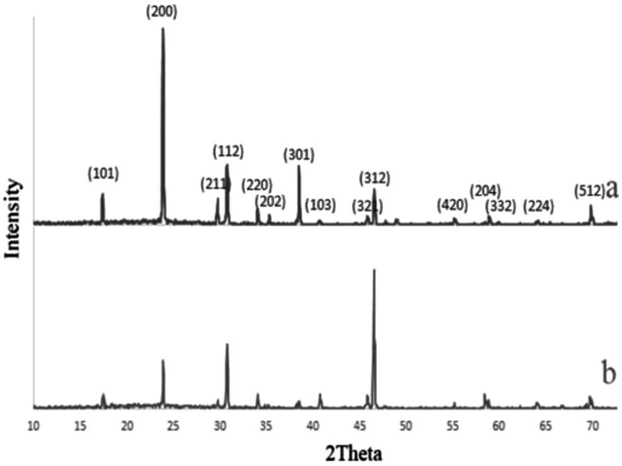

Figure 2: X-ray diffraction patterns of: a) pure KDP and b) 2 M%-K_2CO_3-added KDP single crystals

Slika 2: Rentgenograma: a) čisti KDP in b) KDP monokristali z dodatkom 2 M % K_2CO_3

3.2 Optical transmittance

The optical transmittance spectrum in the wavelength region 200–800 nm was recorded at room temperature using a Perkin Elmer model lambda25 UV-Vis-NIR spectro-photometer on a 1.8-mm-thick plate of the grown K_2CO_3-added KDP crystal in the (001) direction. This property is the most desirable one for an NLO material. **Figure 3** presents a comparison among the transmittance spectra of pure and 5M%-K_2CO_3-added KDP single crystals[7] and a 2 M%-K_2CO_3-added KDP single crystal (present work).

It is clear from the figure that the crystals are highly transparent across the entire UV-visible region. It is also obvious that the transmittance percentage of the doped KDP crystal is higher than that of the pure one. This improvement in the transparency of the KDP crystal after the addition of K_2CO_3 to the solution may be attributed to its ability to suppress the inclusions due to the heavy metals usually present in the starting material.

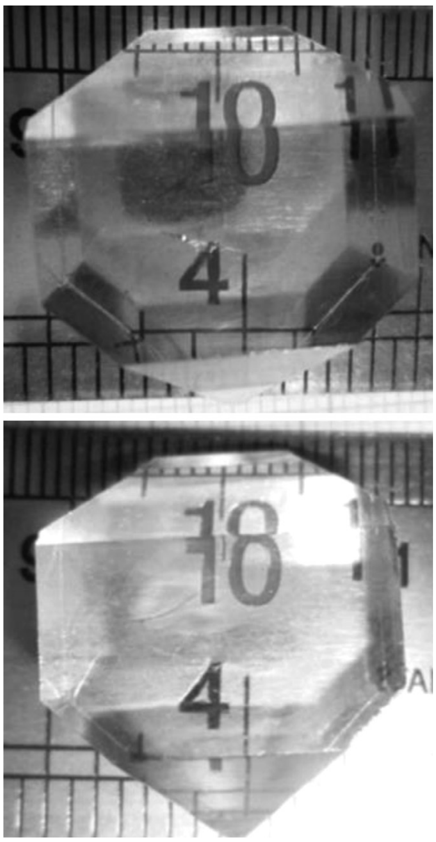

Figure 1: Photographs of: a) pure and b) 2 M%-K_2CO_3-doped KDP crystals

Slika 1: Posnetka: a) čistega in b) z 2 M% K_2CO_3 dopiranega KDP kristala

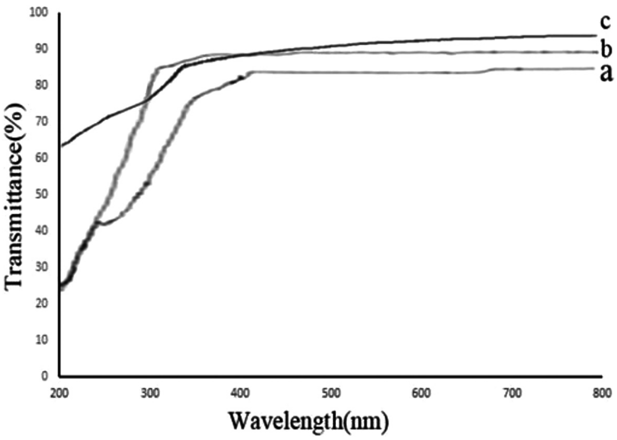

Figure 3: UV-visible transmittance spectra of: a) pure KDP and b) 5M%-K_2CO_3-added KDP single crystals[6], and c) 2 M%-K_2CO_3-added KDP single crystal

Slika 3: Spekter prepustnosti UV in vidne svetlobe: a) čisti KDP in b) monokristali KDP z dodatkom 5M % K_2CO_3[6] in c) monokristal KDP z dodatkom 2 M % K_2CO_3

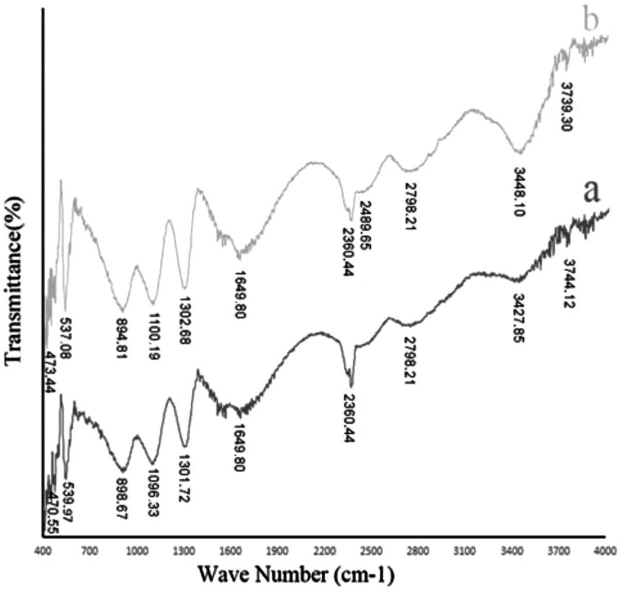

Figure 4: FT-IR spectra of: a) pure KDP and b) 2 M% K_2CO_3 added KDP single crystals

Slika 4: FT-IR-spektri: a) čisti KDP in b) KDP monokristal z dodatkom 2 M% K_2CO_3

3.3 Fourier-transform infrared (FT-IR) analysis

The FT-IR spectra of the pure and 2 M%-K_2CO_3-doped KDP crystals were recorded using a Perkin Elmer model 410 Jasco company spectrometer in the wavenumber range from 400 cm^{-1} to 4000 cm^{-1} using the KBr pellet technique. **Figure 4** represents the FT-IR spectra of the grown crystals. Also, the position of the peaks and their functional group assignments are given in **Table 1**.

Table 1: Observed FT-IR wave numbers (cm^{-1}) and their functional group assignments for the grown pure and 2M%-K_2CO_3-added KDP crystal

Tabela 1: Opažena FT-IR valovna števila (cm^{-1}) in dodeljene funkcionalne skupine pri čistem KDP kristalu in KDP kristalu z dodatkom 2M % K_2CO_3

Wave number (cm^{-1})		Functional group assignments
Pure KDP crystal	2M %K_2CO_3 added KDP crystal	
3739.30	3744.12	Free O-H stretching hydrogen bonded
3448.10	3427.85	O-H stretching hydrogen bonded
2489.65	–	O=P-OH asymmetric stretching
1649.80	1649.80	O-H bending out of plate
1302.68	1301.72	O-P=O stretching
1100.19	1096.33	P=O stretching
894.81	898.67	P-O stretching
537.08	539.97	O-P-O bending
473.44	470.55	PO_4 stretching

The broad band that appears in the range from 3800 cm^{-1} to 2500 cm^{-1} is due to free O-H stretching of the KDP. These functional groups arise at 3739 cm^{-1} and 3448 cm^{-1} in pure KDP and at 3744 cm^{-1} and 3427 cm^{-1} in doped KDP.

The peaks at 537 cm^{-1}, 1100 cm^{-1} and 2489 cm^{-1} in pure KDP and 539 cm^{-1} and 1096 cm^{-1} in doped KDP are due to the O-P-O bending, P=O stretching and O=P-OH asymmetric stretching of the KDP, respectively. The O-P=O stretching, P-O stretching and PO_4 stretching are found at 1302 cm^{-1}, 894 cm^{-1} and 473 cm^{-1} in pure KDP and 1301 cm^{-1}, 898 cm^{-1} and 470 cm^{-1} in doped KDP, respectively.

We can clearly see from the comparison of the FTIR spectrum of the two crystals that the presence of the dopant has led to a change in the intensity of the absorption of the IR frequencies and a slight shift in some of the frequencies. The strong similarities of the two graphs reveal the fact that the peaks corresponding to pure KDP crystal are predominant over those corresponding to the K_2CO_3-added KDP crystal, which may be due to the small amount of doped K_2CO_3 in the compound compared to the KDP.

3.4 Laser damage threshold (LDT)

One of the most important considerations when selecting a material for nonlinear optics applications is its ability to withstand high power intensities.[9]

The laser damage threshold (LDT) of nonlinear optical components depends on physical and chemical factors, particularly imperfections, defects and the concentration and type of the impurities, etc.[10]

The LDT of the grown pure and 2M%-K_2CO_3-doped KDP single crystals was carried out using a Nd:YAG laser with the wavelength 1064 nm and shot-to-shot mode, with an energy per pulse of 50 mJ, a repetition rate of 10 Hz, a pulse duration of 7 ns, a beam waist of 0.0841 mm and a spot diameter of 2.3 mm. The laser beam was focused on the sample with 1-m and 50-cm focal-length lenses. A Tektronic 2430A digital oscilloscope was used to record the energy of every pulse and save the data in a computer.

The damage threshold was calculated for the pure KDP and the 2 M%-K_2CO_3-doped KDP crystals and the value was found to be 12.1083 J/cm^2 and 19.1782 J/cm^2, respectively. It shows that, adding 2M% K_2CO_3 to the KDP solution increased the damage threshold of the KDP single crystal, which can be attributed to the ability of this additive to suppress the inclusions due to heavy-metal impurities like Cr^{3+}, Fe^{3+}, and Al^{3+} that are present in most of the commercially available chemicals.

4 CONCLUSIONS

In this work, pure KDP and 2M%-K_2CO_3-doped KDP crystals were grown by the slow-evaporation solution technique from an aqueous solution at room temperature. Structural studies indicate that both the grown crystals have a tetragonal system with similar XRD patterns. Optical transmission studies showed that using 2 M% K_2CO_3 as an additive increased the optical quality of the KDP crystal compared to the pure crystal. Fourier transform infrared analysis revealed the functional groups of the samples. The laser-damage threshold of the 2 M%-K_2CO_3-added KDP crystal was found to be higher than that of the undoped crystal, indicating the suitability of K_2CO_3 as an additive to enable KDP to withstand high power intensities.

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