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Irradiation effect on second harmonic generation of dyes doped KDP crystals

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Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiation such as UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied. Li^{3+} irradiations lead to the development of a well-defined surface H peak in dye doped KDP crystals. The stability of KDP single crystal was improved by doping organic dyes. The nano-islands of dye in KDP are likely to be dissolved and enhance the non-linear optical properties of these materials. The structural, optical and non-linear optical properties of the doped crystals were analyzed with the characterization studies such as powder XRD, UV-Visible and SHG measurements respectively. The results for doped KDP crystal are compared with the results of the pure KDP crystals.

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Keywords: KDP, Harmonic generation, UV light

1. Introduction

Optical quality KDP crystals can be grown by conventional solution growth methods as well as by fast growth techniques [1]. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket its refractive index for even extreme wavelength range over which it is transparent [2]. Among non-linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication [3].

Irradiation of solids with swift heavy ion (SHI) beams, lead to strong electronic excitation of the target's electron subsystem and the energy loss was mainly determined by the ions interaction with the target electrons [4]. At lower energies (KeV range), elastic collisions are dominant and at higher energies (a few tens of MeV), inelastic collisions dominate the energy loss process [5]. Ion irradiation and the inevitable damage it creates has long been a topic of great interest in the field of semiconductor device fabrication [6]. In particular, the effect of selecting a particular ion during irradiation, determines the mobility of the material.

Swift Heavy Ion irradiation can result in change of optical properties of the crystals by several processes, viz., changes in stoichiometry of new phases [7], structural changes, defects[8] produced by the electronic and nuclear energy loss, volume expansion in the nuclear damage region, stress effects etc.

This investigation was carried out to study the effect of swift heavy ion irradiation on the structural, optical and surface morphology properties of dyes doped KDP crystal. To fabricate optical devices using these materials, a detailed and study of ion-induced changes is necessary.

2. Experimental

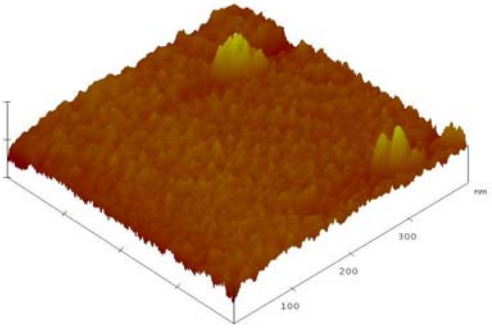
Well-polished, transparent, single crystalline dyes doped KDP samples were used for Li^{3+} irradiation at room temperature. Dyes doped KDP crystals of thickness 500μm were used for the experiment. The samples were irradiated with 50 MeV Li^{3+} ions by using a 15 UD Pelletron Accelerator. These studies were performed at room temperature in an experimental chamber under vacuum better than 10^{-7} torr. The beam was scanned a 10 mm × 10 mm area on the sample using a magnetic beam scanner. The dose of charge accumulated in the sample was measured separately in terms of the fluences and adjusted as 1×10^{11} ions cm^{-2}. According to the calculation of stopping and ranges of ions in matter (SRIM), the projected range (Rp) of the 50 MeV Li^{3+} ions in KDP is 65 μ m (James F. Ziegler, 1984). Also the corresponding end of range lateral distribution of straggling is 4.567 MeV $(mg\ cm^{-2})^{-1}$ and the longitudinal distribution of straggling is 7.5 MeV $(mg\ cm^{-2})^{-1}$.

3. Irradiation effects on dyes doped KDP crystal

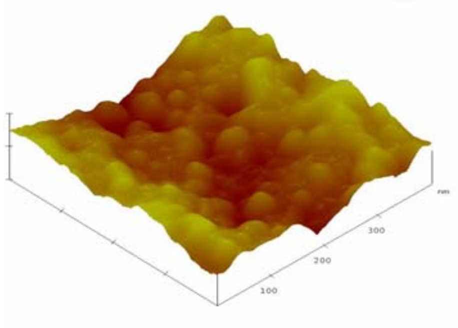
3.1 Atomic force microscopy

The AFM image was obtained using Veeco Digital Nanoscope III atomic force microscopy (AFM) in the contact mode. The Photoluminescence was excited using the 458 nm line of an argon ion laser with typical excitation densities of 10 $mWcm^{-2}$. The samples were mounted in a closed cycle helium cryostat, which can be controlled between 10 and 300 K.

The crystal surface morphology of pure and Li^{3+} ion irradiated doped (Amaranth, Rhodamine B and Methyl orange) KDP samples were analyzed by atomic force microscopy. The crystal surface micrographs of pure and Li^{3+} ion irradiated Amaranth doped KDP were shown in the Figs. 1(a) and (b). The pristine sample appears to be a smooth, ordered arrangement with least dislocation and corresponding root mean square (rms) surface roughness value of 0.114 nm. The Li^{3+} ion irradiated KDP samples demonstrate disturbance of smoothness and ordered arrangement in their surface morphology due to lattice disorder. It appears like twinning with minor cracks and the corresponding root mean square (rms) surface roughness value increases to 5.117 nm.



(a)



(b)

Fig. 1. (a) AFM image of pure KDP sample; (b) AFM image of Li^{3+} ions irradiated Amaranth doped KDP sample with fluence of 10^{11} ions/cm^2.

3.2 UV-Visible transmission analysis of pure and dyes doped KDP after irradiation

The UV-Visible spectra of Li^{3+} irradiated (1×10^{11} ions/cm^2) pure and dyes doped KDP samples were shown in Fig. 2. After the irradiation on dyes doped KDP, optical transmission is totally modified. UV-Visible spectra indicate that swift heavy ions penetrate the crystal along the trajectory of the ion beam and lead to material modification by pushing the atoms from their original positions and distorted lattice. In this process it generates defects and partial amorphization resulting in a non-crystalline nature.

The irradiation process decreases transmittance in pure KDP. Because due to ion-induced disorder in the form of defects and partial amorphization was limited to only a part of the sample exposed to ion beams [9]. Also, the intensity variation can be attributed to the creation of defects like surface tracks. The surface tracks [10] were created from the ion-induced mechanical stress arising from the thermal expansion.

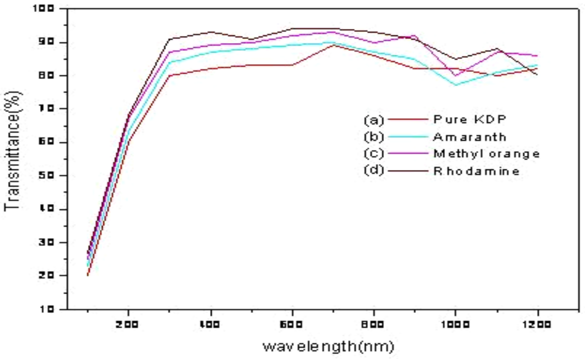


Fig. 2. UV-Visible Spectra for Li^{3+} ion irradiated (a) pure, (b) Amaranth,(c) Rhodamine B and (d) Methyl Orange doped KDP crystals.

3.3 NLO studies of Li^{3+} ion irradiated of pure and dyes doped KDP crystals

SHG measurements were made, using the Kurtz and Perry powder method .The 1064 nm fundamental output from a Q-switched Nd-YAG laser (Quanta Ray) was divided by a beam splitter, where one portion of the light was directed onto a reference cell KDP. The second portion of the fundamental beam was directed on to a second cell containing the sample to be measured. SHG efficiency is improved after the irradiation effect on dyes doped KDP crystal. The SHG efficiency of dyes doped KDP are measured and tabulated in Table 1.

Table 1. SHG of pure and dyes doped KDP crystals after irradiation.

S. No.	Compound	SHG efficiency
1.	Pure KDP	1.00
2.	Amaranth doped KDP crystal	1.56
3.	Rhodamine B doped KDP crystal	1.68
4.	Methyl Orange doped KDP crystal	1.86

4. Results and discussion

AFM indicates that swift heavy ions penetrates the crystal along the trajectory of the ion beam and lead to material modification by pushing the atoms from their original positions and distorts their lattice. In this process it generates defects and partial amorphization resulting in a non-crystalline nature. The extent of ion-induced disorder [11, 12] in the form of defects and partial amorphization is limited to only a part of the sample exposed to ion beams.Optical transparency of irradiated pure and dyes doped KDP [13] have been studied. It has been observed that the cut off wave length is same for pure and dyes doped KDP crystal. Π-conjugations electrons in dyes after the irradiation [14] alter the lattice orientation in the doped crystals.

The relative SHG efficiency of irradiated pure and dyes doped KDP was measured by Kurtz powder technique [15]. During the SHG measurement using 1064 nm laser beam on irradiated pure and dyes doped KDP shows intense emission of green light. The peak intensity of dyes doped KDP was improved after irradiation.

5. Conclusions

Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiation such as UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied.

Li^{3+} irradiations lead to the development of a well-defined surface H peak in dyes doped KDP. The depletion of hydrogen from the –OH groups of KDP sample in terms of the possible bond-breaking mechanism. Due to beam interaction, electron moves to the conduction band leaving behind the free hole, which can get self–trapped and configurationally changes occurring in the neighbouring structural units. Irradiation effects diffuse the dyes uniformly in the crystal due to lattice disorder. The NLO efficiency is increased in dyes doped KDP crystals after irradiation. The stability of KDP was improved by doping organic dyes. The nano-islands of dyes in KDP are likely to be dissolved and enhance the non-linear optical properties of these materials.

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