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Gamma irradiation effect on optical and dielectric properties of potassium dihydrogen phosphate crystals

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ABSTRACT

The effect of Co^{60} gamma-ray irradiation on potassium dihydrogen phosphate crystals is investigated at doses ranging from 1 kGy to 100 kGy with different diagnostics, including UV–Vis absorption spectroscopy, fluorescence spectroscopy, DC electrical conductivity, positron annihilation lifetime spectroscopy and Doppler-broadening spectroscopy. The optical absorption spectra show a wide absorption band between 250 and 400 nm after γ-irradiation and its intensity increases with the increasing irradiation dose. The simulation of radiation defects show that this absorption is assigned to the formation of substitutional impurity defects due to Al, Mg ions substituting for K ions. The fluorescence peak at 355 nm blue shifts after irradiation. The fluorescence intensity is observed to increase with the increasing irradiation dose. The positron annihilation lifetime spectroscopy is used to probe the evolution of vacancy-type defects in potassium dihydrogen phosphate crystal. The variation of size and concentration of vacancy-type defects with the different irradiation dose is investigated. The Doppler-broadening spectroscopy gives direct evidence of the formation of irradiation-induced defects. The dc electrical conductivity of γ-irradiated potassium dihydrogen phosphate crystals increases with the increasing irradiation dose when the dose is less than 10 kGy, whereas keeps constant at high irradiation dose of 100 kGy. The increase of electrical conductivity is associated with the increase of the proton defect concentration in the crystal. A possible explanation about the change of proton defect concentration with irradiation dose is presented.

1. Introduction

KDP (Potassium dihydrogen phosphate or KH_2PO_4) is a nonlinear transparent dielectric crystalline material used in various laser systems for harmonic generation and electro-optic switching [1]. With the increase of laser intensity, laser-induced optical absorption may appear in the KDP crystal and influence the device performance [2,3]. Moreover, the solid-state lasers are often designed to work in the strong external fields with ionizing irradiation which will result in the damage of the laser material [4,5]. Different irradiations on crystalline materials will change their physical and chemical properties [6–9]. Therefore, understanding of irradiation effect on transparent dielectric materials in particular KDP crystal is an important problem and has practical applications in space radiation environments.

An undesired irradiation-induced optical absorption appears in the 300–650 nm spectral region when KDP crystals are exposed to ultraviolet laser or high energy ray irradiation [2,10,11]. Some defects responsible for this optical absorption have been identified using electron paramagnetic resonance (EPR) spectroscopy at low temperature [12,13], such as the hydrogen atoms [14], oxygen vacancies [15], self-trapped holes, and holes trapped adjacent to hydrogen vacancies [16]. On the other hand, some defect centers formed in KDP crystals by impurity ions incorporated in crystal lattice are produced under γ-ray irradiation [17,18]. For instance, Garces et al. reported that the undesired optical absorption bands in the 200–300 nm region are due to Fe ions substituting phosphorus and then forming the $(FeO_4)^{2-}$ defect center after X-ray irradiation [19] and similar behavior of the UV curves in the low wavelength region (200–280) was observed by other authors

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[20,21]. Similar process has been reported in the case of Cr ions substituting phosphorus by Alybakov et al. [22]. Recently, dielectric properties of KDP crystals have been investigated under γ-irradiation to understand the mechanisms of the formation of irradiation defects. Leuchenko et al. reported that the change of electrical conductivity after γ-ray irradiation is attributed to the decrease of L-defect concentration in KDP crystal and disappearance of irradiation-induced defects under thermal, laser, and ionizing irradiation annealing in γ-irradiated KDP crystal containing arsenic ions [23,24].

Positron annihilation lifetime spectroscopy (PALS) is a very valuable nondestructive probe technique which can be used to study vacancy-like defects acting as attractive and deep trapping centers for positrons [25]. Positrons trapped in a vacancy-type defect are accompanied with subsequent changes in annihilation parameters. For instance, the lifetimes of trapped positrons become longer due to the reduced electron density in this defect [26]. Therefore, the positron annihilation lifetime spectroscopy can lead to reliable information on vacancy-related defects. Because the momentum distribution of electrons before annihilation in such defects differs from that of electrons in the bulk material, these defects can be recognized by measuring the Doppler broadening spectra. The changes in the spectra are characterized by S and W parameters, the annihilation intensity with low- and high-momentum electrons, respectively. In general, the variation of W parameter versus S parameter (W–S plot) is used to identify defect due to the slope of the line the S and W parameters form in the (S, W) plane [27]. Implicitly, W–S plots are very usefully for defect identification.

In the present paper, the UV–visible entire absorption and specifically focus on the UV absorption spectra of KDP crystals has been studied with γ-ray irradiation at different doses. The purpose of such study was understood the effect of impurities which cause the formation radiation-induced defects in samples. To characterize the influence of irradiation-induced defects on dielectric properties, the dielectric spectrum is investigated. The variation of vacancy-type defects is also performed by using the positron annihilation lifetime spectroscopy (PALS) and Doppler broadening spectroscopy with high detection sensitivity.

2. Experimental and computational model

The nominally pure KDP crystalline samples were cut to type II frequency conversion orientation and six planes were optically polished. The samples were plane-parallel transparent plates. The samples used for PALS measurement were square with dimensions of $10 \times 10 \times 1$ mm^3; the others were $10 \times 10 \times 4.5$ mm^3. The samples were irradiated at room temperature with Co^{60} γ-ray to the dose of 1 kGy, 10 kGy and 100 kGy at the dose rate of 5.834 Gy s^{-1}. A Lambda 950 (PerkinElmer) spectrophotometer was used to measure optical absorption of the KDP crystals. It uses a gridless Photomultiplier tubes with Peltier-controlled PbS detector to achieve high performance testing across the spectral range up to 3300 nm. The UV/Vis resolution reaches 0.05 nm and the wavelength accuracy is ±0.08 nm. Positron annihilation lifetime measurements were performed using a conventional fast-slow coincidence system with time resolution of about 209.23 ps in full width at half maximum (FWHM). A 13-μCi ^{22}Na radioactive source was sandwiched between two identical samples. All lifetime measurements were achieved at room temperature and a total of about 2 million counts were collected for each spectrum. Then a current LT 9.0 software package was used to analyze the measured positron lifetimes spectra. All the lifetime spectra have adopted three lifetimes fitting with free intensity and lifetime taking into account an additional source subtraction of 340 ps with an intensity of 21.2%. This spectrometer has been used for measurements as a function of irradiation dose. The Doppler broadening spectrum was measured simultaneously using two high purity Ge detectors. The results were analyzed in terms of the *S*- and *W*-parameters. Dielectric conductivity measurement was carried out in the 0.01 Hz–10 MHz frequency range using an Alpha-A LF Analyzer at room temperature. The sample was sandwiched between two external electrodes whose distance should be adjusted according to the sample thickness and no gap was permitted between sample and electrodes. Lastly, a time-of-flight secondary ions mass spectrometry (TOF-SIMS) was utilized to detect the impurity element in KDP crystals. This is a high sensitive (on the order of magnitude of ppm to ppb for most species) and straightforward analytical method that is capable of detecting trace elements.

3. Results

3.1. TOF-SIMS analyses

TOF-SIMS is a powerful analytical technique used for trace elemental determinations. This method is that uses micrometer size $^{16}O^-$ ion beam to remove atoms from the outermost surface of the sample. These atoms are then accelerated into a "flight tube" and their mass is determined by measuring the exact time when they reach the detector. In the test, the analytical area of every point is 200 μm^2. An average value of four test points for each sample is regarded as the final test data of this sample. Fig. 1 shows the evolution of main impurity concentration correlated with the various sputtering time. The lower concentration impurities, such as Ca, Cr, Fe, Cu, As, and Sr, is not shown in Fig. 1. The concentrations of Na, Al, Mg, and Si decrease rapidly with the increasing sputtering time. The concentrations of Ce and La do not change in the sputtering process. The Al element may be from the polishing process and abrasive powder, while other elements may be from process during growth.

3.2. UV–Vis absorption spectroscopy

Fig. 2 shows the optical absorption curves of KDP crystals before and after irradiation at room temperature. It can be seen that there are three week absorption bands near 275 nm, 300 nm, and 355 nm for the pristine and irradiated samples. Compared with the pristine KDP, absorption intensity of γ-irradiated samples increases with the increasing irradiation dose in the whole spectral range, especially in the ultraviolet part of the spectrum (see the

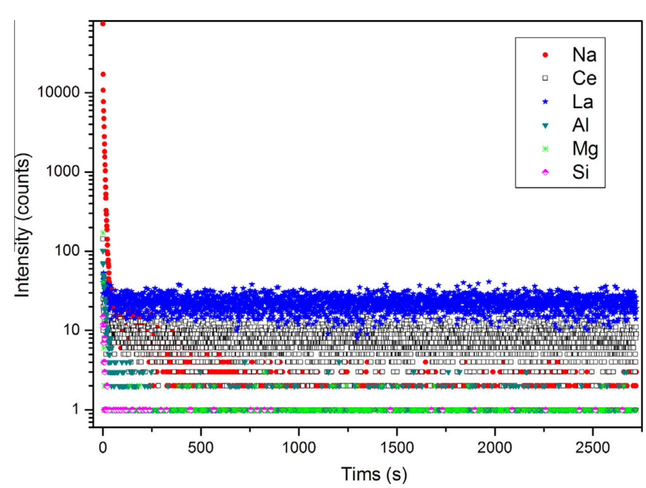

Fig. 1. TOF-SIMS depth profiles of main elements in KDP crystals.