Optics Properties of X-ray Irradiated L-Threonine Crystals

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Abstract: In this work we study optical properties of L-threonine crystals with stables radicals induced by X-ray irradiation. We have measured the absorption spectra, the index of refraction, the second-harmonic generation of irradiated and not-irradiated materials.

(160.4760) Optical properties; (160.4760) Organic materials

1. Introduction

The study of new organic materials with high optical nonlinearities is important because of their potential for applications in devices for harmonic generation, amplitude and phase modulation, switching and signal processing, for instance. Also, some organic crystal have attracted much attention due to their particular properties such low cost productions, environment friendly material and wide variety of new material not study on the nonlinear optical point of view. Among organic materials, the class of amino acids crystal like L-arginine phosphate Monohydrate (LAP) [1], L-threonine [2], L-lysine monohydrochloride dihydrate [3] was already well investigated. Recently, the interest on irradiated organic material with high energy electron (MeV) and γ radiation have increased [4,5]. Such irradiation in the crystals allows formation of stables radicals and changes its absorption and refractive index, especially in the blue and UV spectrum. These effects are proportional to the dose levels and can be used to produce waveguide and photonic bandgap structures. In this work we studied optical properties of X-ray irradiated L-threonine crystals. Due to radical formations there is one visible change in the crystals. Basically, the L-threonine crystal turns to appear yellowish due to formation of an absorption band the blue region of the spectrum. In order to verify how this irradiation affects the crystal we compare the absorption spectra, the refractive indices, dispersion of the refractive indices and second harmonic generation relative efficiency of irradiated and not irradiated materials.

2. Crystal growth and sample preparation

The L-threonine crystals were grown from aqueous solution with the slow temperature decreasing method, as describe in the ref [2]. Using this method, we grew crystal with good optical quality without visible defects with 1 cm^2 transversal area and 5 cm long. The crystal has $P2_12_12_1$ orthorhombic structure with four molecules in the unit cells and a = 13.611 Å, b = 7.738 Å and c = 5.144 Å cell parameters [2]. In the orthorhombic structure the crystallographic axes a, b and c overlap with main refractive index axes y, x, and z, respectively. The negative birefringent crystal has the optical axes in the xz plane. In this work, we used the $n_z > n_y > n_x$ [6] notation for the refractive indices. The crystals were optically aligned and cut parallel to the xy, xz and yz planes in accord to the specific required measurement.

The samples were exposed to X-ray with 8 MeV for 30 minutes long. This time was enough to reach the saturation on the crystal color change. In the Fig. 1 we shown the L-threonine crystal and irradiated sample that was used to measure the refractive indices.

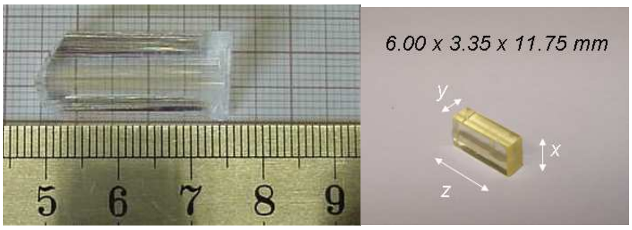

Fig. 1. L-threonine crystal and X-ray irradiated sample cut in main optical directions.

3. Optical properties

The absorption spectrums of irradiated and not irradiated L-threonine crystals are shown in the fig. 2, where the absorbance values are normalized to the same thickness (1 mm). The fresh and irradiated crystals present good transparency from 250 nm up to 1100 nm and from 500 nm up to 1100 nm, respectively. This characteristic allows application on SHG of laser radiation in the near IR range commonly generated in Nd dopped material lasers.

The irradiated crystal does not suffer any significant change in the absorption spectrum in the near IR. The main absorption change only occurs at wavelength bellow 450 nm. One possible explanation for these absorption bands is the formation of a unpaired electron at C-2 carbon atom through C-N bonds breaking and the subsequent electron trapping. Study more precise using EPR and Raman is necessary to determine the mechanism of such change .

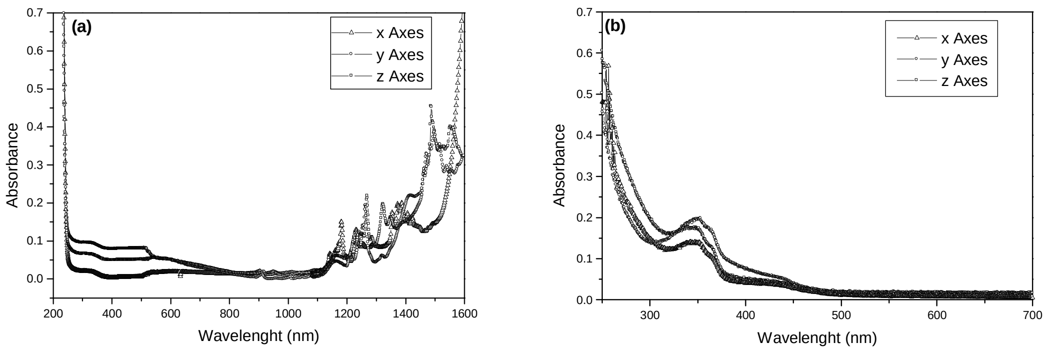

Fig. 2. Absorption spectrum of fresh (a) and irradiated (b) L-Threonine crystal.

The refractive indices were measured in some wavelengths by the minimum angular deviation method using a commercial Pulfrich refractometer at constant temperature of 20 ^{o}C. In table 1 we show the results at 546.1 nm for the fresh and irradiated crystal. As can be seen, the indices decrease when the crystal is irradiated but the change is not enough to change the Hobden class 9 for phase matching *loci* [7] for second harmonic generation (SHG).

Table 1. Index of refractions at 546.1 nm for fresh and irradiated crystals.

	Fresh	Irradiated
n_x	1.5234	1.5233
n_y	1.5952	1.5948
n_z	1.6035	1.6031

The SHG efficiency was measured using pulses with 6 ns at 1064 nm and 10 Hz repetition rate produced by a Q-Switched Nd:YAG laser. In order to avoid time consuming method involving large crystal growing, orientation and cut in the phase matching matching directions, we have used simple and consistent powder method. In this case, the samples are obtained from grind crystals. Also, to make reliable SHG efficiency comparison, we have to be very carefully to use the same beam, sample and detection geometries, for all measurements. The second harmonic at 532 nm was collected by a simple lens and detected by large area PIN silicon coupled to a digital oscilloscope. One BG18 filter was used to remove the fundamental beam signal. The KDP was used as a reference sample. Part of the irradiated L-theonine crystal was ground to be used for efficiency measurements. As a result, we observe that the fresh L-threonine presents SHG efficiency of about 30% higher than the irradiated sample and about 90 % of the reference KDP sample.

Also, we have measured carefully the nonlinear refractive index, n_2, and its dispersion in some of the optical axes using the Z-scan method. To do this, we have used one optical parametric amplifier (OPA) which delivery a tunable femtosecond (fs) light source. The OPA was pumped with 150 fs at 1 KHz repetition rate pulses produced by an amplified Ti:sapphire laser. We carry out measurements with pulses with about 120 fs duration and 0.1 μJ energy from 480 nm to 800 nm. The sample for this measurement was one slab with 1 mm thick, 5 mm wide and 10 mm

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high with optical axes at *y*, *x* and *z*, directions, respectively. This geometry allows determination of nonlinearity at *x* and *z* axes with light propagating in the *y* direction.

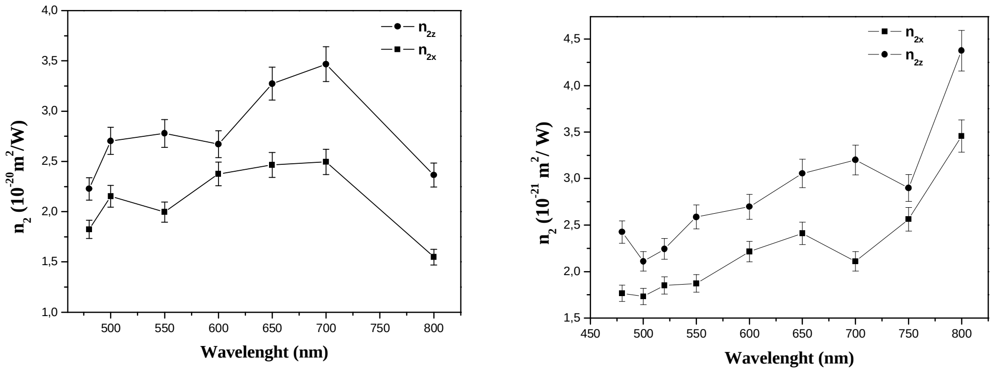

Fig. 3. The value of n_2 for fresh and irradiated crystal.

In summary, we have measured some linear and nonlinear optical properties for L-threonine crystal exposed to high dose of X-ray. Basically, we have observed that the X-ray decrease the linear refractive indices and increase the absorption at 450 nm also decrease the nonlinear refractive indices and SHG conversion efficiency.

4. Acknowledgements

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5. References

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