برگیری اپتیک غیرخطی درجه دوم از نمک های اسیدهای امینه

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چکیده – در مقاله حاضر ساخت و آزمایش نمونه ای از بلور تولید هماهنگ دوم، برومید روی گلایسین، گزارش می شود. بررسی اولیه نشان می دهد که کارآیی تولید هماهنگ دوم این بلور دو برابر یک بلور استاندارد فسفات هیدروژن پتاسیم است. از آنجاییکه این مقرون به صرفه ترین راه تهیه مواد اپتیکی غیر خطی مرتبه دوم است، ساخت این نوع مواد نیمه آلی می تواند مورد نظر تولید انبوه جهت رفع نیاز کشور قرار گیرد.

کلید واژه- اسیدهای امینه، تولید هماهنگ دوم، رشد بلور برمید روی گلایسین، کارایی اپتیکی غیرخطی.

Deriving Large Optical Quadratic Nonlinearity from the Salts of Amino Acids

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Abstract – In the present article, the preparation and testing of a sample of second-harmonic generating (SHG) grown crystal of glycine zinc bromide is reported. The preliminary analysis indicates that the SHG potentiality of the crystal as twice efficient as that of a standard potassium dihydrogen phosphate (KDP) crystal. Since this is the most cost effective avenue ever to produce a class of highly efficient second-order nonlinear optical materials, it would worth considering mass-production of such semiorganic grown crystals to meet the national requirements.

Keywords: Amino acids, Glycine zinc bromide grown crystal, Nonlinear optical efficiency, Second harmonic generation

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1 Introduction

Organic molecules with second-order nonlinear optical properties have various potential in the development of materials for applications for example in second harmonic generation (SHG) and optical switching. In frequency doubling, a pump wave with a frequency of ω generates a signal at the frequency 2ω as it propagates through a medium with a quadratic nonlinearity as:

$$\chi^{(2)}_{\mathrm{SHG}} = \chi^{(2)}(2\omega; \omega, \omega)$$

Since all even-order nonlinear susceptibilities $\chi^{(n)}$ vanish in centrosymmetric media, SHG can occur only in media with no inversion symmetry. Apart from this property, a suitable SHG crystal must meet the requirements like good optical quality, wide transparency region, good mechanical and chemical stability, large birefringence, low absorption, and easy cost-effective fabrication. This latter specification is important from the economical viewpoint to mass-produce efficient SHG crystals at low cost, yet of standard physical quality for usual applications.

An interesting class of potential nonlinear optical materials in this context is amino acids with the glycine being the simplest form. Amino acids contain donor carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group, known as zwitterions, which create strong hydrogen bonds in the form of $N-H^{+}\ldots O-C$. Hydrogen bonds are probably involved in featuring non-centrosymmetric structures in grown crystals. Therefore, in the present investigation, an attempt has been made to prepare and characterize a grown single crystal of glycine zinc bromide (GZB), as a salt of amino acid, and to specifically test its SHG efficiency.

2 γ-Glycine

Glycine exists in six distinct polymorphic forms, i.e., α-glycine, β-glycine, and γ-glycine at ambient temperature and pressure and also δ-glycine, ε-glycine, and β′ -glycine under high pressure. Among the six forms, γ-glycine exhibits strong piezoelectric and nonlinear optical effect. The usual form, α-glycine, is converted into γ-glycine when it is grown in solution. Since γ-glycine crystallizes in a non-centrosymmetric space group $P3_2$, it possesses excellent NLO properties [1]. Also, single crystals of glycine can be grown using additives that show non-centrosymmetric feature. Some prominent examples of such salts are [2,3]: glycine lithium sulfate [$Li_2(SO_4)(C_2H_5NO_2)$], glycine nickel dichloride dihydrate [$NiCl_2(C_2H_5NO_2)(H_2O)_2$], glycine zinc sulfate trihydrate [$Zn(SO_4)(C_2H_5NO_2)(H_2O)_3$], bis(glycine) lithium chromate monohydrate [$CrLi_2(C_2H_5NO_2)_2O_4(H_2O)$], and bis(glycine) lithium molybdate [$Li_2Mo(C_2H_5NO_2)_2O_4$]. Optically active organic amino acids can be mixed with the inorganic salts in order to enhance their physical and chemical properties [4]. Zinc seems to be an appropriate reagent to strengthen γ-glycine grown crystals. For example, the inorganic crystals, such as InAs, InSb, and GaSb, despite their high quadratic nonlinearity, suffer from excessive absorption at the infrared wavelengths around 1550 nm, whereas the laser-induced surface-damage threshold in the transparency window of the zinc-blended grown crystals typically exceeds tens of TW/m^2 for nanosecond pulses [5], depending on the quality of the crystal growth.

3 Preparation of GZB Grown Crystal

Glycine (NH_2CH_2COOH; 98.5%; mp ~ 240ºC, Loba Chemie), zinc bromide dihydrate ($ZnBr_2.2H_2O$; 99% crystalline; mp > 300ºC, Loba Chemie) and distilled water were used for the crystal growth preparation.
Glycine zinc bromide was synthesized by 4:1 ratio of glycine and zinc bromide. The synthesized salt of γ-glycine was grown by the slow evaporation low temperature solution growth technique. The reaction undergoes as: $C_2H_5NO_2$ + $ZnBr_2$ → $C_2H_5NO_2.ZnBr_2$. The saturation of the γ-glycine salt was obtained by dissolving the materials with continuous stirring of the solution using a magnetic stirrer. On reaching saturation, the equilibrium concentration of the solute was determined gravimetrically. The saturated solution was further purified by filtering through the glass filter paper provided with fine pores of 1 μm porosity. The filtered solution was tightly closed with thick filter paper so that the rate of evaporation could be minimized. The solution was kept in an undisturbed condition for 25 days that eventually transparent colorless single crystals with full morphology and good optical transparency were resulted. A UV-visible spectrophotometer (Hewlett Packard 8452A Diode Array) with the measurement range extending from 200 to 1100 nm was employed to record the optical transmittance of a 5 mm thick cut and polished plate of the crystal, as shown in Fig. 1.

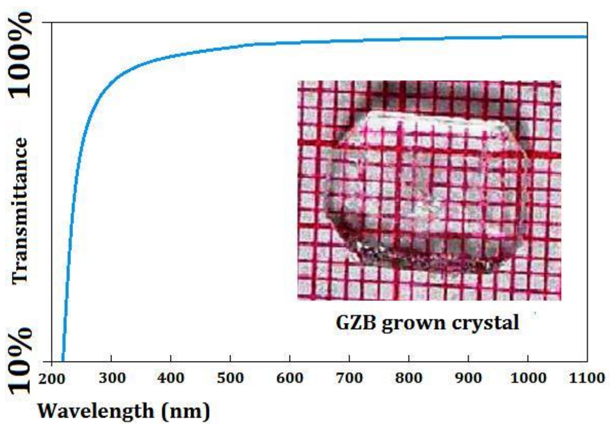

Fig. 1. The optical transparency evaluation of the GZB grown crystal; inset: the snapshot of the crystal.

4 Detection of the SHG Conversion Efficiency

The SHG conversion efficiency defined as the ratio of the emerging second harmonic power to the incident power is one of the most useful measures of the performance of a nonlinear optical crystal. For the present evaluation, the Kurtz-Perry powder technique [6] was employed, which is a crude detection as it probes the sum of all the tensor components of $\chi^{(2)}$. Since each individual particle in the powder is presumed to have arbitrary orientation and the fundamental wave traverses a large number of particles, then the SHG signal is due to an average over all particle angles. Also, the SHG response level depends on a number of parameters, including laser wavelength, bandwidth, particle size, temperature, crystallization solvent, and sample preparation. The proportionality of the intensity of transmitted SHG signal $I_{2\omega}$ to other parameters is [6]:

$$I_{2\omega} \propto \frac{n_{2\omega}^2}{(n_\omega + n_{2\omega})^2}\left[\frac{l_c d_{2\omega} I_\omega}{\lambda(n_\omega+1)^2(n_{2\omega}+1)}\right]^2 r,$$

where n_ω and $n_{2\omega}$ are respectively the refractive indices of nonlinear medium at ω and 2ω and that for most compounds $n_\omega \approx n_{2\omega}$, λ is the wavelength of fundamental laser light, l_c is the coherent length defined as $\lambda/4(n_{2\omega} - n_\omega)$, $d_{2\omega}$ is the nonlinear optical coefficient, and r is the particle size.

The experiment was carried out at room temperature. A pulsed Nd:YAG laser (Quanta-Ray) emitting a continuous train of 8 ns pulse at a repetition rate of 10 Hz was used. The 2 mm radius laser beam of fundamental wavelength 1064 nm was made to fall on the sample normally, as shown in the Fig. 2.

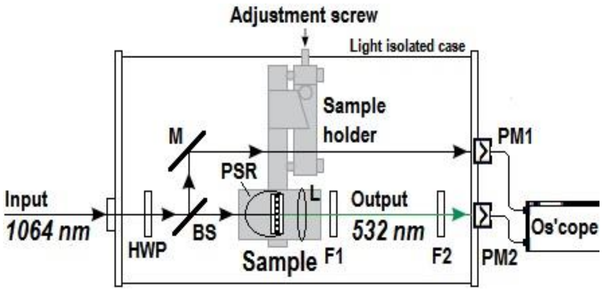

Fig. 2. The experimental setup for measuring the SHG efficiency: M is mirror, BS is beam splitter, HWP is half wave plate, PSR is parabolic scattering reflector, L is lens, F1 and F2 are filters, PM1 and PM2 are identical phoromultiplier tubes.

The GZB grown crystal sample was pulverized into uniform microcrystal particles of ~ 100 μm by using a ball mill and then was packed densely between two high-quality microscope glass slides of ~ 1.0 mm apart. A lens and two filters were used on the emerging path of the beam before reaching the photomultiplier tube 2 (1P28 at 900 V bias): first filter was an IR-cut filter to block the rays above 700 nm and the second one (ZET532-EX) had the bandpass 529-535 nm. The SHG signal was detected by the photomultiplier tube 2 and a fast double trace digital oscilloscope (Tektronix TDS 520 with a bandwidth of 500 MHz). As a reference material, KDP crystal in particle form under the identical condition in the same home-made experimental setup was used. The obtained data has been tabulated in Table 1, confirming the successful sample SHG efficiency as twice that of a standard KDP crystal.

Table 1. The experimental data

Microcrystalline particles	Measured output (mV)	SHG efficiency
KDP	217	1
GZB	443	2.04

Conclusion

We carried out a laboratory scale experiment to grow a physically-defined and transparent single crystal of GZB by solution growth. The powder SHG test confirmed the rich nonlinear optical property of the crystal, and further preliminary analysis revealed its SHG efficiency as roughly twice that of a standard KDP crystal. Since the harmonic generator modules are essential optical components in various laser-based applications, the present grown crystal, or its possible chemically variants, would be beneficial enough, in terms of both the cost-effectiveness and the response superiority, to pursue the study more analytically for a larger plan beyond just a laboratory scale experiment, but in the context of mass production.

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