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Note

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Optical characteristics of bismuth thiourea chloride single crystals

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Abstract : Bismuth thiourea chloride single crystals with molecular formula Bi [CS $(NH_2)_2$ Cl_3 (BTC) have been grown in gels at ambient temperature and characterized by optical techniques. Refractive indices along different crystal axes were determined for different wavelengths of visible light. BTC crystals are optically negative and uniaxial. The optical absorption characteristics of BTC have been measured in the wavelength range 200nm-1400nm. Optical second harmonic generation (SHG) of Nd YAG laser (λ = 1064nm) has been observed in BTC single crystal.

Keywords : Nonlinear optical properties, refractive index, bismuth thiourea chloride, UV vis IR spectra

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In recent years, the nonlinear optical (NLO) properties of some products of thiourea [1,2] have attracted greater interest, because these metal - organic materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. Thiourea crystal belongs to the orthorhombic space group at room temperature [3] and exhibit ferroelectricity between 169K and 202K [4]. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment [5] and due to its ability to form an extensive network of hydrogen bonds. Unfortunately, most of the thiourea complexes known so far, are centrosymmetric and only few crystallize in non-centrosymmetric space group, which is a general requirement of nonlinear optics. The interaction of light with optical crystals depends both on the arrangement and nature of the atoms. The study of optical characteristics of crystal is essential to know the directions of symmetry axes in the crystal. The optical characteristics also provide useful preliminary information on the arrangement of molecules in the unit cell. In this note, room temperature measurements of refractive indices, dispersion, birefringence, optical absorption and second harmonic generation (SHG) in BTC single crystals are presented.

The crystal growth process involves the diffusion of mixture of bismuth trioxide in HCl solution into acidified sodium metasilicate gel impregnated with thiourea solution at ambient temperature. The experiment was carried out in Corning glass tubes of diameter 25mm and length 150mm. The chemicals used were:

(i) Sodium metasilicate (SMS)-----Na_2SiO_3

(ii) Acetic acid------------------- CH_3COOH

(iii) Thiourea------------------------$CS(NH_2)_2$

(iv) Bismuth trioxide------------------------Bi_2O_3 and

(v) Concentrated hydrochloric acid------HCl.

The optimum condition for growing good quality BTC single crystals was established after conducting a series of experiments. The suitable conditions to grow best quality crystals were - gel density of SMS : 1.04gm/cc, gel pH: 4.5, gelling time 24hours, growth temperature: 30°C. The crystals are elongated along *c*-axis direction. The maximum size of the good quality crystal obtained was 12mm × 7mm × 7mm. The morphology of BTC single crystal is shown in Figure 1. BTC crystallizes [6] in hexagonal system with unit cell dimensions a = 13.5335(10) Å; b = 13.5335(10) Å; c = 7.1093 Å; α = 90°; β = 90°; γ = 120° and space group P3.

In order to determine the refractive indices and birefringence samples were prepared with the two mutually perpendicular planes parallel to the BTC crystal axes ($a = b$, c). The refractive

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indices of the crystal within the visible region were measured by the Brewster's angle method. The dispersion characteristics of the crystal were determined by using a monochromator,

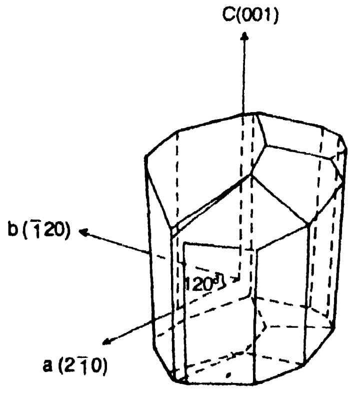

Figure 1. Morphology of BTC single crystal.

mercury lamp, sodium lamp and He-Ne laser as light source. An optical absorption measurement for BTC single crystal with thickness 1.0mm was made with a Cary-14 spectrometer in the range of 200nm-1400nm at room temperature. The SHG experiments were made with a focused, linearly-polarized Nd: YAG laser operating at λ = 1064nm (having peak power P_w = 2.5kW, pulse width = 250ns, the beam diameter W = 0.12mm, power density = 1.3MW/cm^2). Y-cut crystal of thickness 1mm was taken as reference material for the SHG measurements. The generated second harmonics was separated from the fundamentals by a glass filter at 532nm, while blocking completely 1064nm radiation using $CuSO_4$ solution.

The room temperature refractive index variation with wavelength of light for BTC single crystal is shown in Figure 2. The accuracy of refractive index measurement in this case was ± 0.005. The refractive indices were fitted by means of a single term Sellmeier oscillator equation, *viz* $n^2(\lambda)-1 = S_0\lambda_0^2/\left[1-\lambda_0^2/\lambda^2\right]$, where n is the refractive index (for the wavelength λ), S_0 and λ_0 are constants. The relation was found to be appropriate for the region of low absorption [7]. Based upon the measured values, the constants S_0 and λ_0 are

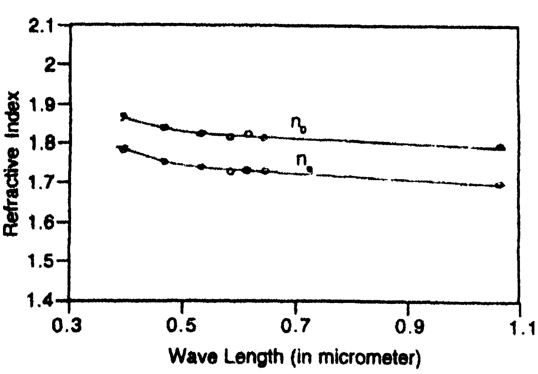

Figure 2. Dispersion of linear refractive indices of BTC single crystals.

evaluated by least square fitting method. The results of this fit are shown in Figure 3, where $1/n^2-1$ is plotted as a function of $1/\lambda^2$. The Sellmeier parameter S_0 (m^{-2}) of BTC single crystals corresponding to n_e and n_0 are 2.309 × 10^{16} and 1.660 × 10^{16} respectively. The Sellmeier parameter $S_0\lambda_0^2$ corresponding to n_e and n_0 are 3.164 and 2.837 respectively. BTC crystallizes in hexagonal system and the optic axis lie along the crystallographic *c* axis. Refractive index study showed that it is an uniaxial crystal with refractive index of ordinary ray is greater than for the extraordinary ray *i.e.* $n_0 > n_e$. The birefringence is 0.08 and found to be small. BTC is optically negative.

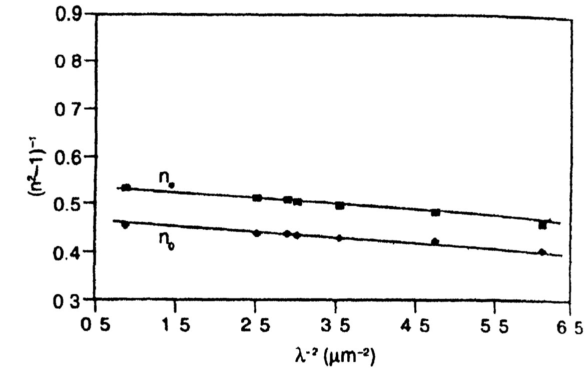

Figure 3. Dispersion of linear refractive indices of BTC fitted to a single term sellmeier oscillator model.

The optical absorption of BTC crystal is shown in Figure 4. Single crystal of BTC is transparent in the wavelength range 250nm-1200nm. BTC has wide transparency window. The absorption spectrum in the visible region shows a small absorption peak around 500nm and is $\lambda/2$ of 1064nm, which may be due to yellow color of the crystal. Frequency doubling may be more efficient in the regions other than 1064nm in the case of BTC. An absorption peak around 320nm may be attributed to the electron excitation from $\pi \rightarrow \pi^*$ orbit which arises due to conjugation.

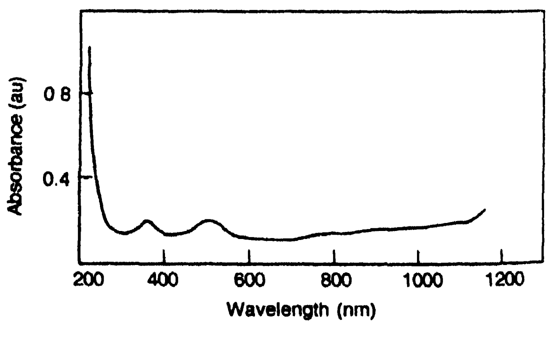

Figure 4. UV *vis* IR spectrum of BTC single crystal.

The SHG experiment revealed that BTC crystal has measurable SHG intensity. The conversion efficiency was calculated from the measured pulse energies, taking into account the filter transmission loss. The energy of the second harmonic pulse was present for fundamental beam pulses of different energies, staying well within the respective damage threshold of the crystals. BTC showed a maximum SHG efficiency of 40% of quartz. The phase matching angle as calculated from the refractive index measurements, is $\theta_m = 32.75^0$ for the fundamental wave of wavelength 1064nm. The optical nonlinearity in BTC may be attributed to the hydrogen bond formation due to conjugation during crystallization. The damage threshold of BTC single crystals for Q-switched Nd: YAG laser radiation was measured to be 0.32GW/cm^2. Surface damage was observed when the intensity of the incident laser radiation was increased beyond this value. The surface damage is said to occur if on radiation, a visible pit is formed on the surface [8].

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