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Thiosemicarbazide Family of NLO Single Crystals for Nonlinear Optical Applications –A Review

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Abstract: Single crystals are the pillars for the development of new generation of devices to meet the demands put forth by the society. This demand requires large high quality homogeneous single crystals along with measurements on variety of properties. Hence, crystal growth and characterization of technologically important materials have evolved into thrust area of research in materials science. This review paper deals with the thiosemicarbazide family of a single crystal, a promising crystal for non-linear (NLO) applications. Non-linear optical studies reveal that the dopant increased the efficiency of the thiosemicarbazide family of single crystal, and several reports are discussed. Recent papers reveal that the thiosemicarbazide family of NLO single crystal possesses excellent optical, thermal, mechanical properties that make it a strong candidate for photonic devices.
Key words: NLO, Crystals, Thiosemicarbazide and Photonic applications.

1. Introduction

Crystals grown nowadays find places ranging from microelectronics, optoelectronics, medical instruments, radar systems, communication systems, defence, and laser sources to the space vehicles viz., satellites. Growth of large size single crystals with quality and perfection has been identified as an important task to meet the requisites of technology development and device applications. In single crystals, charge carriers can move freely, the wavelength associated with a moving charge carriers are long compared with the lattice spacing and not scattered by the individual atoms, which gives the ability for the crystals to interact with electromagnetic waves with little attenuation.

Inorganic materials are much more matured in their applications to second-order NLO than organics. Most commercial materials are inorganic especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long term promise than inorganic materials. Growth of inorganic single crystals has been a subject to perennial concern in order to use these materials for device applications. However, to enable a material to be potentially useful for nonlinear optical applications, the material should also be available in bulk form. The search for new frequency conversion materials over the past decade has led to the discovery of many organic NLO materials with high nonlinear susceptibilities. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganics has been found to be overwhelmingly successful in the recent past. Hence, recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness. Recently, metal complexes of urea and urea analogs have been explored.

Nonlinear optical (NLO) materials find extensive optoelectronic applications such as optical frequency conversion, optical data storage and optical switches in the initially confined laser fusion systems. Incorporation of metals into organic ligand gives a new dimension of study. An important aspect of utilizing these materials for nonlinear optics is their unique charge transfer transitions either from metal to ligand or from ligand to metal. Due to this, in semiorganic materials, the metal – ligand bonding is expected to display large molecular hyperpolarizability, because of the transfer of electron density between the metal atom and the conjucated ligand system. The metal– organic coordination compounds as NLO materials have attracted much more attention for their considerable high NLO coefficients, stable physico-chemical properties and better mechanical intension. The present review focuses on and discusses the important properties of thiosemicarbazide family of NLO single crystals.

2. Materials and Methods

2.1 Growth from solution

Low temperature solution growth method has very good control over growth conditions. It allows growing good quality crystals with fever defects, since the growth occurs at ambient temperature and from free from thermal shock. Materials having melting point at low temperature can also be grown by low temperature solution growth method. Crystallizer used for the growth generally has temperature control accuracy ± 0.01°C. Materials having low solubility can be grown by slow evaporation methods, since small thermal fluctuations lead to drastic changes in super saturation inducing multi-nucleation and hence growth defects affected.

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low.

2.2. Slow evaporation

Evaporation is one of the easiest methods for crystallizing small molecule compounds and works best for compounds which are not sensitive to ambient conditions in the laboratory. Prepare a saturated or nearly saturated solution of the compound in a suitable solvent. The solution is transferred to a crystal growing dish which is covered properly and allowed to evaporate without any disturbance to get best quality crystals. The choice of solvent influences the mechanism of crystal growth. Repeat the experiment to screen a large number of solvents or solvent mixtures to find the optimum for crystal growth. Typical growth conditions involve temperature stabilization to about ± 0.005 °C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of stability.

2.3. Slow cooling

If the solubility decreases with decreasing temperature and solute-solvent systems are less than moderately soluble, then cooling a saturated solution will deposit solid on lowering the temperature. Saturated solution of the compound is prepared and is heated to just its boiling point or a just below it. The solution is transferred to a crystal growing dish and covered it to avoid contamination. Accurately controlled cooling requires an electrically controlled heater-programmer. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

3. Results and Discussion

Single crystals of bulk size with ease of crystal growth process at ambient conditions, good transparency from near IR to deep UV radiation, high laser damage threshold and flexibility in phase matching condition like inorganic crystals and nonlinear property like organic crystals are require to tune the laser sources to generate radiation in UV region with maximum efficiency. Structural and other defects put hindrance to capitalize the advantages offered by the nonlinear optical materials. However suitable crystal growth techniques may allow growth of crystals with minimum defects. The present investigation focuses on the low temperature solution growth method grow crystals since this method offer the growth to occur closeness to ambient temperature and free from thermal shock. While the search of materials with NLO property along with good physical, chemical and mechanical characteristics continues, semi-organic or metal organic crystals, which bridge the outstanding properties of both inorganic and organic crystals have been identified as alternate materials. The present work is focused on the growth and characterization of thiosemicarbazide family of NLO single crystals.

3.1 Thiosemicarbazide Family of NLO Single Crystals

The metal thiocyanates and their Lewis-base adducts are one of the interesting themes of structural chemistry. As second order nonlinear optical (SONLO) materials, bimetallic thiocyanates: Zinc cadmium thiocyanate (ZCTC), Zinc mercury thiocyanate (ZMTC), Cadmium mercury thiocyanate (CMTC), Manganese mercury thiocyanate (MMTC) exhibit efficient SHG at short wavelengths. Spectroscopic and thermal properties of iron mercury thiocyanate (FMTC) crystals were reported [1]. Bis(dimethylsulfoxide) tetrathiocyanato-cadmium(II) mercury(II) (CMTD), a promising organometallic NLO crystal was grown and characterized by Rajarajan et al [2] and the SHG efficiency of the crystal was found to be 15 times that of urea. A highly efficient nonlinear optical crystal of tetrathiourea mercury (II) tetrathiocyanato zinc (II) (TMTZ) was grown by Rajarajan et al [3]. Optically clear manganese mercury thiocyanate (MMTC) crystals have been grown by Joseph et al [4]. The high second harmonic efficiency of nearly 18 times that of urea and the wide optical transmittance window (373 - 2250 nm) of MMTC indicate that this material is an excellent candidate for photonics device fabrication.

The influence of metallic substitution (Mg_2^+ and Cd_2^+) on the physical properties of MMTC was studied by Joseph et al., [5] and it was found that metallic substitution has improved the physicochemical properties. Highly efficient single crystals of zinc cadmium thiocyanate (ZCTC) with SHG efficiency 12 times that of urea was grown by Joseph et al [6]. ZCTC has a UV cut-off wavelength of 290 nm and a high thermal stability of 350 ºC. Nisha Santha Kumari et al., [7] have also grown Zinc Cadmium Thiocyanate (ZCTC) single crystals with dimensions upto $12 \times 2 \times 1.3$ mm^3 in Silica gel.

3.2 Thiosemicarbazide cadmium chloride monohydrate (TSCCCM)

Sankar et al [8] obtained single crystals of thiosemicarbazide cadmium chloride monohydrate (TSCCCM) single crystals were grown from aqueous solution by slow evaporation method. The SHG conversion efficiency of TSCCCM crystal was found to be 14 times higher than that of KDP crystal. In TSCCCM crystal structure, the planer π-organic molecules combine harmonically with inorganic distorted polyhedrons. The chlorine atoms in TSCCCM must be involved in the coordinate polyhedral and have promoted the NLO property. The organometallic complex crystals generally are of good NLO activity and have good thermal stability and are suited for applications.

3.3 Triallylthiourea cadmium chloride (ATCC)

Josephine Usha et al [9] developed single crystals of triallylthiourea cadmium chloride has been grown by slow evaporation technique. The single crystal X-ray diffraction and powder X-ray diffraction studies confirm the trigonal structure of the grown crystal. The NLO behaviour of the ATCC crystal was observed by Kurtz powder method by the emission of green radiation. The optical studies show that the grown crystal can be used for NLO applications. FT-IR analysis confirms the presence of functional groups in the as grown crystal. Thermal analysis reveals that the ATCC crystal is stable up to 200°C. In order to find the mechanical strength of the grown crystal, Vickers micro hardness test was used. SEM and AFM have been employed to investigate the surface and growth morphology of the grown crystal.

3.4 Allylthiourea mercury chloride (ATMC)

Sreekanth et al [10] investigated the crystals of ATMC were successfully grown by the slow evaporation method. The cut of wavelength of ATMC crystal is found to be 355 nm. The dielectric constant and dielectric loss are decreased with increasing frequency at different temperatures. Remnant polarization (Pr) and coercive field (Ec) are found to be 1.25 mC/cm^2 and 26.5 kV/cm, respectively. Electrical conductivity studies were proved that the ATMC crystal is a good conductor at high temperatures. Thermal parameters such as thermal effusivity (e), thermal diffusivity (a), thermal conductivity (k), heat capacity (Cp) are also calculated using the photopyroelectric technique.

3.5 Thiosemicarbazide cadmium acetate (TSCA)

Thiosemicarbazide cadmium acetate (TSCA) single crystals were grown by slow evaporation technique by Selvaraju et al [11]. The crystal system was identified from single crystal X-ray diffraction. It is observed that the grown TSCA crystal belongs to monoclinic system and the lattice parameter values are a = 6.675 Å, b = 10.569 Å, c = 23.689 Å and β = 109.20°. TSCA has a wide transparency window from 300 to 1200 nm, which highlights their prospects of applications as NLO materials. This shows the absence of any overtones and absorbance due to electronic transitions above 280 nm. Thermal analysis clearly illustrates that the crystal undergoes decomposition above 163°C. NLO property was confirmed using ND: YAG laser of wavelength 1064nm and the efficiency was estimated to be two times higher than KDP. It is observed that the measured second harmonic generation efficiency of TSCA crystal was two times that of potassium dihydrogen phosphate (KDP).

3.6 Thiosemicarbazide zinc Acetate (TSCZA)

Sankar et al [12] obtained single crystals of organic NLO material TSCZA has been synthesized and crystals were grown by slow evaporation method. The lattice parameter values have been evaluated by single-crystal XRD analysis. From the XRD analysis, cell parameters were determined as a = 4.93Å, b = 6.01 Å, c = 7.32 Å α = 77.04 Å, β =77.07 Å and γ = 83.66 Å. The cell volume is 205 Å. It was found that grown TSCZA crystal was Triclinic system having Space group P. The UV-Vis spectra reveal that the crystals are transparent in the entire visible region with cut-off wavelength at 280 nm. The TGA/DTA studies showed that this crystal is stable up to 170°C. The emission of green radiation confirms the second harmonic generation. From the observations it is concluded that excellent optical quality, moderate thermal stability, increases in SHG efficiency make the thiosemicarbazide crystals zinc acetate appear to a strong candidate for NLO device fabrication.

3.7 Urea thiosemicarbazide

Jayaprakash et al [13] developed good quality of single crystals of Urea thiosemicarbazide single crystal was grown by low temperature solution growth method from aqueous solution at room temperature. The cell parameters and crystalline nature of the crystals were estimated from X-ray diffraction studies. The unit cell parameters are a = 4.87 Å, b = 5.95 Å, c = 7.25 Å and α = 77.59°, β = 76.69°, γ = 83.74° and volume = 199 $Å^3$. From the data, the grown crystal is belongs to Triclinic with space group is P system. The optical window and low cutoff wavelength are identified from UV analysis. Strong absorption was observed at 255 nm, which indicates that this material is a potential candidate for generating blue-violet light using a diode laser. The second harmonic efficiency of the grown crystals was measured by Kurtz-perry powder method. Emission of bright green light from the tube confirm the generation of second harmonics in the material. Photoconductivity study reveals the negative photoconductivity nature of the crystal.

3.8 Thiosemicarbazone of Benzophenone (TSCBP)

Thiosemicarbazone of Benzophenone (TSCBP) is a semi-organic crystal which is grown by solution growth technique by adopting slow evaporation method from the solvent methanol by Pandian et al [14]. The crystal dimension up to $14X6.5X4mm^3$ obtained. The UV cut off of Thiosemicarbazone of benzophenone (TSCBP) is 310.46 nm and there is no absorbance band between 325-950 nm. The molecular structure was analyzed by chemical environment of magnetic nuclei such as ^{1}H and^{13}C. It confirms the grown crystal Thiosemicarbazone of (TSCBP) is thermally stable up to 184.14°C. Second harmonic generation efficiency of the powdered Thiosemicarbazone of benzophenone (TSCBP) was tested using Nd:YAG laser and it is found to be ~0.8 times that of potassium dihydrogen phosphate (KDP).

3.9 Cadmium chloride incorporated Thiosemicarbazide (CTSC)

Thomas Joseph Prakash et al [15] developed the optical quality of bulk single crystals of cadmium chloride incorporated Thiosemicarbazide crystals were grown by slow evaporation solution growth technique. The grown crystals were subjected to single crystal X-ray diffraction for the estimation of the lattice parameters and it was found that the title compound crystallizes in monoclinic system with Cc space group. The UV Vis NIR spectral analysis provides the information regarding the optical parameters of the crystal. It was found that the title compound possesses a wide transparency window with a lower cut off falling within the visible light region < 300 nm which was confirmed in the excitation spectrum of the Luminescence analysis. Hence it can be concluded that the title material exhibits NLO property. The melting point and the thermal stability were checked by the TG/DTA analysis. This result coincides with the DTA curve that the material is stable up to 147°C which corresponds to the melting point of the crystal. The mechanical stability was evaluated by the Vicker's microhardness test and the results suggest that CTSC crystals belong to the category of soft materials. NLO studies confirm that CTSC crystals are eligible candidates in NLO applications. Powder SHG efficiency obtained for CTSC monohydrate is about 1.9 times that of potassium dihydrogen orthophosphate (KDP) crystal.

3.10 Thiosemicarbazone of benzophenone and of benzaldehyde

Pandian et al [16] investigated the thiosemicarbazone of benzophenone and of benzaldehyde crystals were successfully grown using slow evaporation solution growth technique, using methanol as a solvent. The FT-IR spectral analysis gives an idea about the presence of functional groups. The UV-Visible spectrum proves the transparent nature of the crystal between 320- 800nm.The molecular structure of the thiosemicarbazone derivatives were suitably correlated with the ^{1}H NMR spectral data. Thermal stability of harvested crystals was analyzed by TGA –DSC studies and found that both are thermally stable upto 150^{o}C. The band gap energy and SHG efficiency of thiosemicarbazone of benzophenone and benzaldehyde were correlated. The non-linearity of the both thiosemicarbazone of benzophenone and benzaldehyde crystals was proved by the Kurts and Perry second harmonic generation test. The relative SHG efficiency obtained for thiosemicarbazone of benzophenone is found to be about 2.8 times higher than that of potassium dihydrogen orthophosphate, where as thiosemicarbazone of benzaldehyde is found to be about 5.1 times higher than that of potassium dihydrogen orthophosphate crystals.

3.11 Thiosemicarbazide lithium chloride [TSLC]

Thiosemicarbazide lithium chloride [TSLC] a new semiorganic nonlinear optical crystal has been synthesized by Maadeswaran et al [17].Chemical composition of the synthesized material was confirmed by elemental analysis. Powder X-ray diffraction (XRD) pattern of the grown crystal has been studied. Functional groups present in the materials identified by FTIR spectral analysis. The optical transmission was studied through UV-vis spectrometer. Thermal analysis is carried out on the crystal and infrared to be stable at 176^{o}C. The second harmonic generation (SHG) of the TSLC crystal was confirmed using Nd:YAG laser and also fluorescence spectral analysis is carried out for the TSLC crystal.

3.12 Cadmium thiosemicarbazide bromide (CTSB)

Maadeswaran et al [18] developed good quality Cadmium thiosemicarbazide bromide, a new semiorganic material has been synthesized by solvent evaporation technique at room temperature. Lattice parameter values were determined by using single crystal XRD. The title material CTSB crystallizes in triclinic system with space group P1, the lattice parameter values are a=5.09 Å, b=6.14 Å, c=7.53 Å, α=77.80°, β=77.20 °, γ=84.00 °, V=225 Å^3.The sharp well defined Bragg's peak confirms the crystalline nature of the materials and calculated average crystallite size is about 89 nm. The optical transparency and the lower cutoff wavelength were identified from the recorded UV-Vis spectrum. The lower cut-off wavelength was found to be 236nm.The violet fluorescence emission of the crystal confirms its fluorescence behavior. The Kurtz powder second harmonic generation test shows that the crystal is a promising candidate for optical second harmonic generation applications.

3.13Thiosemicarbazide Potassium Chloride [TSCPC]

Thiosemicarbazide potassium chloride [TSCPC] is one of the potential semiorganic materials for many applications. The crystal growth of TSCPC by slow evaporation method at ambient temperature and its dimension was found to be (5mm×3mm×2mm) by Chandrasekaran et al [19]. The grown crystals where characterized by Fourier transform infrared spectroscopic (FT IR) analysis to find the different modes of vibration due to various functional groups present in TSCPC. The powder X-ray diffraction pattern of the grown crystal has been studied. Thermal stability of the grown crystal was identified at 185°C by using TGA/DTA. The dielectric constant of the crystal was studied as a function of temperature with frequency and the results are discussed. The mechanical property of the grown crystal has been studied using Vicker's microhardness tester. The optical transmission spectrum was investigated to study its linear optical properties using UV–vis spectrophotometer.

3.14Thiosemicarbazide hydrochloride (TSCHCL)

Thiosemicarbazide hydrochloride (TSCHCL) was synthesized by Santhakumari et al [20] using mixing thiosemicarbazide and hydrochloride in 1:1 molar ratio in double distilled water. Single crystals of TSCHCL were grown by slow evaporation at room temperature and were characterized by single crystal X-ray diffraction study to determine the molecular structure and by FT-IR, ^{1}H and ^{13}C NMR spectral analyses to confirm the synthesized compound. Thermogravimetric and differential thermal analyses reveal the thermal stability of the crystal. The transmission spectrum of TSCHCL showed that the crystal is transparent in the wavelength range 380-1100 nm. High resolution X-ray diffractometry (HRXRD) was employed to evaluate the perfection of the grown crystal. Mechanical properties of the grown crystal were studied using Vickers microhardness test. Second harmonic generation efficiency of the powdered TSCHCL was tested using Nd:YAG laser and is 1.5 times that of potassium dihydrogen orthophosphate (KDP).

3.15 Benzaldehyde thiosemicarbazone (BTSC) monohydrate

Santhakumari et al [21] developed single crystals of the organic NLO material, benzaldehyde thiosemicarbazone (BTSC) monohydrate, were grown by slow evaporation method. Solubility of BTSC monohydrate was determined in ethanol at different temperatures. The grown crystals were characterized by single crystal X-ray diffraction analysis to determine the cell parameters and by FT-IR technique to study the presence of the functional groups. Thermogravimetric and differential thermal analyses reveal the thermal stability of the crystal. UV-vis-NIR spectrum shows excellent transmission in the region of 200-1100 nm. Theoretical calculations were carried out to determine the linear optical constants such as extinction coefficient and refractive index. Further the optical nonlinearities of BTSC have been investigated by Z-scan technique with He-Ne laser radiation of wavelength 632.8 nm. Mechanical properties of the grown crystal were studied using Vickers microhardness tester. Second harmonic generation efficiency of the powdered BTSC monohydrate was tested using Nd:YAG laser and it is found to be ~5.3 times that of potassium dihydrogen orthophosphate.

4. Conclusion

Low temperature solution growth method has very good control ones growth conditions. It allows growing good quality crystals with fever defect, since the growth occurs at ambient temperature and freeing from thermal shock. Materials having melting point at low temperature can also be grown by low temperature solution growth method. The nonlinear optical material, thiosemicarbazide family of single crystal growth has been dealt with in this review. The crystals were mostly grown from aqueous solution by slow evaporation technique. This review will provide encouraging inputs to continue the research with various dopants in the growth of thiosemicarbazide family of single crystals that will be highly useful NLO applications.

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