Chapter

Optical Properties of Single Crystals

Senthilkumar Chandran and Srinivasan Manikam

Abstract

Nonlinear optical crystals plays important role in the field of photo electronics, optical communication, optical modulators, laser spectroscopy, frequency conversion and so on. Semi-organic crystals exhibit high NLO response, thermal stability, laser damage threshold, mechanical stability, wide optical window transmittance and structural diversity. Combinations of inorganic and organic molecules yield the semi-organic crystals. Based on its structural diversity it's classified into three categories. In this chapter explains various kinds of semi-organic crystals and their optical, thermal, mechanical, laser damage threshold value and NLO properties and also explains the importance of these crystals in the field of optoelectronics, frequency conversion and other optical applications.

Keywords: nonlinear optical materials, optoelectronics, semi-organic single crystals, laser damage thresholds, optical device

1. Introduction

Over the last three decades, the discovery of new crystals for optical applications has been an emerging area of research. Nonlinear optical crystals are significant in science and modern technology because of their technological importance in the areas of optical communication, optical modulators, laser spectroscopy, frequency conversion, optical bi-stable devices, electro-optical device applications in photonics technology, optoelectronics, information processing, sensors, laser technology, frequency doubling and color displays. Optical applications depend upon various physical features, such as refractive index, birefringence, thermal stability and physicochemical behaviors. Materials with high second-order optical nonlinearity, high optical transmittance with low cut-off wavelength, high laser damage threshold value and easy growth with large dimensions are needed to understand many of these applications. The growth of the new kind of optical crystals with good physical and chemical properties are very important in optoelectronics, photonics laser processing and other applications. The search for high non-linear optical crystals for efficient signal processing has been stimulated by optoelectronics [1–8].

In the field of optoelectronics and photonics, nonlinear optical (NLO) materials are capable of generating the second harmonic frequency. In various device applications, nonlinear optical (NLO) crystals with high conversion efficiency for the second harmonic generation (SHG) and transparent in ultraviolet–visible regions are required. In the current technology world, there is a lot of competition for powerful nonlinear optical devices to satisfy the day-to-day requirements. Usually, organic materials show excellent nonlinear optical (NLO) characteristics. Due to this reason, it becomes important to grow a more and more new organic-based single crystal. Most of the scientists have been focused their research on organic compounds over the past decades as it shows high nonlinear coefficients compared to inorganic materials. But apart from their nonlinearity, the organic molecules are attached with weak van der Walls and hydrogen bonds with π conjugated electrons that make the organic materials are soft, poor physico-chemical stability, low mechanical strength and difficult to polish. Further, these materials have strong absorption in the UV region. On the other hand, the inorganic materials have high laser damage threshold, high melting point and high mechanical strength, but these materials possess moderate NLO behavior. Compare to organic and inorganic materials, the semi-organic materials show combining the properties of both organic and inorganic materials. In this view, semi-organic materials must be analyzed [4–6, 9–12].

2. Selection criteria for NLO materials

In reality, there is no possibility to obtain the perfect nonlinear crystal. The applicability of a specific crystal depends on the nonlinear optical method used, the desired device features and the pump laser. In one application, unique and important material properties may not be relevant in another application. For example, a material with a large angular bandwidth requires the efficient doubling of very high power lasers with poor beam quality. A crystal, which has a lower nonlinearity but permits noncritical phase match angle, will work better than one, which would be more nonlinear, but is critically phase-matched. On the other side, one with a large nonlinearity would be the ideal material for the doubling of femtosecond light signal, even if a very thin crystal can be used to prevent the dispersive expansion of the second harmonic output signals. Nonlinear frequency converters are frequently employed with a capable non-tunable laser source. Kurtz and Perry powder SHG technique was introduced in 1960. In this method, the fine powdered material is irradiated with laser and scattered light is collected and studied for its harmonic capacity with the help of proper filters. This is a rapid and qualitative analyzing method for second-order NLO effect and this technique is suitable for inorganic, organic, semi-organic and new materials. To understand the nonlinear optical effect, the appropriate medium is essential. A non-centrosymmetric crystal, which shows the following characteristics, is required for nonlinear device fabrications (**Table 1**):

1. Good optical quality with large dimensions

2. Wide transmittance with low cut-off wavelength

3. High thermal-mechanical and chemical stability

4. High laser damage threshold value

5. Large birefringence

6. Low absorption cut-off wavelength

7. High second-order nonlinear optical coefficient

8. Easy to device fabrication

S.no	Laser conditions	Crystal parameters
1	Environment	Temperature, Moisture acceptance
2	Beam size	Crystal dimension, spatial walk-off
3	Bandwidth	Spectral acceptance
4	Divergence	Acceptance angle
5	NLO method	Kind of phase- Matching
6	Repetition rate	Surface damage threshold

Table 1.
Parameters for selecting a nonlinear optical crystal.

3. NLO crystal of current interest

Significant developments in new technologies are responsible for the development of new crystals of superior quality. The high-speed and significant amount of optical parallelism would ultimately lead to optoelectronics devices which were a wide range of optical functions will be implemented. The growth of photonic technology, however, depends mainly on the progress made in developing new optical material with improved performance. Crystals with the nonlinear optical response (NLO) are expected to play an important role in facilitating optoelectronic and photonic developments. In optical and electro-optical applications, several NLO crystals have been found out as potential candidates. With the development of many devices using solid-state laser sources, nonlinear optical crystals have received special revolution. For the manufacture of electro-optic modulators that converts an electrical signal into an optical signal and transmission on a fiber optic cable, NLO crystals are very important. Currently, such devices are made with inorganic NLO materials. In this view, further new other crystals should be developed. Recently researcher is showing their keen interest in the development of organic–inorganic salts which show good optoelectronics characteristics [5–12].

4. Semi organic single crystals

Hybrid inorganic–organic structure materials constitute a crucial class of materials that have been extensively analyzed in the last few decades owing to their possible applications in the dielectric, optical luminescence, magnetic, and electronic properties. Because of their tremendous chemical and structural diversity and many technologically applicable properties, these are the fastest-growing fields in materials science. Hybrid inorganic–organic structural materials characterize new generations of crystalline solid-state materials which are formed from metal ions and organic linkers. It is suggested that the semi-organic crystals would have the properties of both inorganic and organic materials. There are three types of semi-organic crystals exist [1–3, 8]:

1. Organic–Inorganic salts

2. Metal–Organic coordination complexes

3. Organometallic compounds

4.1 Organic–inorganic salts

Organic–inorganic salt L-arginine phosphate monohydrate (LAP) was explored in 1971. LAP is a promising biaxial nonlinear optical (NLO) crystal. It crystallizes in the monoclinic crystal structure with P_{21} space group. The chemical formula of LAP is $C_6H_{14}N_4O_2H_3PO_4.H_2O$ [13, 14]. In the past two decades, the growth of LAP crystal and its NLO, electrical, mechanical, optical, surface, thermal and other properties have been well investigated. It has a large effective NLO coefficient. The SHG efficiency is 3.5 times higher than the standard potassium dihydrogen phosphate (KDP) crystal. It has high surface Laser damage threshold (higher than 1GW/cm^2 at 1064 nm), high nonlinear coefficient (>1 pm/V), wide transmission range (220 nm–1950 nm), low hygroscopicity nature and high-frequency conversion efficiency (38.9%). Compared to KDP, it is more sensible and replaces the need for KDP for laser fusion experiments in harmonic frequency generation. The high laser damage threshold of the LAP crystal indicates the advantage of high-power laser devices in frequency conversion and the critical benefit of modern photonic devices. LAP is easy to grow by solution growth technique into a large size single crystal and has improved physicochemical stability than the standard KDP crystal. LAP belongs to KDP family but is particularly hybridized by an amino acid. From the perception of structure, it contains the alternate layers of the acentric tetrahedral inorganic dihydrogen phosphate anionic groups (H_2PO_4), the water molecules (H_2O) and the organic chiral L-arginine molecule [$(H_2N)CNH(CH_2)_3CH(NH_3)^-COO^+$], combined by positive–negative coulomb interactions and hydrogen bonds (**Figure 1**). Planar guanidinium and carboxylate groups are thought to be responsible for the SHG at the two ends of L-arginine. In many aspects, the LAP crystal can match with the inorganic NLO potassium dihydrogen phosphate crystal. Furthermore, it has a larger NLO coefficient d_{21} = 2.14 d_{36}(KDP). It has been analyzed it is one of the good material for ultrafast signal and powerful laser doubling techniques [8, 13–17].

Considerable research has been made to the growth of LAP crystal derivatives, with the expectation of the enactment of NLO performance, surface damage threshold, mechanical strength and optical transmittance. The deuterated LAP (DLAP) is one of its analogues with improved IR transmittance and a wider frequency conversion region. DLAP was assumed to be an efficient material to replace the conversion efficiency of the KDP crystal. DLAP can be used in laser fusion experiment and many high-tech areas. DLAP is the deuterated form of LAP, in which the protons have been replaced. The absorption noted around 1000 nm, in

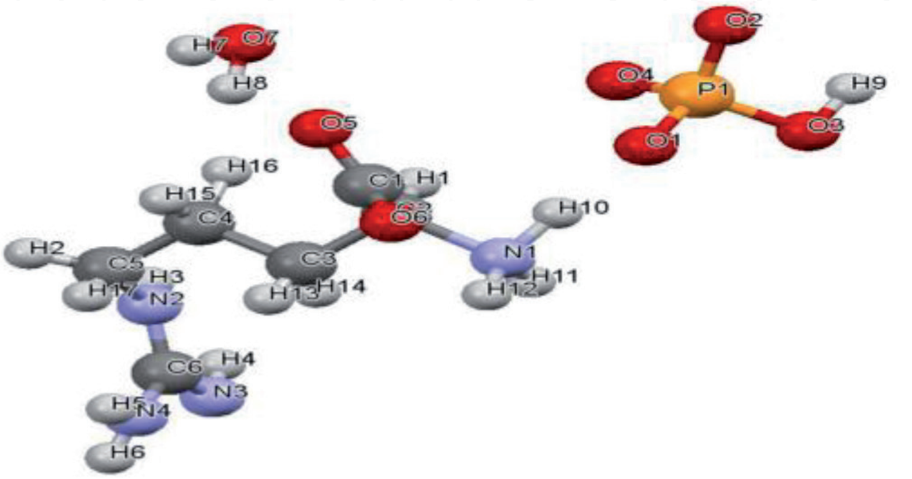

Figure 1.
Molecular structure of L-arginine phosphate monohydrate.

LAP owing to the overtones of vibration linked with hydrogen-containing groups, which is efficiently reduced in DLAP. DLAP also has a higher surface damage threshold than the LAP for Nd: YAG laser light [18].

4.2 Metal–organic coordination complexes

These forms of semi-organic crystals are studied by several polyhedral with a central metal ion coordinated by several organic and inorganic ligands. The common formula of metal–organic coordination complexes is MM' LnLm', where MM'- the various metal ions and LnLm' the organic and/or inorganic ligands. The organic ligand (L) is generally more dominant in the nonlinear optical effect. The II (B) divalent metal (Zn, Cd, Hg) complexes have high transparency in the ultra-violet region because of their locked d^{10} shell. The metal–organic complexes can be categorized into three groups [1, 2, 8]:

1. Island type

2. Chain type

3. Network type

4.2.1 Island type

In this type-specific coordination, polyhedra are held together only by comparatively weak intermolecular interactions (van der Waals forces, hydrogen bonding, long-distance coulomb interactions). Several thiourea complexes were synthesized and tested for their powder efficiencies based on the intuitive approach of incorporating asymmetric conjugated organic molecules into inorganic distorted polyhedra. Bisthiourea cadmium chloride, triallylthiourea cadmium chloride, triallylthiourea cadmium bromide, triallylthiourea mercury chloride and zinc tris(thiourea) sulfate were recognized as the efficient NLO materials. These are some important island type metal–organic coordination complexes. Metal complexes of thiourea have low UV cut -off wavelengths, therefore these materials are suitable for high power frequency conversion applications. These materials can be used as better alternatives for KDP crystals in frequency doubling and laser fusion experiments due to their higher values of laser damage threshold.

Bis(thiourea) cadmium chloride (BTCC) is an efficient NLO material for SHG applications. The chemical formula of BTCC is ($Cd[SC(NH_2)_2]Cl_2$) and belongs to the orthorhombic crystal class with the space group Pmn_{21}. The SHG efficiency of BTCC is almost the same as that of urea. Compared to the other solution-grown NLO crystals, the BTCC crystal has a greater laser damage threshold value. The single-shot damage thresholds resistance of BTCC is 32 GW/cm^2 at 532 nm. The transmission range varies from 285 nm to 1900 nm. Considerable absorption observed around 1500 nm. It has good transmission in the entire visible range. Remarkable transmission in the spectrum is due to the reduction in absorption. This is owing to the number of N-H bonds, which reasons absorption around 1040 nm by vibrational overtones is slighter in BTCC than in ZTS. It also has good mechanical behavior which is comparable with KDP crystal. The NLO coefficient of BTCC is $d_{11} = 2.75d_{36}$(KDP). Along the phase-matching angle, its SHG efficiency is almost similar to that of urea. It is a promising NLO crystal for different applications in the area of laser and optoelectronic [8, 19–21].

Another important island type metal–organic coordination complex is zinc tris(thiourea) sulfate (ZTS). The large size of ZTS crystal can be easily grown using an aqueous solution. The chemical formula of ZTS is $Zn[CS(NH_2)_2]_3SO_4$. It also belongs to the orthorhombic crystal class with space group Pca_{21}. It is a good material for nonlinear engineering applications which has high nonlinearity. It has good optical quality, with low defect densities. The single-shot damage threshold of ZTS crystal is found to be 40 GW/cm^2. BTCC has only two thiourea units while ZTS own three. This decrease in absorption at around 1064 nm which causes significant contribution towards an enhancement in the laser damage resistance of the ZTS crystal. The ZTS has lower cut-off below 300 nm, which is valuable in semi-organic NLO crystals over their organic crystals. It has allowed angular sensitivity that shows useful for type-II second-harmonic generation. It has nearly 1.2 times higher nonlinear than KDP crystal. High surface damage threshold and good transmittance make it a better alternative crystal for KDP crystal in laser fusion and frequency-doubling experiments [22–24].

4.2.2 Chain type

In this kind coordinate polyhedra are connected through chemical bonds, corner by corner or edge by edge, coordinating one-dimensional polymers in the crystal structure. Thiosemicarbazide cadmium chloride monohydrate (TSCCC) and, thiosemicarbazide cadmium bromide monohydrate (TSCCB) are examples of chain type NLO crystals. The chemical formula of TSCCC is $Cd(NH_2CSNHNH_2)Cl_2.H_2O$. Good quality of TSCCC crystal can be easily grown using slow evaporation technique. It crystallizes in the monoclinic system with non-centrosymmetric space group Cc. The SHG efficiency of TSCCC is 14 times more than KDP crystal, this may be due to the chlorine atom must be affected in the coordinate polyhedral. TSCCC crystal has good transmittance in the UV–NIR region and cut-off wavelength is below 280 nm, which is enough for SHG laser radiation of 1064 nm and other optical applications. The laser damage threshold energy value is calculated to be 725 MW/cm at wavelength of 1064 nm. The thermal stability of TSCCC is 148°c which is higher than that of LAP crystal (144°c). It also has good mechanical strength, high dielectric constant and low dielectric losses. TSCC crystals show negative photoconductivity which can be used for IR detector applications. The third-order nonlinear susceptibility of the crystal is calculated to be 2.774×10^{-5} esu which shows it as a suitable material for nonlinear optical applications [8, 25–27].

Another important chain form of NLO material is thiosemicarbazide cadmium bromide monohydrate (TSCCB). The chemical formula of TSCCB (**Figure 2**) is $Cd(NH_2(SNHNH_2)Br_2.H2O$. TSCCB belong to the Cc space group with similar cell parameters and similar molecular packing style of TSCCB. The lower cut-off

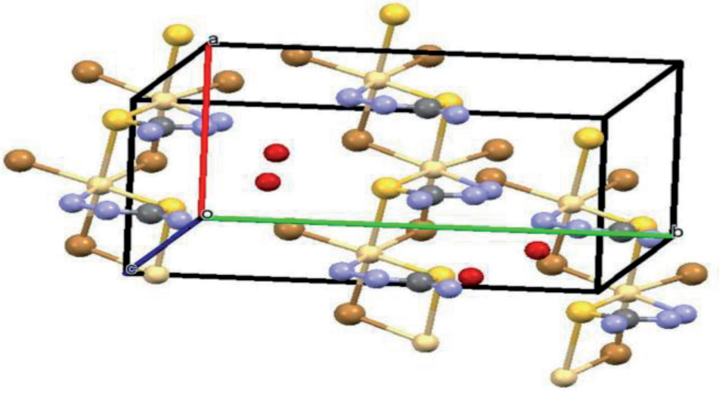

Figure 2.
Packing diagram of thiosemicarbazide cadmium bromide monohydrate.

wavelength is calculated to be 293 nm. The crystal has a wide transparency window in the entire visible region, which confirms the suitability of the TSCCB in NLO device applications. The crystal has high mechanical stability, high thermal stability (190°c), high dielectric constant and low dielectric losses. The SHG efficiency is calculated to be 1.98 times that of standard KDP crystal. The non-linearity of the TSCCB occurs due to the organic–inorganic ring structure of the complex material containing the cadmium ions [8, 28–32].

4.2.3 Network type

In this form, two or three-dimensional coordinative chemical bonds join all polyhedral composed. This is the most referring type because its physicochemical stability and nonlinear optical behavior can be greatly increased compared to organic crystals. The $MHg(SCN)_4$ series complex has three-dimensional networks. This kind of material possesses good NLO properties, which are relevant to their structural features [1–3, 8, 33, 34].

4.3 Organometallic compounds

In the late 1960s, organometallic crystals were brought into use for optoelectronic applications to resolve the physicochemical instability of organic crystals. Based on the concept of combining the inorganic distorted polyhedron with an asymmetric conjugate organic molecule, organometallic compounds can be synthesized. In optoelectronics and nonlinear optical fields, organometallic crystals are of great interest because such crystals have the potential to combine the organics, high optical nonlinearity and chemical flexibility with temporal, thermal stability and strong inorganic transmittance. The high resistance to surface laser damage threshold is another important advantage of organometallic materials. To understand the use of organometallic substances for device applications, the growth of organometallic single crystals has been subject to perennial concern. Like organic molecules, organometallic compounds also offer the advantages of architectural versatility and ease of processing and tailoring.

Recent analysis shows that the organometallic complexes, in particular, the metallic complexes of thiocyanate and their Lewis base have impressed the material scientist because of their strong second-order nonlinear optical efficiency and stable physio-chemical properties. The molecular engineering of bimetallic complexes of thiocyanate crystallizes into non-centrosymmetric space group which affirms the second harmonic generation and also enabled the crystal growers to grow the novel varieties of NLO crystals. Considerable nonlinearity occurs in organometallic thiocyanate crystals because of the delocalized π-electrons from ligand to metal or metal to ligand. Increased NLO properties also occur in the diversity of central metal atoms, oxidation levels, size and nature of the ligand. These materials also have high nonlinearity, high surface damage threshold, low UV cut-off wavelength, moderate thermal and mechanical properties. Crystals such as manganese mercury thiocyanate (MMTC), cadmium mercury thiocyanate (CMTC), zinc mercury thiocyanate (ZMTC), manganese mercury thiocyanate bis dimethyl sulphoxide (MMTD), and zinc cadmium thiocyanate (ZCTC) belong to this type. Most of the organometallic thiocyanate crystals discussed here were grown by solution growth technique (slow evaporation method, slow cooling method and temperature lowering method). Normally, organometallic thiocyanate crystals can be classified into manganese mercury thiocyanate (MMTC), cadmium mercury thiocyanate (CMTC), zinc mercury thiocyanate (ZMTC) and so on [33–45].

4.3.1 Manganese mercury thiyocyanate

The manganese mercury thiyocyanate ($MHg(SCN)_4$) series of crystalline complexes have been known for a century in analytical chemistry for their characteristic shapes and colors. Although SCN ion is a good chromophore for second-order NLO properties, however, these structure type crystals are found to be crystallized in centrosymmetric space groups, which leads them to lose their macroscopic NLO properties or crystallize in a noncentrosymmetric space group, unfortunately, the low energy d-d transitions present in these compounds, normally observed in the visible light region and limit their NLO usefulness. MMTC crystal belongs to the tetragonal crystallographic system with space group $I\overline{4}$. The SHG efficiency of MMTC is 18 times that of urea. Thus, the second harmonic generation efficiency of MMTC is very much higher than that of other organometallic family crystals such as CMTC, CMTD and BTCC and other laser materials like KDP, LAP and BBO. The laser damage threshold of MMTC was found to be 10.5 GW/cm2, which suggests that the MMTC has high damage threshold value than the KDP and BBO. The crystal is thermally stable up to 353°C. MMTC has a large transmission window range from 373 nm to 2250 nm without any absorption peak. The UV cut-off wavelength of MMTC is 383 nm, which is nearly the same as that of CMTC. Third-order nonlinear susceptibility ($\chi^{(3)}$) of MMTC is found to be 3.13×10^{-8} esu. The hardness properties of MMTC (50 kg/mm2) is more than CMTD (47 kg/mm^2) and less than ZTS (116 kg/mm^2) and BTCC (136 kg/mm^2). The high SHG efficiency, wide optical transmittance, high thermal stability and moderate mechanical property of MMTC show that this crystal is an excellent material for photonic device fabrication [33–37].

4.3.2 Cadmium mercury thiocyanate

Cadmium mercury thiocyanate and zinc mercury thiocyanate and are well known efficient phase matchable second harmonic generation single crystals [39]. Bimetallic thiocyanates are semi-organic compounds, with chemical formula AB(SCN)4, that exhibit high nonlinearity. Among the bimetallic thiocyanate materials, zinc mercury thiocyanate (ZMTC) and cadmium mercury thiocyanate (CMTC) is found to have all the important characteristics such as crystallization in a noncentrosymmetric space group, colorless, and high thermal stability. Both ZMTC and CMTC are SHG crystals which can convert 1064 nm radiation. Cadmium mercury thiocyanate ($CdHg(SCN)_4$) is widely studied organometallic crystals. It belongs to the tetragonal system with space group $I\overline{4}$. The crystal is thermally stable up to 251°C. UV–Vis cut-off wavelength of CMTC was found to be 383 nm which indicates the potential of generating blue-violet light using a diode laser. The laser damage threshold value of CMTC is calculated to be 11.14 MW/cm^2. The optical limiting threshold value of the CMTC is calculated to be 31.3 mW, which shows an excellent optical limiting property of CMTC. The phase-matching angles are $\theta = 47.7°$ and $\phi = 0°$, Third-order nonlinear susceptibility ($\chi^{(3)}$) calculated to be 14.27×10^{-6} (esu). The SHG efficiency of CMTC is 11.3 times higher than that of Urea. The results show that this crystal has high NLO coefficient and very high laser damage threshold value which confirms this crystal can be used for many optoelectronic device applications including high power frequency conversion and fabrication of optical limiting devices [8, 33, 40–42].

4.3.3 Zinc mercury thiocyanate

Zinc mercury thiocyanate ($ZnHg(SCN)_4$) is well known NLO material for SHG of 1064 nm radiation. ZMTC (**Figure 3**) belongs to the tetragonal crystal system.

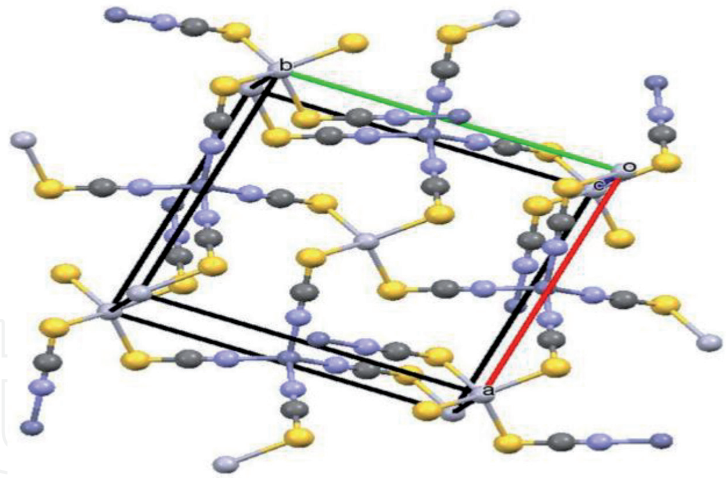

Figure 3.
Three dimensional views of zinc mercury thiocyanate.

UV transparency cut-off wavelength is 257 nm. It is thermally stable up to 310°C. The second harmonic generation efficiency is found to be 14 times greater than that of urea [33, 43, 45].

5. Conclusion

Combination of inorganic and organic material is a potential approach to generate more stable NLO crystals. The chemistry correlated with this group of materials is such that the designing of new systems is extremely versatile and potentially contributing to improved optical response. Various semi-organic crystal satisfies the basic criteria's of NLO applications. The remarkable properties of these crystals suggest that this crystal can be used in various optical device applications.

Acknowledgements

The authors are grateful thank to CCDC for accessing the crystal structures.

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