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Synthesis, growth, structure, optical, mechanical, and electrical properties of an Inorganic new nonlinear optical crystal: sodium manganese tetra chloride (SMTC)

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Abstract

A new inorganic nonlinear optical single crystal of sodium manganese tetra chloride (SMTC) has been successfully grown form aqueous solution by the slow evaporation technique at room temperature. The crystals obtained by the above technique were subjected to different characterization analysis. The crystalline nature of the grown crystal of SMTC was analyzed by powder X-ray diffraction. Single crystal X-ray diffraction study reveals that the crystal belongs to orthorhombic system with non-centrosymmetric space group Pbam. Optical transmission study on SMTC crystal shows high transmittance in the entire UV–Vis region and the lower cutoff wavelength is found to be 240 nm. The mechanical strength of the grown crystal was estimated by Vicker'smicrohardness test. The second harmonic generation (SHG) efficiency of the crystal was measured by Kurtz's powder technique infers that the crystal has nonlinear optical (NLO) efficiency 1.32 times that of KDP.The dielectric constant and dielectric loss of the compound were measured at different temperature with varying frequencies. Photoconductivity study confirms that the title compound possesses a negative photoconducting nature. Growth mechanism and surface features of the as grown crystals were analyzed by chemical etching analyzing.
Key Words :sodium manganese tetra chloride, XRD, second harmonic generation

1 Introduction

The well known properties of laser radiation are important for a wide variety of applications. Laser radiation could be converted into one form of frequency to another through the nonlinear optics, hence the application of nonlinear optics is increased significantly in various fields in science and technology. Generally, nonlinear optical (NLO) interaction is made by one or two laser beam incident on a suitable material in which an output beam of the desired frequency is produced [1-2]. Harmonic generation, sum and difference frequency generation and parametric oscillation are included in the NLO interaction [3]. A Lower frequency pair of tunable output beam can be produced only by suitable material when it is interact (NLO) with high input laser beam. Mostly, NLO interaction imposes several demands on potential NLO materials. The field of nonlinear optics is one of the most attractive fields of current research because of its vital applications in various areas like optical switching, optical data storage for developing technologies in telecommunication and signal processing [4-6]. Since, the first demonstration was done in the year of 1961, which reveals that nonlinear frequency conversion is highly materials-limited field [7]. So materials should be optically transparent, quadratic susceptibility of sufficient

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magnitude, allow for phase matching interaction and withstand the laser intensity without damaging. To date, the most important class of materials used in nonlinear optics is inorganic single crystals.

Inorganic materials, exhibiting second order nonlinear optical properties have attracted in the recent past due to their ability to process into crystals, wide optical transparency domain, large nonlinear figure of merit for frequency conversion, fast optical response time and wide phase matchable angle [8]. These ionic bonded inorganic crystals, easy to synthesis with high melting point and high degree of chemical inertness[9]. Highly polarisable, inorganic quality crystal and their efficient active second order harmonic generation (SHG) have been observed by Franken et al and co-workers in 1961[7].

Inorganic materials have advantages over organic materials, such as architectural flexibility for molecular design and morphology, high mechanical strength and good environmental stability with non toxicity andusability in high power applications. Molecular hyperpolarizability of inorganic nonlinear optical crystal are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro-optic applications especially in EO modulation. Historically, inorganic NLO materials have been chronicled more extensively inorganic oxide crystal, $LiNbO_3$, $KNbO_3$, KDP and KTP, etc., have been studied for device application like piezoelectric, ferroelectric and Electro-optics [10]. This material has also been formed successful usage in commercial frequency doublers, mixers and paramedic generators to provide coherent laser radiation with high frequency conversion efficiency in the new region of the spectrum, inaccessible by other nonlinear crystal conventional sources.

The aim of this research work is to survey the processing and properties of inorganic nonlinear optical crystal sodium manganese tetrachloride (SMTC) with molecular formula Na_2MnCl_4 used in NLO frequency conversion.The structure of Na_2MnCl_4 was determined by Goodyear et al in the year of 1971[11]. The grown crystals of SMTC, chlorine ions coordinated octahedrally with Mn ions and form an infinite chain parallel to c axis and are held with sodium ions. Sodium ions are surrounded by four chloride ions at the corners of a trigonal prism. Binding of Mn-Cl and Na-Cl suggests that the structure is mainly ionic in character.Hence, an attempt hasbeen made on growth of sodium manganese tetra chloride (SMTC) single crystals by slow evaporation solution growth technique and its physical-chemical properties have been investigated for the first time.

2 Experimental Procedure

2.1. Synthesis

SMTC salt was synthesized by taking analytical reagent (AR) grade manganese chloride and sodium chloride in stoichiometric ratio 1:2 with double distilled water as a solvent. The synthesized SMTC salt has been obtained by the following chemical reaction.

$$MnCl_2 + 2NaCl \longrightarrow Na_2MnCl_4$$

Manganese chloride + sodium Chloride $\longrightarrow$ Sodium manganese tetra chloride.

The scheme of the molecular structure of SMTC is as shown below.

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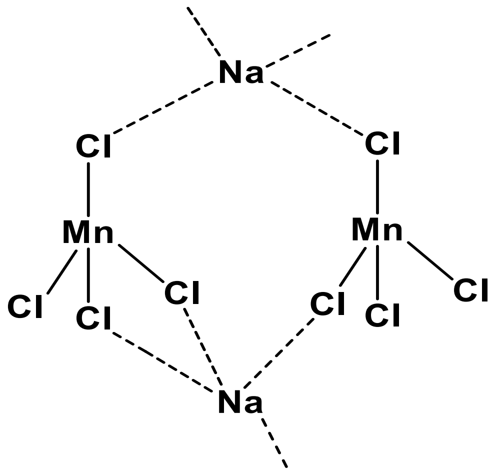

Scheme 1 Molecular arrangement of SMTC crystal

2.2 Solubility study

The growth rate of a crystal depends on its solubility and temperature. Solvent and solubility factors define super saturation, which is the driving force for the rate of crystal growth. The solubility study was carried out by taking an excess quantity of SMTC in the solvent and it was stirred continuously to achieve uniform concentration over the entire volume of the solution. The solubility of SMTC in the solvent of double distilled water was determined for various temperatures 30 - 55 ^{0}C in 5^{o}C intervals using a constant temperature bath with an accuracy of ±0.01^{0}C attached to a cryostat facility. After attaining the saturation, the concentration of the solute was analyzed gravimetrically. The solubility curve for SMTC is shown in figure 1. It is observed that SMTC has a positive solubility (solubility increases linearly with temperatures) gradient in the water.

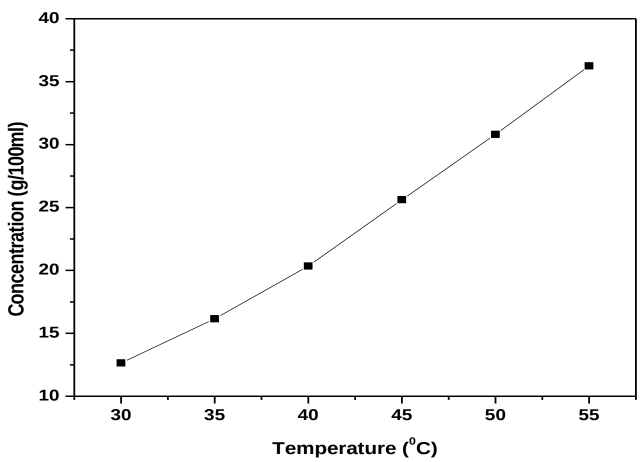

Figure 1 Solubility curve of SMTC

2.3 Crystal Growth

The prepared solutions were stirred vigorously at RT for 4 h. Continuous stirring with slightly rise in temperature ensures homogeneity and avoids co-precipitation of motives. Purification of synthesized salt was achieved by successive recrystallization process. The saturated mixture of solution was filtered two times with micron pore sizeWattmann filter paper. This synthesized clean solution was poured into a Petri dish and covered by polythene paper with pores, and allowed for slow evaporation of the water solvent. After a time span of 35 days, the solvent was evaporated and good quality SMTC crystal of dimensions $2\times2\times1$ mm^3 were harvested from the Petri dish. The growth rate was found to be 0.12mm per day. The grown crystal was defect less, optically transparent and with no inclusions. As-grown crystal of SMTC is shown in the figure 2.

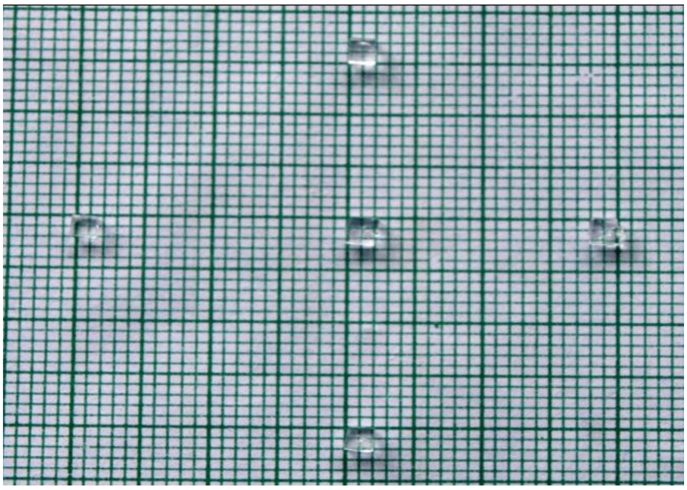

Figure 2 Photograph of as grown crystals of SMTC

3 Characterization of SMTC Single Crystal

The grown crystal of SMTC was subjected to single crystal and powder XRD analysis using ENRAF NONIOUS CAD4 X-ray diffraction meter and BRUKER, Germany (model D8 advance) X-ray diffractometer. Transmission behavior of the grown crystal was studied by using LAMBDA-35 UV-visible spectrophotometer. The NLO efficiency of the grown crystal was tested by KURTZ powder technique using ND:YAG laser of wavelength 1064 nm. Mechanical behaviour of the grown sample was investigated by Vicker's microhardness tester. Dielectric constant and dielectric loss studies were carried out by using HIOKI3532 HITESTER LCR meter. Keithley 485 PICOAMMETER was used to study the photoconductivity of the grown SMTC crystal.

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3.1 Results and Discussion

3.1.1 Single crystal XRD studies.

The Single crystal XRD study confirms the unit cell parameters of as grown SMTC crystals a=6.93 Å, b=11. 82 Å, c=3. 86 Å,$\alpha = \beta = \gamma = 90°$ and volume of the cell is found to be, 316.182 Å^3. Hence the SMTC crystal is Orthorhombic in structure and in thespace group Pbam. The lattice parameters are well coincide with a reported value [11].

3.1.2. Powder XRD studies

Powder XRD of as-grown crystal of SMTC has been studied and XRD pattern is shown in the figure 3. The powder sample was scanned over the range of 10-80° at a scan rate of 0.2°/s, using CuKα radiation of wavelength 1.545 Å. The obtained powder X-ray diffraction data were analyzed and compared with JCPDS data (JCPDS data card number 4137). A limited number of sharp peaks without any broadening in the XRD pattern confirms that the grown SMTC possesses good crystallinity.

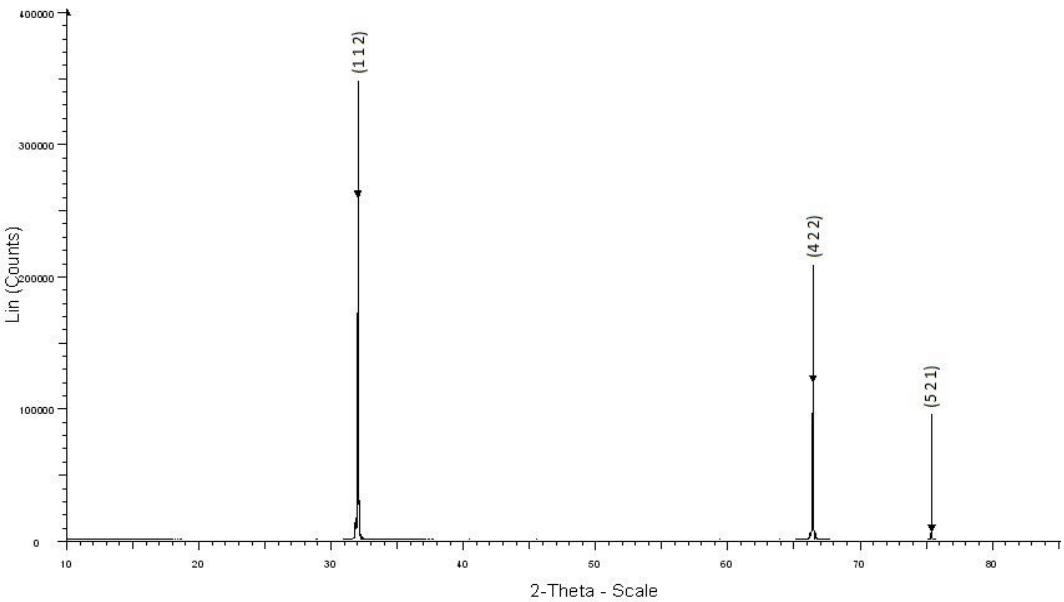

Figure 3 Powder XRD pattern of SMTC

3.1.3 Linear optical transmission studies

Since NLO crystals can be for practical use only when it has wide transparency window. The transmission range of SMTC crystal was determined by recording the optical transmission spectrum in the wavelength region of 200 - 900 nm. The optical transmission spectrum of SMTC crystal is shown in the figure 4. Optically polished single crystal of thickness 2mm was used to study the transmission behavior of SMTC. This recorded spectrum, gives information about the structure of the molecule by absorption of UV and the visible light involves promotion of electrons in the σ and π orbital from ground state to a higher energy state [12]. The transmission spectrum shows that the grown crystal has a lower cutoff wavelength at 240 nm,which attributes the electronic transmission in the SMTC crystal. Absence of absorbance in the region between 240 nm and 900 nm is an essential property of the nonlinear optical crystals. Single crystals are mainly used in optical applications and hence an optical transmittance window and the transparency lower cutoff wavelength (200-400) is very important for the realization of the SHG output in the range for using lasers. Optical width of the as grown crystal SMTC was compared with NaCl and $Mncl_2$ complex inorganic crystals. The grown SMTC crystal has good transparency in UV-visible and IR region which ensures, that crystal can be used as sensor materials from UV, visible in the IR ranges and may be consider as a potential candidate for the photonic and optoelectronic applications [13]. The graph has been plotted to estimate the direct band gap values using Tauc's relation. The Tauc's plot has been drawn between $(\alpha h\nu)^2$ and hν as shown in the figure 5. The band gap value is obtained by extrapolating the straight portion of the graph to hν axis at $(\alpha h\nu)^2=0$. The estimated band gap value of grown sample SMTC is 5.4eV.

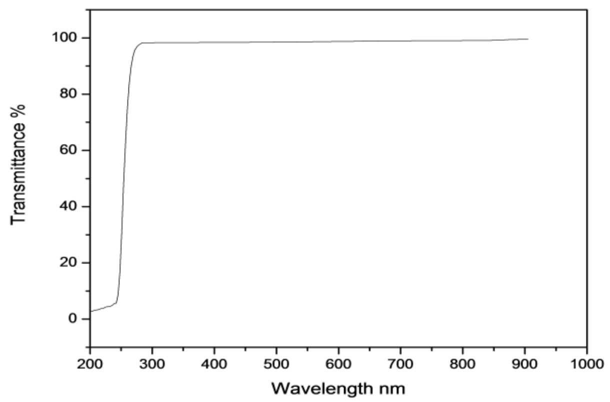

Figure 4 UV-Visible spectrum of SMTC crystal

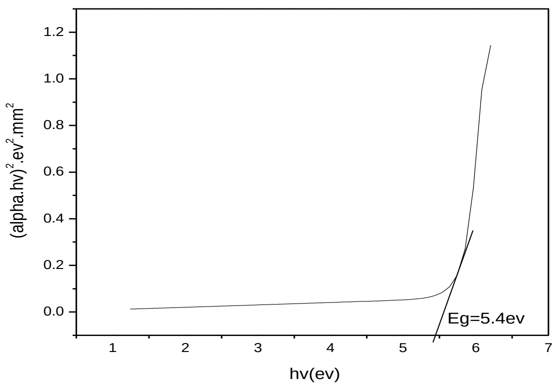

Figure 5 Tauc's plot of SMTC crystal

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3.1.4 Second harmonic generation efficiency measurement

In order to confirm the nonlinear optical property, powdered sample of SMTC was subjected to Kurtz and Perry techniques, which remains a powerful tool for initial screening of materials for SHG [14]. The fundamental beam of wavelength 1064 nm from Q switched mode locked Nd:YAG laser was made to fall normally on the powder from of grind sample which was made available between two transparent glass slides. Pulse energy 2.9 mJ/pulse and pulse width 8 ns with a repetition rate of 10 Hz were used. The photo multiplier tube (Hamamatsu R2059) was used as a detector and 90 degree geometry was employed. The SHG signal generated in the sample was confirmed from emission of bright green (532 nm) radiation from the sample. The measured amplitude of second harmonic generation for SMTC crystal is 11.32 mJ and 8.8 mJ for KDP (KDP crystal was powdered to the identical size of SMTC and used as reference materials). It shows a powder SHG efficiency of SMTC crystal is about 1.3 times of KDP. The SHG efficiency of SMTC crystal is compared to few popular inorganic NLO crystals which are given in the table 1.

Compound	**SHG efficiency**
Potassium dihydrogen phosphate (KDP)	1
Potassium pentaborate	0.79
Ammonium pentaborate	0.2
SMTC(Present work)	1.32

Table 1 comparison of SMTC crystal with other NLO crystals

3.1.5 Microhardness study

Mechanical property of the grown sample was studied by measuring the hardness number with various applied loads. A well polished crystal was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time of 5 s. Here low loads are applied to measure the hardness of the samples. Microhardness analysis was carried out byusing Leitz Weitzler hardness tester fitted with a diamond indenter. The indentations were made on the flat surface with the load ranging from 25 to 100 g using Shimadzu HMV-2T fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time has been kept 5 seconds for all the loads. Several indentations were made on the crystal surface with sufficient space for each load and the diagonal length (d) of the indented impressions is measured. The Vickers hardness number of the materials Hvhave determined by the relation, $Hv=1.8544\ P/d^2\ kg/mm^2$. Where

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P is the applied load in kg and d is the diagonal length of indentation impression in mm. The hardness number was found to be increased with load and above 100 g, significant crack and inclusion are observed, which may be due to the release of internal stress generated locally by indentation [15]. The average value of the Vickers hardness number for the grown crystal is 100 kg/mm^2. The plot drawn between the corresponding loads and hardness values of SMTC is shown in figure 6. The work hardening coefficient (n) of the material is related to the load (p) by the relation $P=Ad^n$, Where A is an arbitrary constant. The work hardening coefficient 'n' of the sample has been determined from the slop of the log p vs log d (figure7) and is found to be 2.278 indicating that the crystal belongs to soft category. From careful observations on various materials Onitschand Hannemanpointed out that the value of n between 1.0 and 1.6 indicates a moderately hard material and n above 1.6 represents a soft material [16-17]. The value of n indicates that the SMTC crystal has higher mechanical strength and useful in device applications.

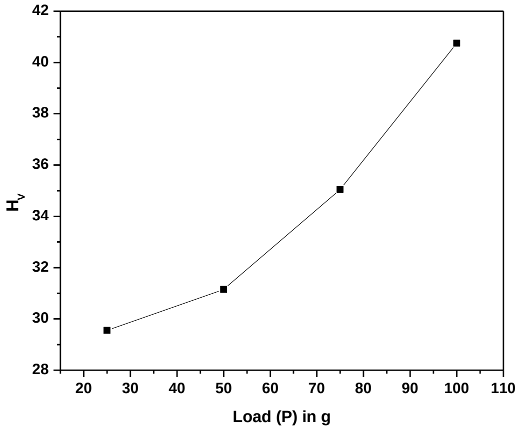

Figure 6 Vickers hardness number against load plot of SMTC crystal

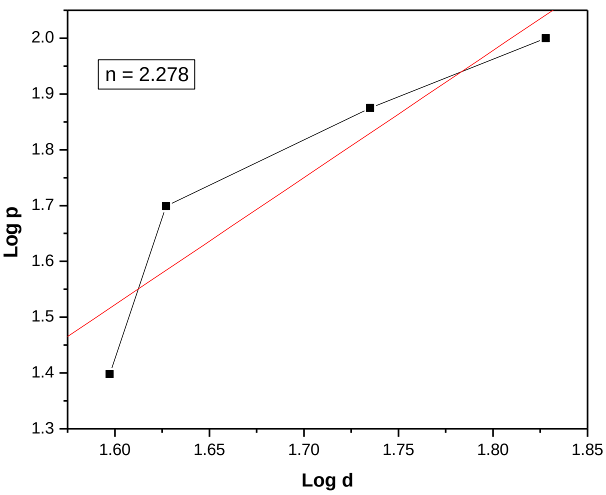

Figure 7 Log p vs log d plot of SMTC crystal

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3.1.6 Dielectic studies.

The behavior of the crystal under the influence of electric field has good relation with the laser irradiation on the sample, hence the power dissipation factor can be studied from the dielectric studies. Dielectric studies for SMTC single crystal were carried out as a function of frequency for various temperatures. The SMTC crystal was coated with graphite on either side to form an electrode of a parallel plate capacitor. The dielectric constant was calculated using the formula

$$\varepsilon_r = Ct/\varepsilon_0 A$$

Where C is the capacitance; t is the thickness of the crystal, ε_0 is the permittivity of the free space and A is the area of a cross section of the sample. The variations of dielectric constant and dielectric loss as a function of frequency (500 Hz to 5MHz) at different temperatures (308 -368 K) are shown in the figure 8 and 9. The dielectric constant as a function of frequency and temperatures are observed, which reveals that the dielectric constant decreases with increasing frequency. This behaviour of the sample referred as anomalous dielectric dispersion. High dielectric constant at low frequency is attributed to various polarization mechanisms of molecules. Generally, the polarization occurs as a function of time. It is obvious that at lower frequency, time taken for polarization is high. Hence, irrespective of the polarization mechanisms, measurement of dipole moment per unit volume would be high, resulting that the dielectric constant is independent of the frequency. At high frequency the change of polarization occurs even at very short time. Therefore, the polarization can occur only by the movement of electronic charge rather than the ions, results low dielectric constant. Electronic and space charge polarization predominantly in the low-frequency region suggest that the grown crystal possesses an enhanced optical quality with lesser defects and this phenomenon is an essential characteristic for nonlinear optical applications [18-20].

From the figure 9, the value of dielectric loss found to be high at low frequency region and dielectric loss found too low at higher frequency. The measure of low dielectric loss at higher frequencies is due to the dipole rotation. Also at high frequencies, the orientation polarization ceases and the energy need not be spent to rotate dipoles. It is also observed that both dielectric constant and dielectric loss depends on the temperature and increases slightly with an increase of temperature at a constant frequency. It is believed that materials with high dielectric constant lead to power dissipation.The Refractive index of the medium is related with dielectric constant according to the equation $n= (\varepsilon_r \mu_r)^{1/2}$. For non-magnetic materials, μ_r is equal to one. This equation explains the electric field based refractive index of the medium could play vital role in nonlinear effect. SMTC crystals possess low dielectric constant and low dielectric loss and hence it will be suitable for electro-optic applications. Also the low value of dielectric loss at high frequency can be taken as a proof of the good optical quality of the crystal. The application part of nonlinear optics demand high quality crystals with lesser defects.

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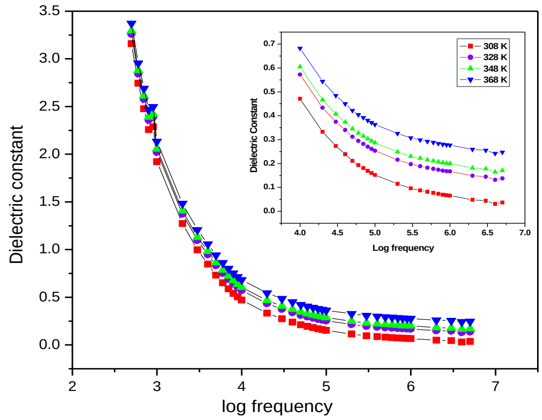

Figure 8 Variation of dielectric constant of SMTC single crystal with log frequency at different temperatures

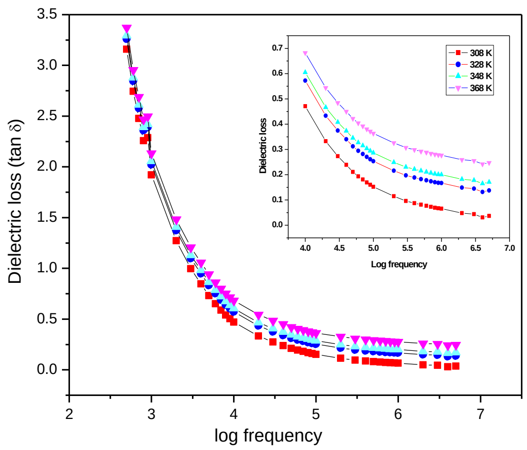

Figure 9 Variation of dielectric loss of SMTC single crystal with log frequency at different temperatures

3.1.7 Photoconductivity studies.

The photoconductivity study of SMTC crystal was carried out by connecting the sample in series with DC power supply and a picoammeter (Keithley 480) at room temperature. The details of the experimental setup are reported elsewhere [21]. By increasing the applied field from 10 to 150 V/cm and corresponding dark current without exposure of radiation was recorded. Photo current was recorded by exposing the crystal with halogen lamp of power 100 W containing iodine vapour for the same applied field. Dark current and Photo current against an applied field of same range were recorded in the same graph [Figure 10]. From the graph, it is observed that dark and photo current of the grown crystal increase linearly with applied field but photocurrent less than the dark current. This phenomenon is termed as negative photoconductivity.

Negative photo conductivity of being as grown crystal SMTC, may be due to decrease in either no number of free change carriers or their lifetime when subjected to radiation. Negative Photoconductivity of the grown crystal explained, according to Stockman model, the forbidden gap in the material contains two energy levels in which one is situated between the Fermi level and the conduction band while another is located close to the valence band. The second state has a high capture cross section for electrons and holes. As it captures electrons from the valence band the number of charge carriers in the conduction band gets reduced and the currentdecreases in the presence of radiation [22-23].

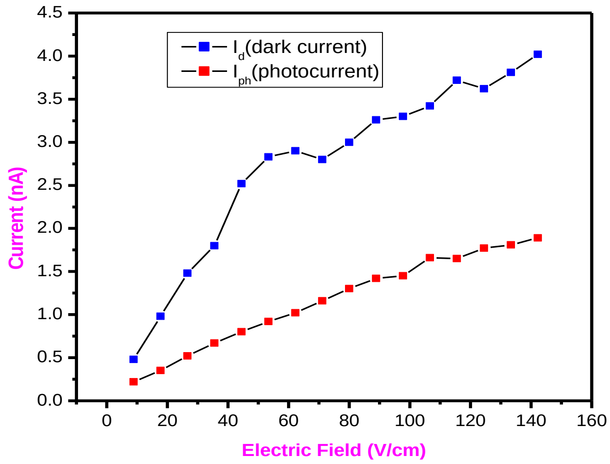

Figure 10 Field dependent conductivity of SMTC crystal

3.1.8 Chemical etching analysis

Chemical etching analyzing is the one of the most convenient and suitable technique for characterizing the growth defects. High quality or well define defect structure crystals are more important for device fabrication and technical applications now a day. Mostly, crystals grown from solution may suffer from imperfections like solvent inclusion, twins, grain boundaries and dislocation. Defects crystals are incident by laser beam, defects cause the scattering and absorption of laser beams. Hence, will affect the performance and use of crystal in laser applications. Generally, the etch patterns are captured at the dislocation sites by etching the crystal surface using suitable etchants [24]. The dissolution of a crystal in an etchant is an essential criterion for the etch pit formation. The region where the dislocations intersect the surface of a crystal is energetically different from the surrounding area. In the present study chemical etching was carried out using ethanol at room temperature. Once the damaged surface layer was removed by means of etching, a fresh surface appeared which in turn gave clear etch pits. The etched surfaces were dried using good quality filter paper and the surfaces were examined immediately. The etching study was carried for different time 5s, 10s and 15 s and observed etch patterns are shown in the figure 11(a, b, c) respectively. In the figure a, it is observed that whiskers type pits are noticed. Also in an etched surface shallow and deep etch pits are observed. By increasing the etching time there is no change of shapes,

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but the size of the pits slightly increased (figure11 b and c). The geometry of an etch pit also depends on the interatomic arrangement on the crystal. The observed etch pitch on the grown crystal surface implies that the crystal undergoes selective dissolution during the growth itself.

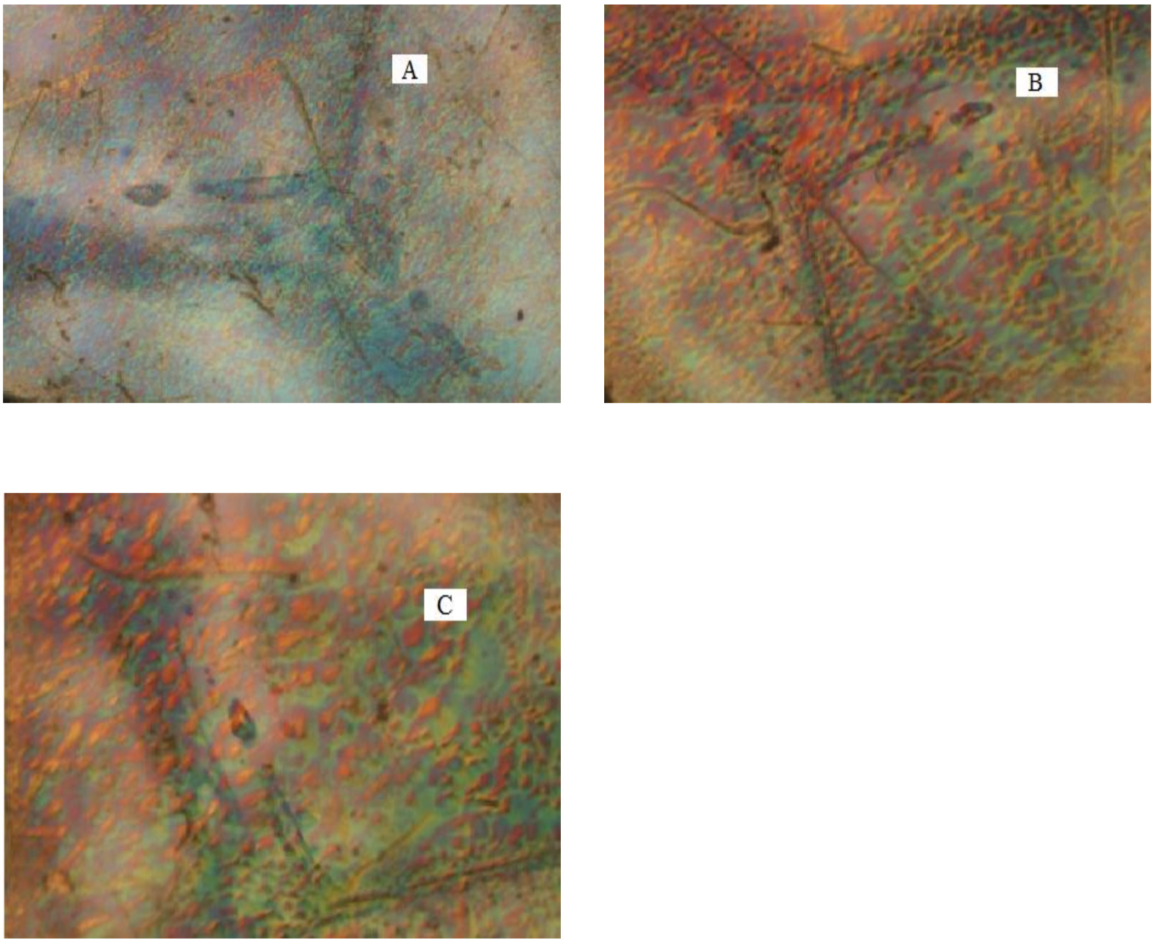

Fig. 11 Etch pattern on the SMTC crystal a) after etching for 5 s b) after etching for 10 s c) after etching for 15s

4 Conclusion

A potential inorganic nonlinear optical single crystal of sodium manganese tetra chloride was prepared at room temperature by slow evaporation of aqueous solutions. The well defined external appearance with bright, transparent and colourless crystals is obtained. The unit cell parameters and the space group were found using single crystal data. The good crystalline nature of the SMTC was confirmed by well defined peaks of powder X-ray diffraction studies. The FT-IR spectrum reveals the functional groups of the grown crystals. The grown crystal shows 99 % transmission with UV cut-off at 240 nm hence suitable for frequency conversion applications. The SHG efficiency of the SMTC was measured to be higher than that of KDP. From the mechanical measurements, it was observed that the hardness increases with increase of load. The dielectric constant and dielectric loss studies of SMTC establish the normal behavior. The above experimental results, viz., bulk size, extremely good crystalline perfection, optical transparency, SHG efficiency and mechanical strength may have possible NLO applications.

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