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RESEARCH ARTICLE

STUDIES ON GROWTH AND CHARACTERIZATION OF PURE AND DOPED
SODIUM CHLORATE CRYSTALS

¹Ajitha Sweetly M., ¹Chithambarathanu T., ²Ramalingom, S. and ^{*,3}Selvarajan, P.

¹Physics Research Centre, S. T. Hindu College, Nagercoil, Tamilnadu, India

²Department of Physics, Vivekananda College, Tamilnadu, India

³Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India

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ABSTRACT

Undoped and sodium chloride-doped sodium chlorate crystals were grown by solution method with slow evaporation technique. The doped crystal was found to be well faceted with high transparency compared to the undoped one. The grown crystals were characterized by structural, FTIR, optical, microhardness, atomic absorption and SHG studies. The results are presented and discussed.

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INTRODUCTION

Nonlinear optical (NLO) materials are used in fields of fiber optic communication, laser technology, optical signal processing, opto-electronics, optical computing and optical storage devices [Prasad and Williams, 1991]. Among NLO materials, the second harmonic generating (SHG) crystals play an important role in the domain of opto-electronics and photonics. For numerous device applications, NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultra violet ranges are required [Aggarwal *et al.*, 2003]. Sodium Chlorate (NaClO_3) crystal is an NLO material and it can be used as a second harmonic generator of laser light. It belongs to cubic structure with a non-centrosymmetric space group [Yulia *et al.*, 2008]. It is transparent, mechanically hard and thermally stable. Various dopants influence the properties of the crystals like growth kinetics, surface morphology, optical, electrical and mechanical properties etc. The dopant effect depends on the solubility of the host and the impurity phase, concentration of dopant, temperature and the pH of the solution. It is known that doping NLO crystals with various dopants can alter physical and chemical properties and doped NLO crystals find wide applications in opto-electronic devices compared to undoped NLO crystals [Seethalakshmi *et al.*, 2012]. Keeping this in mind, an attempt has been made in this work to introduce sodium chloride (NaCl) into the lattice of sodium chlorate crystal to alter its various properties. The aim of this paper is to report solubility and growth, X-ray diffraction studies, UV-visible transmittance studies, SHG, atomic absorption studies and microhardness studies of pure and NaCl doped sodium chlorate crystals.

*Corresponding author: pselvarajanphy@yahoo.co.in

Experimental

Solubility

Analytical reagent grade sodium chlorate, sodium chloride and distilled water were used in the present experiment. 1 mole% of sodium chloride was added into the aqueous solution of sodium chlorate and it was heated upto 50 °C to synthesize the doped sample. The solubility of the samples of this work was measured by gravimetric method. The solution was stirred well continuously in an airtight container maintained at constant temperature and after reaching the saturation, the equilibrium concentration has been analyzed gravimetrically [Lucia Rose *et al.*, 2011] in the temperature range 30- 60 °C. The solubility curves for the samples are shown in the Figure 1 and it is noticed that the solubility increases significantly with increase in temperature. It is observed that the samples have positive temperature coefficient of solubility and sodium chloride doped sodium chlorate sample has more solubility than that of sodium chlorate sample. The solubility data can be used to prepare saturated and supersaturated solutions at any temperature in the given range. The size of a crystal depends on the amount of solute available in the solution and is decided by the material present in that solvent.

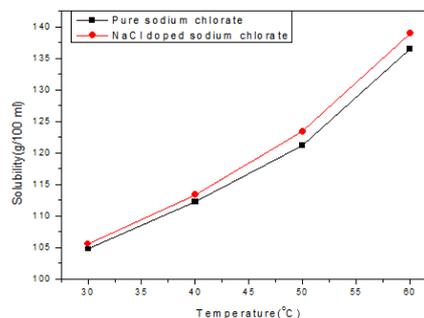
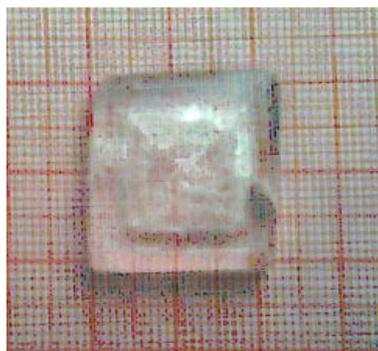


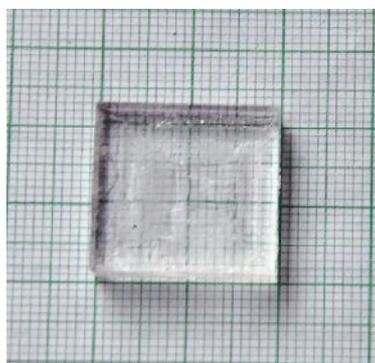
Figure 1. Solubility curves for pure and NaCl doped NaClO_3 samples

Crystal growth

Slow evaporation technique was employed to grow pure and NaCl doped NaClO₃ crystals. The saturated aqueous solutions of the samples were prepared using the solubility data at room temperature (30 °C) and were thoroughly stirred for homogenization. Seed crystals pure and doped samples were harvested separately. Best seed crystals used to obtain big-sized crystals. After a period of 25-30 days, the pure and sodium chloride doped sodium chlorate crystals were harvested and the photographs the grown crystals are shown in the Figure 2. It is observed that the sodium chloride doped crystal has more transparency than undoped sodium chlorate crystal.



(a)



(b)

Figure 2. Harvested (a) pure NaClO₃ and (b) NaCl doped NaClO₃ crystals.

Techniques for Characterization

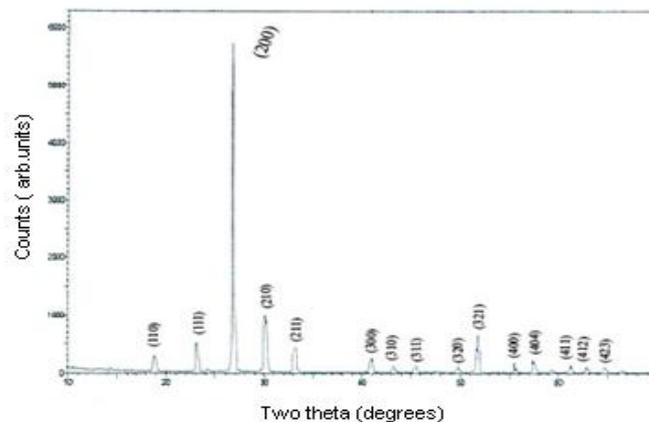
The crystals were characterized by FTIR spectroscopy, powder XRD, Scanning electron microscopy (SEM), Vickers hardness and second harmonic generation (SHG). The FTIR spectra were recorded on spectrometer PERKIN – ELMER in the range from 400 – 4000 cm⁻¹ and powder XRD patterns were obtained on a PHILIPS XPERT-PRO powder diffractometer system. The surface features were characterized by scanning electron microscope (JEOL JSA – 5600R system) under various magnifications. The mechanical strength was measured by Vickers microhardness tester. SHG analysis for the grown crystals was carried out by the Kurtz and Perry powder technique using a Q – switched, mode locked Nd: YAG Laser. The optical property of the sample was assessed by LAMBDA-35 UV-Visible spectrophotometer. The crystals were well polished and the specimens of 2 mm thickness was subjected to transmission measurements in the spectral region 190 – 1100 nm.

Results and discussion

X-ray Diffraction studies

Finely crushed powder of pure sodium chlorate and sodium chloride doped sodium chlorate crystals were subjected to intense X-ray of wavelength 1.5406 Å (Cu – K_α) at a scan speed of 1.2° per minute.

Figure 3 shows the powder XRD patterns of this work. The unit cell parameters were calculated using the software packages such as INDEXING and UNITCELL. The well sharp peaks at 2θ values show high crystallizing of the grown crystals. The powder XRD data for the samples are provided in the Tables 1 and 2. The single crystal XRD data for the samples were also obtained using a single crystal X-ray diffractometer and the unit cell parameters are listed in Table 3. From the data, it is observed that both the samples crystallize in cubic structure and there is no change of crystal structure on doping sodium



chlorate crystal with NaCl

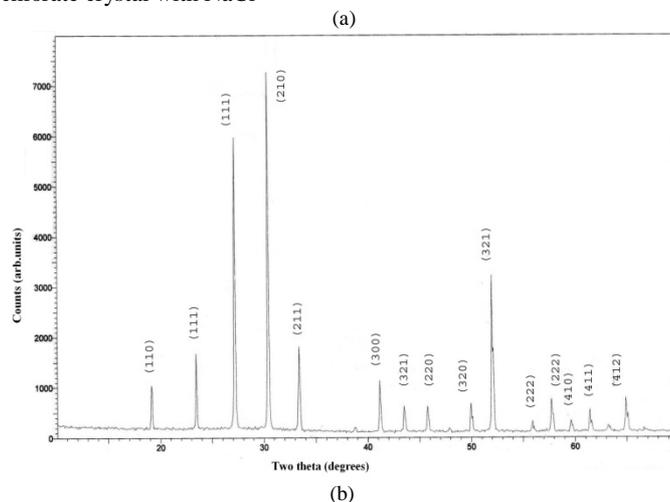


Figure 3. XRD patterns of (a) pure NaClO₃ and (b) NaCl doped NaClO₃ samples

Table 1. Powder XRD data for NaClO₃ sample

d-spacing Å	hkl	2θ (degrees)	Relative Intensity (%) (I/I ₀)
4.71301	110	18.81288	4.53
3.84705	111	23.10037	8.86
3.65877	002	24.30682	0.52
3.32987	200	26.7501	100
2.97341	210	30.02815	16.91
2.70394	211	33.10251	7.34
2.34403	220	38.36926	0.26
2.20392	300	40.91394	4.02
2.09409	3210	43.1644	1.94
1.99415	311	45.44509	1.9
1.90954	222	47.5799	0.45
1.83406	320	49.66746	1.14
1.76353	321	51.79766	11.12
1.65239	400	55.57092	0.74
1.60265	004	57.45297	2.66
1.55762	410	59.27663	0.43
1.51338	411	61.19183	0.99
1.47618	420	62.90707	0.79
1.44076	412	64.63845	1.28
1.10568	323	66.45655	0.4

Table 2. Powder XRD data for NaCl doped sodium chlorate sample

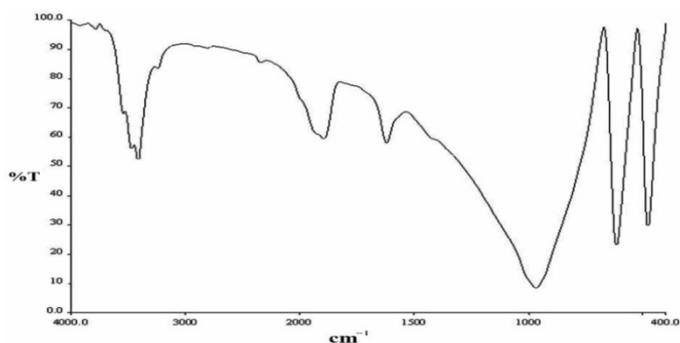
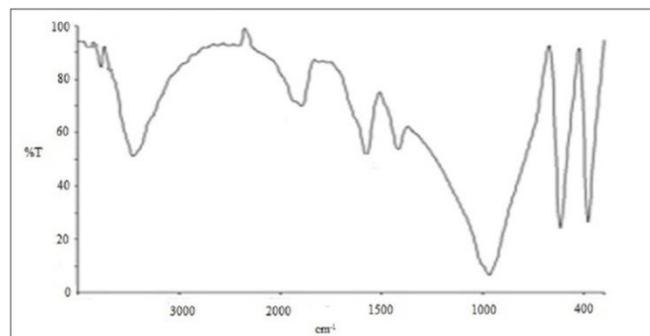
d-spacing Å	hkl	2θ (degrees)	Relative density (%)
4.63798	110	19.12006	12.47
3.78836	111	23.46330	20.80
3.27909	200	27.17228	79.39
2.93545	210	30.42578	100.00
2.68062	211	33.39897	22.51
2.32193	220	38.74895	0.93
2.18979	300	41.18998	10.75
2.07814	321	43.51243	6.43
1.98022	220	45.78290	6.55
1.89682	320	47.91894	0.91
1.82284	320	49.99411	7.09
1.75595	321	52.03795	23.43
1.64286	222	55.92125	2.90
1.59381	222	57.80154	6.37
1.54953	410	59.61717	2.95
1.50819	411	61.42500	5.51
1.46956	420	63.22285	1.58
1.43488	412	64.93570	8.28

Table 3. Crystal parameters for NaCl pure and NaCl doped NaClO₃ crystals

Sample	a =b=c Å	cell volume (Å) ³	α=β=γ (degrees)
Pure NaClO ₃	6.536	279.21	90
NaClO ₃ doped with NaCl	6.566	283.09	90

FTIR studies

The FTIR spectra of pure and NaCl doped NaClO₃ crystals recorded in the range 400 - 4000 cm⁻¹ are shown in Figure 4. The various assignments related to the vibrational frequencies of the functional groups have been identified and provided in the Table 4. It is observed that some absorption peaks/bands are narrowed or broadened due to doping of NaCl into the crystal of sodium chlorate.

(i) NaClO₃(ii) Pure NaClO₃Figure 4. FTIR spectra of (i) NaCl doped NaClO₃ and (ii) pure NaClO₃ crystalsTable 4 (a). FTIR assignments for pure NaClO₃ single crystals

Bands	Vibrational frequency (cm ⁻¹)
OCIO bending vibration	482.04
	619.37
-OCl bending	968.91
OCIO asymmetric vibration	1418.29
Stretching vibration of NaClO ₃ ion	1576.93
O-Cl stretching	1896.24
OH stretching	3543.54

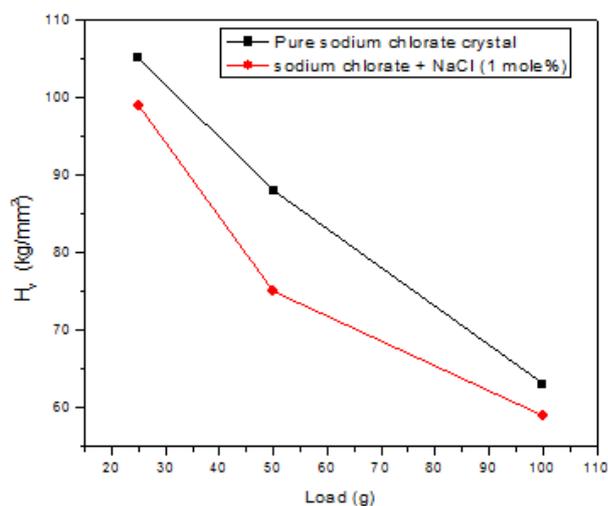
Table 4 (b). Band assignments for NaCl doped NaClO₃ crystals

Bands	Vibrational Frequency cm ⁻¹
-OCIO bending vibration	480.71
-OCIO asymmetric bending	619.37
-OCl bending	969.18
Stretching vibration of NaClO ₃ ion	1620.94
O-Cl stretching	1895.24
OH stretching	3547.40

Vickers hardness test

Vickers microhardness indentation test is used to characterize the hardness of the material. Measurement of hardness is a non-destructive testing method to determine the mechanical behavior of the materials. It is a resistance against plastic deformation. By definition, the indentation hardness is the ratio of the applied load to the surface area generated due to indentation [Sekar and Parimaladevi, 2009]. The hardness number can be evaluated by the knowledge of the load applied and the cross-sectional area of the depth of the impression on the smooth surfaces of as-grown pure and NaCl doped NaClO₃ crystals. In the present study, hardness was measured using LEITZ-WETZLER hardness tester fitted with a Vickers diamond pyramidal indenter. The loads applied are 25, 50 and 100 grams were applied at a time of 10 seconds. Radial cracks were obtained for some indentations. This might be due to the plastic deformation or unique cracks induced in the samples. The Vickers hardness number (H_v) is calculated using the formula

$$H_v = 1.854 * [P/d^2] \text{ kg/mm}^2$$

Figure 6. A plots of load P against hardness number (H_v) for pure and NaCl doped NaClO₃ crystals

Where P is the applied load in kg and d is the average diagonal length in mm of the indented impression [Selvarajan *et al.*, 2009]. Plots of load (P) against Vickers hardness (H_v) for the samples are shown in Figure 5. It is observed from the results that the hardness number decreases with increase in load for both the samples and hardness number for NaCl doped sodium chlorate crystal is less than that for undoped sodium chlorate crystal.

This may be due to weakening the bonds when sodium chlorate is doped with NaCl. The work hardening coefficient (n) or Meyer index of the material is related to the load P by Meyer's law and is given by relation $P = ad^n$ where a is an arbitrary constant and d is diagonal indentation length. The plots of $\log P$ versus $\log d$ are shown in Figure 7. The slopes of straight lines in the Figure 7 (a) and (b) will give the work hardening coefficient (n) and the values are found to be 1.647 for pure NaClO_3 and 3.806 for NaCl doped NaClO_3 crystals. According to Onitsch, if n is more than 1.6, the crystal will be softer and hence it is concluded that the samples of this work belong to soft category of materials [Onitsch, 1947].

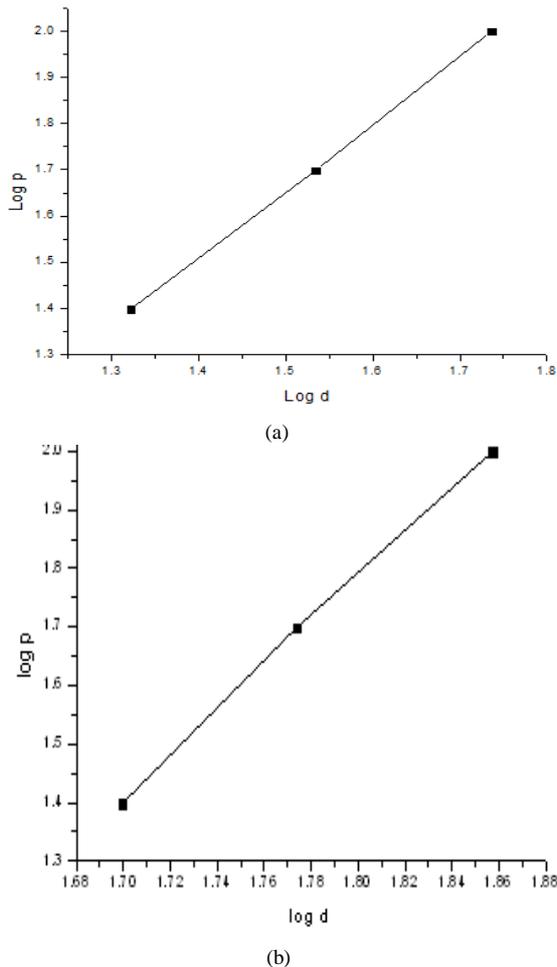


Figure 7. A plots of $\log P$ versus $\log d$ for (a) pure NaClO_3 and (b) NaCl doped NaClO_3 crystals

SHG test

The Second Harmonic Generation (SHG) efficiency of the grown crystals was measured by Kurtz and Perry powder method [Ravishankar *et al.*, 2011]. The second harmonic signal generated in the crystalline samples was confirmed from the emission of green radiation ($\lambda=532$ nm). The output from Nd: YAG laser ($\lambda=1064$ nm) was used as a source and it was illuminated to the powder form of the pure and NaCl doped NaClO_3 crystals. In this experiment, KDP was used as the reference material. The input power of the laser beam was measured to be 0.68 J. Throughout the experiment the laser power was kept constant. The power of SHG signals from of the samples with respect to KDP is given in Table 5. Output power from KDP is measured to be 8.8 mJ/pulse. The results from SHG study reveal that the SHG efficiency for NaCl doped sodium chlorate is more that of undoped sodium chlorate crystal.

Table 5. SHG Efficiency values pure and NaCl doped NaClO_3 crystals

Sample	Power of SHG signal (mJ/pulse)
NaClO_3	7.8
NaClO_3 doped with NaCl	11.3

UV – Visible spectral studies

Single crystals are mainly used in optical applications where the optical transmission range and lower cut-off wavelength are very important. The UV- Visible range from 190 to 400 nm is very important for the realization of SHG output in this range using diode and solid state laser. (Seker.C and Parimaladevi. R, 2009). The UV transmission spectra of pure and NaCl doped NaClO_3 are shown in figure 8. It can be seen from the spectra that the lower cut-off wavelength for both samples lies nearly 330 nm for pure and NaCl doped NaClO_3 crystals. The absence of absorption in the visible region clearly indicates that the grown crystals can be used for opto-electronic application. High transmittance or low absorbance is observed from 400 nm upto 1100 nm and it clearly indicates that both crystals of this work possess good optical transparency for SHG of Nd : YAG laser.

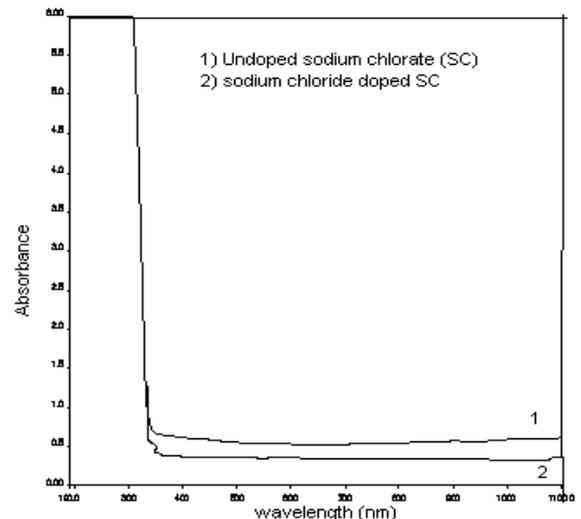


Figure 8. UV-visible absorbance spectra of f (a) pure and (b) NaCl doped NaClO_3 crystals

Atomic absorption studies

Atomic absorption spectroscopy is the most powerful technique for the quantitative determination impurities in the doped samples. Using this method we can find the total metal content of the sample. The absorption of energy by ground state atoms in the gaseous state forms the basis of atomic absorption spectroscopy. Atomic absorption technique is specific because the atoms of a particular element can only absorb radiation of their own characteristic wavelength. The technique makes use of a flame to atomize the sample, but atomizers such as a graphite furnace are also used. In order to analyze a sample for its atomic constituents, it has to be atomized. The sample should then be illuminated by light. The light transmitted is finally measured by a detector. In order to reduce the effect of emission from the atomizer or the environment, a spectrometer is normally used between the atomizer and the detector. The electrons of the atoms in the flame can be promoted to higher orbitals for an instant by absorbing a set of quantity of energy. This amount of energy is specific to a particular electron transition in a particular element. As the quantity of energy put into the flame is known and the quantity remaining at the other side can be measured, it is possible to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured. Atomic absorption studies of NaCl-doped sodium chlorate crystals were carried out using

an atomic absorption spectrometer (Model: AA6300) and the presence of sodium in the doped sodium chlorate crystals was confirmed.

Conclusion

The single crystals of pure NaClO_3 and NaCl doped NaClO_3 were successfully grown by slow evaporation technique. The solubility of the samples was measured by gravimetric method and it is observed that NaCl doped sodium chlorate sample has more solubility than that of undoped sample. The lattice parameters have been determined by XRD method. The functional groups of the grown crystals have been identified from Fourier Transform infrared spectra. The second harmonic generation of the grown crystals was confirmed by Kurtz powder test using Nd:YAG laser as a source. The mechanical property was evaluated by Vickers microhardness method. High transmission indicates the crystals possess good optical transparency. The presence of sodium in the doped sample was confirmed by atomic absorption studies.

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