EFFECT OF THIOUREA DOPING ON A NOVEL AMINO ACID CRYSTAL: GLAHCl

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ABSTRACT

Single crystals of pure and thiourea substituted Glycyl-L-Alanine Hydrochloride (TU-GLAHCl) are successfully grown by slow evaporation solution growth method at constant temperature of 35°C. The effect of thiourea dopant on crystal properties has been studied. Single crystal XRD analysis confirms the structure and change in lattice parameter values for the doped crystals. The doped crystals were quantitatively analysed by EDAX analysis and the presence of thiourea was confirmed. The crystals were characterized by solubility studies, FTIR and UV-Vis-NIR techniques. Second harmonic generations for the grown crystals were confirmed using Nd:YAG laser. Thermal and mechanical stability of crystals were tested by TGA/DTA and microhardness analysis. The surface morphologies of the grown crystals were analysed by scanning electron microcope (SEM).

Keywords: TGA/DTA, SEM, DOPING, GLAHCl

I. INTRODUCTION

Numerous research activities have been in practiceforthe past three decades on nonlinear optical (NLO) crystals, owing to their wide applications in frequencyconver-sion, data storage, optical image processing, optical communication, optical switching, etc.

Recently a number of semi-organic crystals for nonlinearoptical applications have been exploredAmino acids can be used as chiral auxiliaries for nitro aromatics and other donor- acceptor molecules with large hyperpolarizabilities, and as a basis for synthesizing organic and inorganic compounds [1]. A series of studies on semi-organic aminoacid compounds such as Larginiumdinitrate [2], Larginine hydrochloride[3], Lalanineacetate [4], and Glycine sodium nitrate[5] as potential NLO crystals have been reported. L- alanine is an amino acid, and it forms a number of complexes when reacted with inorganic acid and salts to produce an outstanding material for NLO applications. Large crystals of dimensions (3 cm^3) with promising NLO property were reported by Misoguti[6], single crystals of L-alanine were grown from aqueous solution[7].It is very clear from the previous reports that the physical properties of NLO crystals can be enhanced by doping with organic additives .In this paper we report the study of the effect of thiourea on various physical properties of L-alaninesinglecrystals.

II. EXPERIMENTAL

CRYSTAL GROWTH

In the present study Glycyl -L- alanine hydrochloride (GLAHCl) and thiourea doped GLAHCl (TU-GLAHCl) crystals are grown by slow evaporation solution growth method. Stoichiometrically synthesized material was taken a the raw material for growth. Saturated solution of GLAHCl was prepared at room temperature with water as solvent and the prepared solution was filtered using micro filter. The filtered solution was taken in beakers and dried in dust free atmosphere at 35°*C*. In this process 3 drops of hydrogen peroxide were added to the mother solution of GLAHCl to inhibit the growth of microbes[16]. Single crystals of optimum size were grown in 45 days. Similarly crystals are also grown with thiourea as dopant. Saturated solution of GLAHCl was prepared at room temperature and the solution is filtered and thiourea is doped in 2wt% in it. After adding the dopant the solution is again stirred well in a closed vessel for more than an hour.These crystals obtained with thiourea as dopant had no observable morphological changes. The grown crystals are shown in Fig.1a and b.

SOLUBILITY

The recrystallized salt was used for solubility studies. The solubility of pure and thiourea doped GLAHCl in millipore water was determined in the temperature range 30 – 60°C (g/100 ml H_2O) in steps of 5°C using a constant temperature bath of accuracy

$\pm 0.01°C$. Recrystallised salt was used for the studies. The solubility was determined by dissolving the solute in millipore water in an air tight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solution was analysed gravimetrically. The results indicate that there is a positive slope of solubility of pure and doped GLAHCl crystals as shown in Fig.2.

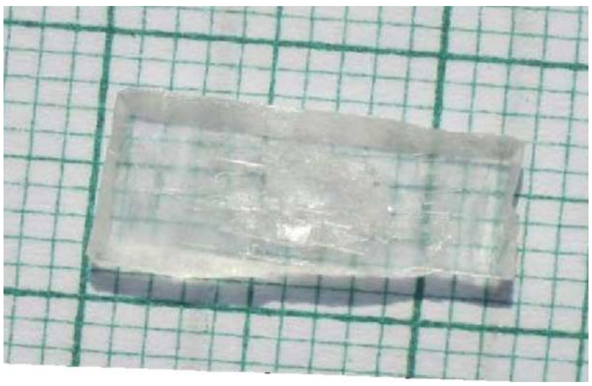

Fig. 1a Photograph of pure GLAHCl

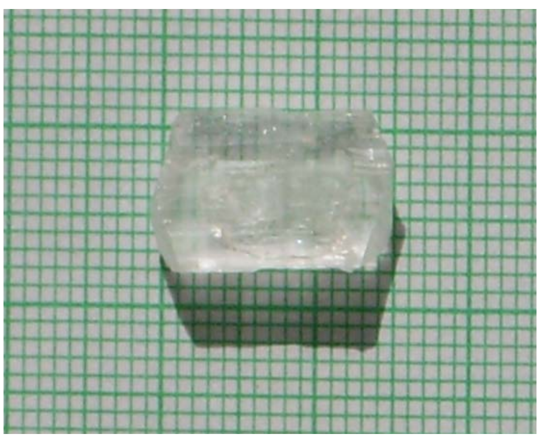

Fig. 1b Photograph of TU- GLAHCl

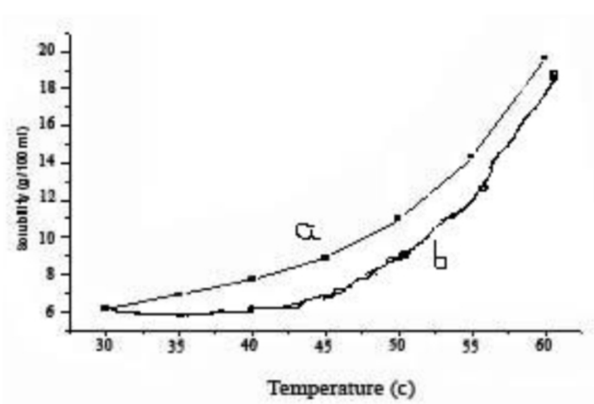

Fig. 2 Solubility curve for pure GLAHCl and TU-GLAHCl

III. RESULTS AND DISCUSSION

Single Crystal XRD analysis

Single crystal X- ray diffraction studies have been carried out using ENRAF NONIUS CAD4 single X - ray diffractometer to calculate the lattice parameters of the grown crystals. It is observed that both pure and thiourea doped GLAHCl, crystallize in the monoclinic system. Both samples belong to $P2_12_12_1$ space group which is recognized as non centrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The calculated lattice parameters for pure GLAHCl are a=5.73Å, b=18.27Å, c=7.87Å and $\alpha = 90°$, $\beta = 96°72"$, $\gamma = 90°$ and the volume of the unit cell is 818 $Å^3$. These values are in good agreement with the data reported in the literature [8]. In the case of thiourea doped GLAHCl crystals slight variations in lattice parameters as well as cell volume values are observed

EDAX ANALYSIS

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals. In the present study, the crystal was analysed by INCA 200 energy dispersive X-ray micro analyzer equipped with LED-steroscan 440 scanning electron microscope. The results obtained in EDAX of the doped crystal is shown in Fig.3 and this confirms the presence of thiourea in the doped sample.

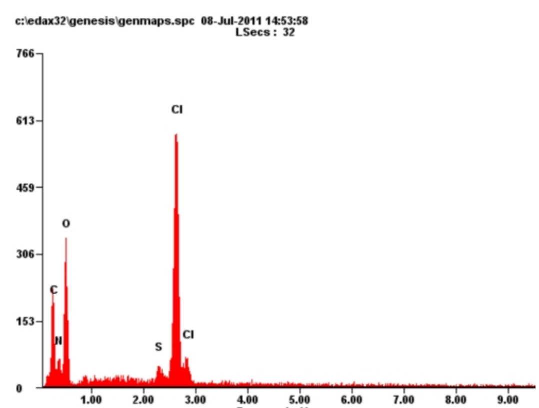

Fig. 3 EDAX Spectrum of TU-GLAHCl

FT-IR ANALYSIS

The presence of the functional groups was qualitatively analysed by the Infra red spectrum.The

FT-IR analysis was recorded in the region 400 – 4000 cm^{-1} using BRUKER IFS 66V spectrometer to confirm the presence of functional groups in the grown crystal. The middle IR spectrum of GLAHCl and TU-GLAHCl is shown in Fig.4a and b. It is observed that the broad envelope between 2508cm^{-1} and 3081cm^{-1} is due to overlapping of NH_3 and CH stretching modes. The NH_2 group is protonated by the COOH group, giving rise to NH_3^+ and COO^- groups [9]. In the overtone region, there is a sharp intense peak at 2112 cm^{-1} which is assigned to combinational and asymmetrical bending vibration of NH_3^+. The bending modes of CH_3 are well resolved sharp peaks positioned at 1362 cm^{-1} and 1505 cm^{-1}. The peak at 1114 cm^{-1} is due to C-O stretch and the O-H bend of COOH group is observed at 1236 cm^{-1}. The lack of any strong IR band at 1700 cm^{-1} clearly indicates the existence of the COO^- ion in zwitterionic form [10]. The symmetric and asymmetric NH_3^+ stretching vibrations appear at frequencies 3081cm^{-1} and 2938 cm^{-1} respectively. The C-H and N-H bending frequency is observed at 1307cm^{-1} and the absorption peak at 1594 cm^{-1} confirms the presence of NH_3 bending [11]. A peptide bond CO-NH is formed between the carboxyl group COOH in L-alanine and amino group NH_2 which is clearly visible in the spectrum at 1620 cm^{-1} [12]. It is due to this peptide bond formation O-H symmetric stretching vibration of water is seen at 1455 cm^{-1}. The IR spectra recorded for the thiourea doped GLAHCl crystals as shown in Fig.5b was similar to those of pure GLAHCl crystals and confirms the presence of all functional groups. The influence and incorporation of thiourea is ascertained from the wavelength assignment at 1413 cm^{-1} which corresponds to C=S stretching vibration.

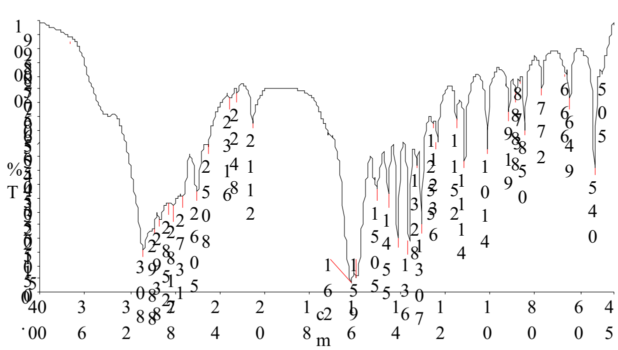

Fig. 4a FTIR spectrum of pure GLAHCl

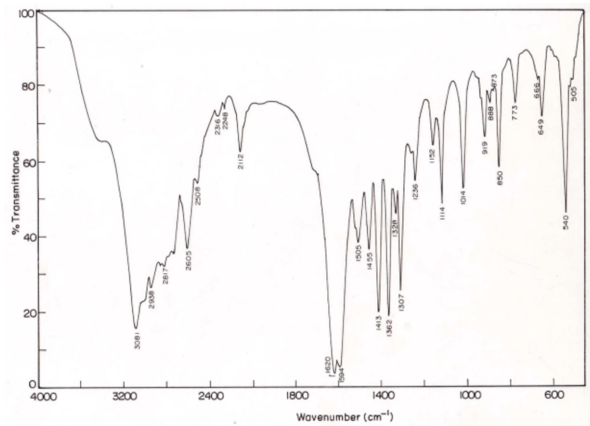

Fig. 4b FTIR spectrum of TU- GLAHCl

UV-Vis-NIR STUDY

The absorption spectrum plays a vital role to identify a potential NLO material which has a wide transparency window without any absorption at the fundamental and second harmonic wavelength. The UV-Vis-NIR analysis of GLAHCl crystal was carried out between 200- 2500 nm covering the entire near ultra violet, visible and near infra- red regions, using a PERKIN-ELMER LAMBDA 25 UV spectrometer. The absorption curves for both doped and pure crystals are shown in Fig.5. The absorbance is very less in the UV and the entire visible region which is an interesting observation in these materials. The absence of absorption of light in the visible region is an intrinsic property of all amino acids [13]. For pure GLAHCl, the crystal is highly transparent in the entire range (280 nm-1500 nm) without any absorption peaks which is an essential parameter for NLO crystals. The maximum absorption lies around 280 nm. But in the case of

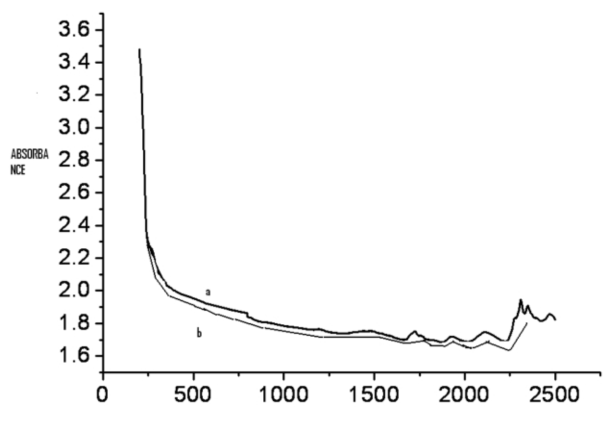

Fig. 5 UV spectrum of pure GLAHCl and TU-GLAHCl

thiourea doped crystals maximum absorption shifted to around 272 nm. Between 272 nm and 1500nm absorbance is almost nil. Hence, it can be concluded that the thiourea dopant play a key role in improving the optical quality of GLAHCl crystals. This transparent nature of crystals in the UV-Vis-NIR region can be exploited for various NLO applications.

NONLINEAR OPTICAL STUDY

In order to find out the NLO property of grown crystals, second harmonic efficiency test was performed by the Kurtz and Perry powder technique [14] using Q-switched, mode locked Nd – YAG laser operating at the fundamental wavelength 1064 nm, generating about 2.5 mJ / pulse. This laser can be operated in two modes. In the single shot mode the laser emits a single 8ns pulse. In the multishot mode, the laser produces a continuous train of 8 ns laser pulses at a repetition rate of 10 Hz. In the present study, the single shot mode of 8ns laser pulses with a spot radius of 1mm was used. The experimental set up used a mirror and 50 / 50 beam splitter, to generate a beam with pulse energy of 6 mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the sample was detected by photo diode detector and oscilloscope assembly. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. The second harmonic generation was confirmed by the green emission of wavelength 532 nm from the crystalline sample. Both thiourea doped and pure GLAHCl crystals were found to possess SHG efficiency. The results obtained by this method shows that the SHG efficiency for pure and doped samples is about 58% and 60% as that of KDP. Hence the SHG efficiency of pure GLAHCl is increased by the inclusion of thiourea.

HR-SEM ANALYSIS

HR-SEM analysis was carried out in order to study the nature and surface features of the grown crystals. The crystals were cut into few mm for observing the surface morphology. The SEM images of both GLAHCl and TU-GLAHCl crystals are shown in Fig.5a and b. Pure GLAHCl shows asmooth surface with closely packed layers as in Fig.5a, while Fig.5b shows the existence of of striations and visible inclusions in the TU-GLAHCl crystals

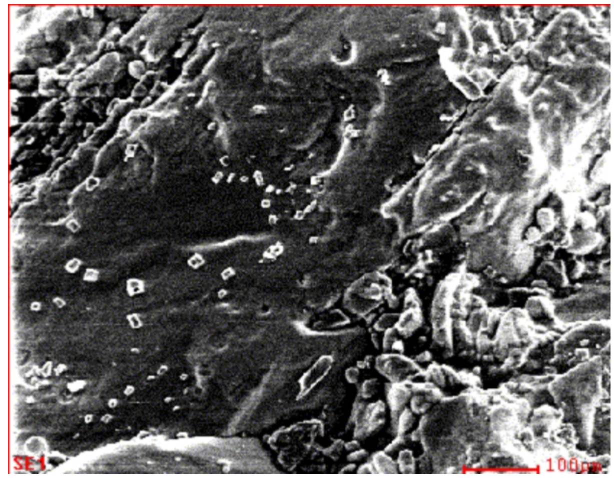

Fig. 5a HR-SEM of pure GLAHCl

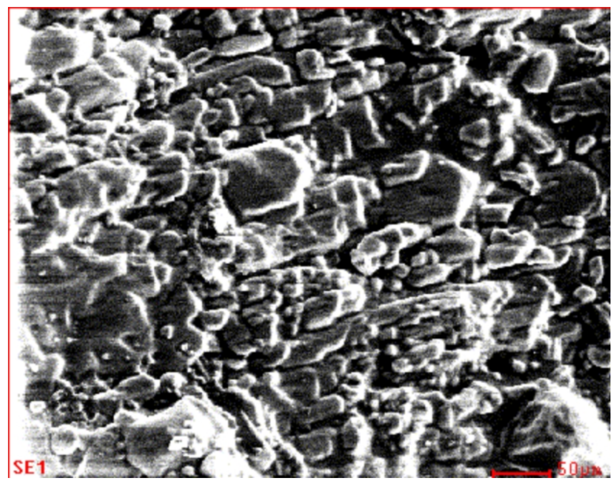

Fig. 5b HR-SEM of TU- GLAHCl

THERMAL STUDIES

The thermal stability of pure and doped GLAHCl single crystal was estimated by TGA and DTA techniques. Simultaneously thermo gravimetric analysis and differential thermal analysis were carried out for the crystal using a NETZSCH STA 409C/CD thermal analyzer. A powder sample of 20.100mg was kept in nitrogen atmosphere in the temperature range 25°C – 1200°C with a heating rate of 10K/min. The crucible used was of alumina (Al_2O_3) which served as a reference for the sample. Thermal characteristic curves for pure and doped GLAHCl crystals are shown in Fig.6 and 7. It is evident from TGA curve that both the grown crystals posses a very good thermal stability upto 243$C when compared with L - alanine oxalate.There is no weight loss upto 243°C and a major weight loss of about 40% is observed at

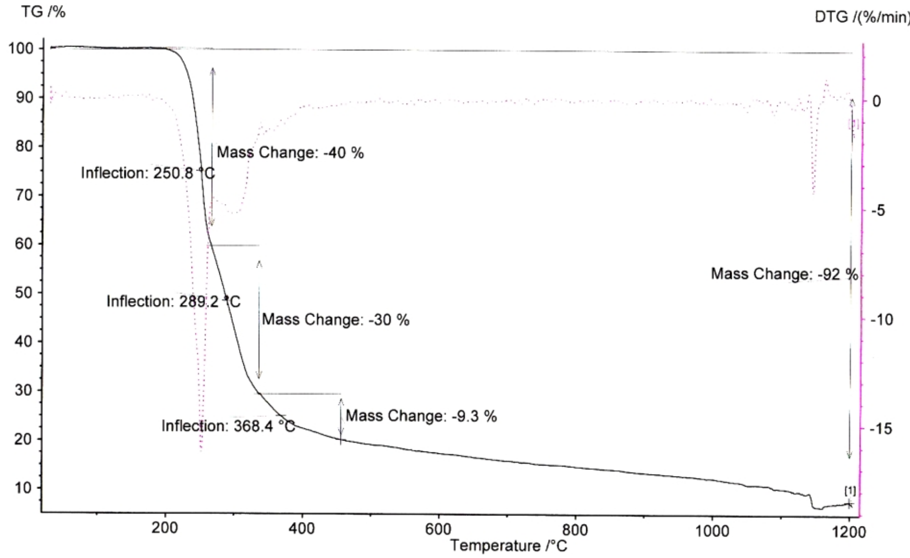

Fig. 6 TGA curve of TU-GLAHCl

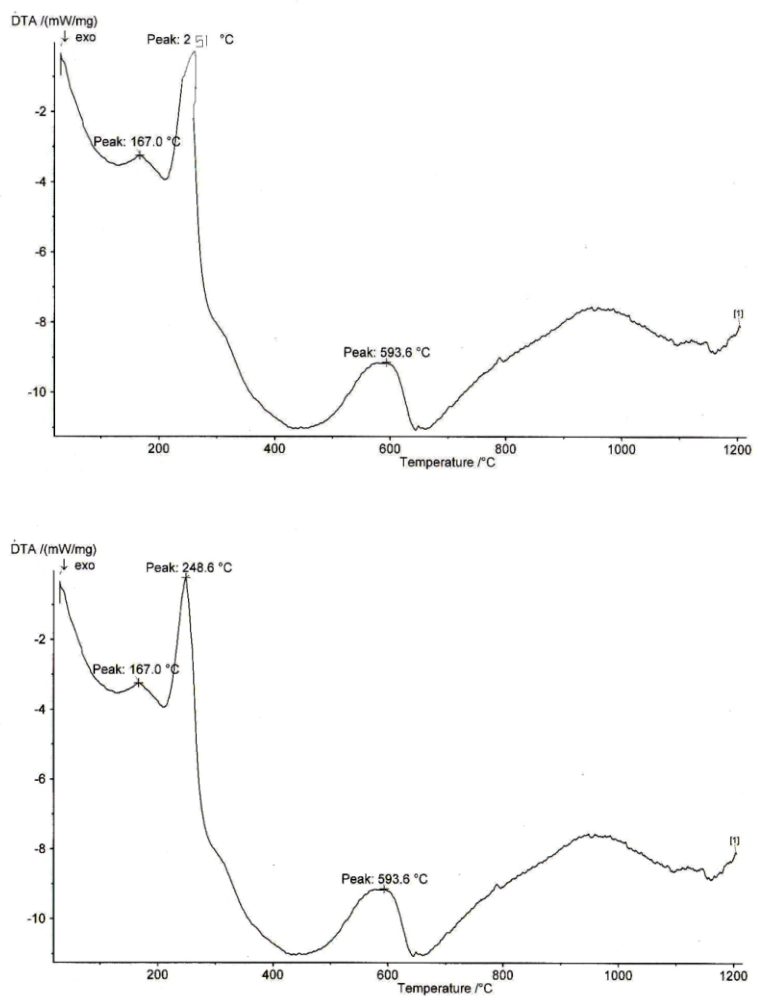

Fig. 7 DTA curve of pure and TU-GLAHCl

250.8°C which may be attributed to the elimination of CO_2 from the crystal. However two stages of weight loss have been observed above 250.8°C. The first stage occurs at 289.2°C with 30% of weight loss, which is attributed to the removal of ammonia. The second stage at 368.4°C with 9.3% of weight loss indicates that the sample has collapsed through the breakage of peptide bond in the crystal. I n the DTA trace of pure GLAHCl a strong exothermic peak is observed at 248.6°C whereas for TU-GLAHCl, the peak is slightly shifted to 251°C.This slight increment in the decomposition temperature is evident for the doped crystals, suggesting that the substitution of thiourea enhances the thermal stability of GLAHCl crystal. Another important observation is that there is no phase transition till the material melts and enhances the temperature range for the utility of the crystal for NLO applications.

IV. CONCLUSION

Single crystals of pure GLAHCl and thiourea doped GLAHCl were grown by slow evaporation technique in a period of 45 days. XRD analysis confirms that both crystals belong to monoclinic system with the space group $P2_1$. However there is a slight increase in the lattice parameter and volume for the TU-GLAHCl crystals.The presence of thiourea in the doped crystal is confirmed by EDAX analysis. Functional groups and the modes of vibrations have been identified by FTIR spectrum and the peak at 1620 cm^{-1} reveals the formation of peptide bond CO-NH between the carboxyl group COOH in L –alanine and amino group NH_2 in glycine which ascertains the coordination of glycine with alanine. The minimum absorption in the entire visible range 272-280 nm for both crystals shows the suitability of these materials for NLO applications. The NLO property analysed with Kurtz Powder technique confirms the grown crystals are non linear in nature. The SEM analysis shows the surface morphology of the grown crystals. The thermal analysis reveal that theGLAHCl is thermally stable upto 248.6°C and its thermal stability is slightly increased when doped with thiourea. It is interesting to note that the incorporation of thiourea dopant has improved the thermal stability, transmittance and SHG efficiency of GLAHCl crystals. These preliminary studies suggest that the thiourea doped GLAHCl crystal is a candidate material suitable for photonic device fabrication.

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