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Impact of $MgCl_2$ on the physio chemical properties of L-HTFB single crystal – an amino acid based semi organic crystal

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Abstract

Low dielectric materials that can take on multiple forms and endure mechanical stress are vital given the rising demand in lightweight and flexible electronics for applications like wearable technology. It is possible to create stretchy dielectric layers with semi-organic crystals that keep their electrical characteristics even when folded or strained. The purpose of this study is to investigate the optical and electrical properties of L-histidinetetrafluoroborate (LHTFB), a semi-organic NLO single crystal with outstanding mechanical properties and strong nonlinearity, through doping with magnesium. Bare and Mg doped crystals were grown by solution growth method and analyzed for its structural, optical, NLO and dielectric analysis. The dielectric permittivity measurements obtained reveal that magnesium drops the value below 4, which is lower than silica. These crystals' low permittivity and low loss factor point to their potential application in the microelectronics industry for elevated device performance, less power usage, optimized signal integrity, and continued semiconductor technological progress towards smaller, quicker, and greater energy-efficient electronic devices.

Key words: Semi organic NLO crystals, solution growth, Low dielectrics, NLO

1. Introduction

Recently, organic and inorganic material blends have developed nonlinear optical (NLO) materials suited for second harmonic generation (SHG), which has sparked great interest in photonic devices [1]. Among these materials, semi-organic single crystals such as L-histidine tetrafluoroborate (L-HTFB) are notable for their high nonlinearity, hardness, and thermal stability [2-4]. L-HTFB, whose formula is C6H10O2N3BF4, is a member of the monoclinic system (P21 space group) and has a transmission range of 230–1600 nm, allowing it to produce green and blue light [3-5]. It also has five times the SHG intensity of KDP. Recent research has highlighted the significance of semi-organic crystals with high nonlinearity and low dielectric permittivity for microelectronics and energy storage, since they increase circuit performance by lowering the RC time factor [6-7]. Examples of the potential for reduced dielectric loss and improved NLO efficiency are doped L-arginine acetate and L-glutamic acid zinc chloride [8–10]. For the advancement of flexible electronics, microelectronics, and photonics, improved materials with low dielectric permittivity and loss are still needed [11–12].

Keeping this in view, for the time, we made an attempt to explore the effect of magnesium chloride ($MgCl_2$) doping on the dielectric properties of L-histidinetetrafluoroborate single crystals grown via solution growth technique. The pure and doped crystals were characterized for their structural, optical, thermal, NLO and dielectric properties. The results are reported herein.

2. Growth of Pure and $MgCl_2$ doped L-histidine tetrafluoroborate single crystals

L-histidine in its raw form and tetrafluoroboric acid in its refined form were obtained from Merck. Supersaturated solution was made by dissolving the precursors in a 1:1 ratio at 50°C for approximately five hours while stirring continuously. The resulting supersaturated solution had a top perforation to allow solvent to evaporate while it was maintained in an undisturbed mode. After 35 days, high-quality crystals were harvested. To develop $MgCl_2$ doped L-HTFB crystals, the used mole percentage of $MgCl_2$ was added during the stirring step. The photograph of the harvested crystals is shown in Figure 1. $MgCl_2$ addition slightly changes the colour to pure white.

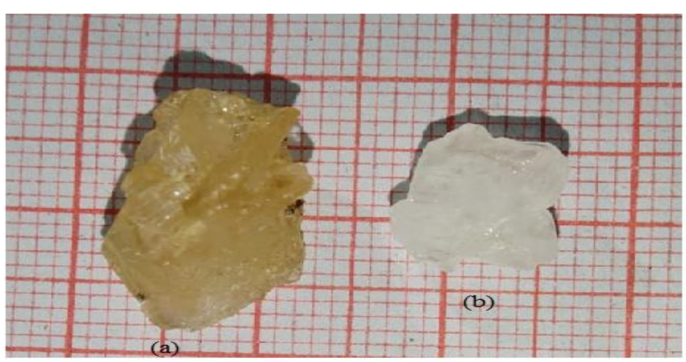

Figure 1: Grown crystals of (a) pure and (b) magnesium chloride doped L-histidinetetrafluoroborate (L-HTFB)

3. Tools and Techniques

To investigate the crystal system and determine the lattice parameters, MgCl2-doped L-HTFB crystals were analyzed using a single crystal X-ray diffractometer. Optical properties were examined in the 200–1100 nm wavelength range with a Perkin Elmer Lambda 35 UV-Visible spectrophotometer for both as-grown and doped crystals. Dielectric properties were measured for pure and doped L-HTFB single crystals after orienting and slicing them appropriately. A thin graphite layer was applied to both sample surfaces for conductivity, and capacitance and dissipation factors were measured using an Agilent 4284A LCR Meter across a frequency range of 1 KHz to 1 MHz. The nonlinearity of the crystals was evaluated through the powder SHG test, performed using a Spectrum Physics Q-switched Nd laser, with a 1064 nm first harmonic input, 10 ns pulse width, and 10 Hz repetition rate.

4. Results and Discussions

4.1 Single Crystal XRD

The obtained values of lattice parameter for doped L-HTFB crystals are listed in Table 1 and compared with the reported values of pure L-HTFB crystal .As reported by previous authors [6], pure the crystal pure L-HTFB crystallized in monoclinic system, whereas $MgCl_2$ doped crystal crystallized in orthorhombic system with space group of P 21 21 21. Also $MgCl_2$ addition increases the lattice volume of pure L-HTFB. Because the atom sizes of the dopant and host differ, doping can cause strain in the crystal lattice. Depending on the precise type and concentration of the dopant, this strain may cause the lattice to grow. Expansion in lattice evident the entry of dopant in L-HTFB crystal lattice. The obtained packing diagram and ORTEP diagram of doped L-HTFB shown in figure 2.

Table 1: Single crystal XRD data of bare and MgCl2 doped L-HTFB crystals

Sample	Parameters (Å)			Unit cell volume (Å^3)	α^o	β^o	γ^o
	A (Å)	B (Å)	C (Å)				
Pure LHTFB crystal [6]	5.032	9.12	10.254	470.21	90	93.39	90
$MgCl_2$ doped LHTFB	6.8453(4)	8.9156(6)	15.2862(3)	932.92(11)	90	93.50	90

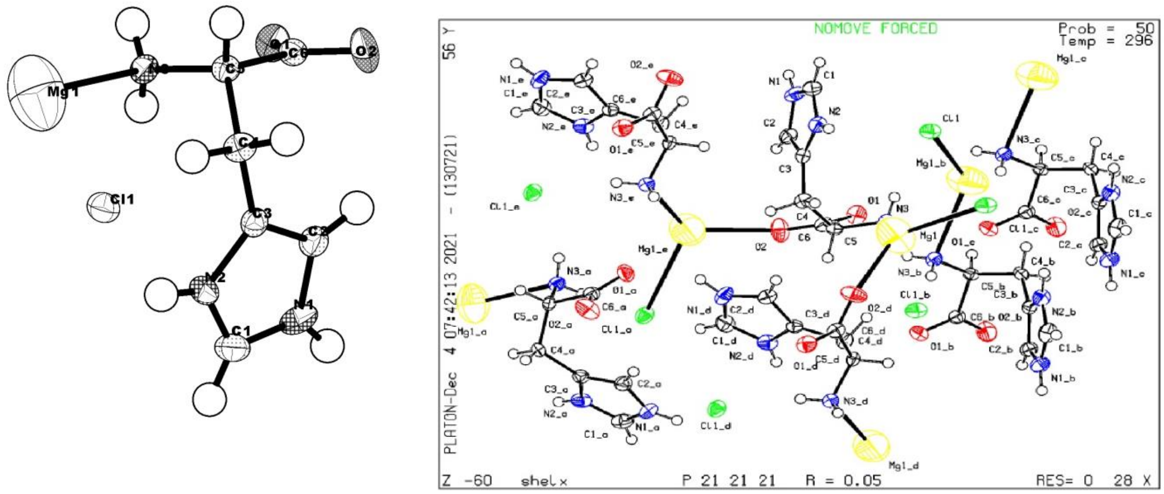

Figure 2: Packing and ORTEP diagram of $MgCl_2$ doped L-HTFB single crystal

4.2 UV-Vis Spectral Analysis

When it comes to optical applications, NLO single crystals are predominantly used because of their high transparency and optical transmission efficiency. The process of absorbing UV and visible light entails elevating electrons from their orbital states to higher ones. This allows the UV-VIS-NIR spectrum to reveal details about the molecular structures within crystals. The spectrum of optical absorption for pure and doped L-HTFB crystals was recorded in the wave length range 190-1100 nm. Recorded UV-Vis absorption spectra of the grown samples are shown in Figure 3.The band edge absorption shifted to high wavelength region with doping. Bandgap energy of the prepared pure and $MgCl_2$ doped L-HTFB crystal was calculated using tauc plot [12] and also shown in figure 4.This high bandgap value indicates that the crystal exhibits dielectric behaviour, which might cause polarisation when intense radiation strikes the substance. The absence of absorption bands in the visible spectrum, confirms that the produced crystals are suitable for photonic and optical applications. Additionally, the high energy bandgap verifies the extremely low defect content in the produced crystal and also the absorption edge in UV region of pure and doped crystals. Semi-organic crystals that are sensitive to UV light can be used in biomedical sensors and equipment for drug discovery, DNA analysis, and fluorescence spectroscopy, besides additional applications.

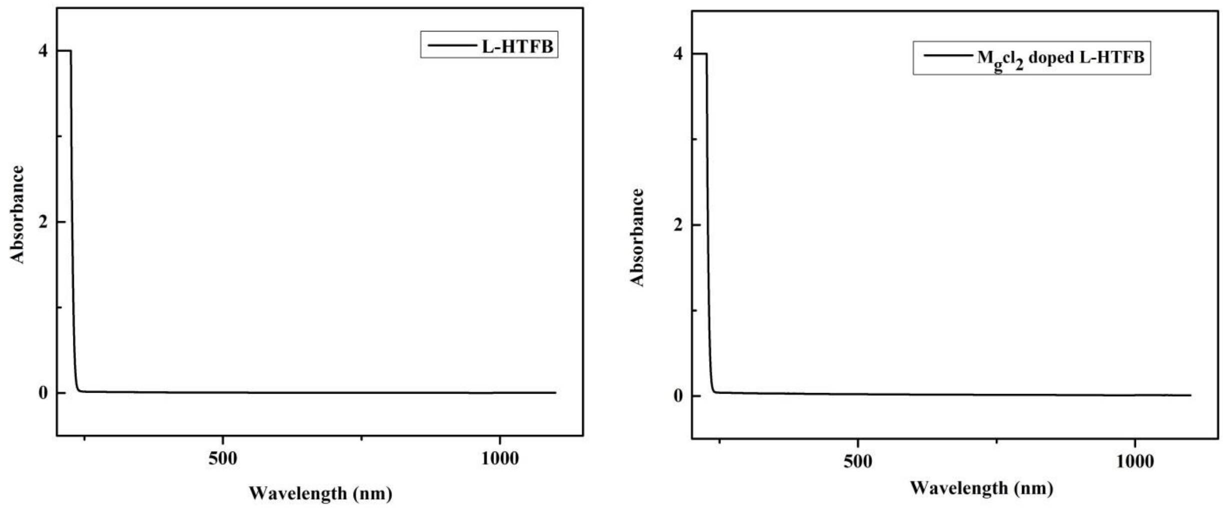

Figure 3: UV-Vis absorption spectra of pure and doped L-HTFB crystals

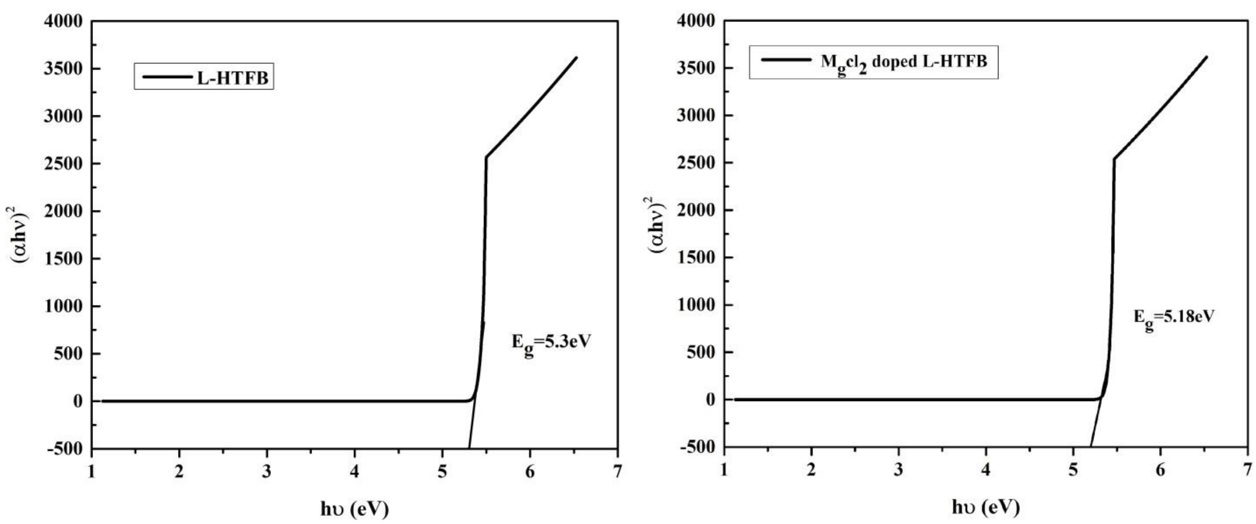

Figure 4: Tauc plot of pure and doped L-HTFB crystals

4.2 NLO Studies

By measuring NLO efficiency precisely, scientists can forecast how well systems and devices that use semi-organic crystals will function. In order to evaluate the practicality and feasibility of using these materials in real-world applications including optical switching, frequency conversion, and optical signal processing, this prediction is crucial. In our present study, NLO efficiency of grown samples was tested through Kurtz-powder technique [13]. The obtained values are depicted in table 2. Entry of $MgCl_2$ in LHTFB crystal lattice reduces the NLO efficiency .When compared with KDP, pure LHTFB crystal has 1.2 times higher NLO efficiency whereas doped sample has only 0.826 times efficiency. The addition of $MgCl_2$ to pure LHTFB crystals alters their structure, as stated in single crystal XRD data. This distortion of the crystal lattice may interfere with the long-range order essential to effective NLO responses [14]. The nonlinear optical response could be caused by excited states or charge carriers being quenched as a result of MgCl2 doping. This quenching can happen via a variety of processes, including nonradioactive decay pathways or energy transfer processes, which will ultimately reduce the crystal's NLO efficiency [15].

Table 2: Output obtained from Kurtz-Powder method for pure and doped LHTFB crystals

Sl. No.	Sample Code / Name of the sample	Output Energy (milli joule)	Input Energy (joule)
1	KDP (Reference)	8.94	0.70
2	Pure LHTFB	10.6	0.70
3	Magnesium chloride doped LHTFB	7.39	0.70

4.4 Dielectric studies

Numerous studies have shown that crystals have emerged as a promising possibility in the electronics industry. It is crucial to investigate the dielectric properties of crystals at all frequencies and to identify potential uses for them in many scientific and technical domains. Ferroelectrics, piezoelectric, optoelectronic devices, LEDs, telephone service, and other industries are among the uses for crystals that are mentioned [16]. In the current work, we use an Agilent 4284 A LCR meter to examine the dielectric characterizations of the formed crystals for various temperature at a range of frequencies, from 100 Hz to 1 MHz [17-19]. A travelling microscope is used to measure the crystal's dimensions. In order to form a suitable conductive layer, the synthesized crystal is polished and coated with graphite on both sides [20]. Using a two probe arrangement, the dielectric constants were recorded [21]. The dielectric constant is calculated using the following relation [19].

$$\varepsilon_r = \left[\frac{A_{air}}{A_{cry}}\right]\left[\frac{C_{cry} - C_{air}\left[1 - \frac{A_{cry}}{A_{air}}\right]}{C_{air}}\right]$$

The dielectric constant and dielectric loss of the pure and doped crystal at different frequencies have been shown in Figures 5 and 6.

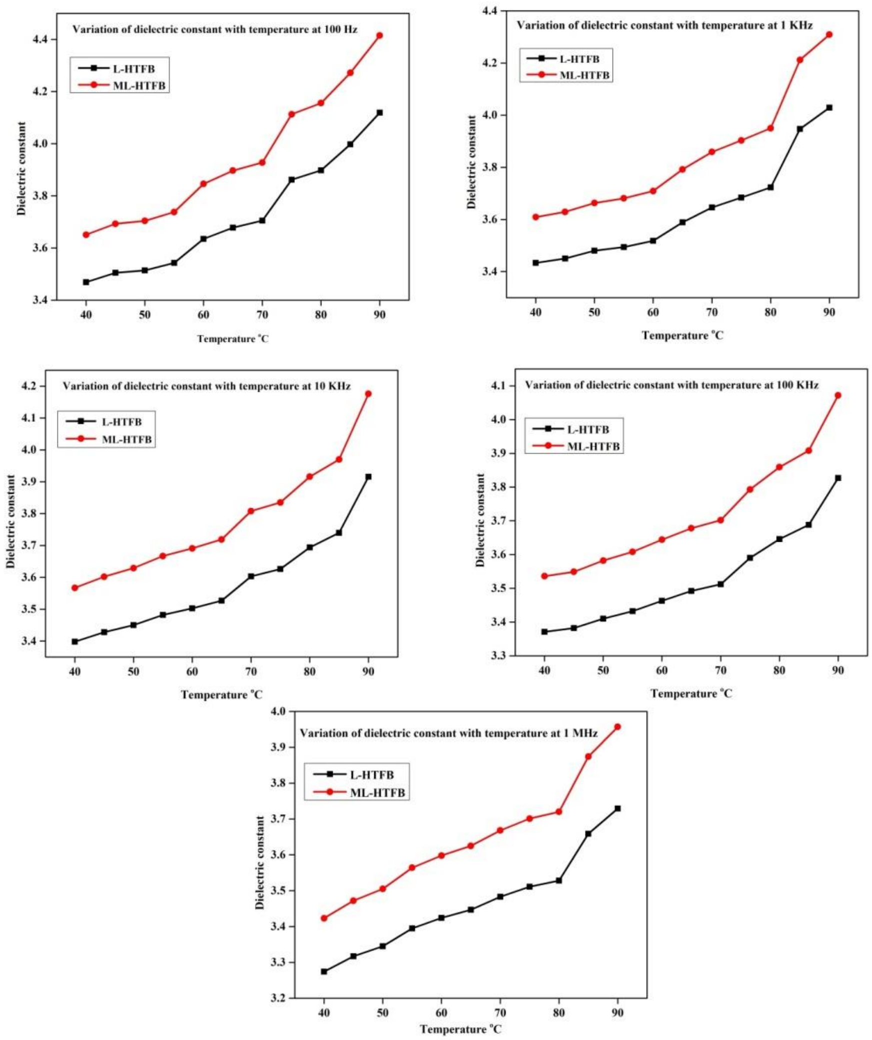

Figure 5: Variation of dielectric constant of pure and doped L-HTFB crystals with temperature for various Frequencies

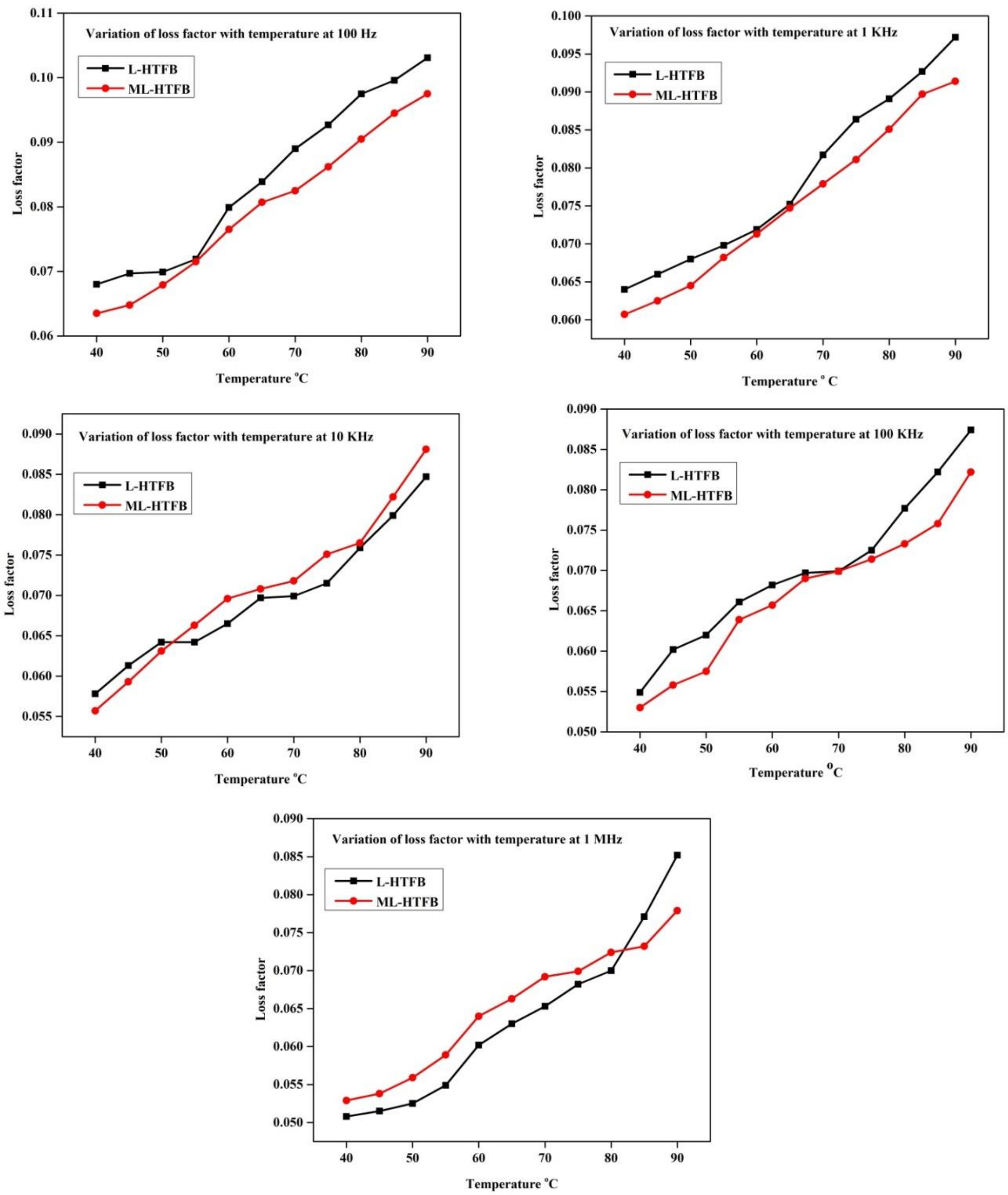

Figure 6: Variation of dielectric loss of pure and doped L-HTFB crystals with temperature for various Frequencies

It has been revealed that for all five frequencies taken into view in this study, dielectric constant as well as dielectric loss for temperature increases along the "a" directions. This is typical behaviour for a dielectric. Given that the polarization mechanism and the conduction process are comparable, this can be understood. The existence of impurities and crystal defects, electrical and ionic polarizations, and crystal expansion are commonly linked to the variation of εr with temperature. The expansions, as well as the ionic and electronic polarizations, are the primary causes of the fluctuation at low temperatures. The primary causes of the rise at higher temperatures are impurity dipoles and thermally produced charge carriers. For ionic crystals, the electronic polarizability essentially stays constant [22]. Ionic polarizability varies with temperature, which is mostly responsible for the dielectric constant's temperature increase. A sample's ability to have a low dielectric constant and high frequency dielectric loss indicates that it has better optical quality and fewer defects. This parameter is crucial for a variety of microelectronic materials, nonlinear optical materials, and their applications [23,24].

Moreover, the doped crystal's dielectric constant value is less than 4, which is lower than that of silicon di oxide. Low dielectric constant crystals can replace silica as interlayer dielectrics in integrated circuits (ICs) to lower power consumption and delays in signal propagation [25]. Crystals having low dielectric constants can be used in energy storage applications by way of capacitors. The energy density and efficiency of energy storage systems, such as supercapacitor and energy harvesting devices, can be raised by using these materials as capacitor dielectrics [26].

Conclusion:

Pure and $MgCl_2$ doped were successfully grown by slow evaporation technique. The grown crystals were subjected to structural, optical, NLO and dielectric measurements. The presence of dopant alters the crystal structure from monoclinic to orthorhombic, by inducing lattice expansion. Also the dopant reduces the optical bandgap by increasing transmission in visible region. Low loss factor with L-HTFB crystals reduced dielectric constant of the doped crystal suggest the use of the grown doped crystal in the development of optical modulators and switches for high-speed optical communication networks. Also by proberly adjusting the concentration of dopant, we may tune the optical and dielectric behavior of pure L-HTFB crystals, which can be not only a NLO crystal but for a low dielectric crystal for energy storage applications.

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