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Research Article

The Study of Structural, Optical, and Dielectric Properties of Magnesium Chloride-Doped Triglycine Sulphate Ferroelectric Single Crystals

Dessale Alemu,[1] **Shita Firehun**,[2] **Tizazu Abza**,[3] **and M. Esthaku Peter**[4]

[1]*Woldia University, Department of Physics, Woldia, Ethiopia*
[2]*Mekdela Amba University, Department of Physics, Mekdela Amba, Ethiopia*
[3]*Hawassa University, Department of Physics, Hawassa, Ethiopia*
[4]*Dilla University, Department of Physics, Dilla, Ethiopia*

Correspondence should be addressed to Dessale Alemu; dessalealemu@gmail.com

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Triglycine sulphate (TGS) and 1 and 2 mol% of magnesium chloride-doped TGS single crystals have been grown by using the slow evaporation solution method at room temperature. Pure and magnesium chloride-doped triglycine sulphate single crystals in a dimension of $12 \times 12 \times 5$ cm^3 have been grown at room temperature. The grown samples have been investigated by various characterization techniques such as single crystal X-ray diffraction, UV-VIS/NIR spectroscopy, dielectric studies, and energy dispersive X-ray analysis (EDAX). The single crystal X-ray diffraction studies revealed that both 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been crystallized in monoclinic crystal structure with space group $P2_1/m$. The UV-VI/NIR spectra analysis confirmed that both pure and 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have wide optical transparency in the wavelength range of 236–1100 nm. The bandgap energy of both samples has been found to be 5.25 eV. The dielectric properties of the grown samples were recorded by measuring the dielectric constant as a function of temperature from 45 to 55°C with various frequencies (100 Hz – 1 MHz). The dielectric studies revealed that the dielectric constants of 1 and 2 mol% of $MgCl_2$-doped TGS single crystals were increased with decreasing frequency and that the transition temperature was found to be 51°C. The EDAX spectrum confirmed the incorporation of $MgCl_2$ into TGS single crystals.

1. Introduction

Nowadays, researchers are giving more attention to crystal growth since it is one of the bases for various technology advancements [1]. Single crystal growth has a vital role in the present era of rapid scientific and technical advancement, whereas the application of crystals has unbounded limits. Single crystals may be defined as the regular ordered repeated array of atoms that show characteristic symmetry elements by which the entire block of the material is built. Single crystals of ferroelectric properties have played a prominent role in various technological devices [2, 3]. All pyroelectric materials are not ferroelectric, but all ferroelectric materials are pyroelectric. Below the Curie temperature, pyroelectric and ferroelectric materials are polar in nature and possess spontaneous polarization. However, this polarity can be reoriented or reversed fully or partially through the application of an electric field with ferroelectric materials [4]. Hence, these crystals have several practical applications in developing capacitors, nonvolatile memory, electro-optic materials for data storage applications, light deflectors, high-performance gate insulators, modulators, displays, etc [5]. Amino acids are strong applicants for optical second harmonic generation (SHG) because they contain chiral carbon atoms and crystallize in noncentrosymmetric space groups [6]. Unlike other amino acids, glycine is in the centrosymmetric space group, and it is optically inactive. Hence, to find the nonlinear optical

(NLO) property, it should be combined with inorganic acids like sulphuric acid, hydrochloric acid, and nitric acid [3]. L-threonine, L-phenylalanine, and L-serine-doped ADP crystals are good linear and nonlinear optical materials. They possess greater second harmonic generation and transparency [7–9]. Triglycine sulphate (TGS) $(NH_2CH_2COOH)_3H_2SO_4$ is one of the most broadly studied ferroelectric materials, which shows ferroelectric transition at ambient temperature (49°C) [10]. It belongs to the monoclinic crystal system associated with polar space group $P2_1$ in the ferroelectric phase, and it crystallizes in the $P2_1/m$ space group in the paraelectric phase [11]. However, pure TGS crystals have some drawbacks over doped TGS crystals such as easy depolarization by thermal and electrical means, ferroelectric properties possessing high mobility, and low Curie temperature [12]. To overcome these unfavorable factors for practical applications, a variety of dopants such as amino acids, organic compounds, and inorganic compounds can be introduced into the TGS lattice [13]. Dopants or additives also influence crystalline perfection, which may in turn influence physical properties like optical and dielectric properties of TGS single crystals [14, 15]. Alkali metal chloride compounds are very important to modify the properties of TGS single crystals [13]. Single crystals of TGS [3], barium-doped TGS [5], sulfuric acid-doped TGS [16], glycine copper nitrate [17], and glycine glycinium picrate [18] have been reported by using the slow evaporation solution growth method.

Although single crystals of TGS are commonly reported, to the best of the author's knowledge, magnesium chloride-doped TGS single crystals are very rarely reported. Rochelle salt-doped TGS crystals are found to have increased optical property and luminescence [19]. In the present work, magnesium chloride-doped TGS single crystals have been grown by the slow evaporation solution method and the results of structural, optical, dielectric, and composition studies of the grown crystals have been reported. The TGS crystal shows a typical second-order ferroelectric phase transition at the Curie point $T_c = 49°C$, but it is found to be increased to 51°C in magnesium chloride-doped triglycine sulphate single crystals.

2. Experimental Details

2.1. Crystal Growth. Commercially purchased Analar reagent (AR) grade glycine, distilled water, and concentrated sulphuric acid (H_2SO_4) were used for the growth of TGS single crystals. The purity of glycine and sulphuric acid that was used for growing magnesium chloride-doped triglycine sulphate single crystals is 99.5% and 98%, respectively. It was 99% in magnesium chloride material. Glycine and sulphuric acid were taken in a molar ratio of 1.5 : 0.5. Initially, the calculated amount of glycine was dissolved in a beaker and put onto a magnetic hot plate regulated at 40°C. Then, sulphuric acid was added into the solution and stirred for 4 hours using a magnetic stirrer until the homogeneous solution was obtained. The solution was filtered by using Whatman filter paper into a beaker. Afterward, the filtered solution was taken in a beaker, which was tightly covered by a perforated sheet so that the rate of evaporation could be minimized and kept in a dust-free environment. To obtain magnesium chloride-doped TGS single crystals, 1 and 2 mol % of $MgCl_2$ were added in two beakers of similarly prepared 1.5 : 0.5 molar ratio solution of TGS. After a period of 30 days, optically transparent crystals were harvested for undoped and 1 and 2 mol% $MgCl_2$-doped TGS crystals as depicted in Figure 1.

3. Result and Discussion

3.1. Single Crystal X-Ray Diffraction Studies. The grown crystals of 1 and 2 mol% of $MgCl_2$-doped TGS have been subjected to single crystal XRD studies using a single crystal X-ray diffractometer with MoKα ($\lambda = 0.7107$ Å) radiation. The single crystal X-ray diffraction analysis revealed that the single crystals of 1 and 2 mol% of $MgCl_2$-doped TGS samples were crystallized in the monoclinic crystal structure with space group $P2_1/m$ and the lattice angle $\alpha = \gamma = 90°, \beta = 105.79°$an d$\beta = 105.81°$, respectively. The lattice parameters (Å) were $a = 9.4173$, $b = 12.643$, and $c = 5.7352$ and $a = 9.4176$, $b = 12.6411$, and $c = 5.7353$, respectively. It is observed that the lattice parameters of 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been in very close agreement with pure TGS crystals reported by authors [3, 10]. However, there is a variation in the space group, and the space group for pure TGS is $P2_1$, so this variation is due to the above Curie temperature. The structure gains an additional set of mirror planes in the $P2_{1/m}$ space group [13]. The grown crystals belong to the non-centrosymmetric space group, thus satisfying an essential material criterion for the SHG activity of the crystal [20].

3.2. UV-Vis NIR Analysis. The optical transmission spectral analysis of grown crystals has been carried out by using a Perkin Elmer Lambda 35 UV-VIS-NIR spectrophotometer in the wavelength range between 200 and 1100 nm to cover near ultraviolet, visible, and near IR regions. The recorded spectrums of pure and 1 and 2 mol% of $MgCl_2$-doped TGS single crystals are depicted in Figure 2. The plot of wavelength versus percentage of transmittance confirmed that crystals have sufficient transmission in the wavelength range of 236–1100 nm. The cutoff wavelength of pure TGS and magnesium chloride-doped TGS crystals is the same as 236 nm. For optical fabrications, the crystal should be highly transparent in the considerable region of wavelength; thus, the optical transmittance range of grown crystals makes them convenient materials for nonlinear optical and opto-electronics applications [21]. The percentage transmittance of $MgCl_2$-doped TGS single crystals has reduced, and the cutoff wavelength for undoped and $MgCl_2$-doped TGS crystals remains the same. The reduced transmission of all samples at 236 nm corresponds to the fundamental absorption edge which is essential in connection with the theory of electronic structure [22]. The bandgap energy was calculated using the relation $E_g = 1240/\lambda_{min}$, where λ_{min} is the cutoff wavelength of light in nm [3], and it has been found to be 5.25 eV for pure and doped crystals.

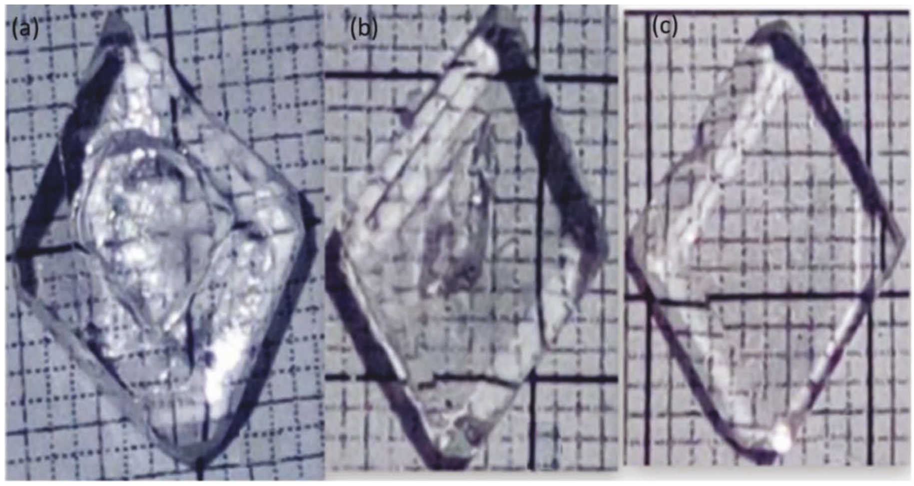

Figure 1: Photographic images of (a) undoped, (b) 1 mol% $MgCl_2$, and (c) 2 mol% $MgCl_2$-doped TGS single crystals, respectively.

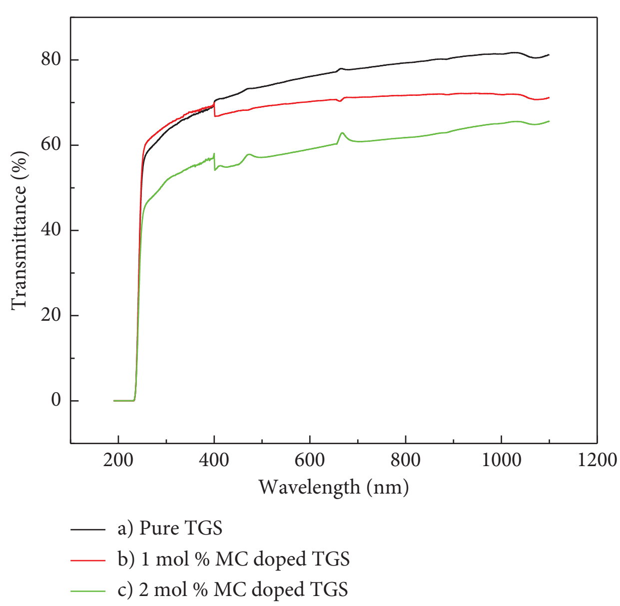

Figure 2: Transmittance versus wavelength for pure and 1 and 2 mol% of $MgCl_2$-doped TGS crystals.

3.3. Energy Dispersive X-Ray Analysis (EDX) Test. Energy dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample [4]. The elemental analysis of 1 and 2 mol% of $MgCl_2$-doped TGS single crystals was subjected to a JEOL-6390LV scanning electron microscope attached to EDX. The EDX spectrum revealed the presence of expected elements such as oxygen, chlorine, magnesium, and sulphur in both 1 and 2 mol% of $MgCl_2$-doped TGS single crystals as shown in Figure 3. Unexpected elements like Na, Ca, and K could have been due to impurities from starting reagents. The weight percentage and atomic percentage of identified elements in doped TGS samples are shown in Table 1. The quantitative and qualitative EDX results clearly showed an increase in the atomic percentage of Mg and Cl, signifying the incorporation of $MgCl_2$ into the TGS single crystal structure. The pure TGS crystal seems to have impurities, which might be due to temperature fluctuations. Good optically transparent crystals have been used for optical studies. It is observed that there are a few impurities like sodium (Na), potassium (K), and calcium (Ca) incorporated into 2 mol% magnesium chloride-doped TGS crystals.

3.4. Dielectric Studies. The dielectric constant is one of the essential dielectric properties of solids. It is important to identify the phase transition and locate the transition temperature in the crystal [23]. The dielectric studies of 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been carried out as a function of temperature (45–55°C) for various frequencies (100 Hz – 1 MHz). 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 sample, A is the area of the face in contact with the electrode, and ε_0 is the permittivity of free space (8.854×10^{-12} F/m) [24]. The variations in the dielectric constant as a function of temperature at different frequencies for 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been depicted in Figure 4. The dielectric study revealed that dielectric constants were small and nearly constant with increasing temperatures up to 49°C. Afterward, it sharply increased and reached a maximum value at a critical temperature (Tc) of 51°C. Then, it rapidly decreased up to 54°C and remained constant until 55°C. The rapid increase in the dielectric constant may be due to the space charge polarization of thermally generated carriers [25]. Also, the dielectric constants of 1 and 2 mol% of $MgCl_2$-doped TGS single crystals increased with decreasing frequency. The large value of the dielectric constant at low frequency suggests that there is a contribution from types of polarizations, such as electronics, ionic, dipolar, and space charge polarization. Electronic and space charge polarizations predominantly in the low-frequency region suggest that the grown crystals possess an enhanced optical quality with fewer defects, and this phenomenon is an essential characteristic for nonlinear optical applications [3, 4].

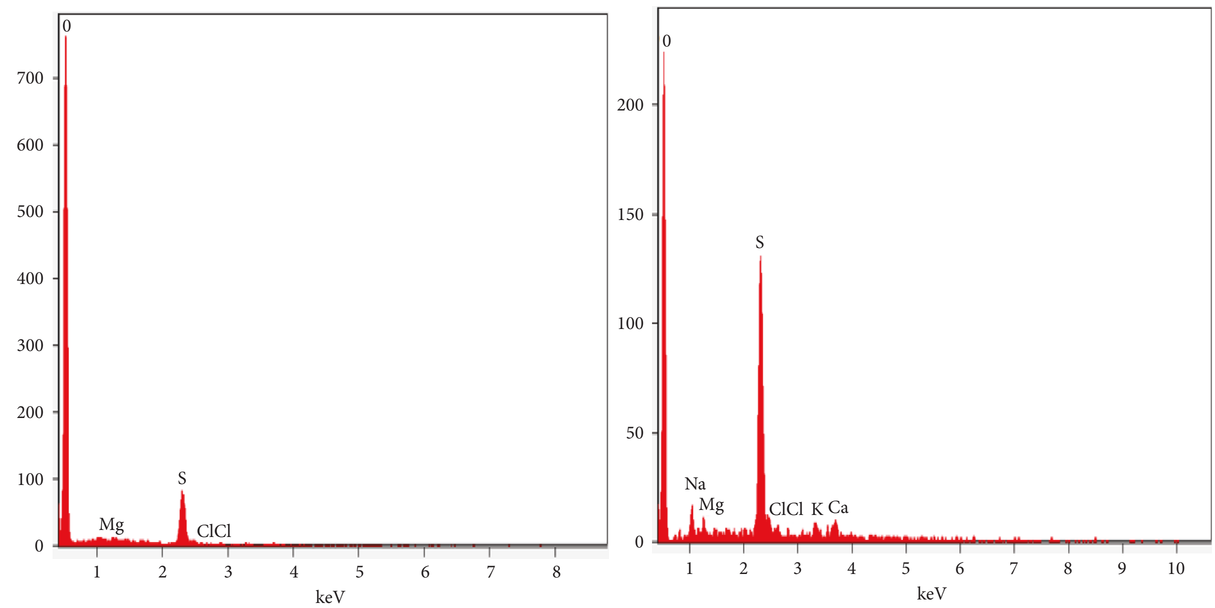

Figure 3: EDX spectrum for 1 and 2 mol% of $MgCl_2$-doped TGS crystals.

Table 1: Energy dispersive X-ray (EDX) analysis.

Elements	1 mol%$MgCl_2$+TGS		Elements	2 mol%$MgCl_2$ +TGS	
	Weight%	Atom%		Weight%	Atom%
OK	90.14	94.79	OK	67.75	80.12
MgK	0.22	0.15	NaK	4.69	3.85
SK	9.64	5.06	MgK	1.34	1.04
Total	100	100	SK	21.21	12.52
			ClK	1.23	0.66
			KK	1.69	0.82
			CaK	2.09	0.99
			Total	100.00	100.00

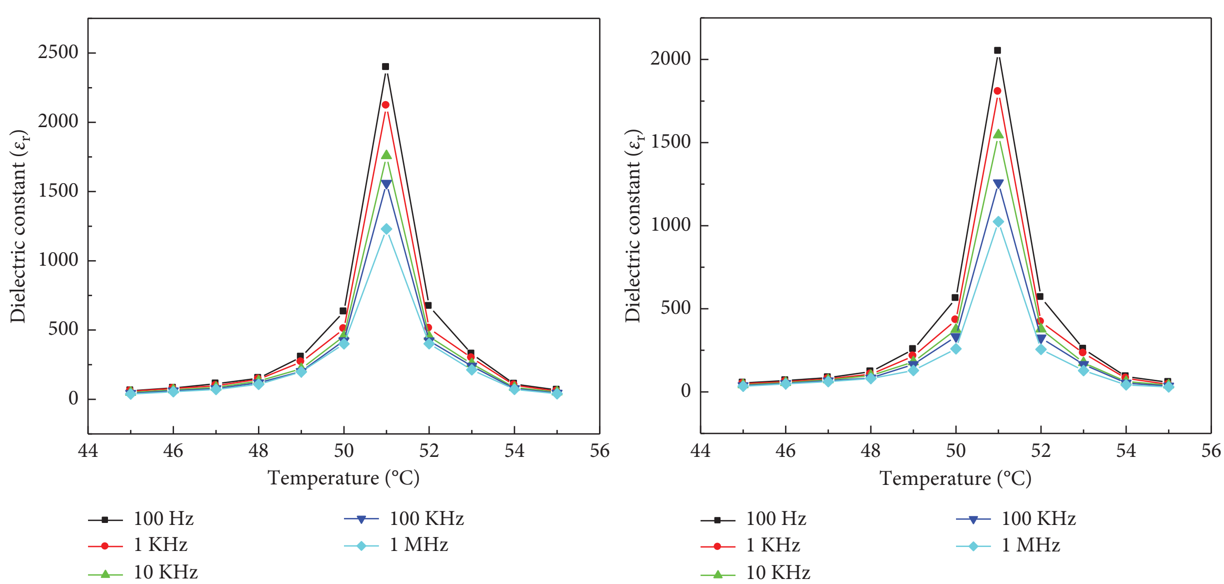

Figure 4: Dielectric constant versus temperature for 1 and 2 mol% $MgCl_2$-doped TGS crystals at different frequencies.

When 2 mol% of $MgCl_2$ was doped into TGS single crystals, the dielectric constant decreased compared with 1 mol% of $MgCl_2$-doped TGS single crystals. This may be due to the presence of metal dopants in TGS crystals [26].

4. Conclusion

Good transparent 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been grown by using the solution growth method at room temperature. The grown samples have been subjected to various characterization studies. The single crystal X-ray diffraction analysis revealed that both 1 and 2 mol% of $MgCl_2$-doped TGS single crystals have been crystallized in the monoclinic crystal structure with space group P21/m. The UV VIS-NIR spectrum confirmed that the λ-cutoff wavelength of the grown samples has been found 236 nm, and the crystal possesses wide transparency even up to the NIR region. The dielectric studies imply that the dielectric constants of the grown samples increase at low frequencies. The ferroelectric phase transition increased from 49°C to 51°C in magnesium chloride-doped triglycine sulphate single crystals. The EDX analysis confirmed the incorporation of magnesium and chlorine into the parent TGS single crystal.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest.

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