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# The effect of cobalt-doping on some of the optical properties of glycine zinc sulfate (GZS) single crystal

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ABSTRACT

Glycine zinc sulfate (GZS) single crystals, pure and doped with three different ratios of cobalt ions were synthesized and grown by the slow evaporation technique of aqueous solutions at 34 °C. Optically transparent single crystals with dimensions up to $2 \times 1.5 \times 1.2$ cm$^3$ were obtained in about four weeks. The optical transmittance was measured and used to study some optical properties for these crystals. Pure GZS crystal has high optical transmittance in the whole visible range and UV transparency with lower cut off wavelength at 300 nm. By adding Co-ions to GZS crystal, the transmittance decreases and the value of cut off shifts to the higher wavelengths with increasing Co ratio. Adding Co-dopants to GZS crystal has other effects like increasing the magnitude of the absorption coefficient ($\alpha$) and forming an absorption band around 2.1 eV. The height of this absorption band increases with increasing Co ratio. The optical energy gap ($E_g$) for pure GZS crystal is about 3.80 eV. This value decreases with increasing Co ratio to GZS crystals. The predominant optical transition for pure and Co-doped GZS crystals is the allowed indirect one. The phonon energy ($E_p$) and the phonon equivalent temperature ($T_p$) at room temperature are 0.20 eV and 2318.84 K for pure GZS crystal, respectively, and these values increase with increasing Co content in GZS crystals.



## 1. Introduction

The search for new materials possessing high optical nonlinearity is an important task because of their practical applications in harmonic generation, switching and other optical signal processing devices. Recent research interest is focused on the search of new semiorganic nonlinear optical (NLO) materials, as they share the advantages of both inorganic (high thermal and mechanical stability) and organic (broad optical frequency range and second harmonic conversion efficiency) materials [1,2].

Some complexes of amino acids with inorganic salts are reported to be promising materials for optical second harmonic generation (SHG) [3–5]. Among the amino acids, glycine is the simplest one. Unlike other amino acids, it has no asymmetric carbon and is optically inactive. It has three polymorphic crystalline forms of $\alpha$, $\beta$ and $\gamma$ under ambient conditions. Narayan Bhat and Dharmaprakash [3] had grown glycine sodium nitrate and reported that the second harmonic generation (SHG) efficiency of this crystal was two times that of potassium dihydrogen orthophosphate (KDP). Nagaraja et al. [6] reported that the (SHG) efficiency of benzoyl glycine crystal was 1.5 times that of KDP. Ferroelectric properties were reported for glycine silver nitrate [7], diglycine manganese chloride [8] and glycine phosphate [4]. Hoshino et al. [9] reported about the dielectric properties of triglycine fluroberyllate. It was also reported that glycine combines with $H_2SO_4$ [10], $CaCl_2$ [11], $CaNO_3$ [12], $BaCl_2$ [13], $SrCl_2$ [13], $CoBr_2$ [14] and $LiNO_3$ [15]. Nevertheless, none of these has nonlinear optical (NLO) property.

Glycine zinc sulfate (GZS), which has the chemical formula: $Zn\,[CH_2NH_2COOH]\,SO_4 \cdot 7H_2O$, is one of glycine complexes and is a nonlinear optical (NLO) material. Balakrishnan and Ramamurthi [16] grew and studied the structural, thermal and optical properties of GZS single crystal. They found that GZS crystal belongs to triclinic system and the cell parameters are $a=5.954(2)$ Å, $b=6.812(2)$ Å, $c=13.272(8)$ Å, $\alpha=85^\circ$, $\beta=83^\circ$ and $\gamma=82.92^\circ$ and $V=529.1(4)$ Å$^3$. They concluded that the transmittance spectrum of GZS has lower cut off wavelength at 300 nm and there is no absorption in the whole of the visible region. This conclusion confirmed that GZS could be used as a material for (SHG). They found that the powder (SHG) efficiency of this crystal is 0.7 times that of KDP. Thermogravimetric study confirmed the elimination of seven water molecules.

Balakrishnan and Ramamurthi [17] also grew single crystal of another glycine complex, glycine zinc chloride (GZC), which is nonlinear optical (NLO) material too. They studied some physical

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properties of this crystal. They found that GZC crystal belongs to monoclinic system. The FT-IR and FT-Raman analyses confirmed the presence of various functional groups. The lower cut off wavelength (230 nm) and the transmittance range (240–1200 nm) observed from the UV–vis–NIR spectrum confirmed the suitability of GZC for (SHG) applications. TGA and DTA revealed that this compound is stable up to about 228.5 °C. They also found that the Vicker's hardness values increase with increasing load and cracks occur for the load of 85 g.

Ravi and Subramanian [18] studied the electron paramagnetic resonance (EPR) of copper ions, Cu (II), as a paramagnetic impurity in GZS single crystal, at ambient temperature. They said that the detailed (EPR) analysis showed the only one site of Cu and entered the lattice substitutionally in place of Zn (II). They obtained the spin-Hamiltonian parameters from the single crystal (EPR) analysis. By using the (EPR) data, they evaluated the molecular bonding coefficient and the Fermi contact interaction terms. They also observed superhyperfine splittings.

To the best of our knowledge, the optical studies on GZS crystal and other nonlinear optical (NLO) materials are focused only on the transmission process and the cut off wavelength, which is important for the (NLO) property and the optical second harmonic generation (SHG) as an application for this property. But, there are no studies on the optical properties for these materials in terms of other important processes such as the absorption spectra, optical energy gab and the transition at fundamental absorption edge. On the other hand, the studies on GZS crystal are little in general and there is no study on the effect of cobalt dopants in this crystal on its properties. In this work we will study some important optical properties of GZS single crystal and the effect of cobalt dopants on these properties which involve the transmission process and the value of cut off wavelength too.

## 2. Experimental

### 2.1. Synthesis

Glycine zinc sulfate (GZS) salt was synthesized by dissolving AR grade glycine and zinc sulfate in the stoichiometric ratio in double distilled water according to the reaction:

$$ZnSO_4 \cdot 7H_2O + CH_2NH_2COOH \rightarrow Zn\ [CH_2NH_2COOH]\ SO_4 \cdot 7H_2O$$

Three different ratios (1–3 mol%) of cobalt sulfate ($CoSO_4$) were added to (GZS) as dopants.

### 2.2. Crystal growth

Three different Co-doped crystals of (GZS), besides the pure one, were grown by the slow evaporation technique of aqueous solutions at constant temperature (34 °C). Large, optically transparent single crystals with dimensions up to $2 \times 1.5 \times 1.2\ cm^3$ were obtained in about four weeks. The grown crystals of GZS pure and doped with cobalt ions are shown in Fig. 1.

### 2.3. Optical measurements

For optical measurements, rectangular plates about $20\ mm^2$ in area and 1 mm in thickness specimens were prepared, and then polished on a wet piece of soft cloth. The prepared plates were clear and free from noticeable defects. Specimens were prepared with these dimensions to fit the sample holder, and the sample was fixed to the holder by special glue.

The optical transmittance was measured using Shimadzu UV–vis-2101 PC dual beam spectrophotometer with unpolarized monochromatic light in the wavelength range 190–900 nm. The spectrophotometer comprises an intelligent photometer unit and a microcomputer software package.

## 3. Results and discussion

### 3.1. Optical transmittance

The dependence of optical transmittance on the wavelength for GZS crystal, pure and doped with Co ions, is shown in Fig. 2. It is clear from part (a) of the figure that the transmittance of pure GZS crystal is high in the whole visible range and the UV transparency lower cut off wavelength occurs at 300 nm which is exactly agreeable to that reported by Balakrishnan and Ramamurthi [16]. For Co-doped GZS crystals, the transmittance in the whole visible range decreases with increasing Co ratio, Table 1 shows a comparison of transmittance at selected values of wavelength ($\lambda$). Part (a) of Fig. 2 also shows that, adding of Co-dopants to GZS crystal leads to another effect on the transmittance spectrum which is the forming of transmission bottom around 592 nm. The depth of this transmission bottom increases with increasing Co ratio. Part (b) of Fig. 2 shows that, increasing Co ratio leads to shift the cut off value to the higher wavelengths. In Table 1 there is a comparison of cut off wavelength between cobalt doped GZS crystals and the pure one. Fig. 3 shows the dependence of the cut off wavelength on Co ratio for GZS single crystals. It is clear from this comparison that Co-doped GZS crystals absorb some ultra violet wavelengths than that of pure GZS crystal. This means that adding cobalt to GZS crystal causes to decrease the transmitted wavelengths and increase the absorbed ones.

### 3.2. Absorption coefficient

The absorption coefficient ($\alpha$) can be calculated from the measured transmittance ($T$) and reflectance ($R$) by using the formula [19]:

$$T = (1-R)^2 e^{-\alpha d} \tag{1}$$

where $d$ is the thickness of the sample. When $R$ is very small, as for our material, Eq. (1) changes to

$$T = e^{-\alpha d} \tag{2}$$

So, the absorption coefficient ($\alpha$) is given by

$$\alpha = \frac{1}{d}\left[\ln\left(\frac{1}{T}\right)\right] \tag{3}$$

The relation between the absorption coefficient ($\alpha$) and the photon energy ($h\nu$) for GZS single crystals, pure and doped with different ratios of cobalt, is clear in Fig. 4. Part (a) of the figure shows the relation at the whole measured range of photon energies and part (b) shows the same relation in the range around the fundamental absorption edges. We can observe from the figure that, Co-dopants affects the magnitude of $\alpha$ and $\alpha$–$h\nu$ shape of the dependence at all energies. In terms of $\alpha$ magnitude, the figure shows that the magnitude of $\alpha$ increases with increasing the cobalt ratio. With respect to $\alpha$–$h\nu$ shape, the adding of Co-dopants to GZS crystal forms an absorption band around 2.1 eV and the height of this band increases with increasing Co ratio.

Table 1 shows the absorption coefficient ($\alpha$) at selected values of photon energy ($h\nu$) for cobalt doped GZS crystals and the pure one. It is clear from this table that adding Co-dopants to GZS crystal leads to increase the absorption coefficient in the measured photon energy range.