Influence of cobalt-doping on the optical properties of zinc tris-thiourea sulfate (ZTS) single crystal

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Abstract
Zinc tris-thiourea sulfate (ZTS) single crystals, pure and doped with different concentrations of cobalt, were synthesized and grown by the slow evaporation technique of supersaturated aqueous solutions at 315 K. Co²⁺ concentration in the solution was 2, 4 and 6 mol%. Optical transmittance was measured for the obtained crystals as a function of wavelength in the range of 190–900 nm. The present investigation shows that doping ZTS crystal with Co²⁺ modifies its optical properties. The absorption coefficient of ZTS crystal exhibits an exponential dependence on photon energy following Urbach relation. Doping ZTS crystal with Co²⁺ changes the values of optical transmittance, cut off wavelength, absorption coefficient, optical energy gap, Urbach tail energy and steepness parameter. The changes are systematic i.e. the mentioned optical parameters increase or decrease continuously with increasing Co²⁺ concentration in the growth solution. The electrical conduction of ZTS crystal is increased with cobalt doping. The Urbach tail energy changes reversely with the optical energy gap.

1. Introduction
Sulfates are less studied materials concerning optical, electronic and other properties and, in the recent years, the great activity appears in this field of materials science [1–6]. Zinc tris-thiourea sulfate (ZTS), Zn[CS(NH₂)₂]₂SO₄, is a desirable semi-organic nonlinear optical (NLO) material for second harmonic generation (SHG). It has high laser damage threshold, low angular sensitivity, wide range of transparency and low dielectric constant at higher frequencies. The optical nonlinearity of ZTS is nearly 1.2 times higher than that of potassium dihydrogen phosphate KH₂PO₄ (KDP) [7–10]. ZTS crystal possesses orthorhombic structure in Pca2₁ space group [11]. The cell parameters are \( a = 11.127 \) (0.001), \( b = 7.7758 \) (0.001), \( c = 15.490 \) (0.001) Å and \( V = 1340.22 \) (0.3) Å³ [12]. The crystal growth and characterization of ZTS crystal have been studied [13–16]. Since ZTS crystal is a promising NLO material, its optical properties were the subject of numerous articles [17–22]. Some procedures have been used in many previous works to modify and enhance the properties of ZTS crystal such as heating [12], mixing [17, 23–25], and doping [18, 22, 26–34]. Previous, in terms of heating, it was found that increasing temperature leads to changing the optical parameters of ZTS crystal [12]. In the same study, the presence of phase transition in ZTS crystal at 323 K was confirmed. In terms of mixing, ZTS crystal has been mixed with different materials in some studies. One from these studies reported that the phosphate mixed ZTS crystal may be a better NLO material for SHG [17]. Another study demonstrated that 10 mol% of phosphate mixed ZTS crystal has better SHG efficiency than pure ZTS [23]. In addition, magnesium sulfate [24] and urea [25] mixed ZTS crystals have been studied and compared with pure ZTS crystal. In terms of doping, various materials have been used as dopants in many studies on ZTS crystal. One from these studies reported that NLO property of ZTS crystal is enhanced by ethylenediamminetetraacetic acid (EDTA) and benzene dopants. However, phenanthroline (Phen) dopant depresses the NLO efficiency of the crystal [18]. Another study confirmed that the second harmonic conversion efficiency of the L-alanine doped ZTS single crystal is better than KDP [22]. Electron paramagnetic resonance (EPR) of vanadyl ion as an impurity in polycrystalline ZTS crystal has been studied and the obtained molecular orbital parameters gave highly covalent character of the bonding in the host lattice [26]. It was found that the optical damage of ZTS crystal in the UV–Vis region could
be reduced by L-arginine doping [27]. It was reported that the SHG efficiency of 1 mol% glycine doped ZTS crystal is 4.14 times higher than that of pure ZTS [28]. In addition, other materials such as KCl [29], KI [30], Mn [31], NaCl [32], L-lysine [33], and L-serine [34] were used as dopants in ZTS crystal. It was found that these dopants improved the properties of ZTS crystal, especially their NLO properties. Recently, some studies used other procedures to enhance the properties of ZTS crystal such as adding L-Ascorbic acid [35] and methyl violet dye [36] to the solution of growth.

Although many publications studied the optical properties of ZTS crystal, the most of these publications focused on the nonlinear optical properties while the works on the linear optical properties are very scarce. On the other hand, to my best knowledge, ZTS crystal was not doped yet with cobalt, although cobalt is appropriate dopant and it changed the properties of many materials [37–39]. The structure and optical properties of these materials have been changed when doping them with cobalt. The optical energy gap of BiSeI single crystals [37], CdS Nanoparticles [38] and NiO thin films [39] decreased as cobalt content increased. The lattice parameters and grain size of CdS Nanoparticles [38] and NiO thin films [39] decreased when cobalt content increased. Therefore, the major aim of the present work is to study the effect of cobalt-doping on the linear optical properties of ZTS crystal.

2. Experimental procedures

Pure (undoped) zinc Tris-thiourea Sulfate (ZTS) salt was synthesized by interaction of Zinc sulfate and thiourea mixed in the molar ratio 1:3, respectively, according to the following reaction:

$$\text{ZnSO}_4 + 3\text{CS(NH}_2)_2 \rightarrow \text{Zn[CS(NH}_2)_2]_3\text{SO}_4$$ (1)

The component salts were well dissolved in double distilled water to obtain an aqueous solution of pure ZTS salt. To synthesize cobalt-doped ZTS salts as aqueous solutions, three different concentrations (2, 4 and 6 mol%) of cobalt sulfate (CoSO_4) were added to the solution of ZTS separately. Here and after, Co^{2+} concentration (x) means the molar ratio Co^{2+}/Zn^{2+} in the solution of growth.

The aqueous solutions of undoped and cobalt-doped ZTS were evaporated slowly at room temperature (293 K) until seeding after several days. Then, good and clear seeds were chosen to employing them for growing large single crystals. Supersaturated solutions were prepared separately for pure and cobalt-doped ZTS salts at constant temperature (315 K). The slow evaporation technique of the supersaturated aqueous solutions was used to grow single crystals at this temperature. Crystal growth process was carried out with use an indigenous crystal growth apparatus (crystallizer) which was fabricated in the laboratory, as it was described in previous study [12]. The crystallizer was multi-jar in order to grow the pure and doped crystals simultaneously at similar conditions. In addition, after preliminary experiments, the optimal growth parameters including solution purity, seed orientation and purity, seed rotational speed, crystallization temperature, and growing period were chosen for the best result. These procedures were achieved to eliminate differences in growth conditions from the discussion.

The harvested single crystals after about 20 days were colorless, transparent, have well-defined edges, and dimensions up to 1.8 \times 1.2 \times 0.5 \text{ cm}^3. Photographs of the grown single crystals are displayed in figure 1.

The grown pure and cobalt-doped ZTS single crystals were used to obtain thin samples for optical measurements. The samples were prepared as rectangular plates 1 mm in thickness. A wet soft cotton was used to polish the samples. The obtained samples were clear, optically transparent and free of noticeable defects. The optical transmittance of the samples was recorded with unpolarized monochromatic light using Shimadzu UV–vis-2101 PC dual beam scanning spectrophotometer. This spectrophotometer comprises an intelligent photometer unit and a microcomputer software package. The optical transmittance was measured in the wavelength range of 900–190 nm (energy range 4.4–6.5 eV). The measurements were performed at room temperature and the surrounding medium was the air.

3. Results and discussion

In figure 2, the transmittance (T) is shown as a function of wavelength (λ) for pure and cobalt-doped ZTS single crystals at λ range between 200 and 900 nm. Transmittance values are high for pure ZTS crystal in the visible range of λ (T ≈ 60%) and these values decrease systematically when cobalt (Co^{2+}) concentration increases. T values decrease to about 40% for the highest Co^{2+} concentration (0.06). Decreasing transmittance (T) with increasing Co^{2+} concentration in figure 2 is reasonable because the doped crystals have transparency lower than that of pure crystal, as it is clear in figure 1.

As seen in figure 2, the cut off wavelength of pure ZTS crystal occurs at 278.5 nm. This value is in good agreement with that obtained in previous works [13, 17, 20, 22]. In addition, it is clear that the cut off wavelength
increases as the cobalt concentration increased. The cut off wavelength values for pure and cobalt-doped ZTS single crystals are listed in table 1. Although the cut off wavelength increases with increasing Co^{2+} concentration, its value remains in the ultraviolet region for all cobalt concentrations used in the present work. Therefore, cobalt-doped ZTS crystals still useful as NLO materials [32].

The absorption coefficient (α) can be determined from transmittance (T) and reflectance (R) by using the following relation [40]:

\[ T = (1 - R)^2 e^{-\alpha d} \]  
\[ (2) \]

where \( d \) is the sample thickness. If \( R \) is very small, as for the material in this work, equation (2) can be changed to:

\[ T = e^{-\alpha d} \]  
\[ (3) \]

The absorption coefficient (\( \alpha \)) can be calculated directly after writing equation (3) as the following simple form:

\[ \alpha = (1/d) [Ln(1/T)] \]  
\[ (4) \]
In addition, the photon energy \((h\nu)\) can be calculated from the wavelength \((\lambda)\) by using the known formula:

\[
h\nu = \frac{hc}{\lambda}
\]

where \(h\) is Planck constant, \(\nu\) is the frequency of photon and \(c\) is the velocity of light in vacuum. Figure 3 shows the absorption coefficient \((\alpha)\) as a function of photon energy \((h\nu)\) for pure and cobalt-doped ZTS single crystals. It is clear that the absorption coefficient \((\alpha)\) increases with increasing \(h\nu\), for all ZTS crystals, and it increases with increasing cobalt concentration.

To study the band gap nature and estimate the optical energy gap \((E_g)\), the following equation proposed by Bardeen et al.\[41\], can be used:

\[
(a\nu)^n = A(h\nu - E)
\]

where \(A\) is a constant independent of photon energy and known as a disorder parameter \[42\]. The transition energy \(E\) is equal to \(E_g\) for direct transitions and \(E_g \pm E_p\) for indirect transitions \((E_p\) is the energy of the associated phonon). The exponent \(n\) characterizes the optical absorption process. \(n = 2\) for direct allowed transition, \(n = 2/3\) for direct forbidden transition, \(n = 1/2\) for indirect allowed transition and finally \(n = 1/3\) for indirect forbidden transition. For the materials under consideration, equation (6) can be well fitted with \(n = 2\) and, therefore, the optical transition in ZTS crystals is of the direct allowed type. This result agrees well to the literature \[19, 20, 29\]. Table 1 shows that \(E_g\) decreases as \(Co^{2+}\) concentration increased. This behavior is expected, and it is in accordance to the fact that the energy gap decreases with increasing defect concentration \[43\]. The observed decrease in the optical energy gap with increasing \(Co^{2+}\) concentration is because of a sp-d exchange interaction, i.e. manifestation of strong exchange interaction presents between d electron of \(Co^{2+}\), and the s and p electrons.

| Co\(^{2+}\) concentration \((x)\) | Cut off wavelength, nm | Optical energy gap \((E_g)\), eV |
|--------------------------------|----------------------|-------------------------------|
| 0 (pure)                      | 278.5                | 3.89                          |
| 0.02                          | 289                  | 3.75                          |
| 0.04                          | 299                  | 3.65                          |
| 0.06                          | 308.5                | 3.56                          |

Figure 3. Absorption coefficient \((\alpha)\) versus photon energy \((h\nu)\) for ZTS single crystals pure and doped with different concentrations of cobalt.
of host matrix \cite{38,44,45}. The optical energy gap \(E_g\) value shows decreasing tendency with increasing \(\text{Co}^{2+}\) concentration. This can be explained as follows: Increasing \(\text{Co}^{2+}\) concentration in the growth solution leads to increasing defects (increasing free charges carriers) in the crystal. Therefore, the optical energy gap \(E_g\) decreases and the electrical conduction of ZTS crystal improves when the crystal is doped by cobalt.

The absorption coefficient near fundamental absorption edge, in the energy region of \(h\nu < E_g\), obeys the empirical Urbach relation \cite{46}:

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu - E_0}{E_U} \right)
\]  

where \(\alpha_0\) and \(E_0\) are constants dependent on material, \(h\nu\) is incident photon energy and \(E_U\) is Urbach tail energy. \(E_U\) is interpreted as the width of the tails due to localized states in the absorption edge. Equation (8) describes the optical transition between occupied states in the valence band tail to unoccupied states of the conduction band edge. The appearance of Urbach tail is due to the structure disorder, caused by defects and doping \cite{47}. The Urbach tail energy \(E_U\) is proportional to temperature \((\text{Temp.})\) by the following relation \cite{48}:

\[
E_U = \frac{K_B \text{Temp.}}{\sigma}
\]  

where \(K_B\) is the Boltzmann constant and \(\sigma\) is a steepness parameter. It is a temperature-dependent parameter characterizing the steepness or width of the straight line near the absorption edge. To simplify the plotting of equation (8), it can be changed to the form:

\[
\ln(\alpha) = \ln(\alpha_0) + \left( \frac{h\nu - E_0}{E_U} \right)
\]

Figure 5 represents the relations between \(\ln(\alpha)\) and \(h\nu\) for ZTS single crystals pure and doped with different concentrations of cobalt. This may be explained as follows: Increasing \(\text{Co}^{2+}\) concentration in the growth solution leads to increasing the defects and forming localized states. Therefore, a band tail will appear.

\[
\text{Figure 4. } (\alpha h\nu)^2 \text{ versus photon energy } (h\nu) \text{ for ZTS single crystals pure and doped with different concentrations of cobalt.}
\]
for the crystals [49]. The absorption edge broadening leads to increasing $E_U$ and decreasing $\sigma$ with dopant concentration increase [48].

It is clear from tables 1 and 2 that $E_U$ changes reversely with $E_g$. Figure 6 shows clearly an excellent linear relation between $E_U$ and $E_g$ with $R^2$ about 0.99. The relation was fitted to the best straight line by using Origin software. The obtained fitted relation between $E_U$ and $E_g$ has the form: $y = 1.333 - 0.0783x$ where $y$ is the Urbach tail energy ($E_U$) in eV and $x$ is the optical energy gap ($E_g$) in eV. The negative slope means that the relation is reverse. This result indicates the state redistribution and the obtained optical band gaps are affected by the difference in disorder [49].

It is clear that, the optical parameter changes with Co$^{2+}$ concentration are systematic (the mentioned parameters increase or decrease continuously with increasing Co$^{2+}$ concentration). This is because the Co$^{2+}$
incorporation into the ZTS lattice is proportional to Co\(^{2+}\) concentration in the growth solution. Therefore, Co\(^{2+}\) concentration in the growth solution represents the concentration of impurities or defects in the crystal lattice.

Comparing the above results with those of the previous work \[12\] leads to deducing that the changes of cut off wavelength, \(E_g\) and \(E_U\), have the same manners in the two works but with different rates. This may be attributed to the reason of the changes that is different in the two works (doping in this work and heating in the previous work). In terms of \(\sigma\), it increases as temperature increased in the previous work \[12\] but it decreases as the cobalt concentration increased in the present work. One can explain this behavior by using equation (9) which shows that \(\sigma\) is a temperature-dependent parameter. Therefore, increasing \(\sigma\) with increasing temperature in the previous work \[12\] is reasonable. In the present work, the temperature is constant and, therefore, \(\sigma\) might be constant. Nevertheless, the Urbach tail energy \(E_U\) changes due to the doping and \(\sigma\) must change too according to equation (9). Therefore, \(\sigma\) decreases with increasing \(E_U\), i.e. \(\sigma\) decreases as Co\(^{2+}\) concentration increased.

The results in this work are reasonable and have well agreement with that reported in other papers \[37–39\] in the field. In these papers, doping the material with cobalt caused some changes in the optical properties of these materials. For example, the optical energy gap decreased, transmittance decreased, and absorbance increased.

4. Conclusions

Good quality pure and cobalt-doped ZTS single crystals have been grown by the slow evaporation technique of supersaturated aqueous solutions at constant temperature 315 K. It was found that doping of ZTS crystal with Co\(^{2+}\) affects its optical properties. The values of optical transmittance \((T)\) are smaller for cobalt-doped crystals than the pure crystal at all measured range of photon energies. The absorption coefficient \((\alpha)\) exhibits an exponential dependence on photon energy according to Urbach relation. The cut off wavelength increases linearly as Co\(^{2+}\) concentration increased and its values range is between 278.5 nm and 308.5 nm. The optical energy gap \((E_g)\) and steepness parameter \((\sigma)\) decrease as Co\(^{2+}\) concentration increased. The optical energy gap is between 3.89 and 3.56 eV and the steepness parameter is between 24.59 and 24. Doping ZTS crystal with Co\(^{2+}\) leads to improving its electrical conduction. The Urbach tail energy \((E_U)\) increases as Co\(^{2+}\) concentration increased and its values range is between 1.028 eV and 1.053 eV. The Urbach tail energy \((E_U)\) changes reversely with the optical energy gap \((E_g)\) as a linear relation.

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