Influence of nickel substitutions on the structural, optical and spectroscopic properties of potassium zinc chloride sulfate single crystals

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ABSTRACT
Crystals of potassium zinc chloride sulfate (KZCS) undoped and doped with Ni\(^{2+}\) ions with different concentrations were crystallized by slow evaporating of saturated aqueous solution. The crystal habit changes considerably by doping. Grown crystals were investigated by various characterization techniques. X-ray powder diffraction analysis was executed to detect the structure parameters of the grown crystals. Slight changes in the unit cell parameters of KZCS crystals after doping with Ni\(^{2+}\) ions have been detected. Different functional groups were detected and assigned from the Fourier transform infrared (FTIR) spectra. Optical properties were investigated in the incident wavelength in the range from 190 to 900 nm. Absorption coefficient was calculated and the grown crystals show indirect allowed inter-band transition and the energy gap decreased continuously with increasing the concentration of Ni\(^{2+}\) ions. The refractive index, extinction coefficient, and other related optical constants were calculated as a function of incident photon energy. The dispersion of the refractive index was analyzed in terms of the single oscillator model for the grown crystals.

1. Introduction
Potassium zinc chloride sulfate trihydrate (KZCS) is a crystalline material isomorphous with the kainite crystalline mineral (KMgCl\(_2\)SO\(_4\).3H\(_2\)O) and crystallizes in the monoclinic symmetry [1,2]. Electron paramagnetic resonance (EPR) investigations of kainite single crystals doped with Mn\(^{2+}\) ions were studied by Subramanian and Haritharan [3], they have reported that Mn\(^{2+}\) ions interacted and influenced by an orthorhombic strong field. Murthy et al. [4] studied the EPR characterization of SO\(_3\) radical in X-irradiated kainite (KMgCl\(_2\)SO\(_4\).3H\(_2\)O) crystals and concluded that SO\(_3\) radical in kainite shows strong power saturation effects as indicated by its Lorentzian shaped and homogeneously broadened EPR lines. They attributed this behaviour to the characteristic spin–lattice relaxation time (\(T_1\)) and spin–spin relaxation time (\(T_2\)) both being large.

Many EPR studies on transition metal ions (Cr\(^{3+}\), Cu\(^{2+}\)) doped potassium zinc chloride sulfate trihydrate [1,5] which considered to be isomorphs of potassium magnesium chloride sulfate and reported that at room temperature, the EPR spectra reveal the substitution of Zn\(^{2+}\) sites in the crystal lattice with two magnetically inequivalent Cr\(^{3+}\) and Cu\(^{2+}\) sites.

Optical single crystals are widely used as ultraviolet (UV) filters and UV sensors. The mechanism of the filters or sensors depends on the passing or blocking of specific spectral wavelengths incident on the single crystal surface. The ideal materials for use in ultraviolet light filter (UVLF) should exhibit high transmittance in the intended UV region which they pass and high absorbance for the rest of the wavelengths. Recently, several crystals were added to the UV filter crystals such as; potassium nickel sulfate hexahydrate (KNSH) [6], cesium nickel sulfate hexahydrate (CNSH) [7], and they are reported as filter crystals.

The optical constants define light interactions with different materials. The optical constants determination is expected to expand the physical analysis for the dependence of different linear optical parameters such as reflectivity, absorptivity, refractive index, and dielectric constant on the incident photon energy which is important in categorizing the material’s usage in the fabrication of optoelectronic devices [8].

KZCS crystals doped with Ni\(^{2+}\) ions with different concentrations belong to the monoclinic crystal system. These single crystals may take the consideration because of their easy growth in excellent purity, reasonable crystal size and desired transparency in the UV region. It could be a candidate for some optoelectronic and (UVLF) applied devices.

The investigations on KZCS crystals are not studied in details. In the present work, the influence of Ni\(^{2+}\) dopant concentration on their optical parameters was studied. The refractive index of the grown crystals showed a normal dispersion which was analyzed...
by the Wemple-DiDomenico single-effective-oscillator approach and the related parameters were calculated to report the full characteristics of the normal dispersion. The vibrational spectroscopic characterizations, X-ray powder diffraction patterns of the grown crystals were also addressed.

2. Experimental techniques

2.1. Crystal growth

KZCS single crystals undoped and doped with nickel ions were grown from aqueous solution using the starting materials ZnSO$_4$.7H$_2$O, NiSO$_4$.6H$_2$O and KCl in a stoichiometric ratio according to the following equations:

$$\text{ZnSO}_4\cdot7\text{H}_2\text{O} + \text{KCl} \rightarrow \text{KZnClSO}_4\cdot3\text{H}_2\text{O} \quad (1)$$

$$(100 - x)\text{ZnSO}_4\cdot7\text{H}_2\text{O} + x\text{NiSO}_4\cdot6\text{H}_2\text{O} + \text{KCl}$$

$$\rightarrow \text{K}_x\text{Zn}_{100-x}\text{NiClSO}_4\cdot3\text{H}_2\text{O} \quad (2)$$

The starting materials of zinc sulfate heptahydrate, nickel sulfate hexahydrate and potassium chloride were dissolved in double distilled water with continuous stirring using magnetic hot plate until obtaining fully dissolved and clear solution. The clear saturated solution was filtered and purified and allowed to cool at room temperature for slow evaporation. Several days later small crystallites were noticeable at the bottom of the crystalizing jar. The most perfect small crystallites were collected as seed crystals for the growing process. The precipitated small clear crystallites were recrystallized three times for more purification. The saturated clear solution was taken into the crystal growth apparatus fabricated in our laboratory and placed on the platform of a constant temperature of an accuracy of $\pm 0.1^\circ\text{C}$ and was allowed to equilibrate at 45°C. Seed crystals were suspended inside the solution using a nylon thread. The jars containing the solutions were covered by a polythene sheet with numbers of small holes which allows the solution to evaporate slowly.

After several weeks the seeds grow to nearly perfect single crystals and the crystals obtained in this way were stable, and having large sizes under normal conditions of temperature and humidity. For growing pure KZCS and KZCS crystals doped with different ratios of nickel ions, we used the last technique having several crystalizing jars to get all crystals to grow at the same time under the same conditions.

A photograph of the grown KZCS crystals pure and doped with different ratios of Ni$^{2+}$ ions are represented in Figure 1. As shown in the figure, there was a changing in the shape and colour between undoped and doped crystals. Perfect colourless crystals were obtained in case of pure KZCS while in case of KZCS crystals doped with nickel ions, different degrees of green coloured crystals were obtained depending on the percentage of Ni$^{2+}$ ions incorporated in the crystal. The crystals with a high percentage of nickel have a darker colour than that of low percentage.

2.2. Characterization method

Powder X-ray diffraction is the first and most important technique in the crystal growth and every field of applied sciences, to investigate the nature of different materials and crystalline structures, the effect of additives/dopants etc. The X-ray diffraction pattern is carried out on a fine powder from samples taken from a perfect single crystal. The diffraction patterns were performed using Philips PW 1710 diffractometer. The diffraction reflections were taken at 2$\theta$ ranging between 4°–80° with a scanning speed of 0.06°/sec. and 1.5418 Å X-ray wavelength, Ni filter was used to eliminate the undesired reflections.

The Fourier transform infrared spectroscopy was performed on the powder of the grounded crystal samples by the KBr pellet method in order to study their functional groups. The spectra were collected in the range 400–4000 cm$^{-1}$ using NICOLET FTIR 6700 spectrometer.

Thin rectangular plates were cut from clear and transparent parts of the grown crystals using a special saw fabricated in our laboratory. Selected crystal plates used for the optical measurements were transparent and free from any noticeable defects. The measurements of transmittance (T) and reflectance (R) were carried at the ambient temperature using (Perkin Elmer Lambda 750 ultraviolet–visible-infrared) scanning spectrophotometer in the wavelength range 190–800 nm.

3. Results and discussion

3.1. X-ray diffraction measurements

The X-ray powder diffraction patterns of pure and doped KZCS crystals are depicted in Figure 2 and the obtained data were treated by Cellref software to get the lattice parameters and unit cell volume and the obtained data are tabulated in Table 1.

Potassium zinc chloride sulfate considered zinc analog of original kainite KMgClSO$_4$.3H$_2$O have monoclinic symmetry with space group (C2/m). The cell dimensions of kainite are $a = 19.72 \pm 0.2$ Å, $b = 16.23 \pm 0.1$ Å, $c = 9.53 \pm 0.01$ Å, $\alpha = 94.55 \pm 5$° and $Z = 16$ [9]. The powder XRD patterns for Ni$^{2+}$ doped KZCS crystals shown in Figure 2 consist of peaks corresponds to KZCS and no other peaks of other phase or element are detected for Ni$^{2+}$ doped KZCS within the detection limit of the instrument. This is the evidence for the incorporation of Ni$^{2+}$ ions into KZCS lattice and the doping does not change the crystal structure of the material.
In general, the unit cell volume decreases with increasing x-value. The decrease in the volume with increasing x-value (increasing Ni-contribution) may be due to the fact that the empirical atomic radii of zinc (1.34 Å) is larger than that of nickel (1.24 Å).

3.2. Optical studies

a. Transmittance (T) and reflectance (R)

The optical transmission spectrum (T) of pure KZCS and KZCS single crystals doped with different concentrations of nickel ions is shown in Figure 3a. The crystals have the good transmission in the entire visible region as observed from the figure and it was reported that similar crystals are applicable in second harmonic generation devices [10,11]. It is also observed from the figure that for pure KZCS the values of the transmittance increase gradually towards longer wavelengths.
and for doped crystals, the transmittance decreased with increasing the concentration of nickel ions and two bands centred at about 390 nm and 675 nm were developed due to nickel doping and the bands were shifted to low energy values (blue shift) with increasing Ni ratio. The KZCS crystals doped with different ratios of nickel ions have a bandwidth in the range 230–310 nm, it is clear from the figure that the samples spectra show an increase of α with increasing the energy of the incident radiation, it is also clear that the value of the absorption coefficient changes from one concentration to another.

Two induced bands centred at about 1.8 and 3.25 eV are observed for crystals doped with different Ni$^{2+}$ ions concentrations as shown in Figure 4a and the intensity of these bands increased with increasing nickel ratios, these bands could be assigned to transition to various field levels in the crystal which cause higher absorption in this range as a result of local defects. It is also noticed that the absorption edge was shifted towards the low energy side with increasing Ni$^{2+}$ ratios.

The values of the optical absorption coefficient (α) of the crystals under study are obeying Tauc’s relation [14] for high photon energies values:

$$\frac{(ahv)^{1/n}}{C(hv - E_g)}$$

Where n is a constant and Eg is the optical band gap of the grown crystal. Here n represents an index that can take any of the values: 2, 3/2, 1/2 or 3 depending on the type of transition responsible for the absorption. For allowed direct transition n = 1/2 while n = 3/2 for forbidden direct transition. For allowed indirect transition n = 2 and for forbidden indirect transition n = 3. In our case, the crystals exhibit indirect allowed transition and hence n is equal to 2. Figure 4b shows the variation of $(ahv)^{1/n}$ versus photon energy hv, where the energy gap Eg is evaluated by taking the intercept of the extrapolation of the linear part to zero absorption with photon energy axis [15]. The band gap is found to be 4.21 eV for pure KZCS and the calculated Eg decreases with increasing nickel ions concentrations in the crystal. The calculated energy gap for pure and doped crystals are tabulated in Table 2 and drawn in Figure 5. Large band gap and good optical transparency shown by the crystals elect them for optoelectronic applications [10,16].

### 3.2.1. Optical constants

1. Extinction coefficient (Kex) and refractive index (n)

Most optical constants can be obtained from transmittance (T) and reflectance (R). The extinction coefficient is directly related to the absorption of the materials by the relation $\alpha = 4\pi Kex/\lambda$, where α is the absorption coefficient and λ is the wavelength of incident light.

Refractive index (n) and extinction coefficient (Kex) of crystalline solids are related by the following equation [17]:

$$R = \frac{(n-1)^2 + Kex^2}{(n+1)^2 + Kex^2}$$

The energy dependence of the extinction coefficient in the photon energy range (1.5–7 eV) is shown in Figure 6a. In case of pure KZCS crystals the extinction

### Table 1. The lattice parameters and unit cell volume of KZCS crystals pure and doped with different concentrations of nickel ions.

| Lattice parameters | a(Å) | b(Å) | c(Å) | V(Å³) |
|--------------------|------|------|------|-------|
| Pure KZCS          | 19.713(2) | 16.230(5) | 9.532(2) | 3038.30 |
| KZCS + 5% Ni$^{2+}$| 19.711(2) | 16.226(4) | 9.530(2) | 3037.89 |
| KZCS + 10% Ni$^{2+}$ | 19.716(1) | 16.229(3) | 9.527(2) | 3038.00 |
| KZCS + 20% Ni$^{2+}$ | 19.719(6) | 16.229(3) | 9.528(2) | 3038.13 |
| KZCS + 30% Ni$^{2+}$ | 19.713(2) | 16.226(4) | 9.530(2) | 3037.89 |

### Figure 2. X–ray powder diffraction patterns of, pure KZCS and KZCS doped with Ni$^{2+}$ ions with different ratios.

### Figure 6a. In case of pure KZCS crystals the extinction coefficient and reflectance decreased rapidly up to 400 nm and then exhibit a small broad minimum before it increases gradually to 800 nm.
Figure 3. Plot of spectral variation of transmittance and reflectance of KZCS single crystals doped with different concentrations of Ni$^{2+}$ ions.

Coefficient ($K_{ex}$) increases slowly or almost constant until the value of $h\nu \approx 5$ eV and after that starts to increase rapidly till the end of photon energy range. In case of KZCS crystals doped with different ratios of Ni$^{2+}$ ions there are two bands centred at about 1.7 and 3.15 eV and also $K_{ex}$ increase more rapid beginning of photon energy $\approx 5$ eV to the end of the studied energy range. Figure 6b shows the refractive index (n) dependence on photon energy. As shown in the figure, the values of the refractive index increases all over the measured range of photon energy.

(ii) Lattice dielectric constant and contribution of charge carrier

Another important optical parameter is the complex dielectric constant $\tilde{\varepsilon}$ which can be described by the equation:

$$\tilde{\varepsilon} = \varepsilon_{\text{real}} - i\varepsilon_{\text{im}}.$$  \hspace{1cm} (7)

Where $\varepsilon_{\text{real}}$ is the real part of the dielectric constant which associated with the speed of light attenuation within the material and $\varepsilon_{\text{im}}$ is the imaginary part of the dielectric constant which explains how a dielectric absorbs energy from the electric field [18].

Refractive index (n) and Extinction coefficient ($K_{ex}$) can be used to determine the lattice dielectric constant as they are related to each other according to the equation:

$$\varepsilon_{\text{real}} = n^2 - K_{ex}^2 \text{ and } \varepsilon_{\text{im}} = 2nK_{ex}.$$ \hspace{1cm} (8)

Variation of the real ($\varepsilon_{\text{real}}$) and imaginary ($\varepsilon_{\text{im}}$) parts of the dielectric constant with photon energy for KZCS crystals pure and doped with different concentrations of nickel ions are shown in Figure 7. The behaviour of the imaginary part ($\varepsilon_{\text{im}}$) against the energy is similar to that of the extinction coefficient ($K_{ex}$) while the real part
Figure 4. (a) Photon energy dependence of $\alpha$ and (b) Photon energy dependence of $(a h \nu)^{1/2}$ of pure KZCS and KZCS doped with different concentrations of Ni$^{2+}$ ions.

The obtained data of refractive index ($n$) can be analyzed to obtain the high-frequency dielectric constant according to the following equation [19]:

$$n^2 = \varepsilon_L - B\lambda^2$$

(9)

Where $\varepsilon_L$ is the lattice dielectric constant, $\lambda$ is the wavelength of the incident radiation and $B$ is given by $(e^2/4\pi^2\varepsilon_0c^2)(N/m^*)$: where $e$ is the electronic charge, $\varepsilon_0$ the permittivity of free space ($8.854 \times 10^{-12} \text{F/m}$), $c$ is the velocity of light, and $N/m^*$ is the ratio of carrier concentration to the effective mass.

Equation (9) can be used to determine the lattice dielectric constant $\varepsilon_L$ and the ratio of carrier concentration to the effective mass $N/m^*$ by plotting $n^2$ on the $y$-axis and $\lambda^2$ on the $x$-axis as shown in Figure 8.
Figure 6. (a) Extinction coefficient \(K_{ex}\) and (b) Refractive index \(n\) versus photon energy for pure KZCS and KZCS single crystal doped with different concentrations of Ni\(^{2+}\) ions.

The intercept represents the lattice dielectric constant \(\varepsilon_L\) while \((N/m^*)\) can be calculated from the slope. The values of \(\varepsilon_L\) and \((N/m^*)\) are listed in Table 2.

### 3.2.2. The dispersion of the refractive index

Wemple and DiDomenico (WDD) model is a way to explain the dispersion of the refractive index which is based on single oscillator formula [20,21]:

\[
n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2} \tag{10}
\]

Where \(E_o\) is the single oscillator energy and \(E_d\) is the dispersion energy.

The parameters \((E_o, E_d)\) mentioned in the above equation can be calculated by plotting \(1/(n^2-1)\) versus \((h\nu)^2\) and fitting the linear part around the optical energy gap and the values of these parameters for KZCS pure and doped with Ni\(^{2+}\) ions can be evaluated and depicted in Figure 9. From the intercept \((E_o/E_d)\) and slope \((1/E_oE_d)\) the dispersion parameters \(E_o\) and \(E_d\) are calculated and listed in Table 2.

For more analysis for refractive index, static refractive index \((n_o)\), single oscillator strength \((S_o)\), oscillator wavelength \((\lambda_o)\) and values of optical moments \((M_{-1}\) and \(M_{-3}\)) can be determined.

By putting \(h\nu = 0\) in equation (10) the equation will take the form:

\[
n_o^2 - 1 = \frac{E_d}{E_o} \tag{11}
\]

The values of \(n_o\) for pure and Ni\(^{2+}\) doped KZCS crystals are calculated and listed in Table 2.

The WDD model also suggests a formula to calculate the oscillator wavelength as follows:

\[
n_o^2 - 1 = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \tag{12}
\]

Where \(\lambda_o\) is the oscillator wavelength and \(n_o\) the static refractive index (determined from eq. (12))
Figure 7. The dependence of the real $\varepsilon_{\text{real}}$ and the imaginary $\varepsilon_{\text{im}}$ parts of the dielectric constant on the photon energy for pure KZCS and KZCS single crystal doped with different concentrations of Ni$^{2+}$ ions.

Figure 8. Variation of $n^2$ versus $\lambda^2$ for pure KZCS and KZCS single crystals doped with different concentrations of Ni$^{2+}$ ions.
Table 2. Optical parameters of KZCS pure and doped with different concentrations of Ni$^{2+}$ ions.

| Optical parameter               | Pure KZCS | KZCS + 5% Ni$^{2+}$ | KZCS + 10% Ni$^{2+}$ | KZCS + 20% Ni$^{2+}$ | KZCS + 30% Ni$^{2+}$ |
|---------------------------------|-----------|---------------------|----------------------|----------------------|----------------------|
| Optical energy gap $E_g$ (eV)   | 4.21      | 3.84                | 3.67                 | 3.44                 | 3.15                 |
| Dispersion energy $E_d$ (eV)    | 2.99      | 2.01                | 1.84                 | 1.37                 | 0.919                |
| Single oscillator energy $E_o$ (eV) | 7.35    | 6.42                | 6.19                 | 5.44                 | 5.01                 |
| Static refractive index ($n_o$) | 1.18      | 1.14                | 1.13                 | 1.11                 | 1.08                 |
| Lattice dielectric constant $\varepsilon_L$ | 2.1069 | 1.90817             | 1.86689              | 1.85255              | 1.74682              |
| N/m·*                          | 7.35 × 10$^7$ | 4.125 × 10$^7$    | 3.75 × 10$^7$        | 3.585 × 10$^7$       | 3.39 × 10$^7$        |
| Oscillator wavelength ($\lambda_o$) (nm) | 3.585 × 10$^7$ | 3.39 × 10$^7$ | 3.12 × 10$^7$       | 2.63 × 10$^7$       | 2.17 × 10$^7$       |
| Oscillator strength $S_{o2}$    | 2.26 × 10$^{-5}$ | 1.83 × 10$^{-5}$ | 1.93 × 10$^{-5}$    | 1.93 × 10$^{-5}$    | 2.17 × 10$^{-5}$    |
| Moment of the optical dispersion spectra $M_{-1}$ | 0.4075 | 0.3133              | 0.2983               | 0.2523               | 0.1835               |
| Moment of the optical dispersion spectra $M_{-3}$ (eV)$^{-2}$ | 7.536 × 10$^{-3}$ | 7.852 × 10$^{-3}$ | 7.784 × 10$^{-3}$   | 8.523 × 10$^{-3}$   | 7.309 × 10$^{-3}$   |

To determine the value of the oscillator wavelength, a parameter $S_{o2}$ can be introduced with rearranging equation (12) so that $S_{o2} = (n_o^2 - 1)/\lambda_o^2$ and the arranged equation takes the form:

$$\frac{1}{(n^2 - 1)} = \frac{1}{\lambda_o^2 S_{o2}} - \frac{1}{\lambda_o^2 S_{o2}} (13)$$

The values of $\lambda_o$ and $S_{o2}$ can be determined from the slope and the intercept of the linear portion of $1/(n^2 - 1)$ versus $1/(\lambda)^2$ as depicted in Figure 10 and the obtained values are tabulated in Table 2.

The moments of optical spectra $M_{-1}$ and $M_{-3}$ are calculated using the following relations [22]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} (14)$$

$$E_d^2 = \frac{M_{-1}}{M_{-3}} (15)$$

The values of optical moments for KZCS pure and doped with nickel ions at different ratios are recorded in Table 2.

3.3. FTIR spectra

The infrared transmission spectra were recorded in the wavelength range 400 cm$^{-1}$ – 4000 cm$^{-1}$. Figure 11 represents the FTIR spectrum of KZCS crystals pure and doped with different concentrations of nickel ions and the infrared frequencies are given in Table 3.

The bands observed around 3229 cm$^{-1}$ are assigned to the stretching of water molecules and these bands were observed for pure and doped crystals and experience a slight shift. The existence of water functional groups in the FTIR spectrum is essential to confirm the crystal formula with 3H$_2$O molecules [23]. Bands of the stretching vibration of water bending and twisting modes were also observed around 1560 and 760 cm$^{-1}$ [24] and the slight shift of these bands indicates that the water molecules weren’t affected much by the substitutions of Ni$^{2+}$ with Zn$^{2+}$ ions.

There were 3 different vibration modes observed for the crystals around 1150, 1100, 980 and 630 cm$^{-1}$ assigned to the vibrations of the sulfate group and the shift in those bands was slight which confirms that the addition of Ni in the crystal structure did not affect the original structure and vibrational modes in the crystal.

![Figure 9. Plot of ($n^2 - 1$)$^{-1}$ as a function of ($h\nu$)$^2$ for pure KZCS and KZCS single crystals doped with different concentrations of Ni$^{2+}$ ions.](image-url)
Figure 10. Plot of \((n^2 - 1)^{-1}\) versus \(\lambda^{-2}\) for pure KZCS and KZCS single crystals doped with different concentrations of Ni\(^{2+}\) ions.

Table 3. FTIR of the main functional groups assignment of KZCS pure and doped with different concentrations of nickel ions.

| Wavenumber (cm\(^{-1}\)) | Pure KZCS | KZCS + 5\% Ni\(^{2+}\) | KZCS + 10\% Ni\(^{2+}\) | KZCS + 20\% Ni\(^{2+}\) | KZCS + 30\% Ni\(^{2+}\) | Assignment |
|--------------------------|-----------|------------------------|------------------------|------------------------|------------------------|------------|
| 3227                     | 3228      | 3227                   | 3227                   | 3230                   | \(v_{as}\) H\(_2\)O stretching |
| 1620                     | 1564      | 1564                   | 1560                   | 1569                   | \(v_{as}\) H\(_2\)O bending |
| 1141                     | 1142      | 1142                   | 1140                   | 1143                   | \(v_{as}\) modes of SO\(_4\) groups |
| 1103                     | 1097      | 1102                   | 1100                   | 1100                   | \(v_{as}\) modes of SO\(_4\) groups |
| 983                      | 982       | 981                    | 984                    | 982                    | \(v_{as}\) modes of SO\(_4\) groups |
| 757                      | 755       | 756                    | 760                    | 761                    | \(v_{as}\) H\(_2\)O Twisting modes |
| 631                      | 630       | 631                    | 632                    | 632                    | \(v_{as}\) modes of SO\(_4\) groups |

\(v_{as}, v_{as}, v_{ab}, v_{ab}\) represents asymmetric stretching, symmetric stretching, symmetric bending and asymmetric bending respectively.

The slight shift in some of the characteristic vibrational frequencies may be due to lattice strains produced as a result of doping. Also, the presence of the functional groups in the compound has been confirmed by FTIR analysis. The assignments of the functional groups appeared in the samples are listed in the Table 3.

4. Conclusion

Single crystals of potassium zinc chloride sulfate (KZCS) pure and doped with different concentrations of Ni\(^{2+}\) ions were successfully grown from aqueous solutions. The crystals were found to crystallize with the monoclinic symmetry and exhibit isomorphism with the kainite crystals. The X-ray powder diffraction patterns proved that the addition of Ni in the crystals didn’t change the crystal structure and the shift in the diffraction peaks and the slight change in the lattice constants were reported. Different functional groups of the crystals were assigned from the FTIR spectra.

The spectral analysis of the crystals was performed and the results confirmed that the optical energy gap (\(E_g\)) of the crystals were in the dielectric range, the value of \(E_g\) is 4.21 eV for the pure sample and decreases with increasing Ni\(^{2+}\) ions ratios and the doped crystals may exhibit filtering for different regions of the visible spectrum. The optical constants were calculated and analyzed and the single oscillator model was employed to
describe the normal dispersion of the refractive index of the grown crystals.

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