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Abstract:
In our investigation, the samples of the empirical formula $K_x^{2+}Ni_1^{2+}Co_{(1-x)}^{2+}(SO_4)_2 \cdot 6H_2O$ are grown with partial occupation of the cations Co and Ni. By using the method based on the growth of crystals per solution with slow evaporation of the solvent, it was possible to obtain mixed crystals with good optical quality. In the decomposition process, these crystals suffer a mass loss of approximately 24%, equivalent to water molecules forming octahedral coordination ions of Ni and Co. The optical characteristics of the grown crystals are measured where transmittance reaches more than 80% in the wavelength range of 190-390 nm. By Raman spectroscopy, the vibrational modes of $SO_4^{2-}, H_2O$ and of the octahedral $Ni(H_2O)_6$ and $Co(H_2O)_6$ were identified. Chemical analyses were performed by ICP-OES technique to measure the proportions of Ni and Co in the samples.

Keywords: Tutton’s salt; Crystal Growth; Characterization; Optical Transmission Spectra; Raman Spectroscopy
1. Introduction:

In recent years the study on the growth and characterization of Tutton salts has drawn considerable attention due to its application in the area of energy absorber of solar collectors, chemical energy storage applications, UV light filters and even in missile approach warning systems. The family of the Tutton’s salts are a group of isomorphic compounds presented by a formula $A_2B(XO_4)_2\cdot 6H_2O$, where $A = K, NH_4, Rb, Cs, Ti; B = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, V, Cr; X = S$ or $Se$. The crystallographic structure of Tutton’s salt belongs to monolithic space group $P2_1/c$ ($Z=2$) [1-2], and this crystal contains two octahedral hexahydrate complexes $[B(H_2O)_6]^{2+}$ in the crystal unit cell, where $B$ is a bivalent cation and $A$ is a monovalent cation.

The Nickel Sulfate hexahydrate (NSH) types crystals exhibits discontinuous optical transmission in the range from ultraviolet to visible light wavelengths and demonstrates its high transmission (almost 80%) efficiency over a narrow band at 200-350 nm, that’s why these types of crystals are used as UV light filters and UV made sensors. There are some studies about the best nickel sulfate hexahydrate crystals, such as ammonium nickel sulfate hexahydrate ANSH [3], rubidium nickel sulfate hexahydrate (RNSH) [4-5], cesium nickel sulfate hexahydrate [6], potassium manganese nickel sulfate hexahydrate (KMNSH) [7-8], $\alpha$-nickel sulfate hexahydrate [9], ammonium iron sulfate hexahydrate [10], zinc magnesium ammonium sulfate hexahydrate [11], potassium and ammonium zinc sulfate hydrate [12]. Recently it was observed that potassium nickel sulfate hexahydrate (KNSH) [13-14] possess same type of optical transmission properties as that of NSHs but with better thermal stability and higher dehydration temperature. But all these above-mentioned crystals have transmission peak near to 500 nm, and this behavior reduces their transmission efficiency in the UV region. To overcome this problem, KCNSH [15-17] (Potassium Nickel Cobalt Sulfate Hexahydrate) $K_2Ni_xCo_{1-x}(SO_4)_2\cdot 6H_2O$ (mixed KNSH crystal) were proposed. The potassium cobalt sulfate (KCSH) crystals are isomorphic to nickel crystals and Ni have UV transmission range 240-290 nm [18], but it has absorption band in the range 350-750 nm, which suppress the transmission peak near to 500 nm.

N.A. Vasilevya et. al [17] studied growth and properties of optically homogeneous mixed KCNSH crystal grown from solutions of different compositions by using the temperature
reduction technique in the static and dynamic range. They have reported the transmittance of this crystal is reaches up to 80% in the wavelength range of 240-290 nm. Whereas, X. Zhuang et al. [15] studied the growth and crystal structure by using X-ray diffraction and optical characteristics of a KCNSH crystal with dimension of $12 \times 12 \times 40 \text{mm}^3$ obtained from temperature reduction technique, and the transmittance of the crystal in the UV range was about 40%. Finally, I. I. Polovinco et al. [16] studied the growth of two crystals with the dimension of $3 \times 3 \times 4 \text{mm}^3$ by using solvent evaporation technique and the transmittance of their crystal were reported in the UV range about 60%. In our work, we have obtained a KCNSH crystal by the solution growth method at 35°C and were characterized by the ICP-OES, EDS, UV-vis, TG-DTG, and Raman spectroscopy techniques.

2. Experimental Methods:

The crystals were grown by slow evaporation of the solvent (distilled and deionized water at pH 6 and resistivity $18.2 \text{M\Omega cm}^{-1}$) with the solution kept static in an oven at 35°C. The crystals of the sample C, shown in figure 1(a) were obtained in about four days, and the crystals of the sample H shown in the figure 1(b) were obtained in about eight days. Crystals of good quality and different sizes were obtained. As growth occurs slowly, without disturbances or large fluctuations in the temperature of the environment (greenhouse), generally the samples obtained have well defined flat faces and high structural perfection. The chemical analysis was performed on an Agilent 725 series Inductive Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) and on a Rigaku-brand automatic sequential. Dispersive energy spectroscopy (EDS) analysis were performed on a Field Effect Emission Scanning Electron Microscope (FEG-SEM) model SIGMA VP, manufactured by Carl Zeiss Microscopy.
Figure 1: Image of the crystals a) Sample C: $K_2Ni_{0.64}Co_{0.36}(SO_4)_2\cdot6H_2O$ b) Sample H: $K_2Ni_{0.76}Co_{0.24}(SO_4)_2\cdot6H_2O$

The thermogravimetric analysis was performed on a simultaneous TG-DTG analysis equipment, model STD2960. Following the protocol: the samples were placed in the form of powder with heating rate of $5^\circ C$ / min in the temperature range of $40^\circ C$ to $500^\circ C$ under atmosphere of synthetic air $N_2O_2$ with flow of $100$ mL/min. The Raman spectra were obtained at room temperature by using Horiba / Jobin-Yvon LABRAM-HR spectrometer, with excitation line of $632.8$ nm (He-Ne laser), with a nominal power of $18$ mW. The light scattered by the sample was collected by an Olympus confocal microscope (100X objective) and analyzed by a spectrograph with 600 and 1800 lines/mm diffraction gratings and a Peltier effect cooled detector. The resolution of the measurements was around $2$ cm$^{-1}$ and acquisition times were typically 20 collections of 10s. The absorption measurements in the UV-VIS-NIR region were carried out by a spectrophotometer: UV-1650 PC, UV-VIS SPECTROPHOTOMETER SHIMADZU which has an operating range of $190 - 1100$ nm, $1$ nm passband, and is Coupled to a computer for acquisition and signal processing. Data measurement were taken place in the wavelengths region from $190$ nm to $1100$ nm in transmittance mode.
3. Experimental Procedure:

2.1 Crystal Growth

\[ \text{K}_2\text{SO}_4 + \text{Ni(SO}_4\text{)}_6\text{H}_2\text{O} + \text{Co(SO}_4\text{)}_7\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{Ni}_{1-x}\text{Co}_x(\text{SO}_4)_{2} \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O} \]

**Sample C**: KCNSH solution of the sample C was prepared by mixing 5g of K\(_2\)SO\(_4\), 3.7705g of Ni(SO\(_4\))\(_6\)H\(_2\)O and 4.0325g of Co(SO\(_4\))\(_7\)H\(_2\)O.

**Sample H**: Sample H was prepared by mixing 4.4632g of K\(_2\)SO\(_4\), 0.9192g of Li\(_2\)(SO\(_4\))\(_3\)H\(_2\)O, 3.3661g of Ni(SO\(_4\))\(_6\)H\(_2\)O and 3.6008g Co(SO\(_4\))\(_7\)H\(_2\)O.

4. Result and Discussion:

The measured proportions of nickel and cobalt in each sample were obtained by means of the (ICP-OES) technique, shown in **table 1** and **table 2**. The thickness of the samples C and H is shown in the **table 3**. Apparently, the ionic radius (0.69Å) the Ni ion is smaller than the Co (0.75Å) ion, as reported by X. Zhuang et al. [8], this would be a possible reason why Ni has a greater ease of accommodation in the crystalline structure. We add the fact that, Nickel has higher electronic affinity than Cobalt, although it can be replaced sometimes by Co ion to form hydrated complexes \([B(H_2O)_a]^{2+}\) (in our case B is Ni or Co) alternately in crystalline structure.

**Table 1**: Proportions of Ni and Co obtained in ICP-OES technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>Ni (g/g)</th>
<th>Co (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.1484</td>
<td>0.0778</td>
<td>0.0444</td>
</tr>
<tr>
<td>H</td>
<td>0.1505</td>
<td>0.0934</td>
<td>0.0292</td>
</tr>
<tr>
<td>Detection Limit</td>
<td>10.08µg/g</td>
<td>5.19µg/g</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2**: Proportions of Ni and Co in samples of mixed crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>K(<em>2)Ni(</em>{0.64})Co(_{0.36})(SO(_4))(_2) \cdot 6\text{H}_2\text{O}</td>
</tr>
<tr>
<td>H</td>
<td>K(<em>2)Ni(</em>{0.76})Co(_{0.24})(SO(_4))(_2) \cdot 6\text{H}_2\text{O}</td>
</tr>
</tbody>
</table>
Table 3: Thickness of the samples C and H.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$K_2Ni_0.64Co_{0.36}(SO_4)_2 \cdot 6H_2O$</td>
<td>1.05</td>
</tr>
<tr>
<td>H</td>
<td>$K_2Ni_{0.76}Co_{0.24}(SO_4)_2 \cdot 6H_2O$</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Next, we have the EDS spectra obtained in the Scanning Electron Microscopy (SEM) as shown in the figure 2, where the peaks for each of the chemical elements appear and confirm their presence in the structure of the studied samples. The gold (Au) peaks in the EDS spectra are due to the fact that all samples had to be metallized with Au to improve the quality of the measurements.

![Figure 2: EDS spectra of the residues of the sample after thermal analysis](image-url)
As reported [19-20], they obtained mixed crystals of K with Zn and Mn and of K with Zn and V, where the EDS technique served to identify and confirm the presence of these elements in the structure of the crystal qualitatively. After the decomposition process in thermogravimetry analysis, the samples were analyzed in the form of powder in order to identify the elements, present in the samples in samples C and H. It can be seen from figure 2 that, even after burning the material of samples, the elements K, O, S, Ni and Co remain present in the sample residues. This is an indication that the samples only suffer loss of water in the decomposition process in the temperature range up to 500 °C. The presence of aluminum may be justified by an oxidation reaction of the sample with the alumina crucible used in the analysis.

The thermogravimetric measurements as shown in the figure 3 of the samples demonstrates a mass loss (dehydration) of 25.3% for sample C and 24.7% for sample H, which corresponds approximately to the percentage of water molecules present in the crystal structure which forms the complexes \([B(H_2O)_6]^{2+}\). The dehydration temperature of the samples is within the expected value, when compared to the reference [15], which is very close to sample C. The above facts indicates that the dehydration process is not affected by the atmosphere used in the analysis.
The optical transmission spectra measurements were performed by sweeping the region of the spectrum that covers the ultraviolet, visible and near infrared regions, comprising the range of 190-1100 nm. In figure 4, the transmittance spectra of the samples C and H are shown, where spectra band is observed where the material exhibits a transparency in the ultraviolet region (190-390nm), followed by two peaks in the visible region (450-650nm) and later in the infrared region (700-1100nm). The UV transmittance of the sample C reaches more than 75% and that of the sample H reaches more than 90%. In principle, the greater transparency of sample H in the UV region is related to the higher concentration of Nickel in the sample. The thickness of the sample H is more than that of the sample C as shown in the table 3, this can be also a possible reason for the higher UV transmittance of the sample H. These characteristics of transmission spectra can be attributed to the
octahedral metal complexes CoO$_6$ and NiO$_6$, due to the electronic transitions involving the electronic configurations d$^7$ and d$^8$, respectively [21].

![Optical transmission spectra of the samples C and H](image)

**Figure 4:** Optical transmission spectra of the samples C and H

Raman spectroscopy performed as shown in the figure 5 in the range of 100 to 4000 cm$^{-1}$ showed the normal vibration modes of the SO$_4^{2-}$ ions, for 9 active modes in Raman Spectroscopy, in which $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$ have 1, 2, 4 and 2 normal modes of vibration, symmetrical respiratory mode, symmetric deformation modes, anti-symmetric elongation modes and anti-symmetric deformation modes, respectively. The tetrahedral SO$_4^{2-}$ are bonded with the ions \([B(H_2O)_6]^{2+}\), by means of bonding type O-H $\cdots$ O, and the potassium atoms are coordinated with the oxygen atoms of SO$_4^{2-}$ [15].
**Figure 5**: Raman Spectroscopy of the samples C and H in the wavenumber range 100-4000 cm\(^{-1}\)

**Figure 6**: Raman spectra of the samples highlighting the regions of the normal modes of vibration of \(\text{SO}_4^{2-}\) and \([\text{B(H}_2\text{O)}_6]^{2+}\). B can be Ni or Cobalt.
The normal vibration modes of the SO$_4^{2-}$ ions are observed around: $\nu_1$ near 990 cm$^{-1}$; $\nu_2$ near 448 and 462 cm$^{-1}$; $\nu_3$ near 1080, 1111, 1129 and 1156 cm$^{-1}$; $\nu_4$ near 614 and 632 cm$^{-1}$ as shown in the figure 6. In relation to the H$_2$O molecules, a broadband is obtained in the 3200-3400 cm$^{-1}$ region where overlapping of normal modes is observed in the spectra of the samples C and H, this occurs due to the O-H interactions of the water molecules [22-23].

The complexes $[B(H_2O)_6]^{2+}$, have the vibrational modes $\nu_1$, $\nu_2$ and $\nu_5$ active in Raman spectra. These vibrational modes as shown in the figure 6 are located in the region below 420 cm$^{-1}$, with $\nu_1$ between 380-410 cm$^{-1}$, $\nu_2$ between 237-267 cm$^{-1}$ and $\nu_5$ between 159-203 cm$^{-1}$. The region between 105-140 cm$^{-1}$ are attributed to libations of SO$_4^{2-}$ and H$_2$O molecules [23-24].

5. Conclusion:

The mixed KCNSH crystals are investigated in this work were grown by the slow evaporation of the solvent and the obtained crystals are transparent and have good thermal stability. TG and DTG data revealed that the two crystals show a thermal stability with measured values were between 95.4° C and 99.6° C, after which the crystals start to show a decomposition of water molecules. The bands of the vibrational modes of SO$_4^{2-}$, water and octahedron $[B(H_2O)_6]^{2+}$ were identified by means of Raman spectroscopy in these two samples C and H and in the obtained results no significant changes observed in the spectra of these samples. These mixed KCNSH crystals exhibit high (more than 80%) UV transmittance, which indicates their high structural quality and better optical properties and can be used in optical filters.
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Highlights

- Potassium nickel cobalt sulfate hexahydrate (KCNSH) crystal growth by slow evaporation of the solvent.
- Inductive coupled plasma (ICP) technique to measure the proportions of Ni and Co in the crystalline structure.
- Scanning electron microscopy (SEM) for dispersive energy spectroscopy analysis.
- Optical transmission spectra to investigate the UV transmittance of the crystals.
- Raman spectroscopy in the wavelength range of 100 to 4000 cm$^{-1}$. 