



Original Article

Growth and characterization of potassium cobalt nickel sulfate hexahydrate crystals: A new UV light filter

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ABSTRACT

Samples of the empirical formula $K_2^+ Ni_x^{2+} Co_{(1-x)}^{2+} (SO_4)_2 \cdot 6H_2O$ were grown with a partial occupation of the cations Co and Ni. Mixed crystals with good optical quality were obtained by the slow evaporation growth method. 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 were measured where transmittance reached 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.

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1. Introduction

In recent years, the study on the growth and characterization of Tutton's salts has drawn considerable attention due to their potential applications in the area of solar energy absorber, chemical energy storage, ultraviolet (UV) light filters and even in missile approach warning systems. The family of the Tutton's salts is a group of isomorphous compounds with the formula $A_2B(XO_4)_2 \cdot 6H_2O$, where $A = K, NH_4, Rb, Cs, Tl$; $B = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, V, Cr$; $X = S$ or Se . The crystallographic structure of Tutton's salt belongs to the monolithic space group $P2_1/c$ ($Z = 2$) [1,2]. 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) crystals exhibit discontinuous optical transmission in the range from ultraviolet to visible light wavelengths and demonstrate their 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], α -nickel sulfate hexahydrate [9], ammonium iron sulfate hexahydrate [10], zinc magnesium ammonium sulfate hexahydrate [11], potassium and ammonium zinc sulfate hydrate [12]. Recently, it has been reported that a potassium nickel sulfate hexahydrate (KNSH) possesses the same type of optical transmission properties as that of NSHs, but with better thermal stability and higher dehydration temperature [13,14]. However, all above-mentioned crystals have a transmission peak near 500 nm, and this behavior reduces their transmission efficiency in the UV region. To overcome this problem, KCNSH (potassium nickel cobalt sulfate hexahydrate) $K_2Ni_xCo_{1-x}(SO_4)_2 \cdot 6H_2O$ (mixed KNSH crystal) was proposed [15–17]. The potassium cobalt sulfate (KCSH) crystals are isomorphous to nickel crystals. Ni has a UV transmission range of 240–290 nm [18], but it has an absorption band in the range of 350–750 nm, which suppresses the transmission peak near 500 nm.

Vasilevya et al. [17] successfully grew an optically homogeneous mixed KCNSH crystal from solutions of different compositions using the temperature reduction technique in the static and dynamic range. They reported the transmittance of this crystal reached up to 80% in the wavelength range of 240–290 nm. In addition, Zhuang et al. [15] studied the growth, crystal structure and optical

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characteristics of a KCNSH crystal with dimension of $12 \times 12 \times 40 \text{ mm}^3$. In the UV range, the transmittance of the crystal was about 40%. Finally, Polovinco et al. [16] studied the growth of two crystals with dimension of $3 \times 3 \times 4 \text{ mm}^3$ by using the solvent evaporation technique and reported the transmittance of about 60%. In this work, the characterizations of the KCNSH crystal obtained by the solution growth method are presented.

2. Experimental

The crystals were grown by slow evaporation of the solvent (distilled and deionized water at $\text{pH} = 6$ and resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$) with the solution kept static in an oven at 35°C . The crystals of the sample C, shown in Fig. 1(a) were obtained in about four days, and the crystals of the sample H shown in Fig. 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), the obtained samples generally 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 was carried out on a Field Effect Emission Scanning Electron Microscope (FEG-SEM) model SIGMA VP, manufactured by Carl Zeiss Microscopy.

The thermogravimetric analysis was taken using a simultaneous TG-DTG analysis equipment (model STD2960). In this case, the samples were placed in the form of powder with heating rate of $5^\circ\text{C}/\text{min}$ in the temperature range of $40\text{--}500^\circ\text{C}$ under atmosphere of synthetic air N_2O_2 with flow of $100 \text{ mL}/\text{min}$. The Raman spectra were recorded at room temperature by using Horiba/Jobin-Yvon LABRAM-HR spectrometer with an excitation line of 632.8 nm (He–Ne laser) and a nominal power of 18 mW . The light scattered by the sample was collected by an Olympus confocal microscope ($100\times$ 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 10 s. The absorption measurements in the UV–VIS–NIR region were carried out by a spectrophotometer UV-1650 PC, UV–VIS SPECTROPHOTOMETER SHIMADZU operating in the range of $190\text{--}1100 \text{ nm}$, 1 nm passband. All data were taken place in the wavelengths region from 190 nm to 1100 nm in transmittance mode and are coupled to a computer for acquisition and signal processing.

3. Experimental procedure

3.1. Crystal growth

For sample C, the KCNSH solution was prepared by mixing 5 g of K_2SO_4 , 3.7705 g of $\text{Ni}(\text{SO}_4)\cdot 6\text{H}_2\text{O}$ and 4.0325 g of $\text{Co}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ via the chemical reaction: $\text{K}_2\text{SO}_4 + \text{Ni}(\text{SO}_4)\cdot 6\text{H}_2\text{O} + \text{Co}(\text{SO}_4)\cdot 7\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$.

For sample H, an attempt was made to dope the crystal with lithium. In this process, the percentage of potassium was reduced to 90% and was placed 25% Lithium. Then, the KCLNSH solution was formed by mixing 4.4632 g of K_2SO_4 , 0.9192 g of $\text{Li}_2(\text{SO}_4)\cdot \text{H}_2\text{O}$, 3.3661 g of $\text{Ni}(\text{SO}_4)\cdot 6\text{H}_2\text{O}$ and 3.6008 g $\text{Co}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ via the chemical reaction: $\text{K}_2\text{SO}_4 + \text{Li}_2(\text{SO}_4)\cdot \text{H}_2\text{O} + \text{Ni}(\text{SO}_4)\cdot 6\text{H}_2\text{O} + \text{Co}(\text{SO}_4)\cdot 7\text{H}_2\text{O} \rightleftharpoons \text{K}_{1.8}\text{Li}_{0.25}\text{Ni}_x\text{Co}_{(1-x)}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$.

4. Result and discussion

The measured proportions of nickel and cobalt in each sample obtained by means of the ICP-OES technique are shown in Table 1. Thus, the samples C and H are formed in the formula $\text{K}_2\text{Ni}_{0.64}\text{Co}_{0.36}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{Ni}_{0.76}\text{Co}_{0.24}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$, with the thickness of 1.05 and 0.95 mm , respectively. Attempts to dope lithium with the intention to obtain a mixed crystal of nickel/cobalt with potassium/lithium were not successful. However, we believe that lithium has influenced in some way on the crystal growth. Otherwise, the two samples should have the same proportions of nickel and cobalt, since they were grown under the same conditions. Apparently, the ionic radius (0.69 \AA) of the Ni ion is smaller than that of the Co (0.75 \AA) ion [8]. This would be a possible reason why Ni has a greater ease of accommodation in the crystalline structure. In addition, we can propose that, nickel has higher electronic affinity than cobalt, although it can be replaced sometimes by Co ion to form hydrated complexes $[\text{B}(\text{H}_2\text{O})_6]^{2+}$ (in our case B is Ni or Co) alternately in crystalline structure.

The EDS spectra obtained by the scanning electron microscopy (SEM) are shown in Fig. 2, where the peaks for each of the chemical

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

Sample	Mass (g)	Ni (g/g)	Co (g/g)
C	0.1484	0.0778	0.0444
H	0.1505	0.0934	0.0292
Detection limit		$10.08 \mu\text{g}/\text{g}$	$5.19 \mu\text{g}/\text{g}$

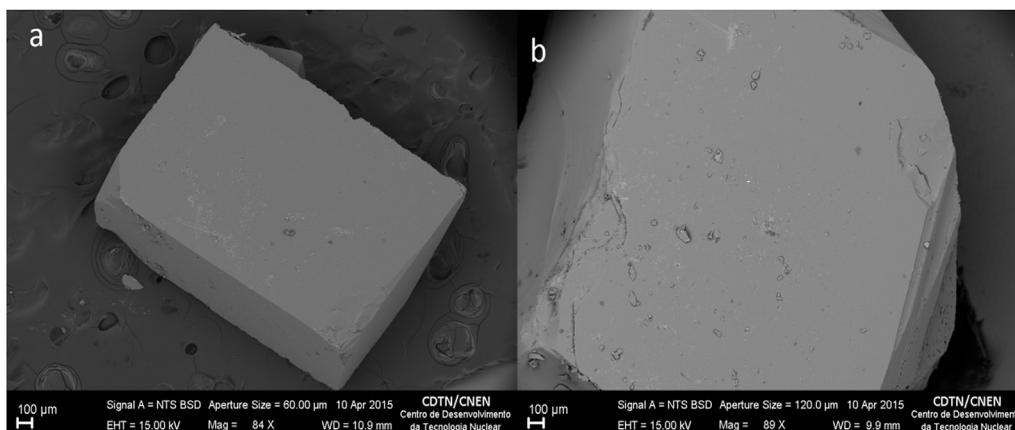


Fig. 1. Images of the crystals (a) sample C: $\text{K}_2\text{Ni}_{0.64}\text{Co}_{0.36}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ and (b) sample H: $\text{K}_2\text{Ni}_{0.76}\text{Co}_{0.24}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$.

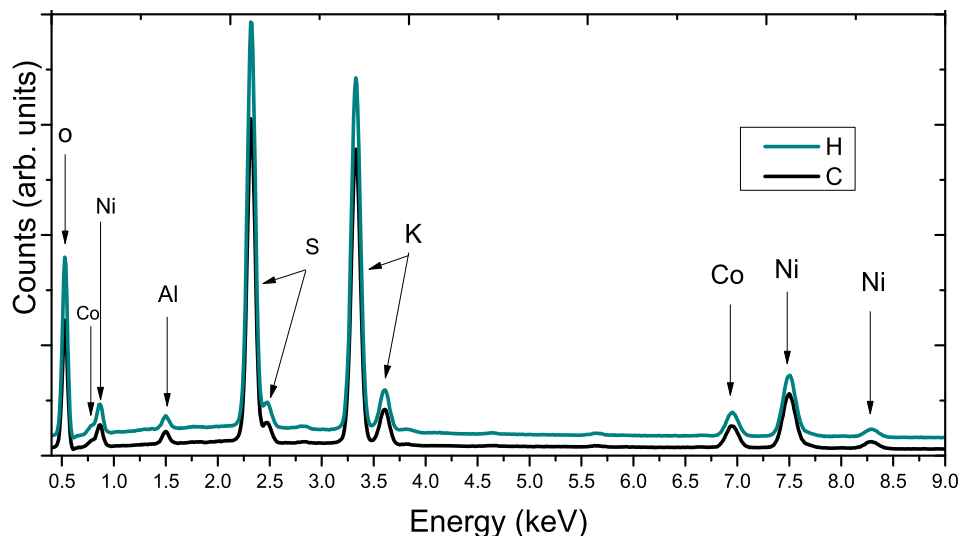


Fig. 2. EDS spectra of the residues of the samples C and H after thermal analysis.

elements appear and confirm their presence in the structure of the samples under investigation. In the spectra, the gold (Au) peaks might appear due to the fact that all samples had to be metalized with Au to improve the quality of the measurements.

As reported in [19,20], the samples contain 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 existing in the samples C and H. As can be seen from Fig. 2, even after burning the samples, the elements K, O, S, Ni and Co remain in the sample

residues. This indicates 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 results of thermogravimetric measurements are presented in Fig. 3. TG and DTG data revealed that the two crystals show a thermal stability below 100 °C, after which the crystals start to show a decomposition of water molecules. The mass loss (dehydration) is 25.3% for sample C and 24.7% for sample H, which corresponds approximately to the percentage of water molecules used to form the complexes $[B(H_2O)_6]^{2+}$ in the crystal structure. The dehydration temperature of the samples is comparable to that

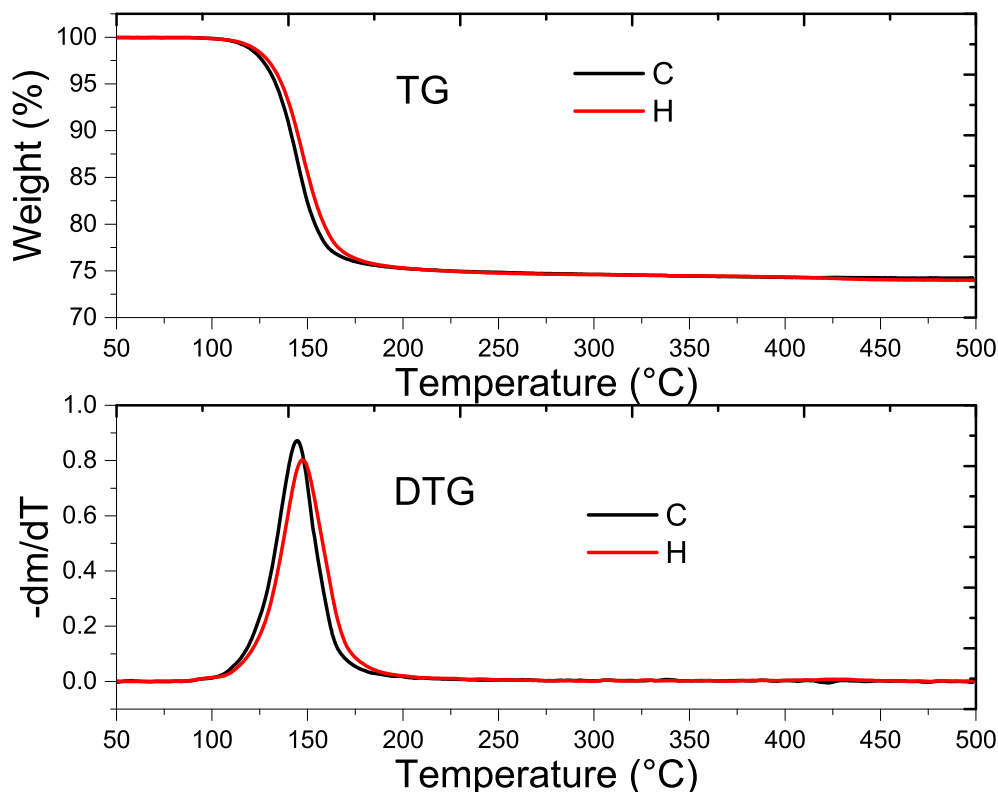


Fig. 3. Thermogravimetric analysis (TG-DTG) of the samples C and H.

reported in [15], in particular for the sample C. These findings indicate that the dehydration process is not affected by the atmosphere used in the analysis.

The optical transmission spectra were recorded by sweeping in the region of 190–1100 nm that covers all the ultraviolet, visible and near infrared regions. In Fig. 4, the transmittance spectra of the samples C and H are shown. It is clearly seen that, the spectra band appeared where the material exhibits a transparency in the ultraviolet region (190–390 nm), followed by two peaks in the visible region (450–650 nm) and later in the infrared region (700–1100 nm). The UV transmittance of the sample C reaches more than 75% and

that of the sample H is more than 90%. In principle, the greater transparency of sample H in the UV region can be related to the higher concentration of nickel in the sample. In addition, as above mentioned, the sample H is thicker than that of the sample C. This can also be a possible reason for the observed 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].

Raman spectroscopy shown in Fig. 5 presents the normal vibration modes of the SO_4^{2-} ions. The observed 9 active modes in

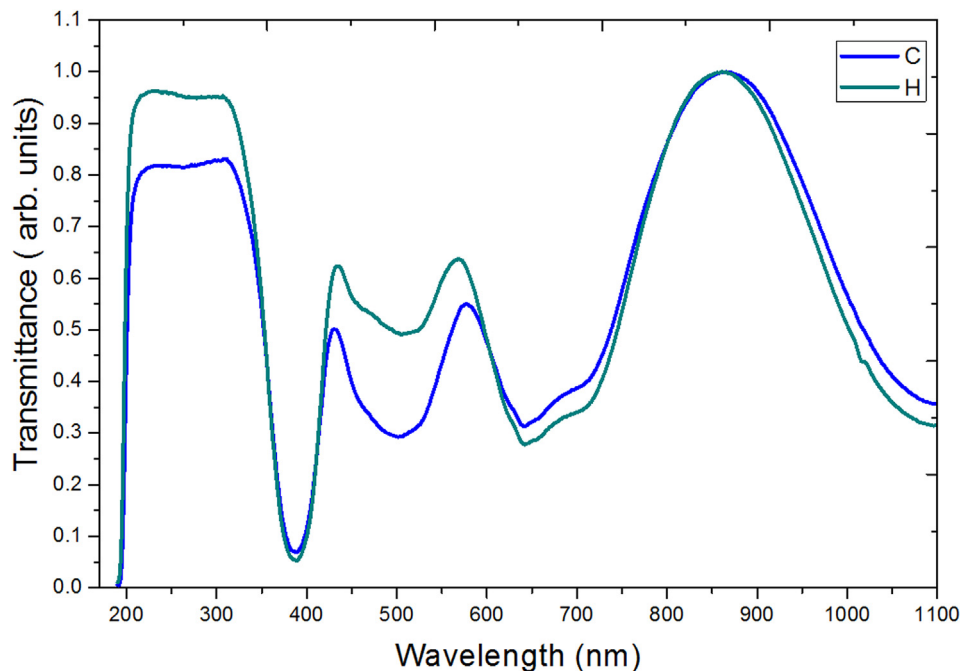


Fig. 4. Optical transmission spectra of the samples C and H.

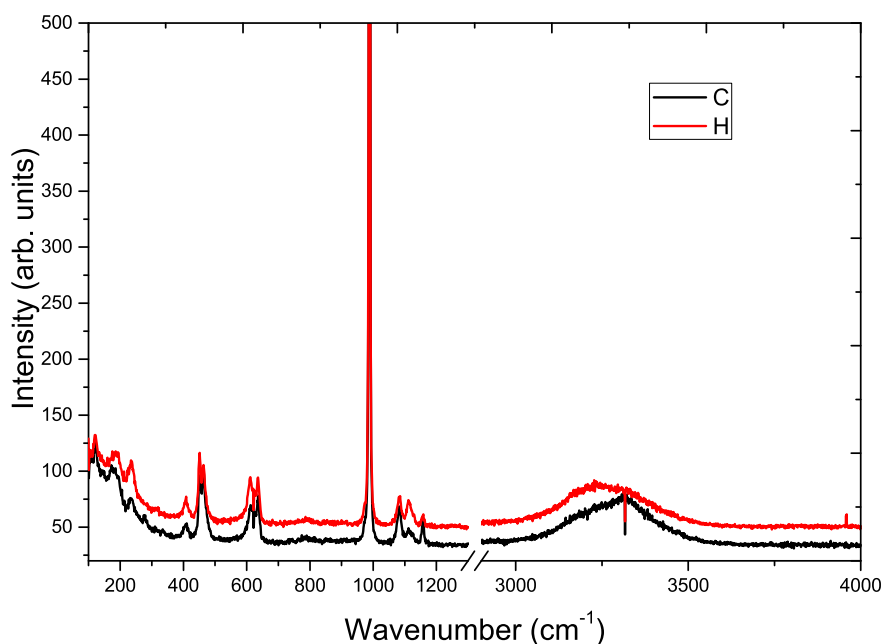


Fig. 5. Raman spectra of the samples C and H in the wavenumber range of 100–4000 cm^{-1} .

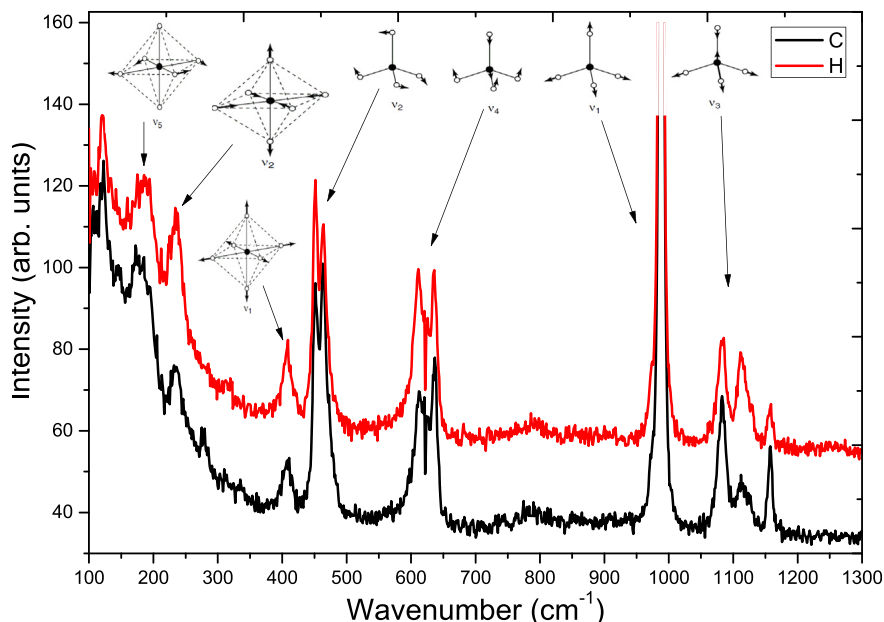


Fig. 6. Illustration of the normal vibration modes in the Raman spectra for SO_4^{2-} and $[\text{B}(\text{H}_2\text{O})_6]^{2+}$. B can be Ni or Co.

Raman spectroscopy, in which ν_1 , ν_2 , ν_3 and ν_4 have 1, 2, 4 and 2 normal modes of vibration, correspond well to symmetrical respiratory mode, symmetric deformation modes, anti-symmetric elongation modes and anti-symmetric deformation modes, respectively. The tetrahedral SO_4^{2-} is bonded with the ions $[\text{B}(\text{H}_2\text{O})_6]^{2+}$, by means of bonding type $\text{O}-\text{H} \cdots \text{O}$, and the potassium atoms are coordinated with the oxygen atoms of SO_4^{2-} [15].

The normal vibration modes of the SO_4^{2-} ions observed around ν_1 near 990 cm^{-1} ; ν_2 near 448 cm^{-1} and 462 cm^{-1} ; ν_3 near 1080 , 1111 , 1129 and 1156 cm^{-1} ; ν_4 near 614 and 632 cm^{-1} are shown in Fig. 6. In relation to the H_2O molecules, a broadband is obtained in the $3200\text{--}3400 \text{ cm}^{-1}$ region, where the overlapping of normal modes is observed in the spectra of the samples C and H. This relates to the $\text{O}-\text{H}$ interactions of the water molecules [22,23]. The complexes $[\text{B}(\text{H}_2\text{O})_6]^{2+}$ have the vibrational modes ν_1 , ν_2 and ν_5 active in Raman spectra. These vibrational modes shown in Fig. 6 locate in the region below 420 cm^{-1} (with ν_1 between 380 and 410 cm^{-1} , ν_2 between 237 and 267 cm^{-1} and ν_5 between 159 and 203 cm^{-1}). The region between 105 and 140 cm^{-1} is attributed to librations of SO_4^{2-} and H_2O molecules [23,24].

5. Conclusion

The mixed KCNSH crystals were successfully grown by the slow evaporation of the solvent. The obtained crystals are transparent and exhibit a good thermal stability. The bands of the vibrational modes of SO_4^{2-} , water and octahedron $[\text{B}(\text{H}_2\text{O})_6]^{2+}$ were identified by means of Raman spectroscopy for the samples under investigation. These mixed KCNSH crystals exhibit high (more than 80%) UV transmittance, which indicates their high structural quality and better optical properties. They can be used in optical filters.

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