Optical Materials 85 (2018) 425–437

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Growth and characterization of ammonium nickel-copper sulfate hexahydrate: A new crystal of Tutton's salt family for the application in solar-blind technology

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ARTICLE INFO

Keywords:
Solar-blind filters
Crystal growth
Hirshfeld surface
Thermogravimetric analysis
UV–Vis spectroscopy
Near-infrared spectroscopy

ABSTRACT

We have obtained the mixed crystals ammonium nickel-copper sulfate hexahydrate compounds which exhibits 98% transmittance in the ultraviolet region, a promising material for UV light filters and UV sensors for solar-blind technology. These crystals belong to the family of Tutton's salt having empirical formula $(NH_4)_2Ni_xCu_{(1\text{-}x)}(SO_4)_2.6H_2O$ and they were synthesized by employing growth from the slow evaporation of aqueous solution technique. The crystallographic parameters, three-dimensional Hirshfeld surface analysis and the calculation of two-dimensional fingerprint plots of the sample crystal $(NH_4)_2Cu(SO_4)_2.6H_2O$ were determined with the help of single crystal X-Ray diffraction. The X-ray powder diffraction of the pulverized samples were carried out at ambient temperature, 200 °C and 350 °C with the purpose to observe the change in the crystalline structure when subjected to higher temperatures. The thermal analysis of the samples was conducted in the temperature range 30–900 °C with the help of thermogravimetric analysis (TGA), which provides the information about the thermal stability and decomposition process during the heat treatment. Some of our sample crystals demonstrated high dehydration temperature up to 108 °C and they can be considered as an excellent candidate for UV light filters for high temperature applications. The direct and indirect band gaps of the samples were determined from UV–Vis spectra with the help of Tauc's equation. The overtones and combinations of fundamental vibrations of the functional groups our sample crystals were investigated by utilizing near-infrared spectroscopy in the wavelength range 830–2500 nm.

1. Introduction

The ultraviolet region from 200 to 300 nm wavelength range is solar-blind because it is strongly absorbed by the ozone layer in the upper atmosphere, as a result of that, the intensity of solar UV radiation in the solar-blind region near to the surface of the earth is almost zero. The utilization of certain kind of materials as UV light filters which provides full absorption in other subbands of the UV and visible region, offers a unique opportunity for the design of a whole new class of highly sophisticated devices for diagnostic equipment. Development of this type of technology was termed as "solar-blind" technology [1,2] and is widely used for the defense purposes. These types of devices are extensively used in the area of remote sensing as required for missions like aircraft protection, sniper shoot detection, modern missile approach warning system, terrorist attack surveillance, as well as in nuclear reactor. On the other hand, due to the man-made chemical activity there is a depletion in ozone layer [3], as a result we are suffering an interrelated impending health risks [4–7] by the increasing level of harmful UV radiation in our environment [8,9]. The solar-blind UV sensors can be used for UV inspection in everyday usable food products and the detection of UV radiation in hazardous industrial waste.

UV light filters exhibits maximum transmission in the ultraviolet region and strong absorption in all other wavelengths. Initially glass filters were used for UV light filters, since they are transparent in the wavelength range 300–500 nm, but this reduces the efficiency of the glass light filters used in the solar-blind devices based on the detection of UV radiation in the 200–300 nm spectral region. After that, various materials, such as aluminium gallium nitride (AlGaN) [10–13], silicon carbide (SiC) [13–16] and diamonds [17–19] have been used for the next-generation solar-blind photodetectors. In recent years it has been

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https://doi.org/10.1016/j.optmat.2018.09.004
Received 28 July 2018; Accepted 2 September 2018

observed that, the crystals of Tutton's salt can be used to locate and track the sources of ultraviolet light energy and can be used as a promising material for UV light filters [2,20] in solar blind technology.

The family of Tutton's salts are the isomorphic hydrated complexes crystalize in the monoclinic system with centrosymmetric space group $P2_1/c$ [Z = 2] [21,22], with empirical formula $M_2M'(SO_4)_2.6H_2O$ or $M_2M'(SeO_4)_2.6H_2O$, where M is an univalent cation which may be Cs^+, K+, NH_4^+, Rb^+, Tl^+ and M′ is a bivalent cation of the first transition series metals Co^{+2}, Cr^{+2}, Cu^{+2}, Fe^{+2}, Mn^{+2}, Ni^{+2}, V^{+2}, Zn^{+2}. The unit cell of Tutton's salt contains one or more octahedral hexahydrate complexes $[M'(H_2O)_6]^{2+}$ in the crystal unit cell where, M′ is situated at the inversion center and surrounded by six water molecules through a slightly distorted octahedral formed by the Jahn–Teller effect [23–26]. The Jahn-Teller effect is a geometric distortion; if the ground state electronic configuration of a non-linear complex is orbitally degenerate the complex will distort so as to remove the degeneracy and achieve a lower energy. This type of distortion is typically observed among octahedral complexes [27,28] where the two axial bonds can be shorter or longer than those of the equatorial bonds.

The low dehydration temperature and high hygroscopicity are the main drawbacks of the crystals of the Tutton's salt for the applications in solar blind filters. It has been observed that, nickel sulfate hexahydrate (NSH) crystals demonstrates same type of UV transmission characteristics as that of other Tutton's salt, but they also exhibit better thermal stability and higher dehydration temperature, which is suitable for UV light filters for high temperature applications. For the first time, α-nickel sulfate hexahydrate crystal (α-NSH) was studied for solar blind UV light filters [29]. There are some very important studies about the crystal growth, morphological and structural analysis, optical spectroscopy and vibrational spectroscopies of NSH crystals, such as, potassium cobalt nickel sulfate (KCNSH) [30–38], potassium nickel sulfate hexahydrate (KNSH) [39–41], cesium nickel sulfate hexahydrate (CNSH) [42], rubidium nickel sulfate hexahydrate (RNSH) [43,44], guanidine carbonate doped nickel sulfate hexahydrate [45], α-nickel sulfate hexahydrate (α-NSH) [29,46–49], potassium manganese nickel sulfate hexahydrate (KMNSH) [50,51], zinc nickel sulfate hexahydrate (ZNSH) [52], Zn (II) doped ammonium nickel sulfate hexahydrate [53], potassium zinc nickel sulfate hexahydrate (PZNSHH) [54], ammonium nickel sulfate hexahydrate (ANSH) [2,55–57], ammonium nickel cobalt sulfate hexahydrate (ACNSH) [58–61].

There is a considerable amount of studies of the crystals of copper Tutton's salt. Stoneham et al. [62] reported a calculation of the spin-lattice relaxation of Cu^{+2} in potassium zinc copper Tutton's salt on the basis of crystal field model. Breen et al. [63] and Hoffman et al. [64] investigated the spin-lattice relaxation of the octahedral complex of copper by using electron paramagnetic resonance (EPR) and electron-spin-echo (ESE) methods; Zhou et al. [65] used EPR spectroscopic measurements to determine the magnitude of the electron-electron exchange energy of Cu atoms in ammonium copper Tutton's salt. Bosi et al. [66] and Ballirano et al. [67,68] reported the structural features of Cu Tutton's salt, whereas Simmons et al. [69] reported high pressure and low temperature single crystal neutron diffraction study of deuterated and hydrogenous hexaaquacopper sulfate. Schultz et al. [70] reported the influence of pressure on the unit cell parameters of deuterated ammonium copper(II) sulfate hexahydrate at various temperatures from 50 to 325 K obtained from pulsed neutron powder diffraction. Cha et al. [71]investigated infrared hole burning of ammonium copper Tutton's salt with the help of tunneling kinetics and Jahn-Teller distortions. Soumati et al. [72] presented the growth, characterization and thermal analysis of potassium copper sulfate hexahydrate crystals. In addition, there are some computational studies also available, such as, Beagley et al. [73] performed *Ab initio* molecular orbital calculations on the free octahedral copper complex in D_{2h} symmetry, on the other hand Chandler et al. [74] calculated the structure factor by using ab initio quantum-mechanical calculations on individual isolated ions near to the Hartree-Fock limit in a deuterated copper Tutton's salt and compared their results with the neutron diffraction experiment performed at 9 K.

In the present article, we are reporting the crystal growth of ammonium nickel copper sulfate hexahydrate crystals by using growth from the aqueous solution by slow evaporation technique. The morphological and structural characterization of our sample crystals were carried out with the help of X-ray diffraction and thermogravimetric analysis. The optical spectroscopy of the samples has been investigated with the help of UV–Vis and near-infrared spectroscopy.

2. Materials and methods

There are different techniques available to grow the crystals of the Tutton's salt, such as, diffusion gel technique in silica hydro-gel media [53], Sankaranarayanan–Ramasamy (SR) method [47] and super-cooling and forced convection technique [75]. In our present work, sample crystals were obtained by employing conventional isothermal evaporation of aqueous solution crystal growth method. For the preparation of the solution reagents, ammonium sulfate were $(NH_4)_2SO_4$ fixed at 5 g, and the mass of the nickel sulfate $NiSO_4.6H_2O$ and the copper sulfate $Cu(SO_4)7H_2O$ were obtained from the stoichiometric ratio given by the empirical formula $(NH_4)_2Ni_xCu_{(1\text{-}x)}\ (SO_4)_2.6H_2O$.

$$(NH_4)_2SO_4 + Ni(SO_4)_6H_2\ O + Cu(SO_4)_7H_2\ O \rightleftarrows (NH_4)_2NixCu_{(1-x)}(SO_4)_{2}._6\ H_2\ O + \uparrow H_2O$$

The purity of nickel sulfate is 99%, whereas purity of ammonium sulfate and the copper sulfate is 98%. The quantities of the reagents were used in the crystal growth process is shown in the Table 1. To obtain the mixed ammonium nickel-copper sulfate hexahydrate (ANCUSH) crystals, we have varied the concentration of Cu(II) by 10%, 30%, 50%, 70% and 90%. In addition, we have also prepared the solution to obtain pure crystals of ammonium nickel sulfate hexahydrate (ANSH) and ammonium copper sulfate hexahydrate (ACUSH). The calculated masses of the reagents were placed in a beaker and then we have added approximately 100 ml deionized water (resistivity = 18.2 MΩ and pH = 7). The dilution of the reagents was occurred with the help of magnetic stirrer, where the temperature was varied from 60°C to 70 °C throughout the process. After dilution, the solution was filtered and then brought to a greenhouse where the temperature was maintained at 40 °C.

The single-crystal X-ray diffraction measurement for ammonium copper sulfate hexahydrate crystal ($(NH_4)_2Cu(SO_4)_2.6H_2O$) have been performed using a Supernova Agilent diffractometer with CCD detector through MoKα radiation at room temperature. The data collection, reduction, unit cell refinement, and absorption correction have been obtained by using Crysalis RED software (Oxford Diffraction Ltda, version 171.38.41) [76]. The structures have been solved and refined using the SHELX-14 program package [77] and the figures have been produced using Mercury 3.9 [78], ToposPro package [79,80] and CrystalEXplorer [81] softwares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms connected to oxygen were placed in idealized positions and treated with the rigid model. Hydrogen atoms from water molecules were directed by difference maps and refined

Table 1
The variation of nickel and copper compositions and the masses of $NiSO_4.6H_2O$ and $CuSO_4.7H_2O$ used in the preparation of the solutions.

Ni x (%)	$NiSO_4.6H_2O$ (g)	Cu (1-x) %	$CuSO_4.7H_2O$ (g)
100	9.9450	0	–
90	8.9520	10	0.9430
70	6.9740	30	2.8340
50	4.9746	50	4.7224
30	2.9850	70	6.6123
10	0.9940	90	8.5020
0	–	100	9.4475