

A New Hydrothermal Route to Prism-shaped $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ Single Crystals

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Prism-shaped $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals, with sizes of $0.64\text{--}0.77 \times 0.45\text{--}0.67 \times 0.26\text{--}0.33$ mm, were synthesized via a new hydrothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and Se powder in aqueous ammonia at 180°C . The double crystal X-ray diffraction rocking curve shows that the single crystals have high quality. And optimum conditions for the growth of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals are discussed.

In the past few years, the transition metal selenites afforded attractive perspective in the general area of solid-state physics and related technologies because of their novel structures and unusual physical properties.^{1,2} The crystal structure analysis of the studied transition metal selenites indicated the presence of hydrogen bonding between water molecules and oxygen atoms of the selenite group.³ The interaction of adjacent molecules by hydrogen bonding might provide a route for facilitating semiconductor. Copper selenite dihydrate, owing to its optical, electrical and magnetic properties, could be applied as anisotropic semiconductive coatings, photovoltage sources, or photoelectric devices.^{4,5} Therefore, bulk and perfect single crystals of copper selenite dihydrate were expected to be rewarding and were widely studied for several years.

Many methods have been adopted to prepare copper selenite dihydrate, including sol-gels⁶ and hydrothermal processes.^{5,7} Salib et al. prepared it by precipitation from copper acetate with selenium dioxide in hot glacial acetic acid (60°C),^{4,8,9} and obtained the product powders. Asai and co-worker hydrothermally synthesized the crystals with dimensions of $0.05 \times 0.08 \times 0.12$ mm.⁵ Robinson et al. obtained the crystals through sol-gels processes for a year,⁶ and dimensions of the crystals were $0.15 \times 0.10 \times 0.12$ mm. Here, we reported a new hydrothermal route to the single crystals of copper selenite dihydrate with sizes of $0.64\text{--}0.77 \times 0.45\text{--}0.67 \times 0.26\text{--}0.33$ mm based on the hydrothermal reaction in aqueous ammonia at 180°C for 3 days. Compared with the above-mentioned, this route can obtain the objective products with larger size for shorter time.

An appropriate amount of analytically pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and elemental selenium were added to a Teflon-lined autoclave with dilute aqueous ammonia ($\text{pH} = 11\text{--}12$) up to 90% of its capacity (85 mL). The autoclave was heated to 180°C in 60 min, and maintained at the temperature for 72 h. Then it was gradually cooled to room temperature at $1.0\text{--}2.0^\circ\text{C}/\text{h}$. The blue crystals on the inner wall were collected, and then washed several times with distilled water and absolute ethanol to remove impurities. The final products were dried in vacuum at 60°C for 4 h.

The phase and crystallographic structure of the products were determined by X-ray powder diffraction (XRD) with a Philips X'Pert X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The XRD patterns of the polycrystalline powders ground from single crystals are shown in Figure 1a. All the reflection peaks can be indexed to the orthorhombic chalcocomenite

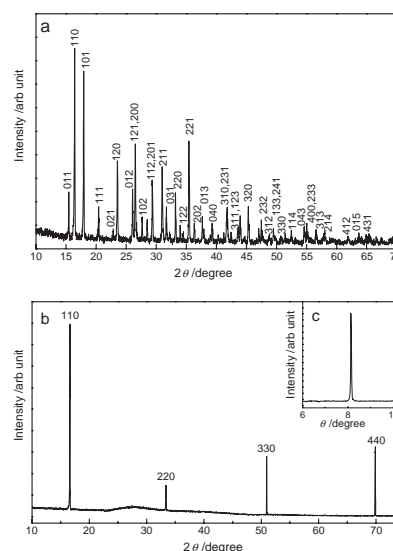


Figure 1. (a) XRD patterns of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ polycrystalline powders ground from single crystals. (b) XRD patterns of single crystals $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$. (c) Rocking curve of (110) reflection for single crystals $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$.

structured $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ with no impurities detected. The calculated cell constants, $a = 6.675$, $b = 9.193$, and $c = 7.394 \text{ \AA}$, are very close to the reported values ($a = 6.671$, $b = 9.193$, $c = 7.384 \text{ \AA}$, JCPDS Card No.17-523). Rocking curve of the (110) reflection for $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals was performed by XRD with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). The XRD patterns (Figure 1b) of prism-shaped single crystals $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ only exhibit four peaks at 16.6° , 33.4° , 50.9° , and 69.9° , which can be assigned to the orthorhombic 110, 220, 330, and 440 planes. The presence of a broad and weak peak between the (110) plane and (220) plane is due to the adsorbed water on the sample, which is proved by comparison with XRD patterns of water. The above results show that the (110) plane of the orthorhombic single crystals $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ parallels the shaft of the prism-shaped single crystals. And the double crystal X-ray diffraction rocking curve of the (110) reflection for $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals (Figure 1c), showing a single symmetrical peak at 8.135° with the FWHM (full width half maximum) of 0.04° , indicates that the products have high crystal quality and perfect orientation of the single crystal.

The morphology and size of the crystals were examined by scanning electronic microscopy (SEM), performed on an X-650 scanning electron microanalyzer. The SEM images of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals (Figure 2) show that the single crystals have prism-shaped morphology with dimensions of $0.64 \times 0.45 \times 0.33$ mm (Figure 2a) and $0.77 \times 0.67 \times 0.26$ mm (Figure 2b), respectively.

The FT-IR spectrum (Figure 3), recorded on a MAGNA-

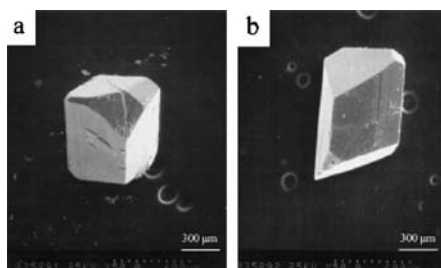


Figure 2. SEM images of single crystals $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$.

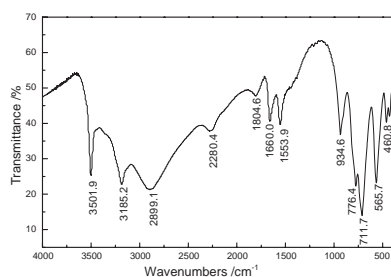
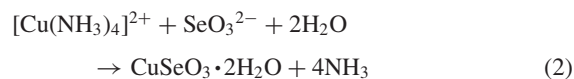
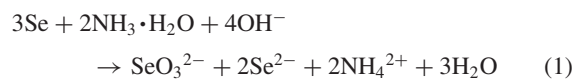


Figure 3. Infrared spectrum of the sample $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$.

IR750 spectrometer, is in good agreement with that reported in the literature.¹⁰ The two bands at 1553 and 1660 cm^{-1} are the O–H bending modes. The bands at 3501, 3185, and 2899 cm^{-1} suggest three distinct O–H stretching modes. The bands at 2899 and 2280 cm^{-1} indicate the presence of hydrogen bonding between water molecules and oxygen atoms of the selenite group.¹¹ Hydrogen-bonding formation presumes the possibility of transfer of a proton along the line of the hydrogen bonding, which may suggest the mechanism of proton conduction of hydrogen-bonded materials.¹² $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ exhibits semiconducting properties owing to the presence of hydrogen bonding, for the transfer of protons along the lines of the hydrogen bonds during dehydration is considered to be the main source participating in the conduction processes.⁴

In the hydrothermal process, $\text{NH}_3 \cdot \text{H}_2\text{O}$ acts as both alkali and ligand. In aqueous ammonia, elemental selenium disproportionates to Se^{2-} and SeO_3^{2-} , and NH_3 is coordinated to Cu^{2+} to form complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Thus, SeO_3^{2-} can combine steadily with Cu^{2+} , homogeneously released from $[\text{Cu}(\text{NH}_3)_4]^{2+}$, to produce $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals adhered to the wall of the Teflon-lined autoclave. Meanwhile, Se^{2-} is transformed into the precipitate CuSe_2 , which was identified by XRD patterns (not shown). These processes can be described by the following equations:



In addition, $\text{NH}_3 \cdot \text{H}_2\text{O}$ may be favorable to control of the crystalline morphologies under the hydrothermal conditions. When dilute aqueous ammonia was substituted with sodium hydroxide solution under the same conditions, only green amorphous CuSeO_3 was obtained, as confirmed by XRD patterns.

As reaction media $\text{NH}_3 \cdot \text{H}_2\text{O}$ possibly matches the nucleation and growth of nuclei, which is propitious for the growth of the prism-shaped $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals.

A pH range of 11–12 is optimal in the initial reaction system. Some impurities such as elemental Se were obtained at pH lower than 9 because the disproportionation of elemental selenium is restrained when the pH is lower (Eq 1). If the pH value is higher than 12, the obtained products were copper selenides, as proved by XRD analysis. From the above results, the pH of the reaction system is believed to be critical for the crystallization of products.

In our experiments, optimum condition for preparing $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals was 180 °C for 72 h. Lower temperature (<140 °C) or shorter time (<48 h) led to incomplete reaction with elemental selenium in the final products, as observed from the XRD. At reaction time longer than 72 h, the size of the crystal was not obviously enlarged. When the reaction temperature was elevated over 200 °C, the products were CuSe_2 powders rather than the desired $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals. A temperature of 140–180 °C is beneficial for the formation of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals under the hydrothermal conditions.

Prism-shaped $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ single crystals were successfully synthesized via a new hydrothermal method using aqueous ammonia as reaction media at 180 °C and characterized by various techniques. The double crystal X-ray diffraction rocking curve shows that the single crystals have high quality. The reaction media, reaction temperature and time, and pH values have influence on the formation of the single crystals. This method may be convenient and is expected to be applicable for preparation of other selenite single crystals. However, growth of inorganic bulk single crystals by this technique needs further study.

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