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Unidirectional growth of $CoNi(SO_4)_2.12H_2O$ single crystal by Sankaranarayanan–Ramasamy (SR) method

S. Karvar, H. Rezagholipour Dizaji*

Crystal Growth Lab., Physics Department, Semnan University, Semnan-35195-363, I. R. Iran

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Large cylindrical [010] cobalt nickel sulfate twelvehydrate (CNSH) crystal with 18 mm diameter and 150 mm length was grown from an aqueous solution by Sankaranarayanan–Ramasamy (SR) method. The grown crystal was examined by X-ray diffraction, UV-Vis spectroscopy and TGA/DTA analysis methods. The grown crystal was found to possess high transmission efficiency in UV region and high absorption in the other regions introducing it as a good candidate for use as UV band-pass filter. The grown crystal showed dehydration temperature higher than that of commercially available nickel sulfate hexahydrate (NSH) crystal.

Key words: Growth from solution, Transmission, X-ray diffraction, UV filter, Thermogravimetric analysis

INTRODUCTION

Crystalline materials having narrowband transitive in particular wavelength region and strongly absorptive over all others are usually used in band-pass filters. Generally, most optical crystals have continual optical transmission characteristics in the range from UV to near IR wavelengths. There are few exceptional crystals in this sense. Those crystals showing discontinue in the UV to near IR wavelengths region can be used as optical filter in UV region.

Nickel sulfate hexahydrate (NSH) crystal is a well-known UV band pass filter crystal having high transmission efficiency over a narrowband at 250-340 nm, moderate transmission at 450-600 nm, and strong absorption over all other wavelengths [1].

The ultraviolet light filters and UV sensors of NSH crystals are already commercially available [2]. However it has some drawbacks among which the most important one is its low dehydration temperature [73 ºC]. This parameter is very important when considering an optical system employed to detect the UV signal characterizing the jet engine of a missile to operate at various climate conditions, including those associated with elevated temperatures, which might be experienced in the desert. Also, temperature of 85 ºC or higher and low relative humidity conditions can be reached when aboard an aircraft, armored vehicle or a ship, as a combined result of both solar heating and engine-generated heat. Thus, the crystal should have not only proper spectral transmission but thermal stability. Accordingly, it is desirable to provide a crystal having optical properties similar to that of NSH but having greater thermal stability. Therefore, other NSH – based compounds such as cobalt nickel sulfate twelvehydrate (CNSH)[2], iron nickel sulfate twelvehydrate (FNSH)[3], potassium nickel sulfate hexahydrate (KNSH)[4], rubidium nickel sulfate hexahydrate (RNSH)[5], ammonium cobalt nickel sulfate hexahydrate (ACNSH)[6], potassium cobalt nickel sulfate hexahydrate (KCNSH)[7], and potassium manganese nickel sulfate hexahydrate (KMNSH)[8] were grown possessing dehydration temperature higher than that of NSH crystal.

Crystals of cobalt nickel sulfate twelvehydrate $CoNi(SO_4)_2.12H_2O$ (CNSH) belong to the monoclinic system with the space group C2/c and crystal lattice parameters a=9.996(Å), b=7.2265(Å), c=24.218(Å) and β=98.32(3)º [2].

In the present investigation, CNSH crystal has been grown in the [010] direction using a novel technique called Sankaranarayanan-Ramasamy (SR) method [9]. The main advantages of this technique over conventional solution growth method employed by Su et al to grow CNSH crystal [2] are the ability to grow a crystal unidirectionally as well as to convert solution to crystal with 100% efficiency. The grown crystal was subjected to X-ray diffraction, UV-Vis and TGA/DTA analysis.

EXPERIMENTAL

Experimental set-up

The SR set-up for crystal growth shown in Fig. 1 consists of two ring heaters positioned at the top and bottom of the growth ampoule each connected to a temperature controller maintaining constant temperature.

* To whom all correspondence should be sent:

E-mail: hrezhgholipour@semnan.ac.ir

The entire SR set-up is placed in a water bath in order to avoid temperature fluctuations during the growth process. The top heater provides the necessary temperature for solvent evaporation, while the bottom one is used to maintain the solid-liquid interface at the saturation temperature. It is moved upwards depending on the growth rate of the crystal.

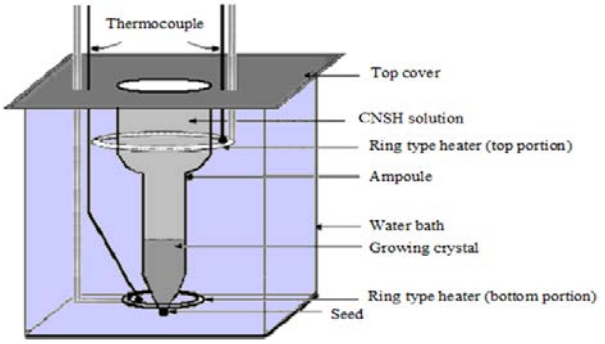

Fig. 1. SR growth set-up

Crystal growth

The equal molar proportion $CoSO_4.7H_2O$ and $NiSO_4.6H_2O$ powders of 98% purity were dissolved in twice distilled water. The saturated CNSH solution was prepared at room temperature (27 °C) and filtered using a membrane filter of 0.45μm porosity at the same temperature.

The vessel containing the prepared solution was placed in a constant temperature bath set at saturation temperature and left for several days in order to obtain seed crystal through solvent evaporation. After 14 days, brown transparent CNSH crystal grew. A disk shape seed with 4 mm thick and 5 mm diameter was cut from the already grown crystal and mounted at the bottom of the ampoule. The plane was so fitted not to allow other faces to grow. The ampoule was filled with saturated solution of CNSH at 27 °C.

The temperature of the bottom and top portions was set as 27 °C and 29 °C respectively. Gradual evaporation of the solvent from the top portion of the solution caused the seed to grow. After 40 days, cylindrical shape CNSH crystal of 150 mm height and 18 mm diameter was grown which is shown in Fig. 2.

Fig. 2. CNSH cylindrical crystal (a) after removing from ampoule and (b) Cut and polished piece.

RESULTS AND DISCUSSION

The physical phase and structure of the product was confirmed by X-ray diffraction (XRD) analysis using an X-ray diffractometer with intensity Cukα radiation (λ=1.5406 Å). The grown crystal was ground and pestle in order to determine the crystal phases by XRD. Figure 3 shows the X-ray diffraction pattern of CNSH grown crystal. According to the results obtained from XRD data, the CNSH crystal belongs to the monoclinic space group C2/c and lattice parameters of a = 9.97 Å, b = 7.24 Å, c = 24.23 Å, β = 98.34°, V = 1729.78 $Å^3$.

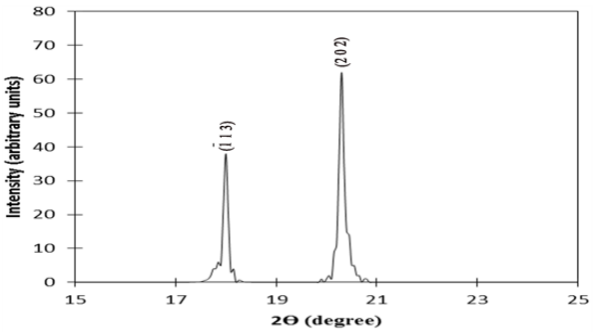

Fig. 3. X-ray diffraction pattern of CNSH crystal.

Figure 4 represents the optical transmission of 2mm thick CNSH crystal obtained in UV-Vis spectrophotometer (Model UV-1650 PC) with performing wavelength ranged from 190 to 1100 nm. The grown crystal has two sharp transmission bands centered at 292.5 and 496.5 nm. Transmission efficiency at 292.5 nm is about 77.44% which is higher than the reported value [2]. It is also observed that the other wavelengths are strongly absorbed. This transmission behavior is the characteristics of a UV band pass filter.

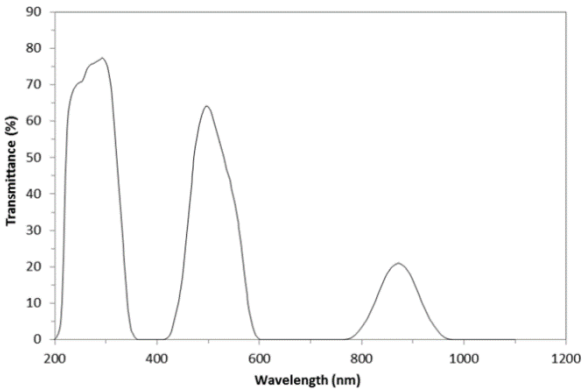

Fig. 4. Transmission spectrum of the CNSH crystal.

The thermo-gravimetric analysis on freshly grown CNSH crystal was performed by using Perkin-Elmer diamond TGA/DTA instrument in air atmosphere. It is observed from TGA/DTA curve shown in Fig. 5 that the dehydration temperature of

CNSH crystal is about 85.25 °C which is higher than that of NSH crystal and nearly the same as reported by Su et al [2].

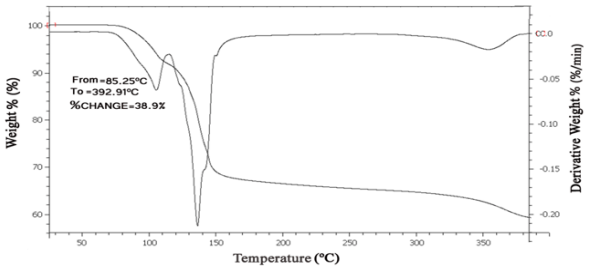

Fig. 5. Thermo-gravimetric and differential thermal analysis curves of CNSH crystal.

CONCLUSIONS

CNSH single crystal in cylindrical shape with 18 mm diameter and 150 mm length was grown by SR method. The XRD analysis proved good crystalinity of the grown crystal. Optical transmission spectrum of this crystal showed its high transmission efficiency at UV region and high absorption in the other regions making it suitable for use as UV band-pass filter. The transmission of the CNSH crystal grown by SR method was found to be slightly higher than that grown by conventional solution technique. Thermal analysis of the grown crystal revealed its dehydration temperature of 85.25 °C, well higher than that of NSH crystal.

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ЕДНОПОСОЧЕН РАСТЕЖ НА ЕДИНИЧЕН МОНОКРИСТАЛ ОТ $CoNi(SO_4)_2.12H_2O$ ПО МЕТОДА НА Sankaranarayanan–Ramasamy (SR)

С. Карвар, Х. Резаголипур Дизаджи*

Лаборатория по кристален растеж, Департамент по физика, Университет в Семнан, Семнан -35195-363, И.Р. Иран

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(Резюме)

Израстван е голям цилиндричен кристал [010] от кобалто-никелов сулфат додекахидрат (CNSH) с диаметър 18 mm и дължина 150 mm length из водна среда по метода на Sankaranarayanan–Ramasamy (SR). Полученият кристал е изследван с рентгено-структурен анализ, UV-Vis спектроскопия и TGA/DTA-анализ. Полученият кристал притежава голяма предавателна ефективност в UV-областта и висока абсорбция за останалите дължини на вълната. Затова тези кристали са добър кандидат за филтри на UV-вълни. Полученият кристал показва по-висока температура на дехидратиране отколкото на комерсиално достъпния никелов сулфат-хексахидрат (NSH).