

Low temperature luminescence and scintillation characteristics of SrWO₄ crystal



Hua Jiang^a, Gul Rooh^{b,c}, H.J. Kim^{c,*}, J.M. Lee^a, Y.J. Lee^a, Wansong Zhang^d, Sunghwan Kim^e

^a Department of Engineering Physics, Tsinghua University, Beijing 100084, China

^b Department of Physics, Abdul Wali Khan University, Mardan 23200, Pakistan

^c Department of Physics, Kyungpook National University, Daegu 702-701, Republic of Korea

^d College of Science, China University of Petroleum, Beijing 102249, China

^e Department of Radiological Science, Cheongju University, Cheongju 360-764, Republic of Korea

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ABSTRACT

We have successfully grown a SrWO₄ single crystal using the Czochralski pulling method. X-ray diffraction (XRD) showed a single phase of the grown crystal. Luminescence spectrum under X-ray excitation of a bulk SrWO₄ single crystal showed a broad emission band from 300 to 700 nm at room temperature. The decay time spectrum contained two components of 2.6 ns (5.7%) and 522 ns (94.3%) at room temperature. A change in the light yield and decay time is observed between 10 and 300 K. The luminescence yield of SrWO₄ at 125 K is found to be 8 times higher than at room temperature. The decay time gets longer by a factor of 51 as the temperature decreases down to 10 K.

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1. Introduction

In recent years, the divalent metal tungstates have attracted a great deal of interest due to their potential applications in photo-luminescence, solid state optical masers, optical fibers, scintillating materials, humidity sensors, and so on [1–6]. Moreover they are the first-chosen materials for some applications under some extreme environments, since they maintain their tetragonal structure over a wide range of temperatures and pressures. The luminescence properties of these materials were intensively investigated during the past half century. SrWO₄ has attracted particular attention due to its potential applications; for example, it can be used as a laser host material in quantum electronics and scintillators in medical applications. SrWO₄ exhibits a scheelite-type tetragonal structure with WO₄^{2−} molecular ions loosely bound to Sr²⁺ cation [7]. The space group of SrWO₄ is C_{4h}⁶ (I4₁/a) with four formula units per tetragonal cell, with *a*=5.40 Å and *c*=11.90 Å. Its luminescent properties are mainly connected with charge-transfer transitions within the WO₄^{2−} complex [8]. Films and powders of SrWO₄ have been prepared by different methods, such as pulsed-laser deposition [9], novel electrochemical method [10], and co-precipitation technique [11]. In the novel electrochemical method, AMO₄ (A=Ca, Sr, Ba; M=Mo, W) films are prepared using the energy supplied in

the forms of currents or potentials by an electrochemical apparatus. In the co-precipitation technique, 5 × 10^{−3} mol of tungstic acid (H₂WO₄), 5 × 10^{−3} mol of strontium acetate [(CH₃CO₂)₂Sr] and 0.1 g of polyethylene glycol are dissolved in 75 mL of deionized water. As a result, SrWO₄ powders are precipitated.

In addition, reports have been published by various authors related to the growth of pure and rare-earth-doped SrWO₄ crystals [12–17]. The optical transmission spectrum of pure SrWO₄ crystal was studied by Jia et al. [14] and luminescence excitation spectra were measured in a wide temperature range by Nikl et al. [18]. To the best of our knowledge, the luminescence properties under laser excitation down to a temperature of a few degrees Kelvin of SrWO₄ single crystals have not yet been studied.

In the present paper, we report on the luminescence properties of SrWO₄ single crystal grown by the Czochralski technique. X-ray diffraction is used to verify the crystallographic structure of the grown crystal. Luminescence properties include the measurements of X-ray induced emission at room temperature, and laser induced emission down to 10 K. Energy resolution, light yield and decay time measurements are performed between 10 and 300 K.

2. Experimental procedure

High purity powders of SrCO₃ (99.99%, Alfa Aesar) and WO₃ (99.998%, Alfa Aesar) are used as starting materials for the crystal

* Corresponding author. Tel.: +82 53 950 5323; fax: +82 53 956 1739.

E-mail address: hongjoo@knu.ac.kr (H.J. Kim).

growth of SrWO_4 . The raw materials are weighed in an argon-filled glove box according to the reaction



The weighed powders are thoroughly mixed using a ceramic ball at a grinding speed of 120 rpm for 20 h. After mixing, the raw material is loaded into a platinum crucible and placed in a furnace for sintering at 900 °C for 20 h. After sintering, the polycrystalline powder of SrWO_4 is transferred to an iridium crucible (25 mm in diameter and 25 mm in height) for the growth of SrWO_4 single crystal. The whole powder is melted around 1520 °C. A SrWO_4 seed crystal with an arbitrary crystallographic direction is slowly lowered, and the tip of the seed is dipped a few millimeters into the melt. During the growth, the pulling and rotation rates are kept constant at 1 mm/h and 6 rpm, respectively. The growing crystal diameter is controlled by changing the melt temperature. The thermal gradient in the crucible is about 1–3 °C/mm. From the melt, we have successfully pulled a single crystal up to 15 mm in length and 10 mm in the diameter. To eliminate cracks in the crystal, the grown crystal is cooled down to room temperature at a rate of ~ 20 °C/h. However, a few cracks appeared in the ingot. Dark greenish color appearing at the bottom of the grown samples might be due to unspecified impurities. A package of as-grown samples of SrWO_4 single crystals is shown in Fig. 1. Finally, we have successfully obtained a sample of $5 \times 5 \times 8 \text{ mm}^3$ dimensions from the ingot.

The crystal structure of the grown crystal is determined by X-ray diffraction (XRD), using a Philips XPERT-MED X-ray diffractometer, where Cu K α is used as an incident X-ray. The X-ray tube was operated at 40 kV and 30 mA. For the XRD measurement, a little section of the grown sample was hand-milled in an agate mortar at room temperature. The XRD analysis is carried out in a 2θ range from 10° to 80° at a scanning rate of 1.2°/min. An X-ray tube from a DRGEM Co. having a W anode and a power setting of 90 kV and 1 mA is used to excite the sample crystal at room temperature. The X-ray induced luminescence spectrum is measured by using an Ocean-Optic model QE65000 fiber optic spectrometer. A 266 nm UV solid state laser system: MPL-F-266 made by Changchun New Industries (CNI) Co., is used to study the low temperature luminescence. The laser pulse energy was maintained constant at about 4.13 μJ , and the pulse duration was about 10 ns. A sample of SrWO_4 crystal is mounted onto a copper cold finger. A quartz tube is used as a light guide, and spectra are obtained and analyzed by the QE65000 fiber optic spectrometer. The decay time of the SrWO_4 crystal luminescence at room temperature is obtained by the coincidence method using a ^{60}Co source whose decay includes two mutually coincident gamma rays (1173 keV and 1332 keV). Two Hamamatsu H6610 photomultipliers are coupled to lutecium

yttrium silicon oxide (LYSO) and SrWO_4 single crystals. Each photomultiplier is connected to a 400-MHz flash analog-to-digital converter (FADC). The ^{60}Co source is placed at the middle of the PMTs attached with the LYSO and SrWO_4 crystals, and the LYSO crystal is chosen as a time reference detector. The decay time of SrWO_4 crystal is recorded with coincidence timing in the reference LYSO crystal. Data is recorded by coincidence trigger logic of the two pulses input. We have directly registered many pulses of the PMT output to the 400-MHz FADC and calculated the decay time spectrum by using average of the recorded pulse shape information.

We measured the temperature dependence of the emission light yield and its mean decay time in the SrWO_4 crystal down to 10 K under the γ -ray excitation from a ^{137}Cs source with emission photon energy of 662 keV. The experimental setup used for the measurement of the low temperature luminescence properties can be found in Ref. [19]. Fig. 2 shows the experimental setup used for the measurement of the low temperature luminescence properties. A sample of SrWO_4 crystal is mounted onto a copper cold finger with four faces of the crystal covered by several layers of 0.1 mm thick Teflon using a quartz tube as a light guide, where its one end is coupled with the entrance window of the PMT and the other is positioned at the top face of the crystal. The whole assembly is wrapped with several layers of Teflon followed by black tape to make a firm attachment of the light guide to the sample crystal during the measurements.

3. Results and discussion

The X-ray diffraction (XRD) pattern of the SrWO_4 single crystal powder is shown in Fig. 3. The XRD pattern shows that the SrWO_4

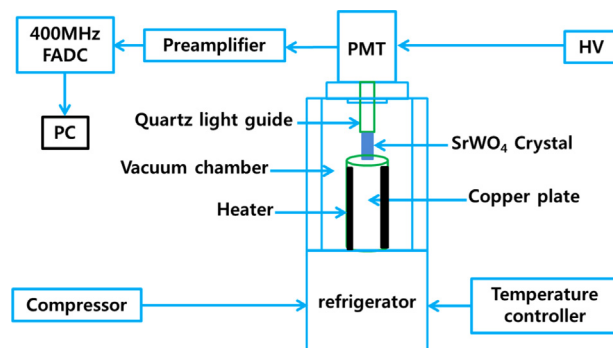


Fig. 2. Schematic representation of the low temperature measurements of luminescence decay time and light emission yield. PC is personal computer. FADC is flash analog-to-digital converter. PMT is the photomultiplier tube. HV is high voltage.

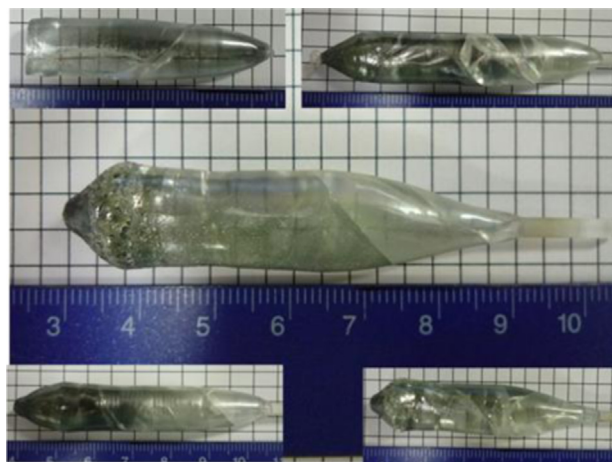


Fig. 1. The grown samples of SrWO_4 single crystal.

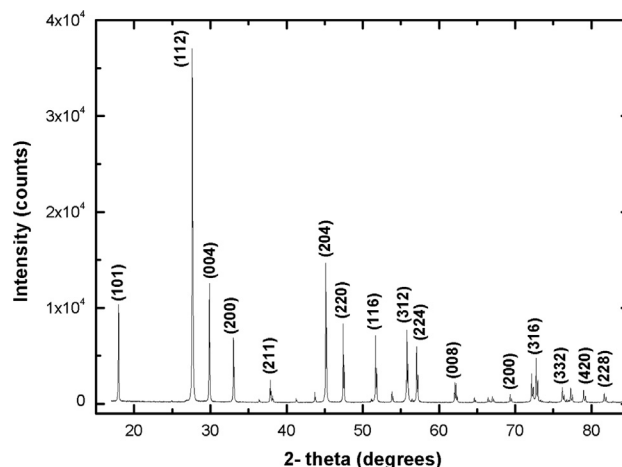


Fig. 3. X-ray diffraction pattern (XRD) of the SrWO_4 single crystal powder.

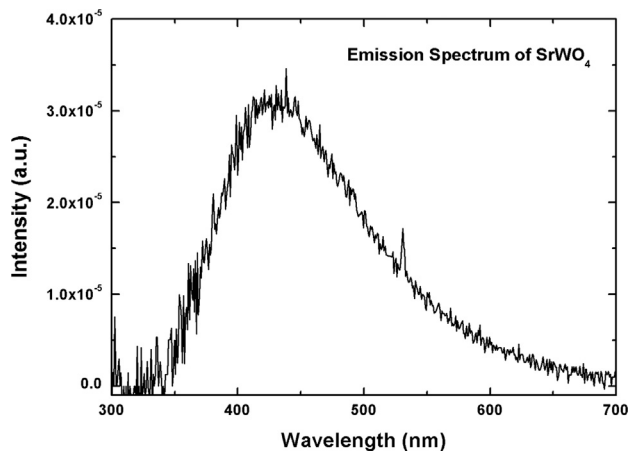


Fig. 4. Luminescence emission spectrum of SrWO₄ crystal at room temperature excited by X-rays.

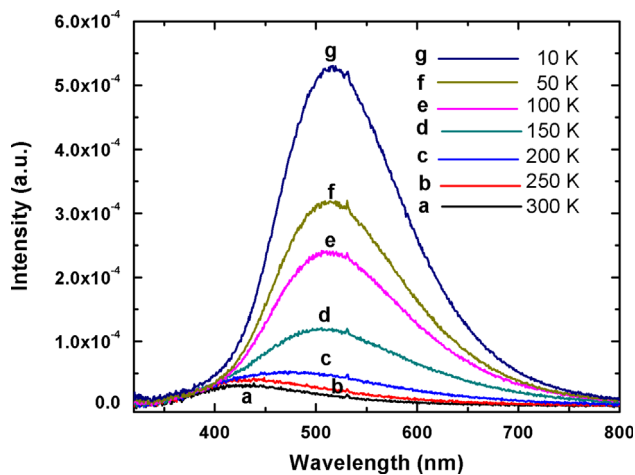


Fig. 5. Laser induced emission spectrum of SrWO₄ crystal at different temperatures.

single crystal has a tetragonal structure. The unit cell parameters obtained from the XRD data are $a=5.40$ Å and $c=11.93$ Å. These values are in agreement with the published result [14,17].

Measured X-ray induced emission spectrum of SrWO₄ single crystal is shown in Fig. 4. The spectrum consists of a broad wavelength band ranging from 300 nm to 700 nm and peaking at 430 nm.

The laser induced luminescence spectra of SrWO₄ single crystal at different temperatures are shown in Fig. 5. When the temperature decreases from 300 K to 150 K the spectral shapes show significant change, and the maximum emission peak position is shifted to a longer wavelength (from 430 nm to 510 nm), as shown in Fig. 5. This shift ends up at 150 K, but the peak intensity increases with further cooling to 10 K. Very similar observations are reported with PbWO₄ and BaWO₄ in a similar temperature range [18] and assigned to the excitonic luminescence and is due to the radiative transition with tetrahedral (WO₄)²⁻ group where the exciton is autolocalized. Therefore, we also attributed our observations to the explanation given in Ref. [18]. The possible reason of the weak peak intensity of SrWO₄ emission at high temperature (300 K) might be due to the low probability of the formation of exciton due to the higher energies of electrons and holes produced after getting laser excitation. The produced electrons and holes after thermalization formed excitons. When the temperature is lowered from 300 to 10 K the probability of bonding of isolated electrons and holes to an exciton increases, which subsequently increases the emission peak intensity, since

the mean free path of electrons and holes in the lattice matrix decreases and the effective radius of the recombination sphere increases with the decrease of temperature [20,21]. The emission peak around 510 nm at 10 K is consistent with the observation of Nikl et al. [18] at 5 K. However, we do not observe a narrower central peak surrounded by two shoulders under X-ray and laser excitations as reported in Ref. [18].

The pulse height spectra of the SrWO₄ crystal irradiated with 662-keV γ -rays from ¹³⁷Cs source at room temperature are shown in Fig. 6. Due to the smaller sample size of SrWO₄ ($5 \times 5 \times 8$ cm³) used in this study, the intensity (counts in the lower channel numbers) of the Compton scattering is higher than that of the 662 keV photopeak. The recorded photo-peak is fitted to a Gaussian function to evaluate the peak position and full-width at half maximum (FWHM) to obtain the energy resolution. The energy resolution measured at 662 keV is 29% (FWHM).

Fig. 7 shows the decay time curve of the SrWO₄ single crystal under ⁶⁰Co γ -ray (with energy of 1173 keV and 1332 keV)

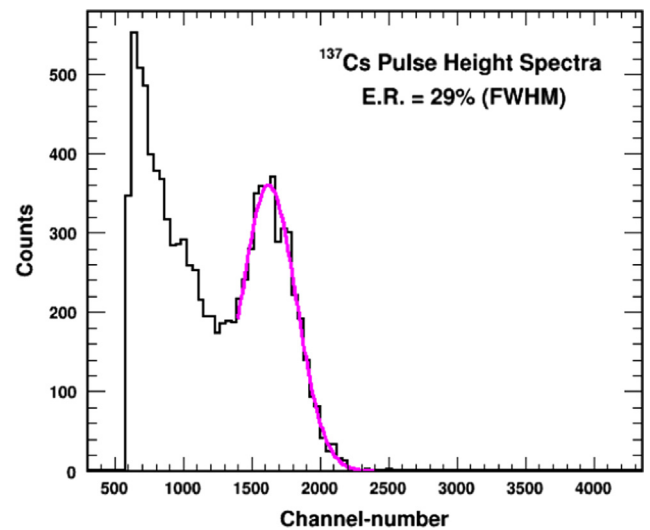


Fig. 6. Pulse height spectrum of the SrWO₄ crystal excited with 662 keV γ -rays from a ¹³⁷Cs source at room temperature. The photon peak is fitted to a Gaussian fitting. E.R. is energy resolution.

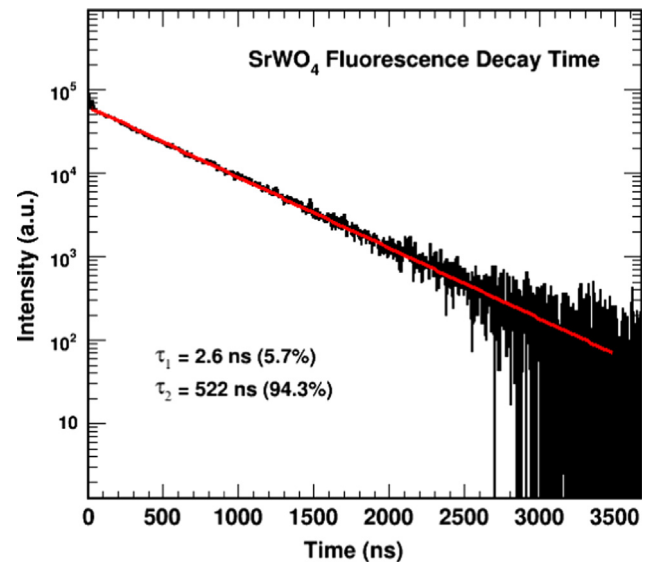


Fig. 7. Luminescence intensity vs. time at room temperature with 1173 keV and 1332 keV ⁶⁰Co γ -rays. The solid line drawn through the data shows the best fit to the data.

excitation at room temperature. The decay time curve is characterized by two exponential decay time components. The short and long decay time constants are obtained as 2.6 ns and 522 ns with 5.7% and 94.3% relative light yield intensities, respectively. The origin of the fast component is unknown, therefore further investigation is mandatory for the in depth study of the scintillation mechanism responsible for this component.

Fig. 8 shows the temperature dependence of the light response of SrWO₄ measured between 10 and 300 K by 662 keV γ -ray excitation. At first, decreasing the sample temperature from 300 to 125 K shows a steep increase of the light output. Below 100 K the light output has almost remained constant. A similar trend at low temperature is also reported in BGO which is attributed to the lesser thermal quenching [22]. The total light output of the SrWO₄ increases by a factor of ~ 8 from 300 K to 10 K and a maximum light yield is obtained at 125 K.

Mean decay time of SrWO₄ crystal is shown in Fig. 9. The following relation is used for calculation of the mean decay time of SrWO₄ crystal.

$$\langle \tau \rangle = \frac{\sum A_i t_i}{\sum A_i} \quad (2)$$

where t_i is the time when amplitude $A_i y_i$ is recorded by the FADC. From Fig. 9, it is clear that the value of luminescence decay time gradually increases with the decrease in temperature from 300 to

10 K. The mean luminescence decay time of the SrWO₄ crystal at 10 K is about 25.28 μ s. This is 51 times longer than the mean decay time value obtained at 300 K. The observed lengthening of decay time with the decrease of temperature reveals that non-radiative decay is a dominant process at low temperatures, since other tungstate and molybdates show similar behavior at low temperatures [23].

4. Conclusions

SrWO₄ single crystal is successfully grown by the Czochralski method. A broad luminescence emission band spanning from 300 to 700 nm is observed by X-ray excitation at room temperature. With laser excitation the peak intensity increased while its position shifted from 430 nm to 510 nm as the temperature decreased down to 10 K. Energy resolution of SrWO₄ crystal at 662 keV is obtained to be 29% (FWHM) at room temperature. With γ -ray excitation the luminescence decay curve of SrWO₄ shows two decay time components. Light yield increased while the mean decay of the sample crystal got slower with the decreased of temperature down to 10 K. The light emission yield increased roughly by a factor of 8 between 300 K and 10 K and 51 times longer mean decay time was observed in the same temperature range. Further investigations are underway to measure the luminescence quantum efficiency under different excitation processes and to improve the crystal quality of SrWO₄.

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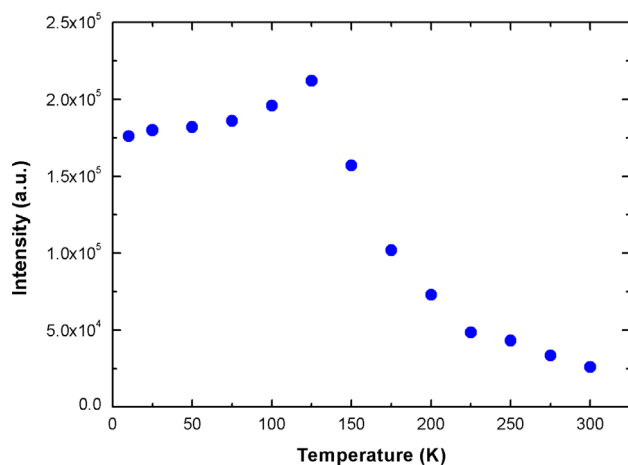


Fig. 8. Temperature dependence of the luminescence light yield of SrWO₄ single crystal.

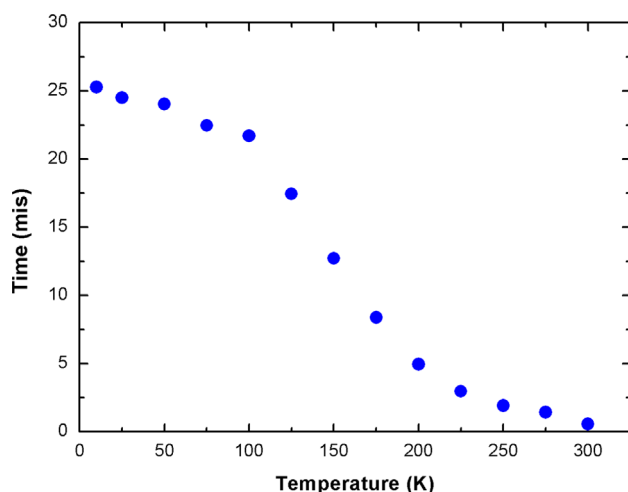


Fig. 9. Temperature dependence of the mean decay time of SrWO₄ single crystal.