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# Studies on triboluminescence emission characteristics of various kinds of bulk ZnS crystals

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ABSTRACT

ZnS crystal, as a semiconductor material with wide band gaps, has been investigated for a long time, due to its wide applications in many fields, like electroluminescence devices, photodiodes, functional nanomaterials, optical thin films and so on. Understanding the luminescence mechanisms of ZnS is of fundamental importance since many methods were used on the exploration of luminescence properties of ZnS. Up to now, triboluminescence properties of undoped ZnS crystals are rarely reported. Thus, we explored the luminescence emission characteristics of ZnS crystals based on triboluminescence method, and the results reveal that multi spectra and hot pressed ZnS crystals presented different fluorescence peaks at 420 nm and 475 nm respectively. This phenomenon may be due to the structural differences between different kinds of ZnS crystals, and it provides a new perspective for the study of luminescence properties of ZnS material.

**Contents**

## 1. Introduction

Luminescence of solid materials with wide band gaps has been investigated for a long time [1] because these measurements yield information about the energetic positions of the electronic states in the gap [2]. ZnS, as an important luminescence material with a wide band gap [3], widely used in flat panel displays, infrared windows, sensors, optical thin films for anti-reflection [4] and so on, appears to have been investigated more than any other phosphor [5]. In addition, many works have been carried out to explore the luminescence properties of ZnS crystals, with various experimental methods: photoluminescence (PL) [6], thermoluminescence [7], electroluminescence [8], optical absorption (OA) [9] and so on. In spite of this, the processes involved in luminescence are still not very clear.

Many of the previous works are focused on the photoluminescence properties of ZnS. In 1983, researchers discovered that

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ZnS presented three distinct photoluminescence bands, of which two blue emissions (BL1, 428 nm, BL2, 418 nm) are attributed to sulfur vacancy and interstitial sulfur lattice defects, respectively [10]. Scocioreanu et al. [11] investigated photoluminescence evidence for mechanico-chemical interaction of a polyaniline-emeraldine base with ZnS in cubic and hexagonal phase. The results revealed that the charge collection processes occurred in the composite materials. In recent years, luminescence in blue (450 nm) and green (530 nm) has been found in ZnS ceramics due to the formation of zinc vacancies and sulfur interstitials [12]. Apart from photoluminescence, many other methods have also been used to explore the luminescence properties of ZnS crystals. Grasser et al. [13] explored thermoluminescence properties of ZnS, and the results showed that the emission bands of luminescence were at about 475, 580 and 620 nm respectively. In terms of electroluminescence properties, emission of ZnS crystals was caused by ionization of luminescent centers in a barrier region [8]. Over the past years, although the luminescence properties of ZnS have been widely investigated, the influences of micro structural changes of ZnS crystal on the luminescence properties are rarely reported.

Triboluminescence(TL), the emission of light caused by solid materials subjecting to mechanical stress [14], may show evidences of microscopic characteristics of solid materials. In recent years, some researchers have investigated luminescence properties of doped ZnS materials by triboluminescence method. TL may be classified into two different categories: the luminescence caused by gas discharges, and fluorescence or phosphorescence from solid material itself [15]. Sweeting et al. [16,17] investigated the crystal structures and triboluminescence of 9-anthryl carbinols and anthracenecarboxylic acid, while asymmetric and non-centrosymmetric crystals showed different TL properties. In the past few years, Hollerman et al. [18] have done a lot of researches on luminescence properties of ZnS:Mn. An experimental apparatus was developed to measure the TL emission spectrum from ZnS:Mn generated during impact velocity 410 m/s, while the TL emission wavelength was found to be 586 nm. Their work indicated that the annealing temperature of ZnS:Mn affected the TL emission intensity [19]. In 2016, Fontenot et al. [20] explored the triboluminescence properties of ZnS:Mn encapsulated elastomer, and TL emission from impact scales with phosphor concentration was not affected by the encapsulating medium. The effects of micro structure on TL have not been completely researched. In addition, the existing TL work was focused on doped ZnS materials.

The luminescence properties of undoped ZnS still need much further researches. In the 1950 s, Researchers at Kodak developed a powder hot pressed (HP) version of ZnS, which was enhanced by Raytheon with a chemical deposited (CVD) version [4,12]. These two versions of ZnS have different transmission ranges and defect content [21]. Due to the light transmittance difference, CVD ZnS crystals have been divided into multi spectral and single spectral ZnS. For the low absorption and scatter properties over its broad transmission of multi spectral ZnS, the single spectral is rarely used as an infrared window material [4]. In this work, the luminescence properties of ZnS crystals including multi spectral CVD, single spectral CVD and hot pressed ZnS were investigated through the TL method. We found that CVD ZnS and hot pressed ZnS presented dramatically different TL characteristics.

## 2. Experimental

The experimental setup is established to measure the images and spectrums of emitted photons in real time during sliding contact between solid materials, as showed in Fig. 1. The light detection system consists of an optical fiber, a spectrograph, and a charge-coupled Device (CCD) camera. Photons emitted during the sliding friction process of two kinds of solid materials were gathered by optical fiber, and then transmitted to the spectrograph (SP2500; Princeton Instruments, America) and CCD (100BR, Princeton Instruments, America). Finally, images and spectrums of photons are obtained. The normal force(F) was applied to the solid materials and detected by a pressure sensor (LTW-W2-5 kg, Lungday, China) with combined 0.5% F.S, including hysteresis, nonlinearity and non-repeatability error. The integration time (T) of CCD was 10 min and the spectrums of photons were in the range from 300 to 800 nm.

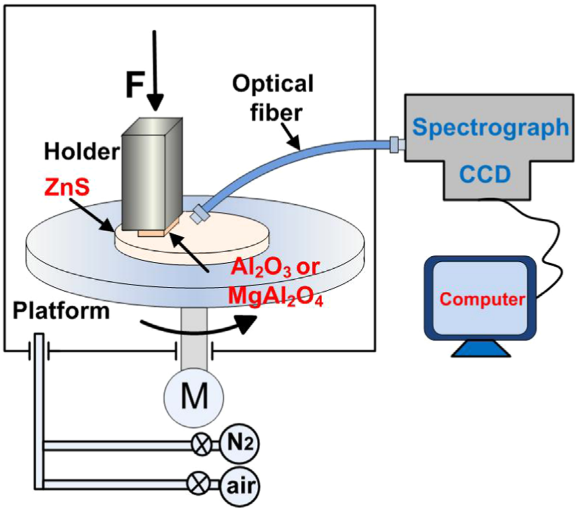

**Fig. 1.** The experiment setup for measuring the images and spectrums of emitted photons.

The $Al_2O_3$ and $MgAl_2O_4$ crystals with width of 3 mm and thickness of 2 mm were provided by Shanghai Daheng Optical & Fine Mechanics Co. Ltd, while the ZnS crystals with diameters of 25 mm and 2 mm were purchased from Beijing Sinoma Synthetic Crystals Co. Ltd. Multi spectral, single spectral and hot pressed ZnS crystals were used in the experiments. ZnS crystals as lower materials were adhered to the rotating platform along the adjustable-speed motor (4GN5K, Devoter, China), while $Al_2O_3$ and $MgAl_2O_4$ as upper materials were fixed on a holder. Then, a normal force having been applied on the holder, lower material slid over the upper material continuously. The normal force throughout the experiments was $F = 15 \pm 0.0375$ N, and the relative shear velocity (V) between sliding materials was 27.5 mm/s. The sliding experiments were carried out both in ambient air and $N_2$ gas in the dark. In order to confirm the spectra of ZnS, all experiments were done no less than three times on different dates. The purity of $N_2$ gas was 99.99%, the humidity of air was10% ± 0.5, and the temperature was 23 ± 0.5 °C.

## 3. Results and discussion

### 3.1. TL of ZnS and $Al_2O_3$

The spectrums of photons emitted during sliding contact between $Al_2O_3$ and ZnS crystals are shown in Fig. 2. Many sharp peaks at region 300–450 nm as well as two characterize peaks at 695 and 776 nm in the near infrared region are appeared in the spectrum of multi spectral ZnS. The spectrum peaks of photons in the region 300–450 nm are assigned to $C^3\pi \rightarrow B^3\pi$ electron transitions of $N_2$ [22,23]. Other sharp peaks of the spectrum are mainly due to $B^3\pi \rightarrow A^3\Sigma$ electron transitions of $N_2$ and $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ electron transition in $O_2$ [24,25]. In addition, one broad fluorescence peak is shown in the vicinity of 420 nm. Spectrum sharp