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Invited article

# Mechanically induced phase transformation of zinc sulfide

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ABSTRACT

Molecular dynamics (MD) simulations of the consecutive compression–decompression cycles of hexagonal zinc sulfide (wurtzite) nanoparticles predict an irreversible phase transformation to the cubic polymorph. The phase transformation commences at the contact area between the particle and the indenter and proceeds with the number of compression cycles. Dislocations are visible for a particle size above 5 nm.

Results from wet grinding and dry powder compression experiments on a commercial wurtzite pigment agree qualitatively with MD simulation predictions. X-ray diffraction patterns reveal that the amount of cubic polymorph in the compressed samples increases with pressure applied to the powder. In comparison with powder compression, wet milling leads to a more pronounced phase transformation. This occurs because the particles are exposed to a large number of stress events by collision with the grinding media, which leads to the formation of defects and new surface crystallites by particle fracture. According to the MD simulations, phase transformation is expected to occur preferentially in surface crystallites because they experience the highest mechanical load.

Because of the phase transformation, the wet ground and compressed samples exhibit a lower photoluminescence intensity than the feed material. In comparison with powder compression, milling reduces the photoluminescence intensity more substantially. This occurs because a higher defect concentration is formed. The defects contribute to the phase transformation and photoluminescence quenching.

## Introduction

Zinc sulfide is a luminescent semiconductor material. Because of its electronic and luminescence properties, it is used to manufacture electroluminescence displays, solar cells, field effect transistors, sensors, and safety signs (Lan, Hong, Wang, & Wang, 2003; Park et al., 2007; Toyama, Adachi, Fujii, Nakano, & Okamoto, 2002). The photoluminescence intensity of zinc sulfide is enhanced significantly by doping, for example with copper or manganese. The type and concentration of doping element influence the spectral features and photoluminescence lifetime (Bhargava, Gallagher, Hong, & Nurmikko, 1994; Curie, 1963; Hsia, Wuttig, & Yang, 2011; Kang, Beverley, Phipps, & Bube, 1967; Keshari & Pandey, 2009; Klausch et al., 2010; Manam, Chatterjeh, Das, Choubey, & Sharma, 2010; Mu, Gu, & Xu, 2005; Peng, Cong, Qu, & Wang, 2006; Sapra, Prakash, Ghangrekar, Periasamy, & Sarma, 2005; Small, Johnston, & Clark, 2010; Wang, Xu, & Yuan, 2010; Warad, Ghosh, Hemtanon, Thanachayanont, & Dutta, 2005; Yu, Isobe, & Senna, 1996; Zhuang et al., 2003). The doping, particle size and crystal structure influence the photoluminescence behavior of zinc sulfide significantly (Curie, 1963; Komada, Kobayashi, Arao, Tsuchiya, & Mori, 2012; Nanda, Sapra, Sarma, Chandrasekharan, & Hodes, 2000). Zinc sulfide exists as cubic and hexagonal crystalline polymorphs. In the non-doped state, both polymorphs exhibit photoluminescence, which can be attributed to the recombination of charge carriers trapped in sulfur or zinc vacancies (John & Florence, 2009; Tang, Xu, Weng, Pan, & Wang, 2004; Lu, Chu, & Tan, 2004). The hexagonal wurtzite phase luminesces more strongly than the cubic phase. Highly luminescent zinc sulfide nanoparticles are prepared mainly by chemical precipitation, and many of these synthesis routes are described in the literature. Most syntheses yield zinc sulfide nanoparticles with cubic crystal structure.

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Mechanochemical synthesis by dry grinding of mixtures of zinc salts with sulfides in high-energy planetary ball mills also yields cubic zinc sulfide (Wang et al., 2010; John & Florence, 2009; Balaz, 2008; Balaz et al., 2013; Dutkova et al., 2009). Zinc sulfide nanoparticles with hexagonal lattices can be obtained by hydrothermal synthesis in the presence of thioglycolic acid (Salavati-Niasari, Loghman-Estarki, & Davar, 2009). Temperature and pressure changes can induce polymorph transformations: Yang et al. (2008) have shown experimentally that cubic zinc sulfide is transformed into wurtzite at 1 GPa and 250 °C. At atmospheric pressure, this phase transformation is observed at ~1020 °C (Trigunayat & Chadha, 1971). The heating of cubic zinc sulfide quantum dots with starting sizes of 2–3 nm to 400–600 °C yields wurtzite nanoparticles. This indicates that there is a strong quantum size effect on the phase transformation temperature (Tiwary, Kumbhakar, Mitra, & Chattopadhyay, 2009). The hexagonal wurtzite phase is metastable at ambient temperature whereas the cubic polymorph is the thermodynamically stable phase at low temperature. Besides temperature and pressure changes, mechanical activation can induce phase transformations (Balaz, 2008; Balaz et al., 2013). In contrast with thermally induced phase transformations, where all atoms in the lattice are activated to almost the same degree, in mechanically induced phase transformations, a limited number of atoms are activated (Balaz et al., 2013). These activated atoms can act as nucleation centers to initiate the phase transformation (Balaz et al., 2013). Zinc sulfide is known to undergo phase transformations by mechanical activation (Balaz, 2008; Balaz et al., 2013; Dutkova et al., 2009; Senna, 1981), and applying a mechanical stress to cubic zinc sulfide particles may result in amorphization (Balaz, 2008). The dry milling of hexagonal zinc sulfide microparticles in a planetary ball mill resulted in its transformation to cubic zinc sulfide according to Balaz (2008), Balaz et al. (2013), and Dutkova et al. (2009). As a reason for this phase transformation, the motion of dislocations has been discussed (Balaz, 2008; Avvakumov, 1986). The transformation of wurtzite particles 12–21 nm in diameter to cubic polymorphs was studied by molecular dynamics (MD) simulations and no size dependence of the transformation process was indicated (Morgan & Madden, 2006). Mechanically induced phase transformations of zinc sulfide are not well understood and it is not clear which parameters (particle size, defects) contribute to the phase transformation. During the production of devices, zinc sulfide particles may be exposed to mechanical forces, such as in the dispersing steps. In previous work we showed for a number of oxidic materials that stirred media milling can induce mechanochemical changes, which lead to a strong modification of material properties (Damm & Peukert, 2009; Stenger, Götzinger, Jakob, & Peukert, 2004; Romeis et al., 2014). Therefore, an improved understanding of the influence of mechanical forces on the microstructure and photoluminescence behavior of zinc sulfide particles is essential.

In this paper, we investigate the mechanically induced phase transformation of hexagonal to cubic zinc sulfide by a combination of MD simulations and experiments. MD simulations allow for the investigation of microstructure evolution under mechanical load on an atomistic level and a temporal resolution in the order of the Debye frequency (Armstrong et al., 2009). Powder compression experiments and mild wet milling experiments were conducted to verify the predictions of the MD simulations. The combination of MD simulations and experiments provides increased insight into the mechanism of the mechanically induced phase transformation of zinc sulfide. The influence of the mechanically induced changes in microstructure on the photoluminescence behavior of zinc sulfide is also discussed.

## Experimental

### Materials

Storelite RNS, a copper-doped luminescent zinc sulfide (ZnS:Cu) pigment, was supplied by RC Tritec AG, Teufen, Switzerland. Absolute ethanol was purchased from Carl Roth GmbH, Karlsruhe, Germany. Polyvinylpyrrolidone (PVP-10) with a molecular weight of 10,000 g/mol was supplied by Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany. All materials were used as received.

### Wet grinding process

The LAU-disperser DAS H 200-K shaker table (LAU GmbH, Hemer, Germany) was used for the mild wet grinding of the zinc sulfide pigment, Storelite RNS, in absolute ethanol. The zinc sulfide concentration in suspension was 5 wt.%. PVP-10 (0.25 wt.%) was used as a stabilizing agent against agglomeration. The grinding process was conducted at ambient temperature. The diameter of the $ZrO_2$ grinding media was varied from 0.5 to 1.2 mm. For a typical grinding experiment, six 30-mL glass bottles were loaded with 20 mL of absolute ethanol, 40 mg of PVP-10, 800 mg of zinc sulfide, and 30 g of yttria-stabilized $ZrO_2$ beads. The sealed bottles were mounted on the disperser plate and shaken. Individual bottles were removed from the disperser at different processing times. The suspension was separated from the grinding media using a sieve and analyzed as described below.

### Powder compression experiments

The as-supplied zinc sulfide powder (2.5 g) was placed into the chamber (2 cm diameter, 3.14 $cm^2$ cross section) of a pressing tool used for the preparation of samples for infrared spectroscopy analysis. The stamp of the pressing tool was moved downwards at 50 mm/min using a Z020 stress-strain tester (Zwick GmbH & Co. KG, Ulm, Germany) until the desired pressure was reached and the zinc sulfide powder was compressed to a pellet. After maintaining the desired pressure for 10 min, the stamp was moved back up to its original position. The pellet was removed from the pressing tool, ground to a powder using an agate mortar, and analyzed by X-ray diffractometry and photoluminescence spectroscopy.

### Sample characterization

For X-ray diffraction (XRD) patterns, specific surface area, and photoluminescence spectra measurements, the zinc sulfide was separated from the ground suspensions by centrifugation (17,000 g, 10 min) using a centrifuge 5418 (Eppendorf Zentrifugen GmbH, Leipzig, Germany), washed five times with absolute ethanol, dried at room temperature and ground to a powder. Powder XRD patterns were recorded from a $2\theta$ of $15^\circ$–$80^\circ$ using a D8 "Advance" X-ray diffractometer (Bruker corporation, Billerica, MA, USA). The instrument uses Cu K$\alpha$ irradiation with a wavelength of 0.154 nm. A Cu K$\alpha$2 correction was conducted prior to evaluating the XRD patterns. The specific surface area was measured by nitrogen adsorption at 77 K using a Nova 4000 BET-analyzer (Quantachrome GmbH & Co. KG, Odelzhausen, Germany). A scanning electron microscope (SEM) "Gemini Ultra 55" (Carl Zeiss AG, Oberkochen, Germany) was used to study the particle morphology. Before the SEM investigation, powder was deposited onto a conductive rubber sheet and loosely bound powder particles were removed from the substrate using compressed air. Photoluminescence spectra of the feed material and of the ground and compressed samples were recorded from 350 to 650 nm with an excitation wavelength of 337 nm using