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Combustion synthesis of ZnSe with strong red emission

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ABSTRACT

A fast and furnace-free way is reported to synthesize ZnSe from self-sustained combustion reaction between Zn and Se. The synthesized ZnSe shows a zincblende structure and large particle size of >100 μm, which can be reduced by two magnitude to 1.4 μm by using NaCl as diluent. It is proposed that the added NaCl can lower the reaction temperature and diminish the interfacial area of ZnSe grains by a steric hindrance effect. The ZnSe samples show the characteristic band-edge absorption in visible region, and the band gap energy is estimated to be 2.43–2.58 eV. Under an ultraviolet excitation, the ZnSe samples do not show the near-band-edge blue emission but exhibit strong red emission, which is likely related to the intrinsic point defects in ZnSe. Compared with previous studies, the ZnSe samples synthesized in this work show red emission peaks at even larger wavelength up to 730 nm.

1. Introduction

Zinc Selenide (ZnSe) is an important II—VI semiconductor with a direct band-gap of $E_g = 2.7$ eV at room temperature. With a wide band-gap, high luminescence efficiency, and low absorption coefficient, ZnSe has potential for a variety of applications such as short-wavelength lasers, light-emitting diodes, thin film solar cells and other photoelectronic devices [1]. As many other II—VI compounds, ZnSe has two polymorphs with different lattice structures, viz. cubic zincblende (ZB) and hexagonal wurtzite (WZ). The two structures are identical with the same tetrahedral building units, in which each Zn (or Se) atom is tetrahedrally coordinated by Se (or Zn) atoms, but differs in the stacking sequence of successive closely-packed layers, with an ABCABC (3C) stacking sequence in the ZB structure and ABAB (2H) in WZ. For bulk crystals of ZnSe at room temperature and atmospheric pressure, the ZB structure is the stable form and energetically more favorable than the WZ one [2]. It is pointed out that, at high temperatures near the melting point of ZnSe, the WZ phase does exist but later transforms into ZB during the cooling process through a solid phase transition [1]. High-temperature X-ray diffraction has revealed that the ZB-WZ phase transformation occurred at a high temperature of 1425 °C [3]. In this way, ZnSe usually exists in the ZB polymorph and the WZ structure is less reported, and most of the reports on WZ are limited to nanostructures [4].

Up to now, a large variety of methods have been reported to synthesize ZnSe in different forms such as bulk crystals, thin films, nanoparticles and quantum dots [5–7]. These methods include direct reaction between elemental Zn and Se [8], wet chemical route by reaction between Se^{2-} and Zn^{2+} in solutions [7], chemical vapor deposition [9], and so on. The direct reaction between Zn and Se may be the most straightforward way to synthesize ZnSe, but it requires long-time heat treatment at high temperatures by furnace, which means a long processing time and large energy consumption. The wet chemical route, which is widely used to prepare ZnSe nanoparticles and quantum dots, operates at relatively low temperatures and does not require complex equipment, but it usually involve the use of toxic and sometimes explosive starting materials, thus causing environmental or safety problems. The chemical vapor deposition technique also uses expensive or toxic raw materials and moreover requires sophisticated equipment, which increases the cost of production.

In this paper, we report an alternative approach to synthesize ZnSe, which is known as combustion synthesis. Combustion synthesis is a method to synthesize inorganic compounds from self-sustained exothermic combustion reactions [10,11]. Combustion synthesis can be carried out in two different modes of volume combustion synthesis (VCS) and self-propagating high-temperature synthesis (SHS), and the latter is applied in this work. Once the combustion reaction is triggered, it continues in a self-sustained way requiring no external heating. The combustion front passes through the sample quickly and the combustion reaction completes in only a few seconds, during which the reactant is converted into product. Up to now, combustion synthesis has been mostly used to produce materials for structural applications [12,13], and not so widely applied for preparing functional materials

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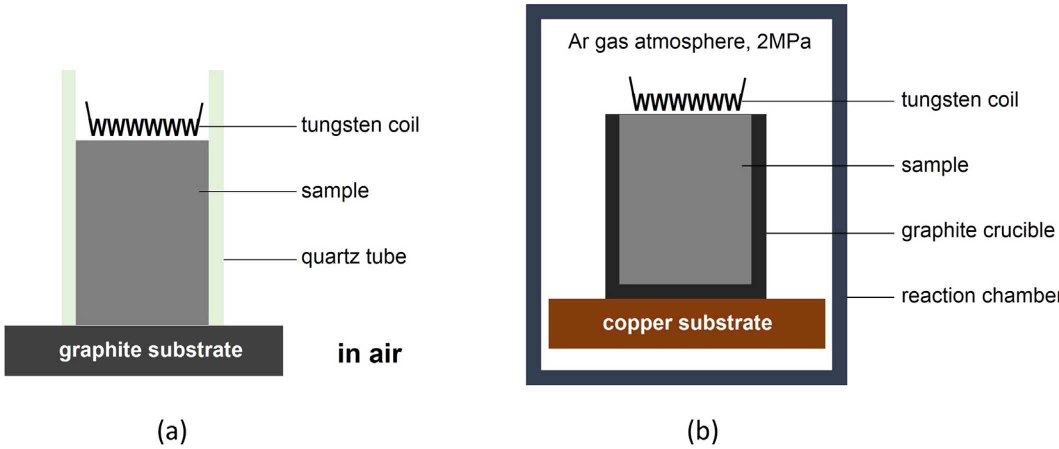

Fig. 1. An illustration of combustion synthesis of ZnSe: (a) in air; (b) in Ar gas atmosphere with a pressure of 2 MPa.

Table 1
Related thermodynamic data for Zn, Se, ZnSe, and NaCl (under a pressure of 1 atm) [15].

Substance	T_m (K)	T_b (K)	$\Delta H_{f,298}$ (kJ/mol)	ΔH_m (kJ/mol)	ΔH_v (kJ/mol)	C_p (J/mol)
Zn	693	1180	0	7.3		
Se	493	958	0	5.9		
ZnSe	1799		−159	51.9		50.17 + 0.0058 T (298–1300 K)
NaCl	1074	1738	−411	28.2	161	45.94 + 0.0163 T (298–1074 K) 77.74–0.0075 T (1074–1500 K) 66.94 (1500–1738 K)

T_m: melting point, T_b: boiling point, $\Delta H_{f,298}$: standard formation enthalpy at 298 K, ΔH_m: enthalpy of melting, ΔH_v: enthalpy of vaporization, C_p: specific heat.

[14]. Here, we demonstrate that combustion synthesis is effective in preparing crystalline ZnSe materials. The reaction mechanism in combustion synthesis of ZnSe is discussed, and the optical properties of the synthesized ZnSe samples are investigated.

2. Experimental

High-purity element powders of Zn (purity > 99.9%, 200 mesh) and Se (purity > 99.9%, 200 mesh) were weighed and mixed in an agate mortar according to the stoichiometric molar ratio of Zn:Se = 1:1. In some cases, commercial NaCl (Analytical Reagent) was added into the (Zn + Se) mixture with weight percent of 10, 20, 30, 40, and 50 wt% in order to decrease the reaction temperature. The reactant powder mixture was cold pressed into a compact with a porosity of about 40% under a uniaxial pressure of 20 MPa. The combustion synthesis experiment was carried out in air or in Ar gas atmosphere. For combustion synthesis in air (Fig. 1(a)), the reactant compact was loaded in a quartz tube placed on a graphite substrate. A tungsten coil was fixed above the

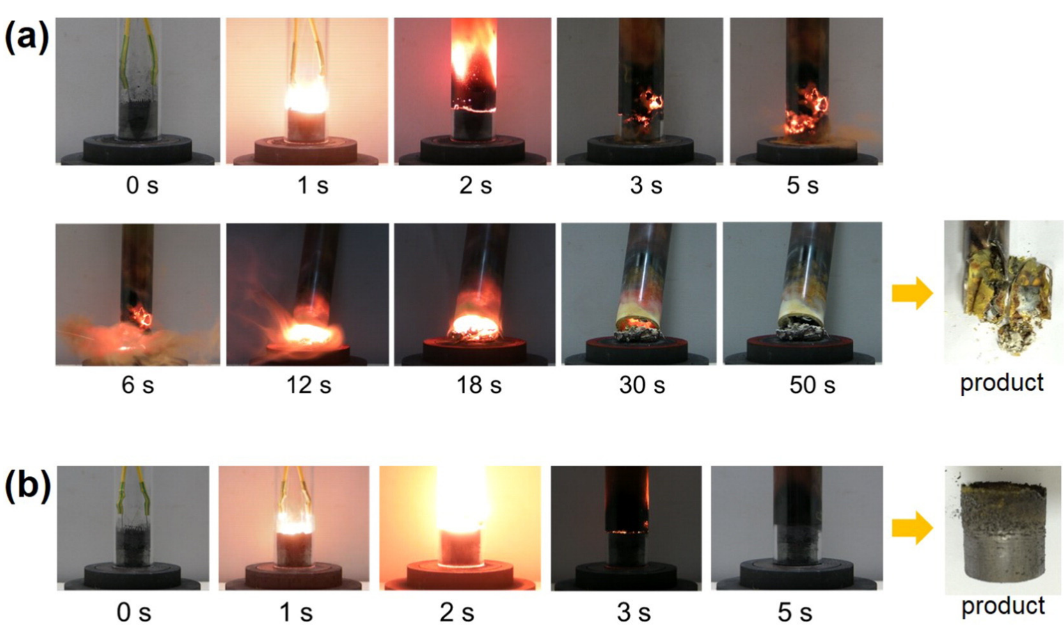

Fig. 2. Photographs showing the reaction process and products for combustion synthesis of ZnSe in air from different reactants: (a) (Zn + Se) powder mixture with a molar ratio of Zn/Se = 1; (b) powder mixture of 70 wt% (Zn + Se) plus 30 wt% NaCl.