Journal of Crystal Growth 476 (2017) 25–30

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

Nanoscale zinc silicate from phytoliths

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ARTICLE INFO

Article history:
Received 7 July 2017
Received in revised form 9 August 2017
Accepted 10 August 2017
Available online 12 August 2017
Communicated by T.F. Kuech

Keywords:
Nanomaterials
Oxides
X-ray diffraction
Characterization
Crystal structures
Phosphors

ABSTRACT

We report a faster, less expensive method of producing zinc silicate nanoparticles. Such particles are used in high volume to make phosphors and anti-corrosion coatings. The approach makes use of phytoliths (plant rocks), which are microscopic, amorphous, and largely silicate particles embedded in plants, that lend themselves to being easily broken down into nanoparticles. Nanoparticles of Zn_2SiO_4 were produced in a two stage process. In the refinement stage, plant residue, mixed with an appropriate amount of ZnO, was heated in an argon atmosphere to a temperature exceeding 1400 °C for four to six hours and then heated in air at 650 °C to remove excess carbon. TEM shows 50–100 nm nanoparticles. Raman scattering indicates that only the -Zn_2SiO_4 crystalline phase was present. X-ray analysis indicated pure rhombohedral $R\bar{3}$ phase results from using rice/wheat husks. Both samples luminesced predominantly at 523 nm when illuminated with X-rays or UV laser light.

1. Introduction

There is a need for a less expensive and faster method to produce zinc-silicate (Zn_2SiO_4) nanoparticles. Zinc silicate (Zn_2SiO_4) is an important chemical compound with many industrial applications. It is used as an anticaking additive for various types of foods. It is widely used in anticorrosion coatings for ships, buildings, and vessels that are exposed to high levels of saltwater; in these types of applications, zinc silicate is also used as a primer for the paint that is applied to the surfaces. Zinc silicate, a semiconductor with a wide band gap of 4.1 eV, is used as a scintillating material in cathode ray tubes and fluorescent electronic devices. Manganese doped Zn_2SiO_4 is an efficient green emitting phosphor and is used extensively in fluorescent lamps and plasma display panels [1–7]. Mn-doped zinc silicate (Zn_2SiO_4:$Mn2^+$), has been used as a phosphor in fluorescent lamps, neon discharge lamps, oscilloscopes, black-and-white and color televisions, and many other displays and lighting devices for a long time [8–13]. At present, Zn_2SiO_4:Mn^{2+} is consumed in high volume for the most advanced televisions; plasma display panels (PDPs), due to its high luminescence efficiency, high color purity, and its high chemical and thermal stability [13,14]. In addition to the phosphor characteristics of zinc silicate, it has been shown that nano-rod like structures of Zn_2SiO_4 are capable of adsorbing heavy metals such as Fe, Cd, Hg and Pb in water [15]. With these findings, there is added incentive to study the properties and performance of Zn_2SiO_4 and its applicability to purifying water by removing heavy metals.

There are two commercial processes for synthesizing zinc silicate. One consists of a solid state reaction at high temperature to produce large pieces of zinc silicate followed by ball milling and grinding to obtain desired powder [16]. The other is a wet-chemistry multistep process to produce the powder product [17]. Both processes are time consuming and cost intensive.

The new process to produce Zn_2SiO_4 nanoparticles introduced here uses agricultural plant residue (specifically rice and wheat husks) as a source of SiO_2. The phytoliths that naturally occur in these plant residues provide the needed SiO_2. Plants absorb water from the ground along with nutrients. Minerals not needed by the plant are secreted as microscopic solid minerals within the structure of the plant; these are called phyto-liths (plant-rocks). Different plants and even different parts of a plant produce different shapes and sizes of phytoliths. Their composition is largely non-crystalline SiO_2, with some water and a plant dependent <1–5% by weight of other plant nutrients. There is a subfield of archaeology that uses phytoliths to learn (1) what plants grew and (2) where they grew in ancient times. But in the present work the interest is to use these phytoliths to produce zinc-silicate. Rice and wheat husks are available in abundance as agriculture residues around the world. Rice husk (RH) and wheat husk (WH) have high C and Si contents, so they can be used as low-cost Si and C sources for synthesizing advanced materials. When WH and RH are burned

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http://dx.doi.org/10.1016/j.jcrysgro.2017.08.015
0022-0248/Published by Elsevier B.V.

at a certain temperature in air, carbon and other elements are released leaving silicon dioxide (SiO_2) as the major component of the end product known as rice husk ash (RHA) or wheat husk ash (WHA). Recently Xiong et al. [18] showed, using a multistep process, that SiO_2 extracted from RHA can be mixed with Zinc Oxide (ZnO) and combusted to produce Zn_2SiO_4 and, when doped with $Mn2^+$, yield an efficient phosphor. The following equation describes the solid state reaction that results in zinc silicate:

$$2ZnO + SiO_2 \Rightarrow Zn_2SiO_4$$

Previous work on agriculture residues has shown successful conversion of rice husks, wheat husks, sorghum leaves, and corn leaves into silicon carbide (SiC) and Si_3N_4 by pyrolyzing in argon atmosphere or in nitrogen atmospheres respectively [19–25]. An important feature of this type of synthesis is that it involves a single step process in which no additives are involved.

This paper focuses on producing nanoparticles of Zn_2SiO_4 by mixing SiO_2 from wheat and rice husks with ZnO in the correct weight ratio and growing nanoparticles of Zn_2SiO_4. A major difference, compared to Xiong et al. [18], is that the process introduced in this work starts with a solid state reaction in which the plant residue and ZnO are pyrolyzed in an argon atmosphere with carbon acting as a catalyst; the remaining carbon present in the sample is then removed by heating at an appropriate temperature in air to produce an amorphous mixture of Zn_2SiO_4. Also different from Xiong et al. [18] is that the final Zn_2SiO_4 nanocrystal growth stage is also a solid state reaction in an argon atmosphere. The structural parameters and composition of the Zn_2SiO_4 produced are investigated using X-ray diffraction (XRD) and Raman scattering spectroscopy. In addition, transmission electron microscopy results are presented to obtain the size and shapes of the nanoparticles of zinc silicate. The phosphor characteristics were determined in-situ using 8 keV x-rays and an optical spectrometer, and also by room temperature photoluminescence (PL) and PL imaging.

2. Experimental details

Samples were made from raw wheat and rice husks after they were thoroughly washed in distilled water, dried, and then mixed with ZnO powder in the appropriate weight ratios to produce zinc silicate. The amount of ZnO of 0.242 g was chosen to be the maximum that left no remnant ZnO in the resulting material.

By weighing the wheat and rice samples before and after heat treatment in air and using X-ray diffraction scans, the presence of crystalline phases of SiO_2 was found to have a weight percentage of 16% for the rice husk and 14% for the wheat husks. It took 0.242 g of ZnO mixed with 1.54 g of wheat husk to produce Zn_2SiO_4 with no remnant ZnO, whereas it took 0.20 g of ZnO mixed with 1.54 g of rice husks to produce Zn_2SiO_4 with no remnant ZnO. The ZnO and wheat or rice husks mixtures were thoroughly mixed and pulverized using ball milling which produced a very homogenous fine powder. The fine powder was pressed into disks having diameter of 1cm and 2–3 mm thickness using a hydraulic press. The pellets were heat treated in a conventional furnace at temperatures above 1400 °C in an argon atmosphere for a period of 2–4 h and subsequently treated in air at 650 °C to remove the excess carbon. The samples were then pulverized into powder using a SPEX 8000M high energy mill with stainless steel milling media. Pellet samples of 1 cm diameter were prepared again from the resulting powder. The samples in the form of pellets were heated in an argon atmosphere using a conventional tube furnace to a temperature between 1400 and 1500 °C. The processed samples were characterized using X-ray diffraction, Raman scattering and photoluminescence spectroscopy, and electron microscopy techniques. X-ray diffraction profiles were collected using a Rigaku 18 kW generator and a high resolution powder diffractometer. Monochromatic Cu Kα radiation was used for all X-ray diffraction scans. Optical emission spectra were collected during X-ray irradiation using a USB2000 Ocean Optics spectrometer equipped with a fiber optic probe with a 1000 μm core. The fiber optic probe was positioned perpendicularly ~2 mm from the sample surface while the X-ray incident angle was 45°. For TEM analysis, the pyrolyzed sample was added to ethyl alcohol and the mixture was placed in an ultrasonic cleaner for a period of 30 min. A carbon coated 200 mesh copper grid was immersed in the mixture to pick up the Zn_2SiO_4 powder samples. The specimens were examined in a FEI Tecnai G2 TEM operated at 300 kV.

A home-built confocal micro-Raman spectrometer, comprised of single-mode 488 nm and 532 nm lasers, a half meter Acton spectrometer with an 1800 groove/mm holographic grating, and a Princeton Instruments back-thinned, deep depleted, Nitrogen cooled CCD (1340 × 400 pixel array) was employed to verify sample structure and composition. The spectral resolution of this configuration of the system is 2.5 cm^{-1}, and the repeatability with which a line position can be determined is within 0.1 cm^{-1}. Neutral density filters were employed to control the laser power. Room temperature PL spectra were acquired with a small UV-enhanced CCD fiber optical spectrometer covering the UV-NIR spectral region. The samples were excited with the 325 nm line of a HeCd laser; low power density (~64 mW/cm^2) was employed to prevent sample heating and luminescence bleaching and/or saturation. Real color and monochromatic luminescence images of the samples, using 325 nm laser line excitation, were acquired with a home built luminescence imaging set up.

3. Results and discussion

The pellet samples prepared from the milled wheat or rice husks were subjected to uniaxial pressures in excess of 2.0 GPa

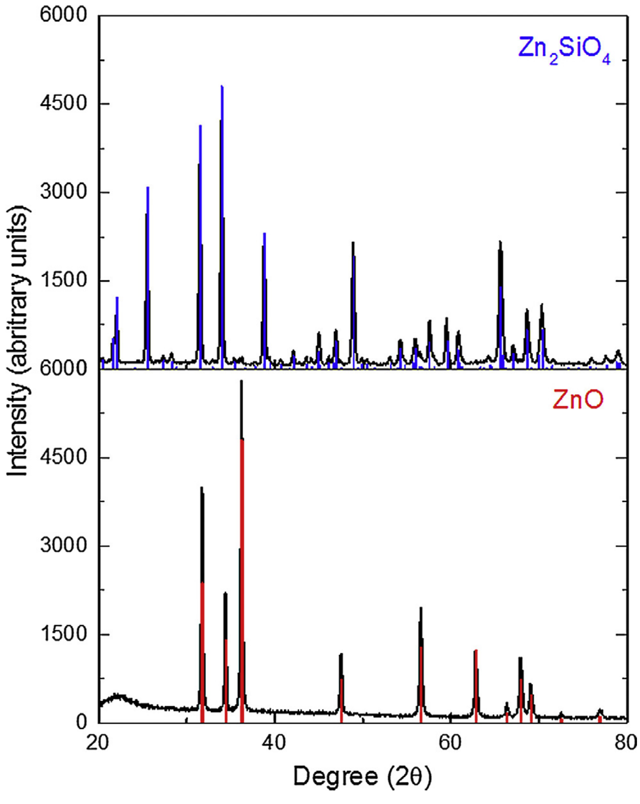

Fig. 1. An overlay of X-ray diffraction patterns taken with Cu Kα radiation of as-received wheat husk plus zinc oxide (lower half) and the processed sample showing the diffraction pattern of Zn_2SiO_4 (upper half).