Radiation Physics and Chemistry 104 (2014) 93–99

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Production and characterization of spodumene dosimetric pellets prepared by a sol–gel route

H.R.B.R. Lima [a], D.S. Nascimento [a], G.F.C. Bispo [a], V.C. Teixeira [a,b], M.E.G. Valério [a], S.O. Souza [a,*]

[a] Universidade Federal de Sergipe, Departamento de Física, P. O. Box 353, 49100-000 São Cristóvão, SE, Brazil
[b] Universidade Federal de Sergipe, Departamento de Engenharia de Materiais, 49100-000 São Cristóvão, SE, Brazil

HIGHLIGHTS

- β-spodumene can be successfully produced by the proteic sol–gel method.
- Sintered pellets produced by the proteic sol–gel method are sensitive to beta rays.
- β-spodumene produced by the proteic sol–gel method with SiO_2 is more sensitive to radiation detection than the one produced with TEOS.

ARTICLE INFO

Article history:
Received 9 July 2013
Accepted 21 March 2014
Available online 19 April 2014

Keywords:
Spodumene
Proteic sol–gel
Gelatin

ABSTRACT

Spodumene is an aluminosilicate that has shown good results for high-dose TL dosimetry for beta or gamma rays. Due to its chemical composition ($LiAlSi_2O_6$) it has potential to be used as a neutron dosimeter. The synthetic spodumene is usually produced by solid state reaction and conventional sol–gel, whose shortcomings arise from the need to employ high temperatures and high cost reagents, respectively. Proteic sol–gel method is promising, because it can reduce production costs and the possibility of environmental contamination. This work reports the production of the spodumene by the proteic sol–gel method using edible unflavored gelatin as a precursor. The product is characterized physically and morphologically, and investigated its applicability as a TL dosimeter. Two sets of samples were prepared using different sources of silicon, one with TEOS ($Si(OC_3H_5)_4$) and one with SILICA (SiO_2). The materials produced were characterized by X-ray diffraction, differential thermal analysis and thermogravimetry in order to evaluate the structural properties, as well as possible changes in physical or chemical properties depending on the temperature. The production of spodumene was successful, with generation of the crystals in the β-phase with tetragonal structure. Sintered pellets produced from these crystals were irradiated with a ^{90}Sr–^{90}Y source and their TL glow curves were evaluated. Although the samples prepared by the proteic sol–gel method with TEOS presented a lower forming temperature, the samples produced with SILICA showed higher sensitivity to radiation.

1. Introduction

The safe application of ionizing radiation in many areas requires the use of radiation detectors capable of detecting its presence or to quantify it. Thermoluminescent (TL) crystals are extensively used as passive dosimeters. However, a unique material hardly exhibits all the desired characteristics to ensure the safe use of ionizing radiation.

In the search for new materials some most striking features such as high sensitivity to irradiation and linear response of the emission to dose, temperature and wavelength of the emission should be the focus of the research. Spodumene is an aluminosilicate that has shown good results for high-dose TL dosimetry for beta or gamma rays. The thermoluminescent properties of natural crystal of spodumene have been exploited in applications of dating and dosimetry of ionizing radiation (d'Amorim et al., 2012; Ferraz et al., 2008; Souza et al., 2004; Lima et al., 2010). Due to its chemical composition ($LiAlSi_2O_6$), the natural crystal is one of the main sources of Li, and has potential to be used as neutron

* Corresponding author. Tel.: +55 79 2105 6630
E-mail addresses: hestialima@gmail.com (H.R.B.R. Lima), deborasiqueiran@hotmail.com (D.S. Nascimento), gfredericoc@gmail.com (G.F.C. Bispo), vctbell@gmail.com (V.C. Teixeira), megvalerio@gmail.com (M.E.G. Valério), sosouza@ufs.br (S.O. Souza).

http://dx.doi.org/10.1016/j.radphyschem.2014.03.022
0969-806X/

dosimeter as well. Its electronic structure and basic optical properties have been investigated theoretically on the basis of Density Functional Theory (Lima et al., 2008, 2009).

Despite the spodumene has been synthetically produced by a solid state reaction, the process has been limited due to high melting point of the spodumene (1421 °C). The conventional sol–gel process appears as an alternative in the production of various materials such as crystals, glass, ceramics and thin films. The method is effective because, in general, lower processing temperatures are needed compared with those in traditional methods of crystal growth. Moreover, the sol–gel route facilitates stoichiometric control of porosity and crystalline structure or particle size, thus generating crystals of high purity and homogeneity. Samples of synthetic β-spodumene have been produced by various authors by the conventional sol–gel method (Brovetto et al., 1993; Gutierrez et al., 2009; Xia et al., 2009). However, the conventional method is expensive due to usage of specific reagents and its usability is limited by the solubility of alkoxides, which makes the process unfeasible on a large scale and generates health risks because solutions exhibit high degree of toxicity during calcination (Brinker and Scherer, 1990).

Over the last decades some alternative procedures of preparing materials have been studied with objective to reduce production costs, environmental impacts and also to facilitate manufacture of devices such as radiation dosimeters. One of them is the proteic sol–gel process, proposed by Macedo (1998) as a modified route from the conventional process. The essential novelty introduced by this process is application of the coconut water as a substitute for conventional alkoxides used in the conventional processes (Macedo, 1998; Macedo and Sasaki, 2002). On the basis of this idea, the edible gelatin started to be used due to its rather significant concentrations of protein (Meneses et al., 2007), reducing the production costs and the possibility of environmental contamination.

The present work reports production of the beta-spodumene via the proteic sol–gel method, using edible unflavored gelatin and SiO_2 or $Si(OC_3H5)_4$ as the silicon source. The product is characterized both physically and morphologically and investigated its applicability in TL dosimetry.

2. Experimental

The proteic sol–gel method using gelatin as organic precursor was applied to obtain the samples. Two different reagents were used as source of silicon: (SiO_2) and ($Si(OC_3H_5)_4$), called in this work SILICA and TEOS, respectively. The molar concentration for both was 0.25 mol/L, varying only the stoichiometry due to the use of different reagents and temperatures of pre-calcination. Table 1 shows which reagents have been used and their respective purities.

For samples prepared with SILICA, 1.515 g edible unflavored gelatin (Royal®) and 20 ml of distilled water were mixed at approximately 70 °C and constant stirring. Then, 2.1 g $Al(NO_3)_3 \cdot H_2O$, 0.37 g $LiNO_3$ and 0.65 g of SILICA were added to the mixture.

Table 1
Reagents.

Reagent	Manufacturer and purity
$[Al(NO_3)_3 \cdot H_2O]$	Vetec 98%
$[LiNO_3]$	Fluka 98%
$[Si(OC_2H_5)_4]$ (TEOS)	Sigma-Aldrich 98%
$[SiO_2]$ (SILICA)	Sigma-Aldrich 98%
Edible unflavored gelatin	Royal

For samples prepared with TEOS, initially it was made a solution of 2.24 g of TEOS with ~18 mL of ethyl alcohol with a molar concentration of 0.52 mol/L (whose purpose was to dissolve the silica reagent). Subsequently, another solution was made with 1.515 g unflavored edible gelatin (Royal®) and 20 mL of distilled water at a temperature of about 70 °C constantly stirring. Then, 2.01 g $Al(NO_3)_3 \cdot H_2O$, 0,37 g $LiNO_3$ and TEOS solution were added.

The final solution prepared with SILICA or with TEOS underwent the same following procedures: they were heated at ~200 °C for 1 h to release part of the existing water. A solid gel was formed. It was dried in a kiln at 100 °C for 48 h. After drying, the xerogel formed was ground in a mortar with a pestle, both of porcelain.

An aliquot of the xerogel was separated for thermal analysis and the remainder was lead to pre-calcination at 600 °C for 2 h to remove the organic material. Aliquots of 0.2 g were calcinated at different temperatures maintained for 2 h in muffle-type electric furnaces, EDG 1800, using a heating rate of 10 °C/min and a cooling free rate. Once calcinated, the samples were again ground and sieved to select grains between 150 μm (100 mesh) and 75 μm (200 mesh).

The aliquots removed from xerogel were submitted to differential thermal analysis (DTA), thermogravimetry (TGA) and differential thermogravimetry (DTG), in order to evaluate changes in physical or chemical properties depending on temperature. The measurements were performed in TA Instruments Model equipment SDT 2960, with a system of simultaneous TG/DTA. The samples were placed in a platinum crucible, under a flow of synthetic air of 100 mL/min and a heating rate of 10 °C/min.

To confirm the thermal measurements and to obtain information on the structure of the samples identifying their crystalline phases, X-ray diffraction (XRD) of powders was performed with particle sizes smaller than 75 μm. The diffraction patterns were obtained with a Rigaku diffractometer RINT Ultima Plus 2000/PC with angular Cu Kα radiation ($\lambda = 1.5406$ Å) from tube operating at 40 kV/40 mA, in a range of 10° to 80°, with a speed of 1°/min and 0.05° step in a continuous mode. The diffraction peaks were compared to patterns available in ICSD (Inorganic Crystallography Structure Database).

Pellets were produced with aliquots of 0.04 g and a particle size between 75 and 150 μm. To increase their mechanical strength, the powder of each aliquot was mixed with one drop of PVA (in the ratio of 1 g of PVA in 10 mL of water) in a porcelain mortar until obtaining a homogenized powder. Then, it was pressed with ~90 kgf/m² in a hydraulic press inside an aluminum cylindrical mold with 6 mm diameter.

Once pressed, the pellets were subjected to sintering, which consisted of a heat treatment to develop contact between the particles and to eliminate the porosity. The sintering process was realized at 300 °C for 30 min, and then at 400 °C for 2 h, following the same procedure reported by d'Amorim et al. (2012, 2013).

The TL measurements were carried out in a Harshaw model 3500. TL measurements with a heating rate of 4 °C/s were performed with two different pellets for each dose evaluated, thirty minutes after having been irradiated at room temperature.

3. Results and discussion

3.1. Thermal analysis

TGA is a technique used to measure changes of mass of a sample during the heating (or cooling) under specific and controlled temperatures. DTA is a technique that records the difference in temperature between a substance and a reference material as both being subjected to the same thermal cycle. Figs. 1 and 2