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

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HIGHLIGHTS

- β-spodumene can be successful produced by Proteic Sol-Gel and Pechini Methods.
- Syntherized pellets produced by proteic sol–gel method are sensitive to beta rays.
- Pellets produced by proteic sol–gel and SiO_2 is more sensitivity to radiation.
- Pellets of β-spodumene produced by Pechini Method is more sensitivity to radiation.

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ABSTRACT

Spodumene is an aluminosilicate that has proven suitable for high-dose TL dosimetry of beta or gamma rays. Due to the presence of lithium in its chemical composition ($LiAlSi_2O_6$ – β-LAS), it has potential as neutron dosimeter as well. This silicate may be obtained naturally or synthetically. The synthetic LAS has been produced by solid state reaction and conventional sol–gel, whose difficulty arises from the need to employ high temperatures and high cost reagents, respectively. Alternative routes like Pechini and proteic sol–gel methods are promising, because they can reduce production costs and the possibility of environmental pollution. This work aimed at producing spodumene with the proteic sol–gel method using edible unflavored gelatin as a precursor and also with the Pechini method. The products were characterized physically and morphologically, and their applicability as TL dosimeter was investigated, comparing the sensitivity of samples produced by different methods. Two sets of samples were produced using different sources of silicon, tetraethyl orthosilicate (TEOS, $Si(C_2H_5O)_4$) and silica (SiO_2). The materials produced were characterized by X-ray diffraction and by thermal analysis in order to evaluate their structural properties, as well as possible temperature-dependent changes in physical or chemical properties. The syntherized pellets produced with these crystals were irradiated with a ^{90}Sr–^{90}Y source and their TL glow curves were evaluated. The production of β-LAS was successful by both methods, either using silica or TEOS as a silicon source. The crystals were obtained using much lower temperatures than by methods described in literature. We observed that the method of powder production was critical to develop a radiation detector: the best TL material was the powder produced using silica and the Pechini Method.

1. Introduction

Thermoluminescent (TL) crystals are extensively used as passive dosimeters (TLD – thermoluminescent dosimeters) in several industrial and medical applications of ionizing radiation. In the search for optimal dosimeters, many studies have attempted to clarify the correlation between structure and composition of the TL materials and features such as high sensitivity, linearity of dose-response with temperature, and emission wavelength. However, the method of production may also introduce important differences, such as size of crystals, crystalline phases and others, that affect the dosimetric features of the TLD. These may result in a viable dosimeter or not, especially because it is well known that

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both the intensity and the position of the TL glow peaks depend on the lattice defects of the material.

Spodumene ($LiAlSi_2O_6$) is an example of aluminosilicate that has shown good results for high-dose TL dosimetry of beta and gamma rays. This material is a member of the LAS (Li_2O–Al_2O_3–SiO_2) family of solid solutions. The various phases of the LAS systems present high thermal stability, which allowed their use in manifold applications such as mirror substrates for telescopes, cookware, turbine engine, heat exchangers (Guedes et al., 2001). The TL properties of natural crystals of spodumene have been exploited in dating and dosimetry of ionizing radiation (d'Amorim et al. 2012; Ferraz et al. 2008; Souza et al. 2004). Due to its chemical composition, the natural crystal is one of the main sources of Li, and has the potential to be used as neutron dosimeter as well. Several theoretical models have been developed to correlate the physico-chemical properties of spodumene and its electronic transitions (Lima et al. 2008, 2009).

Spodumene is widely produced by solid state reactions, but it is mainly the requirement of high temperatures (Li and Peacor, 1968; d'Amorim, 2012) which prevents its large scale production. The synthesis of spodumene has been also tried by conventional sol–gel method; however, this creates mixtures of many other polymorph silica derivatives such as eucryptite, petalite or virgilite, among others, part of the LAS family (Correcher et al., 2009; Sanchez-Munoz et al., 1999). Alternative methods of synthesis, such as the proteic sol–gel and polymeric precursor protein (Pechini) routes, are promising because they can reduce production costs, the lower synthesis temperature and decrease possible environmental contamination. Proteic sol-gels were successfully employed to produce spodumene crystals (Lima et al., 2014).

The proteic sol–gel route is an alternative to the conventional sol–gel method in which an organic precursor replaces alkoxides. In this work, edible unflavored gelatin was the precursor of choice due to its significant protein content (Meneses et al., 2007). Also used was the Pechini method, which is based on the formation of a polymer chain through chelation reactions and polyesterification with uniformly distributed metal ions (Jesus, 2011).

This work aimed at producing spodumene through the proteic sol–gel route, using edible unflavored gelatin, and also through the Pechini method, using different sources of silicon. The products were characterized physically and morphologically, and their applicability as TL dosimeter was investigated, comparing the sensitivity of samples produced by different methods.

2. Materials and methods

Lithio-aluminosilicate (LAS) samples were prepared using either tetraethyl orthosilicate (TEOS, $Si(C_2H_5O)_4$) or silica (SiO_2) as a source of silicon. The proteic sol–gel method was used with a 1:0.5 ratio of reagents:gelatin. A solution was first prepared with distilled water and unflavored edible gelatin (Royal®) dissolved at about 70 °C under constant stirring. Then the following reagents were added: $Al(NO_3)_3 \cdot H_2O$ [Vetec, 98% purity], $LiNO_3$ [Fluka, 98%, purity] and either silica [Sigma Aldrich, 98%, purity] or TEOS with ethyl alcohol. The final solution was heated up to ~200 °C for one hour to release the water and form a gel. The gel was dried on a heating plate at 100 °C for 48 h. After drying, the resulting xerogel was ground in a porcelain mortar with a pestle. An aliquot of the xerogel was separated for thermal analysis and the remainder was subjected to pre-calcination at 600 °C for 2 h to remove the organic material. Different aliquots were calcinated for two hours each at different temperatures, in a muffle-type electric furnace (EDG 1800, EDG Equipamentos), using a heating rate of 10 °C/min and a free cooling rate.

For the production of samples by the Pechini method, a 4:6 ratio of ethyleneglycol:reagent was used. One solution was prepared for each reagent, $Al(NO_3)_3 \cdot H_2O$ [Vetec, 98% purity], Li_2CO_3 [MaxiFlux, 99% purity] with HNO_3 [Impex, 65% purity], silica or TEOS with ethyl alcohol, and mixed with distilled water, citric acid [Vetec, 99.5% purity] and ethyleneglycol [Neon, 99.5% purity]. The amount of citric acid used was proportional to the atomic valence of the final spodumene sample. The reagents were mixed under constant stirring and heating to 70 °C to form a final solution with a molar concentration of 0.25 mol/L. The final solution was allowed to dry at 100 °C for 24 h. After drying, an aliquot of the formed polymer was removed for thermal analysis. The remaining material was pre-calcinated at 500 °C for 2 h to promote the breakdown of the polymer chain. Then, aliquots were separated and calcinated for two hours each at different temperatures.

X-ray diffraction measurements were performed in a DMAX2000 powder diffactometer (Rigaku), with CuK_α ($\lambda = 1.5418$ E) radiation. Thermal analysis was done at a heating rate 10 °C/min with an SDT 2960 unit (TA Instruments) performing simultaneous thermal gravimetric analysis (TGA) and differential thermal analysis (or DTA). Thermoluminescence glow curves were acquired from room temperature up to 400 °C, at a heating rate of 4 °C/s, with a Harshaw 3500 TL reader. Two different pellets were evaluated for each dose and the measurements were done 30 min after irradiation with three $^{90}Sr/^{90}Y$ β-particle sources positioned around the pellets, in order to yield dose rates of 0.1395, 0.0775 and 0.2235 Gy/min.

The pellets had 6 mm diameter, 0.04 g of LAS (particle size between 150 and 75 μm) agglutinated with PVA (1 g PVA:10 mL water), pressed at ~90 kgf/m^2 in a hydraulic press and sintered at 300 °C for 30 min, followed by heating at 400 °C for 2 h.

3. Results and Discussion

3.1. Thermal analysis

Fig. 1a and b shows the results of the thermal analysis of the samples produced by the proteic sol–gel with silica and TEOS, respectively, whereas Fig. 2a and b shows the results of the thermal analysis of the samples produced by the Pechini method with silica and TEOS, respectively.

Five regions (denoted I to V) associated with different exothermic processes are shown in Fig. 1a The regions correspond to the following: I – thermal processes related to mass and water loss; II – decomposition of nitrates used in the synthesis; III – loss of organic matter from the gelatin by pyrolysis; IV – peak ascribed to the release of carbon dioxide. Finally, in region V, the peak is assumed to derive from the LAS phase formation.

Although the curves are somewhat different, almost the same thermal processes of Fig. 1a happen with the sample shown in Fig. 1b. Thus, the same mass loss events are attributed to the regions I to V in Fig. 1b.

In Fig. 2a, regions I, II and III relative to the mass loss are associated with the following processes: I – water loss; the endothermic peak relates to hydrolysis; II – evaporation of nitrate from the acids used in the synthesis; III – loss of residual organic matter, release of carbon dioxide and beginning of LAS phase formation. In regions II and III, the exothermic peaks relate to condensation reactions, decomposition, oxidation, combustion and crystallization.

In Fig. 2b, only 2 regions are denoted but the processes are very similar to those shown in Fig. 2a. The regions relate to mass loss in the following processes: I – evaporation of water and loss of nitrate from the acids used in the synthesis; the peak relates to hydrolysis and condensation; II – loss of organic matter, releasing carbon