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Topaz synthesis using Al_2O_3, $Al(OH)_3$ or $Al_2Si_2O_5(OH)_4$ and color centers promoting its radioluminescence response

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ABSTRACT

A first study on the radioluminescence (RL) response of topaz synthesized is reported. Using three alternative and different compact reactants separately, i. e., aluminum oxide, aluminum hydroxide and kaolinite, synthesis tests by chemical vapor deposition (CVD) were conducted varying systematically processing temperature and time, incidence angle, and atmosphere. Results show the feasibility to form topaz using the three types of reactants, in varying amounts of 60%, 100% and 47%, respectively. Synthesized topaz exhibits a variety of morphologies: fibers and rectangular bars using Al_2O_3, cross needle shape compacts using $Al(OH)_3$ and needle-shape phases using $Al_2Si_2O_5(OH)_4$. Irradiation with ^{90}Sr beta-source revealed that only samples prepared using aluminum hydroxide exhibit RL response. The emission band centered at 390 nm of thermally untreated samples and the lack of RL emission of samples treated thermally at 500 °C confirm that the RL response is due to the $(H_3O_4)^0$ color centers. The RL response showing the highest RL intensity at 390 nm is promoted by processing at 700 °C for 90 min, used for sample H3. A set of reaction pathways for topaz formation using the three alternative compact reactants is proposed.

1. Introduction

Radioluminescence (RL) is the phenomenon by which a material produces light by bombardment with ionizing radiation. Some minerals like topaz [1], which pertains to the group of alumino-silicates, exhibit this property. Topaz is one of the main fluorine bearing minerals that comprises a solid solution between a fluorine end member, $Al_2SiO_4F_2$ (fluor-topaz) and a hypothetical hydroxyl end member, $Al_2SiO_4(OH)_2$, with the empirical formula $(Al_2SiO_4(OH,F)_2)$ [2–5]. Topaz crystallizes in the orthorhombic system, reported for crystalline materials within space group No. 62, more specifically, to the group Pbnm (62) [6]. It has a hardness of 8 in the Mohs scale and is highly resistant to a number of chemicals including hydrofluoric acid [7]. Its reported luminescent properties and effective atomic number similar to that of human tissue, makes of topaz a potential material for the field of dosimetry [4,7–10]. And although the past and recent literatures have informed on the thermoluminescent properties of natural topaz (mineral and synthetic) [11–18], thus far, no studies have reported its RL properties.

Owing to variations in composition when mined in different locations, the presence of impurities in topaz will influence its response when exposed to different radiation conditions [19]. It is thus reasonable to think that synthesized topaz would help exploiting its full potential in its response to radiation. Recently, authors synthesized topaz $(Al_2SiO_4(OH,F)_2)$ by CVD and reported its structural characteristics, formation pathway and optimum processing conditions [5].

Although several routes have been put forward for synthesizing topaz, most of them turn out to be unattractive from the economic and technological standpoints [20–24]. Owing to the relatively low processing times, pressures and temperatures, chemical vapor deposition (CVD) is an attractive alternative route for synthesis of topaz. Several precursors have been used in the synthesis of a variety of phases by CVD [25]. Sodium hexafluorosilicate (Na_2SiF_6) has been successfully used as a precursor in different investigations due to its relatively low decomposition temperature, good stability at

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atmospheric pressure and at room temperature [26,27]. This precursor can be dissociated thermally at low temperature (≈550 °C) to generate SiF_4 (g) (according to reaction 1), which can subsequently react with the compact reactant used. In addition to SiF_4, sodium fluoride (NaF) is obtained as solid by-product but it does not participate in the reactions because it is left behind as an ash.

$$Na_2SiF_6(s) \rightarrow 2NaF(s) + SiF_4\,(g) \quad (1)$$

The aim of this work is to study the effect of compact reactant (aluminum oxide (Al_2O_3), aluminum hydroxide ($Al(OH)_3$) or kaolinite ($Al_2Si_2O_5(OH_4)$) and processing conditions by chemical vapor deposition (CVD) on topaz formation and its RL response, using sodium hexafluorosilicate as solid precursor. In addition, establish the processing conditions (temperature, time, atmosphere, and incidence angle) as well as aluminum compound compact reactant that promotes the best RL response.

2. Experimental procedure

The present investigation was carried out in two stages. In the first step, topaz was synthesized by CVD. In the second stage, the specimens were characterized by radioluminescence. The samples were prepared using aluminum oxide (A series), aluminum hydroxide (H series) or kaolinite (K series) as compact reactants and sodium hexafluorosilicate (Na_2SiF_6) as a solid precursor. The Na_2SiF_6 and the compact reactants were prepared weighing 10 g of each reagent powder and adding approximately 0.2 ml of distilled water, followed by a careful and thorough mixture with a mortar and pestle, separately. Using a uniaxial Carver press model 4350L, the Na_2SiF_6 and reactant powders were then pressed at 40 and 20 bar, respectively. Synthesis trials were conducted in three replications according to an L8 Taguchi standard experimental design. The synthesis tests were carried out in a reactor consisting of a Thermolyne tubular furnace, model 59300, provided with a 304-type stainless steel tube (the chamber) of 3.8 cm in diameter x 76.2 cm long. The Na_2SiF_6 and compacts (aluminum hydroxide, aluminum oxide or kaolinite) were positioned in the reactor, as shown schematically in Fig. 1. Table 1 shows the sample code and the experimental conditions used in the study. The tests were conducted with and without a flow of high purity nitrogen during the dwell and cooling stages (flow rate of 5 cm^3/min), at 700 and 750 °C, for 60 and 90 min. Nitrogen is used to displace the oxygen present initially in the reactor chamber and avoid formation of $Al_2SiO_4(OH)_2$, serve as gas carrier and to direct SiF_4(g) towards the reactant compact within the reactor.

Furthermore, the position of the compact reactants – Al_2O_3, Al $(OH)_3$ or $Al_2Si_2O_5(OH)_4$ –, the so called incidence angle henceforth, was varied with respect to the gas flow direction at 0 and 90°. The CVD reactor presents thermal gradients along the longitudinal axis of the tube. Based on the measured temperature profiles, the experimental temperature levels used – close to the tube ends –, were 700 and 750 °C.

After the synthesis of topaz, samples were ground in an agate mortar and sieved to-100 mesh for characterization.

The percent contribution of the abovementioned processing parameters to the variability in the amount of topaz synthesized was determined using analysis of variance (ANOVA).

In order to identify the formed phases, specimens were characterized by XRD using a diffractometer Philips model 3040 under the following conditions: excitation voltage of the anode 40 kV and current of 30 mA: monochromatic Cu K_α radiation ($\lambda = 1.5418$ E); 2θ range of 10–80°, at a scanning speed of 0.02°/s. The samples were characterized by FTIR spectroscopy using an equipment NICOLET model Avatar 320. The measurements were carried out between 4000 and 400 cm^{-1}, using KBr pellets. Morphology, distribution and composition of the samples were analyzed by SEM and energy dispersive X-ray spectroscopy (EDS) using a scanning electron microscope Philips XL30 ESEM provided with an EDX microanalysis device. Both, secondary and backscattered electron modes were used in the analysis, at an acceleration voltage between 20 and 30 kV.

The enthalpy change and Gibbs free energy change of proposed reactions for topaz formation with each of the compact reactants (A, H and K) were computed using the FactSage™ program and databases.

In the second stage of the investigation, the samples were weighed and subsequently the RL measurements were performed. RL curves were recorded at room temperature and as function of time during beta-particle irradiation with a 3.7×10^8 Bq ophthalmic ^{90}Sr beta-source placed 1 cm away from the samples. The ^{90}Sr source rendered a dose rate of 0.022 Gy/min at the sample position. The emitted light was collected by means of a $\phi = 1$ mm communication grade optical fiber (PMMA – polymethyl methacrylate) and projected onto a Sens-Tech P25PC-02 photon counting tube having sensitivity between 180 and 630 nm [28].

3. Results and discussion

The XRD patterns of A8, H8 and K8 specimens after processing by CVD can be observed in Fig. 2, allowing the identification of the reflections pertaining to AlF_3 (symbol ●) (ICDD01-080-1007), $Al_2F_{1.44}(OH)_{0.56}SiO_4$ (symbol ◊)(ICDD 01-076-0480) and Al_2O_3 (symbol □)(ICDD 00-043-1484) and $Al_2F_2(SiO_4)$ (symbol ◆)(ICDD

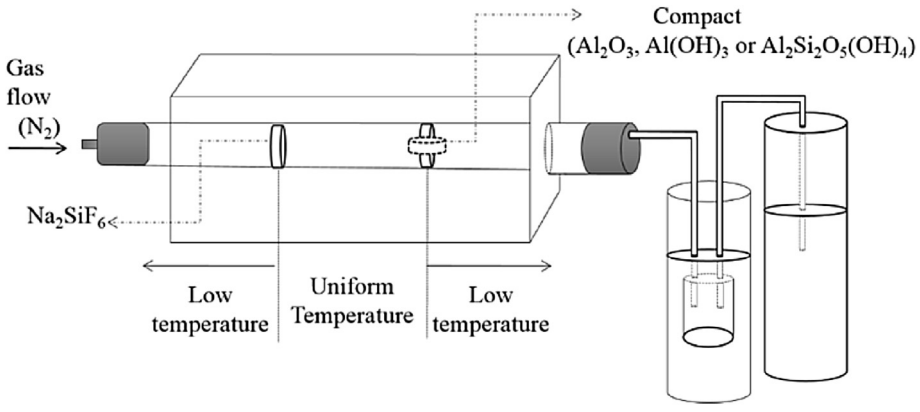

Fig. 1. Schematic diagram of the tubular reactor with solid precursor of Na_2SiF_6 and reactant compact (aluminum hydroxide, aluminum oxide or kaolinite).