

## LA-UR-13-26612

Approved for public release; distribution is unlimited.

Title: Optical and structural investigation of GSO gels made via sol gel method

Author(s): Torres, Joseph A.

Intended for: Report

Issued: 2013-08-21



**Disclaimer:**

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

# Optical and structural investigation of GSO gels made via by sol gel method

## 1. Introduction:

Silica and doped silica materials that are produced by a solution gelation (sol gel) process create versatile materials that have a large range of applications[1]. Coatings, thin films and fibers, nanomaterials, energy conservation materials and optical materials can be synthesized with this technique. Specifically, silica gels have many advantages for optical materials. The gels are transparent and possess a high homogeneity and density. In addition, silica materials can be doped with different compounds to enhance scintillating properties. Gadolinium Oxyorthosilicate (GSO) is a promising candidate as a host for rare earth ions for scintillating applications because of its high stability, density and fast decay time[2, 3].

When a sol gel is dried conventionally, it often shrinks or cracks, forming a xerogel. This work will first focus on forming a transparent GSO host xerogel with sol gel chemistry. Once a transparent GSO xerogel is formulated and characterized,  $Ce^{3+}$  will be doped into the GSO network. Non-radiative energy transfer from the Gd matrix ions to the  $Ce^{3+}$  ions occurs because the GSO crystals activated are close in energy to the  $Ce^{3+} f \rightarrow d$  transition[4]. GSO:  $Ce^{3+}$  crystals are currently produced by growing single crystals via Bridgeman and Czochralski methods, which are expensive. Optical ceramics offers a cheap alternative method for making scintillating materials.

Structural and thermal characterization of the xerogel will be investigated using X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The materials' optical properties will be examined by UV-Vis absorption spectroscopy. XRD will be utilized to determine the crystal structure. This will tell determine if the gel is amorphous or crystalline. FTIR was be used to identify functional groups in the gel. DSC and TGA will be used to thermally characterize the gel's crystallization temperature.

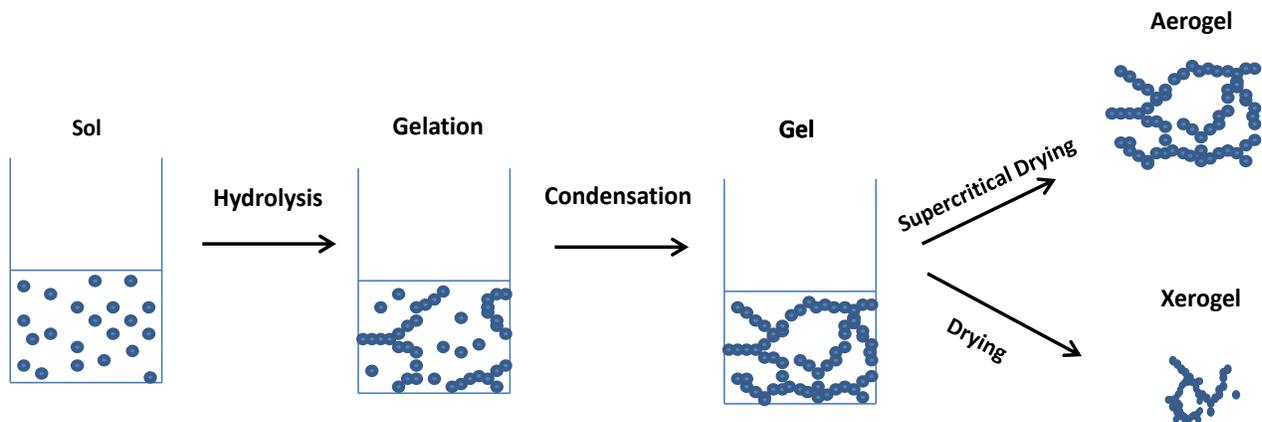


Figure 1 Illustrates reactions that take place in making materials via sol gel route

Sol gel materials are generally synthesized via hydrolytic polycondensation, of silica precursors at room temperature, such as TMOS or TEOS, under controlled conditions[1]. Figure 1 illustrates the process of forming a gel. A catalyst is often needed because the gelation process is slow due to low polarity of the Si-O bond[1]. The catalyst can be an acid or base depending on the properties of the gel that is desired.

A base will push the equilibrium of the reaction towards condensation. This will produce a more colloidal gel. An acid will favor hydrolysis and produce more of a polymeric type gel. A challenge in forming the gel is the solubility of the precursors within the solution. This requires mixing of the precursors before the gel vitrifies. A xerogel is formed when the gel is allowed to dry conventionally. The solvent will evaporate and this will cause shrinkage or cracking in the silica network. However, when the solvent is brought to its critical point and is replaced by a gas, an aerogel is produced. An advantage to aerogel is that it will not shrink or crack. A reactor is used to bring the solvent, usually methanol or CO<sub>2</sub>, to its supercritical point. At this point, the solvent is gaseous or gas-like and can be removed without exerting any capillary forces on the gel network.

## **2. Experimental:**

### *2.1 Gel Preparation*

GSO will be formed by the following reaction:



The starting materials used in the present work were reagent grade Gadolinium Nitrate (99.98%), Tetraethyloxyorthosilicate (TEOS, 99.5%), Ethanol (EtOH, 99.8%), and Nitric Acid (35 M). Gadolinium nitrate was used because of the high solubility compared to gadolinium oxide. The ratio of Gd(NO<sub>3</sub>)<sub>3</sub>:TEOS was set at 2:1. Two moles of Gd(NO<sub>3</sub>)<sub>3</sub> which will decompose into 1 mole of Gd<sub>2</sub>O<sub>3</sub>. As the moles of Gd(NO<sub>3</sub>)<sub>3</sub> increases, additional phases of gadolinium silicate will start evolving[3]. The precursors were made in two parts. Part A contained stoichiometric amounts of Gd(NO<sub>3</sub>)<sub>3</sub>, H<sub>2</sub>O, EtOH, and HNO<sub>3</sub>. The solution was mixed for 1 hour at room temperature. Part B contained stoichiometric amounts of TEOS, H<sub>2</sub>O, and EtOH. The solution was mixed for 1 hour at a temperature of 70°C. Part A was then slowly added to part B and allowed to mix at room temperature for 1 hour. The gel was poured into a glass petri dish and was allowed to vitrify for 2 days. The gel was further dried in a vacuum oven at 100°C for 3 days to yield a xerogel. A piece of as made xerogel was selected and grinded to a fine powder for XRD, FTIR, and DSC measurements.

## 2.2 Characterization

A powder XRD profile was obtained on a RigakuUltima III diffractometer with  $\text{CuK}_\alpha$  ( $\lambda=1.542 \text{ \AA}$ ) radiation, using an applied voltage of 40 KV and 20 mA anode current, calibrated with Si at a rate of 2 deg/min.

A FTIR spectrum using Attenuated Total Reflectance (ATR) with a diamond crystal was measured over the  $400\text{--}4000 \text{ cm}^{-1}$  range by a Bruker Vertex 80V FTIR spectrometer [5] with  $4 \text{ cm}^{-1}$  spectral resolution.

The thermal stability of the xerogel was evaluated by DSC on a Netzsch DSC 404 F1. The measurement was carried out under nitrogen atmosphere with a covered Pt–Rh crucible; with a heating rate of 10k/min. Calibration with a sapphire standard was performed. The xerogel was further investigated with TGA (TA instruments Q 500)[6]. The UV–Visible absorption spectrum of the xerogel was measured on a Varian Cary 5000 double-beam spectrophotometer.

## 3. Results and Discussion:

### 3.1.XRD

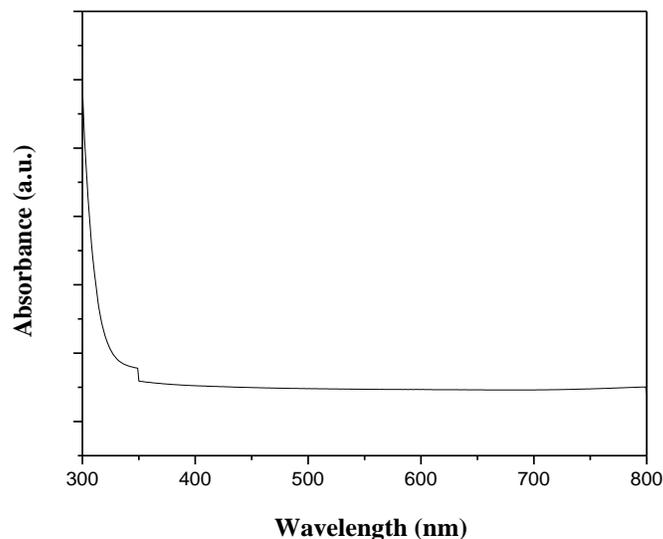
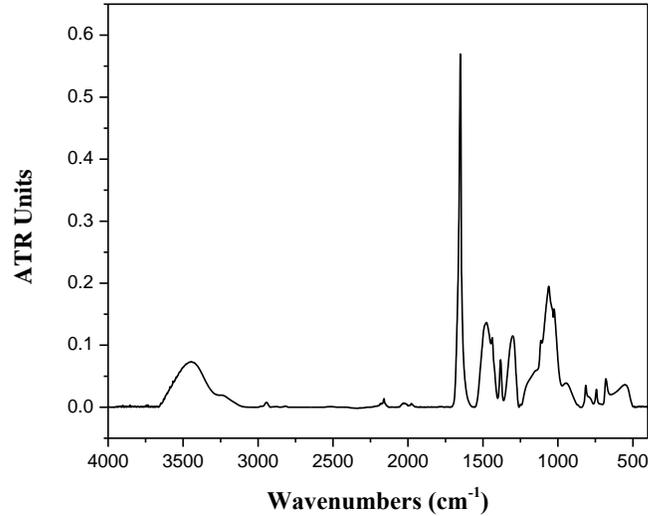


Figure 2\_XRD profile of GSO xerogel

The broad humps in Figure 2 indicate the amorphous nature of the xerogel. Further XRD experiments will be used to confirm the GSO phase after heat treatment is completed. This heat treatment temperature will be selected based on the crystallization temperature from DSC.

### 3.2. FTIR Spectroscopy



Figure\_3 FTIR spectrum of the studied xerogel

Figure\_3 presents the FTIR spectrum of the studied gel within the wavenumber range of 4000-400  $\text{cm}^{-1}$ . The peaks common to Silica are 3300, 1650, 900-1200, and 800  $\text{cm}^{-1}$ . The broad peak centered at 3300  $\text{cm}^{-1}$  is assigned to OH bending and stretching vibrations [7, 8]. The broad peak centered at 1060  $\text{cm}^{-1}$  is the Si-O-Si and Si-O vibration modes. The sharp peak at 1650  $\text{cm}^{-1}$  is from  $\text{N}_2\text{O}_5$ . This is a product in the decomposition of the Gadolinium Nitrate.

### 3.3. Thermal Analysis

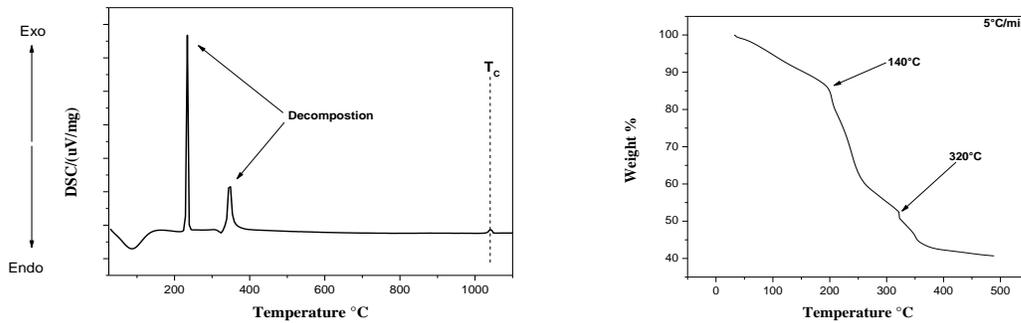


Figure 4 (a) DSC profile of the as made gel ran at a heating rate of 10°C/ min. (b) TGA profile of the gel ran at 5°C/ min.

DSC was utilized to determine thermal properties: Glass transition ( $T_g$ ) and Crystallization ( $T_c$ ). Figure 4 illustrates a  $T_g$  around  $125^\circ\text{C}$ . There are two sharp peaks at  $225^\circ\text{C}$  and  $350^\circ\text{C}$  which represents an exothermic event. TGA was utilized to confirm that this event is decomposition since crystallization would show no weight loss and decomposition would show loss in weight. The spectrum does show that the sample loses 60% of its weight between  $197^\circ$  and  $337^\circ\text{C}$ . These temperatures correspond to the 2 exothermic peaks in the DSC spectrum. The loss in weight can be attributed to the decomposition of Gadolinium Nitrate which produces  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$ [9]. The FTIR spectrum confirms the presence of these compounds in the gel.

The crystallization peak ( $T_c$ ) of the GSO is actually seen at  $1030^\circ\text{C}$ . Using this information, the temperature for heat treatment was selected as  $1000^\circ\text{C}$ .

### 3.4. UV-Vis Spectroscopy

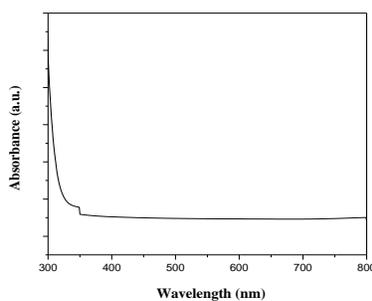


Figure 5 UV-Vis absorption spectrum of studied gel.

The UV-Vis absorbance spectrum was taken to determine if the gel is transparent throughout the visible range. The GSO host is transparent in the visual range and begins to absorb around 300 nm. It is important for scintillators to be transparent in this region in order to emit light in this region.

## 4. Conclusion:

In this work, a transparent GSO xerogel was prepared using a sol gel processing method. The gel was characterized using XRD, FTIR, DSC, TGA, and UV-Vis absorption. FTIR and XRD were utilized for structural analysis of the gel. DSC and TGA were used in tandem to thermally characterize the gel. The crystallization temperature of the gel was determined. The DSC spectrum also shows decomposition of impurities. Therefore, heat treatment above the decomposition temperature will serve to purify the gel. Further XRD experiments on the heat treated gel will be performed to determine if the GSO phase is being formed.

## 5. Future Work:

Scintillators are materials that convert energy from incoming particles or radiation into electron-hole pairs which leads to emission of light[10].  $Ce^{3+}$  will also be doped into the gel matrix and the scintillating properties will be investigated. GSO doped with  $Ce^{3+}$  possesses high scintillation yield and short decay time (40 ns)[11]. The concentration of  $Ce^{3+}$  will be determined to see the optimal amount that will produce high yield. At a certain concentration, the luminescent properties will begin to quench. Cerium Nitrate will be used to dope  $Ce^{3+}$  into the matrix. A challenge will be to keep  $Ce^{3+}$  from oxidizing to form  $Ce^{4+}$ . Antimony Oxide will be added as a reducing agent to prevent  $Ce^{4+}$  from forming.

Future work will also focus on making a GSO aerogel via supercritical drying. Aerogels are an interesting material given the low density and low thermal conductivity characteristics. They are coherent, porous solids made by the formation of a colloidal gel followed by removal of the liquid within the pores of a gel via supercritical drying[12]. Aerogels are super lightweight and are transparent in the visible spectrum. A good scintillating material typically needs to be high density, to increase stopping power, and a high refractive index close to glass. Until now, very little work has been done on using aerogel as a scintillating material due to the low refractive index and density. Aerogels are commonly  $SiO_2$  but can be made from different materials such as titanium and carbon. If an aerogel contains high Z material, then the stopping power of the scintillator may be increased.

## 6. Reference:

1. Ciriminna, R., et al., *The Sol–Gel Route to Advanced Silica-Based Materials and Recent Applications*. Chemical Reviews, 2013.
2. Blasse, G., *Scintillator materials*. Chemistry of Materials, 1994. **6**(9): p. 1465-1475.
3. Seema Shinde, M.G., Shashwati Sen, S. G. Singh, S. C. Gadkari, *Synthesis of gadolinium silicate by hydrothermal method*. AIP Cpmference proceedings, 2013: p. 1192.
4. V.G. Baryshevsky, D.M.K., MV. Korzhik, V.B. Pavienko, A.A. Fedorov, *Mechanism of scintillations in cerium-doped gadolinium orthosilicate  $Gd_2SiO_5$  : Ce crystals*. Elsevier Science, 1994.
5. BrukerOptics. *Vertex 80/80V*. 2013 [cited 2013; Available from: <http://www.bruker.com/products/molecular-vibrational-spectroscopy/ftir/vertex-series-research-ft-ir/vertex-8080v/overview.html>].
6. Instruments, T., *TGA Thermogravimetric Analyzer Q series getting started guide*. TA, 2006.
7. Stoch, A., et al., *FTIR study of silica sol-gel deposited films on anodically oxidized aluminium*. Journal of Molecular Structure, 1993. **293**(0): p. 287-290.
8. M. Waseem, S.M., A. Naeem, K.H. Shah, Irfan Shah, Ihsan-ul-Haque, *SYNTHESIS AND CHARACTERIZATION OF SILICA BY SOL-GEL METHOD*. J Pak Mater Soc, 2009.
9. P. P. Melnikov, V.A.N., and L. Z. Zaroni Consolo, *Computerized Modeling of Intermediate Compounds Formed During Thermal Decomposition of Gadolinium Nitrate Hydrate*. Russian Journal of Physical Chemistry A,, 2012. **86**(11): p. 1659-1663.
10. Blasse, G., *Scintillators materials*. Chem. Mater., 1994. **6**: p. 1465.
11. ISHIBASHI, H., *Mechanism of luminescence from a cerium-doped gadolinium orthosilicate ( $Gd_2SiO_5$ ) scintillator*. Nuclear Instruments and Methods in Physics Research, 1990. **A294**: p. 271-277.
12. Gesser, H.D. and P.C. Goswami, *Aerogels and related porous materials*. Chemical Reviews, 1989. **89**(4): p. 765-788.