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Project Plan

1. Aim of the Project

This document summarizes the various objectives I would like to address in my project. They have been split into "Main Objectives" that will characterize the projects direction and "Additional Objectives" which will be addressed if there is additional time or if any issues occur in the project, meaning alternative provisions needs to be made.

1.1. Main Objectives

-Fabricate transparent silica glass using fumed silica by using "Solid-State Sintering"

- Fabricate transparent silica glass using fumed silica by using "Pressure-induced Sintering"

-Investigate the electronic states and defects that are believed to contribute to White Light Emission. This requires using software (Games or Vasp) to stimulate different models and perform calculations. This will be compared with experimental data.

1.2. Additional Objectives

-Photoluminescence decays dynamics. This could include mixing different particle sizes, changing pellet size and evaluating temperature dependence.

- Other sintering methods which could include "Spark-Plasma sintering". Note if this is undertaken it would include experiments outside of Aberystwyth. After discussions with my project supervisor Martin Wilding, there is availability to do this as a result of new research being done into material properties linked to Aberystwyth.

-Raman spectroscopy of the bulk silica glass to investigate the R line and the D lines.

2. Resource Section

Equipment: - Pressure-induced sintering apparatus brought in and set up (has arrived at Aberystwyth and a certain date has already been arranged for when a skilled technician is coming to Aberystwyth to help set it up).

-Furnace (located in the Materials Laboratory) should be booked for Weeks 3-5.

- Spectrometer, Photography and Microscope to view structure. The Microscope with camera (Ground floor Laboratory, IMAPS) and the Spectrometer (1st Floor IMAPS) are both readily available to use after discussions with Steve Fearn.

-X-ray diffractometer (located in the Materials Laboratory should be booked for Weeks 3-5 and 8-9)

Laboratory Access:

- Materials Laboratory (Weeks 3-5 and 8-9)

-1st Floor Laboratory (Available anytime)

Software: -Gamess or Vasp (both available)

Materials: - Due to preliminary work in Semester 1 indicating issues with the particles, new particles have been brought in from Sigma (See Figure 1 for descriptions). We note possibility a third particle size might be introduced for additional results, namely 20nm.

Figure 1: Information of the Fumed Silica

Particle Size (nm)	Surface Area (m^2/g)	Density (lb/cu.ft)	Product Identification from Sigma
7	390 ∀ 40	2.3	S5130
14	200 ∀ 25	2.3	S5505

3. Additional Information

-Continue weekly meetings with project supervisor Martin Wilding to discuss project progress (Semester 1: Tuesdays 4pm, Semester 2: Tuesdays 2pm)

-Weekly Thursday workshops on HPC Wales, (beginning 30th January 2014) 4pm-5pm, C4, Cledwyn Building.

-As a result of the date for the Pressure-induced sintering being postponed due to availability of the technician, the experimental data obtained from Pressureless sintering will be first compared to the stimulations. Once the data is then obtained from Pressure-induced sintering this will then be compared. However, we will take into account that there might be limited time and consequently only the spectral analysis might be achievable.

Figure 2: Weekly Plan for the Project

Week	Dates	Milestones/Aims	Additional Information
1	27th January- 2nd February	Discussions with supervisor on materials.	
2	3rd February -9th February		
3	10th February- 16th February	Set up initial pressureless, Solid state sintering experiments.	
4	17th February-23rd February		Literature Review and Project Plan Deadline :Monday 17th February 2014, 2pm
5	24th February-2nd March	All samples using pressureless sintering must be created by 2nd March. Analysis of Spectra	
6	3rd March-9th March	3rd March: Begin data analysis using software and comparison with experimental results.	
7	10th March-16th March		
8	17th March-23rd March	Begin pressure induced sintering experiments.	Technician arriving 17th March
9	24th March-30th March	Pressure induced sintering experiments analysed.	
10	31st March-6th April	Data Analysis and comparison with the experimental data must be completed by 31st April	
11	7th April- 13th April		Oral Presentations
-	-	-	Final Report Deadline: Tuesday 6th May 2014, 2pm

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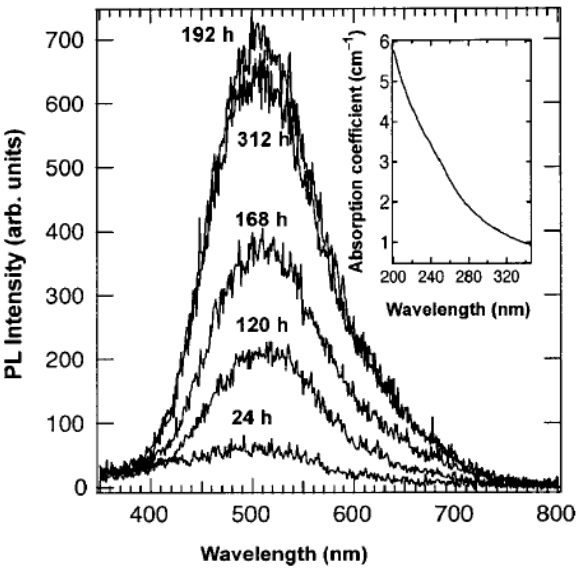
White Light Emission from SiO_2 Nanoparticles

Many experiments have demonstrated silica exhibits optical properties. For this reason different types and forms of this material have been investigated to harness this behaviour[1]. For example, after porous silica was first explored by Canham, amorphous SiO_2 was analysed[1]. In particular, Uchino discovered white light can be emitted from a non-porous glass formed from silica nanoparticles called Fumed Silica[2]. However, in the Si/SiO_2 films this phenomenon is not present. For this reason, scientists now seek to answer the question as to why white light is emitted from bulk silica glass and not from the films themselves. To evaluate this mystery individuals have sought answers through investigating both the structure of fumed silica and the bulk glass as well as developing different thermal treatments to obtain the glass.

1. White Light Emission from Bulk Silica

White light emission is the emission of light across the whole visible region of the electromagnetic spectrum (400nm-700nm). For any sample to emit white light a radiation source of sufficient energy needs to be applied to cause electronic transitions. Uchino identifies a UV source is sufficient to cause bulk silica glass to emit white light, with the spectral feature of white photoluminescence(PL) at 510nm [2] as shown on Figure 1. Figure 1 clearly indicates how the peak has its intensity dependant on the duration of the thermal treatment. In fact recent experiments have developed this further, by demonstrating how the peak can be decomposed into three individual peaks in the region 360-510nm [3]. Another significant result that is apparent is that the sample age

Figure 1: Photoluminescence spectra for bulk silica glass[2]



and wavelength of the source do not affect the spectra[2]. This information is therefore important for any experiment into white light emission and should be noted in my experiment.

Although, fumed silica does not emit white light, results have demonstrated PL emissions at "652 and 523nm"[2]. From this property, Uchino argues this is the reason why fumed silica does not emit white light, as these PL emissions cause low emissions in the green region of the visible spectra. He develops this suggestion further by implying different processes cause photoluminescence in fumed silica and the glass. However, in each case, Uchino does not indicate the exact origin[2]. One suggestion proposed by Vaccaro, is that fumed silica's nanodimensional structure causes its blue PL emission[4]. This gap in the literature offers availability for further study, as perhaps through identifying the structural

difference between fumed silica and the glass we can determine the origin of the white light emission. Through directly contacting Uchino, he informed me he has made no progress in identifying that this is the cause [5]. Consequently, this means work still needs to be done.

2. Production

Before considering the possible origins of the white light emission, we must first identify how bulk SiO_2 glass is produced. Previous methods of production include Sol Gel which causes the problem of high OH concentrations[3,6] and Melt-quenching which is not only difficult to control, but inefficient as it requires temperature above 2000 ^0C [3,6] to melt a large sample. Alternatively, using the process of hydrolysis which breaks bonds in an oxygen-hydrogen flame, we can produce amorphous SiO_2 nanoparticles [7]. These nanoparticles known as Fumed Silica can also form a glass through a two stage process of Pellitization and Sintering, while not including the disadvantages of the other methods as stated above.

2.1 Pellitization

The first stage of producing a silica glass from nanoparticles is Pellitization. Initially through compacting the powder, the nanoparticles combine to form aggregates [8]. Then by building up these aggregates, a weakly bound pellet of certain shape is created. At this stage no permanent structural change occurs, enabling us to carefully control the size and dimensions of the sample. Of course during pellitization there are a number of factors we must consider. These can include particle size, pressure and the pellets final size. Kang addresses the significant factor that "shaping techniques"[9] affect sintering. For instance, by compacting the powder to a smaller size, there are fewer pores between nanoparticles and hence fast densification. Nevertheless, we should note when sintering the sample decreases in size and surface area[10]. Uchino noted a significant decreases in area from "400 -190(120)m^2/g"[7]. Therefore, this might be why since Uchino's first experiments, samples of similar initial surface area have been used in other experiments. In light of this, a balance between pellet size and surface area must be acknowledged in my experiment.

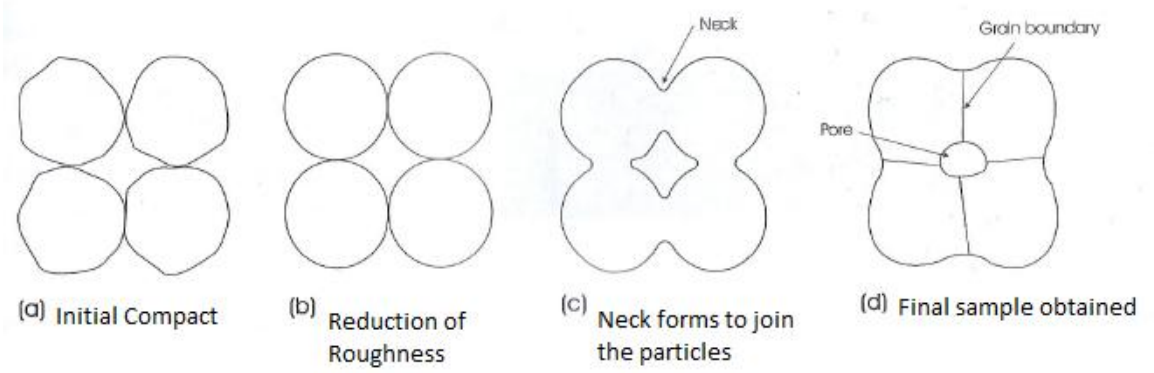
In old[11] and recent[8] experiments a uniaxial press has been used to apply the pressure which can vary from 300MPa[8] to 530MPa[11] depending on the geometry. Consequently, its frequent use demonstrates its reliability and suitability for an experiment. However not all experiments have used this apparatus. Before white light was first observed, Yong-Taeg fabricated a silica pellet using Slip-Casting[6]. This method requires mixing the powder with water, before placing in moulds and drying. In illustrating this method, Yong-Taeg notes its advantages for producing large samples[6]. Consequently, as pellitization does not affect white light, both methods can be applied. Although, as I will be producing small samples in the range of a few mm's, a uniaxial press will be used.

Moreover, it is apparent that predominantly cylindrical pellets have been produced [2,3,12] Although, some experiments have used rectangular pellets[4,8,13]. This identifies how the glass's transparency which could affect the white light is independent of the shape. However, cylindrical pellets have the advantage when applying pressure due to their geometry and for this reason this shape will be used in my experiment.

2.2 Sintering

Once a pellet is obtained Sintering can be conducted. During this process a temperature "below the melting point"[14] must be applied

Figure 2: The four different stages of sintering[14]



to cause the pellet to maintain a permanent structure. Figure 2 shows how sintering can be decomposed into four stages. It illustrates that the particles need not be spherical and how there is disruption at the grain boundaries causing them to disappear and reform.

An important remark Tilley addresses is how different reactions cause Sintering[14]. There are in fact many different reactions with a few including diffusion, viscous flow and evaporation[14]. Hence, one might assume the white light emission from silica glass is process dependant. Tilley disproves this possibility by specifying only the resulting shape is affected by the reaction[10]. Consequently, this means different methods can be tested to obtain the glass.

2.2.1 Types of Sintering

Kang points out how Solid state and Liquid phase sintering characterize the different thermal treatments[15]. Solid state sintering is when the pellet undergoes densification without changing its state. Therefore only the shape should change and all other parameters should remain constant. Kang clearly addresses how this is not the case in Liquid phase, with the microstructure changing due to a liquid being present in the pellet[16]. As scientists such as Uchino[7] and Buscarino[8] imply white light is due to the microstructure, this gives a strong explanation as to why no experiments have used this method. However, as the origin is still unknown there is no evidence to support this. Thus future work could involve using Liquid phase sintering to investigate the glass's white light emission.

In 2004, Uchino's experiment which first saw white light emission from bulk silica used pressureless, Solid state sintering. It involved applying a constant temperature of 980^{o}C and sintering for different durations[2]. In fact temperatures can reach 1200^{o}C [7] and a transparent glass will be obtained. Although, from 1300^{o}C onwards the samples become crystalline and white light is not observed[2]. As a result, careful control of temperature should be done.

Nevertheless, this method appears to be reliable with Buscarino recently applying it where he was able to reduce the sintering time from 192hrs[2] to 75hrs[8] and still observe an intense emission. However, Buscarino suggests in this method particle size affects sinterability[8], which was not previously acknowledged[2]. It is implied smaller particles cause modifications to the structure whereas larger particles do not. In fact the particle size in previous experiments has often ranged from "7nm-50nm"[1-4,7,8,13, 17] with the predominant size of 7nm being used, suggesting at this scale we induce a change. In light of this the 7nm particles will be

investigated in my experiment as well as sizes that have small perturbations from this.

A very recent, alternative method is Spark Plasma Sintering[18]. This is similar to the previous method with a constant temperature being used, but differs by placing the powder in graphite die, before a uniaxial press and DC current are applied[18]. This method reduces sintering time, yet it is disadvantaged by limiting the shapes produced and requiring expensive equipment[19]. Furthermore, Zhang compares this method to Pressureless sintering. Although, he does not indicate whether it was solid or liquid state[18]. Therefore we cannot compare to Uchino[2] or Buscarino's[8] work as other factors might have been present.

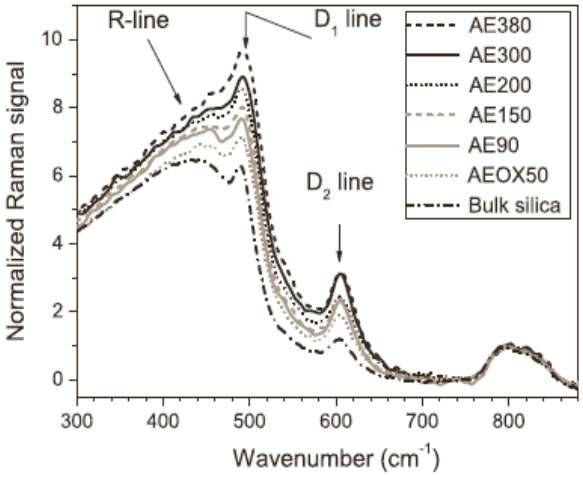
Noting the above methods have all used pressureless, Solid state sintering, Uchino argues that Pressure sintering at 6GPa and ambient temperature can also obtain the glass[2]. White light emission has not been considered in-depth using this method. For this reason, I would like to investigate this, along with Solid state sintering at low temperatures.

Moreover, we should note in any method control of the impurity content and sintering variables such as pore size and density must occur[9]. Consequently, this must be taken into account during my experiment.

3. Origins of White Light Emission

As alluded to earlier, Uchino proposes the origin of white light could lie in a structural difference between fumed silica and bulk silica glass[7]. Noting bulk silica glass is the fusing of SiO_2 nanoparticles that are proposed to have a "chainlike"[11] structure, one might assume that their structure is identical. Clémer identifies how previously the bulk glass was viewed to have the same surface and interior structure as fumed silica[17]. Uchino draws on this weak argument by highlighting that for each form of SiO_2, little work has been done into the structure[7]. From performing experiments, he proposes fumed silica has the structural difference of more 3-4 membered rings[7]. Vaccaro supports this in Figure 3 by the Raman spectrum having the D1 and D2 lines lowered for the glass.

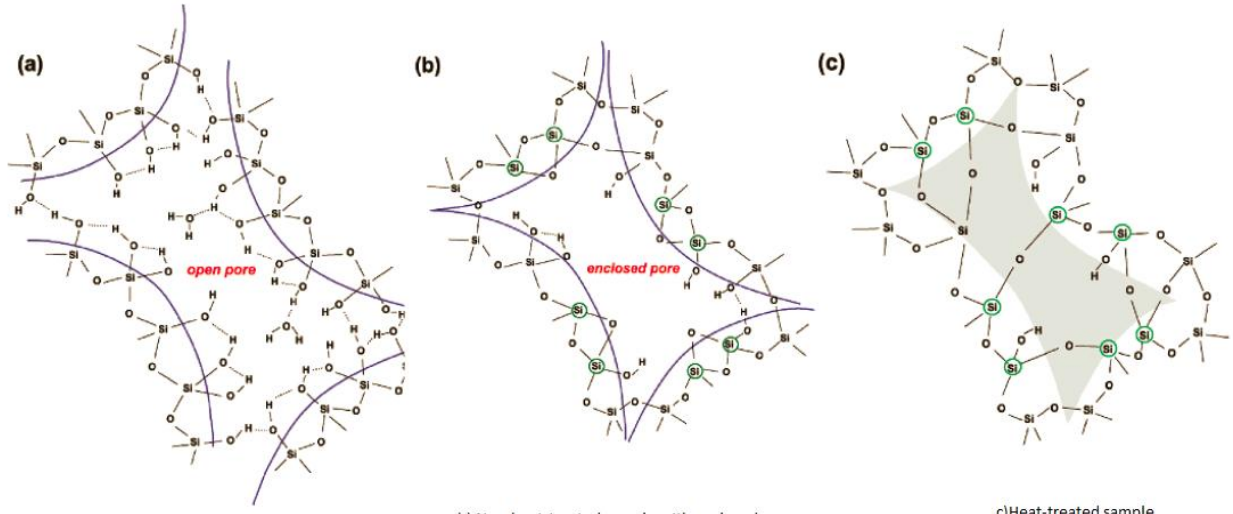
Figure 3: Raman spectra for different particle sized fumed silica samples and bulk silica glass[4]



Ivanda addresses the important concept that the D1 and D2 lines characterises these rings, with the former associated with the 4-membered and the latter with the 3-membered[20]. Rings are small structures formed by the bonding of atoms. Hence, in silica the 3 and 4-membered rings have 3 or 4 silicon atoms bonded to oxygen, forming a tetrahedral structure.

Developing this even further, Vaccaro proposes fumed silica has the 3-4 membered rings located in the external shell of the particles, causing a stressed network in comparison to the interior[13]. This point is backed up by Figure 4 that illustrates the structural change of fumed silica during thermal treatments. It indicates the core has

Figure 4: The structure of fumed silica during thermal treatments[3]



a) Non-heat-treated sample with open pore

b) Non-heat-treated sample with enclosed pore

c)Heat-treated sample

space (a) for the structure to reorganise, causing it to be different to bulk silica glass (c). In addition, Figure 3 demonstrates that there is a shift in the frequency for the peak of the R line. Buscarino clarifies this behaviour through his recent experiments[8]. Therefore perhaps either one of these characteristics is the reason for the white light emission. However, as no literature has identified this, future work could be performed here. This might involve a more detailed analysis of the Raman spectra or analysis of the rings.

A contrary explanation to the origin of the white light emission has been proposed to lie in the existence of Midgap states[12] which are believed to cause a one-photon excitation[2]. Midgap states are states that are located in the bandgap of the material. Consequently, as the bandgap is the region of forbidden states, they must arise from defects. Noting 9eV [12] is the bandgap energy for SiO_2, Yamada and Uchino's proposition gives a strong indication that Midgap states play a role, as under a 5eV source photoluminescence occurs, as well as discarding a previous suggestion that a self-trapped exciton caused the white light emission[12].

Moreover, it is suggested the Midgap states are created from the Si-O bond changing in angle[13] and increasing in length[12], causing strained ≡Si-O-Si ≡ bonds. This is a strong explanation as one would expect from fewer 3-4 membered rings, there would be a strained network of SiO_2. Yamada supports this argument by the lengthened Si-O bonds on part c) of Figure 4. After interviewing Uchino, he still maintains that this is the most probable cause of the white light emission. In spite of this, he notes he has no current work to clarify it because his interest has shifted to materials that emit coloured light due to defective oxides such as MgO [5]. This gap in the literature indicates that future work into midgap states should be conducted which might be achieved through a more detailed investigation into the band structure.

As there has been no solid evidence to indicate this particular defect causes midgap states and hence white light emission, it has resulted in a significant development into the different defects present in SiO_2[1,11,21,22]. One branch of this includes the paramagnetic point defects called E-centres. Often referred to as Dangling bonds they contain an unpaired electron in the configuration of a single silicon atom and three oxygen atoms[21]. Uchino identifies the significant difficulty in identifying which defect might be causing the

white light emission as many E-centres in SiO_2 have been found[22] along with the possibility that even more might be present and unaccounted for. Another issue is that the bulk SiO_2 glass is amorphous, meaning determining the defect is also difficult due to the structure having no periodic ordering.

Clémer has made a significant contribution to investigate the defects through using Electron Spin Resonance[17]. His results give a strong indication that the E_γ defect $O_3{\equiv}Si{\bullet}\ldots{}^{+}Si{\equiv}O_3$ is the cause. Nevertheless, no other evidence has clarified this, illustrating this argument could be weak. Although, Clémer develops his idea further by suggesting the defect combines two defect systems of E_γ which are located at the centre and surface of the SiO_2 particles[17]. This could be a strong argument as Figure 4 supports it. One might also argue the slow and fast PL dynamics that have also been investigated supports this[12].

Another way the problem has been tackled involves density functional theory to perform quantum chemical calculations[21,22] in order to understand these defects. Programs to perform this have included Gaussian-98 [21] and Gaussian03 [11]. Therefore by modelling the defects and comparing to experimental data we could perhaps identify the origin of the white light emission. Through using software such as Gamess or Vasp, it will allow me to take my project in this direction.

4. Applications

Despite the glass having the disadvantages of it being amorphous and containing defects, which would cause difficulty in controlling the structure and the white light emission, it has a number of useful applications. Buscarino alludes to the possibility that the glass could be used in electronics[8], however the glass's unique white light emission would also enable it to be used as a material for optical devices.

On the other hand, there is also evidence for temperature dependence of the PL emission for the glass. Uchino clearly indicates there are changes in the PL spectra at 200K [1]. Therefore, perhaps the glass could have applications in temperature sensitive devices. Nevertheless, Zhang identifies how bulk silica has the properties of low electrical conductivity and thermal expansion in addition to its transparency[18], highlighting that it is a worthwhile material to investigate. For this reason, I believe it is fundamental to understand the reason behind the white light emission from the bulk silica glass.

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