SOL GEL PREPARATION OF BARIUM OSUMILITE GLASS

.

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THIS DISSERTATION IS SUBMITTED TO FULLFILL THE

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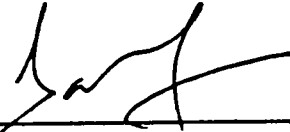
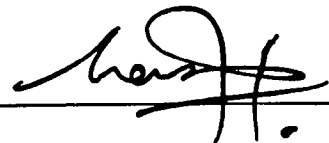16 May 2008

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ABSTRACT

Partial alkoxides are used in the sol gel preparation of stoichiometric barium osumilite ($BaMg_2Al_6Si_9O_{30}$). TEOS applied as in acidic condition to increase its hydrolysis rate. Utilization of acetic acid and ethylacetoactate to chelate Al butoxide are controlled the precipitation. Two samples are prepared from the resultant sol: one dried and aged at room temperature and another one at 75°C. This is to analyse the influence of the temperature on the crystallisation of barium osumilite. Gelation and aging at different temperatures influenced the composition of final product. Amorphous gel clusters are produced after calcination at 650°C. FTIR analysis is performed to analyse the evolution of gel. The analysis shows the expulsion of some content and some carbonaceous residuals in the gel matrix. Barium osumilite crystallizes above 1200 °C and the crystallization initialised by mullite. Other phases also present during crystallization such as cordierite, MAS osumilite and hexacelsian.

ABSTRAK

Alkoxida-alkoxida separa telah digunakan untuk penyediakan barium osumilit $(BaMg_2Al_6Si_9O_{30})$stoikometrik secara sol gel. TEOS berasid telah digunakan untuk mempercepatkan kadar hidrolisisnya. Penggunaan etilasitoasitat untuk mengelat Al butoxide dan penggunaan asitik asid telah mengawal pemendakan. Dua sampel telah disediakan daripada sol yang dihasilkan: satu daripadanya dikeringkan pada suhu bilik dan yang lagi satu pada suhu $75^{\circ}C$. Ini adalah untuk mengkaji pengaruh suhu ke atas penghabluran barium osumilit. Pengeringan pada suhu yang berbeza telah mempengaruhi komposisi hasil terakhir. Kelompok-kelompok amorf telah dihasilkan setelah rawatan haba pada suhu $650^{\circ}C$. Analisis FTIR telah dilakukan untuk mengkaji evolusi gel. Ia telah menunjukkan kehadiran bahan-bahan berkarbon id dalam kelompok tersebut. Barium osumilit menghablur pada suhu lebih $1200^{\circ}C$ dan penghablurannya dimulakan dengan fasa mullit. Fasa-fasa lain juga hadir semasa penghabluran seperti celsian, MAS osumilite dan hexacelsian.

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LIST OF ABBREVIATIONS / SYMBOLS

AAR	All alkoxide route
Al / Al^{3+}	Aluminium / aluminium (III) ion
$\overset{\circ}{A}$	Angstrom
a_0	Unit cell dimension
Ba / Ba^{2+}	Barium / barium (II) ion
BuO	Butoxide
Ca / Ca^{2+}	Calcium/ calcium (II) ion
Cu	Copper
Cl_2	Chlorine
CCl_4	Tetrachloromethane
cm	Centimeter
c_0	Unit cell dimension
°C	Celcius degree
etac	Etylacetoacetate
Fe / Fe^{2+} / Fe^{3+}	Iron / iron (II) ion / iron (II) ion
FTIR	Fourier transform infrared
g	Gram
H / H^+	Hydrogen / proton
H_2O	Water
HCl	Hydrochloric acid
HF	Hydrofluoride
K	Kelvin

K / K$^+$	Potassium / potassium (I) ion
KBr	Potassium bromide
KOH	Potassium hydroxide
KF	Potassium fluoride
M	Metal
Mg / Mg^{2+}	Magnesium / magnesium (II) ion
MPa	Mega Pascal
N	Coordination number of metals
NaCl	Sodium chloride
nm	Nanometer
O	Oxygen
OH / HO	Hydroxyl ion/group
OR / RO	Alkoxide ion/group
PAR	Partial alkoxide route
R	Alkyl group
R	Water to silicon molar ratio (H$_2$O:Si)
Si	Silicon
Sr / Sr^{4+}	Serenium / Serenium (IV) ion
SN$_2$	Nucleophilic substuition: second mechanism
TEOS	Tetraethylorthosilicate
TMOS	Tetramethylorthosilicate
TG	Thermogravimetry
DTA	Differential Thermal Analysis
XRD	X-ray diffraction
Z / z	Valence number of metals

CHAPTER 1

INTRODUCTION

1.1   INTRODUCTION

Barium osumilite ($BaMg_2Al_6Si_9O_{30}$) has many attractive physical and chemical properties that make it the most favourite in composition of high temperature utilities. It has also gained high recognition in the glass industry as it has very stable predominance in the glass.

Barium osumilite glass has usually been prepared by conventional melting of a mixture of the oxide components. Beall *et al.* (Beall *et al.*, 1984), for instance, made their osumilite containing glass article by melting their batches at 1650°C for six hours. However, through this traditional solid state sintering technique it is almost impossible to obtain dense material without special equipment (Hu & Tsai, 2000; Jais *et al.*, 1995; Venkatachalam *et al.*, 2007).

Later, several approaches including glass ceramics (crystallised glass) and multiphase ceramics (glass + ceramics) have been taken. For multiphase ceramics, glasses are added to crystalline ceramic fillers and then fired at elevated temperatures. In this approach, a low softening temperature glass is used as sintering flux to enhance densification of the materials at low temperature. However, these approaches require very high temperature by conventional melting methods (>1400°C). Loss on ignition and phase separation sometimes become the main problems in the glass processing (Hu & Tsai, 2000). Furthermore, this method is expensive and at the same time, the highly viscous liquid melt present in the crucible may leach impurities from the crucible or be more susceptible to other routes of contamination (Newport et al., 1998).

The sol gel process for forming glass ceramics has been widely studied in recent years. Sol gel methodology provides a more convenient route to high purity silica glasses which negates such problems (Hu & Tsai, 2000; Livage, 1993). It involves a chemical preparation of a polymeric porous gel structure (Livage, 2004). Such materials can then be sintered rather than melted at a considerably low temperature to produce more homogeneous high purity vitreous solid. Sol gel process has been rarely used for preparation of barium osumilite glass powder (Jais et al., 1995).

According to Jais et al. (1995), R. Veltri and his colleagues prepared the barium osumilite type powder for their SiC–barium composite was derived from ethyl silicate, aluminium tri sec-butyl alcohol, barium nitrate and magnesium

nitrate. However, barium nitrate has low solubility in the mixture (Jais *et al.*, 1995).

In most studies, TEOS (tetraethylorthosilicate), a silicon source, is mixed together with other alkoxides during hydrolysis. This leads to inhomogeneity in gels and oxides because these alkoxides have different hydrolysis rates (Hu & Tsai, 2000; Livage, 2004). Especially the TEOS has very low hydrolysis rate relatively. Fumed silica powder was used to solve the problem of inhomogeneity also did not give any improved result (Hu & Tsai, 2000). Similarly, aluminium of $Al(BuO)_3$ has very high hydrolysis rate which readily leads to immediate precipitation in presence of water (Livage, 2004).

According to Jais *et al.* (1995), some precipitations upon gelation are unavoidable. The X-ray diffractometry (XRD) analysis of wet gels also shows that presence of barium acetate, magnesium acetate and barium carbonates. Appropriate amount of water is added to the gel in order to dissolve metal acetates but precipitation of carbonates could not be stopped. This is may be due to the CO_2 in the air reacts with molecules in the gel.

Most researchers have attempted or extended the earlier research in order to improvise their outcome and increase the knowledge in their research field (Hu & Tsai, 2000; Jais *et al.*, 1995). Meanwhile, they also advertently or inadvertently found some errors or problems in their research. In this investigation, the problems that are found by earlier researchers will be encountered or at least will be minimised. This investigation is concerned with

the preparation of barium osumilite glass powder by the sol gel process and its crystallization as the predominant phase of the glass composition.

1.2   RESEARCH OBJECTIVES

The objectives of this research are:

(a)   To use sol gel technique in the preparation of barium osumilite glass.

(b)   To analyze the crystallization of the barium osumilite glass powder.

1.3   SCOPE OF RESEARCH

The study focuses only in the preparation of sol gel glass which is mostly constituted by barium osumilite as the predominant crystal phase in the glass (Hu & Tsai, 2000; Jais *et al.*, 1995). Partial alkoxide route is used to prepare the sol gel. The resultant gel from the sol is crystallized insitu and the dried gel and the powder are then analysed their crystallisation by FTIR.

CHAPTER 2

LITERATURE REVIEW

2.1   SOL GEL PROCESS

2.1.1   Introduction

In the past decades, a process that has gained much notoriety in the glass and ceramic fields is the sol gel reaction. However, in recent years it gains recognition in the ceramic-glass and material science (Sakka, 1994). It is a chemical technique to prepare mostly the glass and ceramic samples (Brinker & Scherer, 1985; Livage, 2004). Before the sol gel process, chemically, given its full definition, some of the sol gel related terms should be defined first in order to comprehend the concept of sol gel process.

Sol is a colloidal suspension of solid particles or clusters in a liquid. Colloid is a suspension in which the dispersed phase is so small (1-1000 nm) that gravitational force is negligible and interactions are dominated by short range forces such as van der Waals attraction and surface charges. The dispersed

phase is usually known as the precursors for the sol gel process. The sol gel process or technique, by the name implies, involves the evolution of inorganic network through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) (Hu & Tsai, 2000; Laughlin *et al.*, 2000; Sakka, 2004).

2.1.2 Historical background

The first sol gel synthesis of silica was described by J.J Ebelmen about 150 years ago (Livage, 2004). He noticed that silicic esters or alkoxides hydrolysed slowly in the presence of moisture to give hydrated silica. Later, in the seventies, the properties of alkoxides were studied extensively. Then it was rediscovered again in the late 1800s and extensively studied since the early 1930s (Livage, 2004).

Then, a renewed interest surfaced in the early 1970s when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process (Livage, 2004). Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, optical transparency, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperatures, as opposed to the much higher melting temperatures required in the production of conventional inorganic glasses. Sol gel process, thereafter, with burgeoning knowledge and understanding properties of alkoxides, have studied widely by chemists and material engineers.

2.1.3   Principle of sol gel process

Sol, the word originated from solution, is a stable colloidal suspension can be formed by alkoxide precursors (Hu & Tsai, 2000; Jais *et al.*, 1995; Livage, 2004; Lorenzo *et al.*, 2003; Newport *et al.*, 1998). The precursors consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS = $Si(OCH_3)_4$) and tetraethoxysilane (TEOS = $Si(OC_2H_5)_4$) (Hu & Tsai, 2000; Livage, 2004; Newport *et al.*, 1998). However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process, often mixed with TEOS (Livage, 2004).

At the functional group level, two reactions are generally used to describe the sol-gel process: hydrolysis and condensation (Hu & Tsai, 2000; Jais *et al.*, 1995; Livage, 2004; Newport *et al.*, 1998; Richerson, 1992). Since silicon alkoxides are the main component of the sol, it is appropriate if the hydrolysis-condensation reaction is explained with silicon alkoxides $M(OR)_z$ (where M is metal or metalloid but in this case is silicon, R is an alkyl group and z is the valence of the metal). Hydrolysis gives reactive silanol groups (equation 2.1) whereas condensation leads to the formation of bridging oxygen (equation 2.2 and 2.3) (Aelion *et al.*, 1950; Livage, 2004).
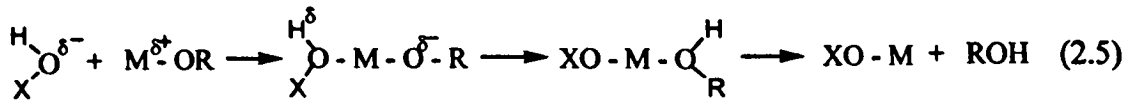
$$\equiv Si\text{-}OR \ + \ H_2O \ \rightleftharpoons \ \equiv Si\text{-}OH \ + \ ROH \tag{2.1}$$

$$\equiv Si\text{-}OH \ + \ RO\text{-}Si\equiv \ \rightleftharpoons \ \equiv Si\text{-}O\text{-}Si\equiv \ + \ ROH \qquad (2.2)$$

$$\equiv Si\text{-}OH \ + \ HO\text{-}Si\equiv \ \rightleftharpoons \ \equiv Si\text{-}O\text{-}Si\equiv \ + \ H_2O \qquad (2.3)$$
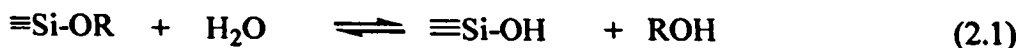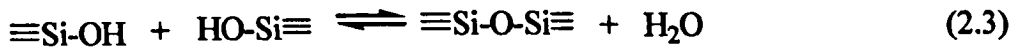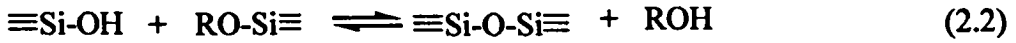
Generally, the chemical reactions involved in sol gel chemistry correspond to the nucleophilic substitution of alkoxy ligands by hydoxylated species XOH (equation 2.4) (Livage, 1993; Livage, 2004; Venkatachalam *et al.*, 2007):

$$M(OR)_z \ + \ XOH \ \rightleftharpoons \ [M(OR)_{z\text{-}x}(OX)_x \ + \ x\,ROH \qquad (2.4)$$

where X stands for hydrogen (hydrolysis), a metal atom (condensation) or even an organic ligand (complexation). The reactions can be described by an associative SN_2 mechanism as in equation 2.5.

$$\underset{X}{\overset{H}{\diagdown}}O^{\delta^-} + \ M^{\delta^+}\text{-}OR \ \longrightarrow \ \underset{X}{\overset{H}{\diagdown}}\overset{\delta}{O}\text{-}M\text{-}\overset{\delta^-}{O}\text{-}R \ \longrightarrow \ XO\text{-}M\text{-}O\underset{R}{\overset{H}{\diagup}} \ \longrightarrow \ XO\text{-}M \ + \ ROH \quad (2.5)$$

The reaction starts with the nucleophilic addition of negatively charged HO^{δ^-} groups onto the positively charged metal M^{δ^+}, leading to an upsurge of the coordination number of the metal atom in the transition state. The positively charged proton is then transferred toward an alkoxy group and the protonated ROH ligand is finally removed (Livage, 2004).

Condensation is the primary stage of gelation wherein the precursor molecules or particles react forming a three dimensional network of cation-

oxygen bonds (Lorenzo *et al.*, 2003; Pettit & Brinker, 1986; Richerson, 1992). The gel aging is an extension of the gelation step that will allow gel networks to be reinforced through further polymerization, possibly at different temperature and solvent conditions. Syneresis, the expulsion of solvent due to gel matrix shrinkage, can occur during gel aging (Liu *et al.*, 2000). Hitherto the gel exhibits shining gelatinous character, it is called wet gel.

Thereafter drying process of gel continues. Herein, water is removed from the gel system with simultaneous collapse of the gel structure, under conditions of constant temperature, pressure, and humidity (Lorenzo *et al.*, 2003). During this stage, possibly other liquids are added or produced. Usually additive chemicals are added in order to tailor the pore structure of a sol gel derived silica. Such chemicals are known as Drying Control Chemical Additives (DCCA) and some of the common additives are dimethyl formamide and oxalic acid (Livage, 2004; Lorenzo *et al.*, 2003). They produce more uniform pore size distribution preventing the formation of cracks upon further drying.

The dried gel in powder form will be treated thermally to enhance the crystallinity of the powder and it also an expulsion way to remove some residues from the condensation in the gel powder. Besides the thermal treatment, the powder also undergoes densification and the densification temperature will be decided by the precursors employed and the production process (Lorenzo *et al.*, 2003). Usually the densification temperature will be lower for the sol gel powder (Hu & Tsai, 2000; Jais *et al.*, 1995; Newport *et al.*, 1998; Richerson, 1992; Venkatachalam *et al.*, 2007).

As it is well known in recent studies, during the thermal treatment for complete densification of the dry gel, it is possible to include operations for its chemical cleaning (Lorenzo *et al.*, 2003). By these treatments, it is feasible to take advantage of the porosity of the dry gel for gas phase 'washing' steps capable of removing organic impurities left in the gel from organometallic precursors (such as TMOS and TEOS), as well as water, hydroxyl groups bound to cations in the gel network, or atoms of undesired metals. (Lorenzo *et al.*, 2003)

In general, the removal of organic impurities is achieved by calcination treatments, pouring an oxidizing atmosphere (oxygen and air) in the dry gel. On the other hand, by pouring Cl_2, HCl or CCl_4 into the gel, water hydroxy groups and foreign metals will be removed (Lorenzo *et al.*, 2003). This is called purification treatment. Following this step is the washing treatment wherein inert gases such as nitrogen, helium, or argon are used to completely remove chlorine or chlorine containing gases from the gel pores (Lorenzo *et al.*, 2003; MacChesney & Johnson, 2004). The washing treatment is effective in cleaning the gels to such a degree that the glasses resulting upon their densification are suitable for most application (generally, mechanical or optical parts) (Lorenzo *et al.*, 2003; MacChesney & Johnson, 2004).

Actually, most researchers conduct their heat treatment and densification without going through the calcinations, purification, washing or any dry gel treatment (Hu & Tsai, 2000; Jais *et al.*, 1995; Newport *et al.*, 1998). At last, the dried gel powder after densification (and treatments) will be sintered at lower

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