



Contents lists available at [www.sciencedirect.com](http://www.sciencedirect.com)

## Journal of the European Ceramic Society

journal homepage: [www.elsevier.com/locate/jeurceramsoc](http://www.elsevier.com/locate/jeurceramsoc)



# Role of thermodynamic miscibility gaps in phase selection in sol-gel synthesis of yttrium silicates

Surendra B. Anantharaman<sup>a,1</sup>, V.B. Rajkumar<sup>a</sup>, S. Raghunandan<sup>a</sup>, K.C. Hari Kumar<sup>a</sup>,  
R. Suresh Kumar<sup>b</sup>, Ashutosh S. Gandhi<sup>c,\*</sup>

<sup>a</sup> Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600 036, India

<sup>b</sup> Materials & Manufacturing Entity, Liquid Propulsion Systems Centre, Indian Space Research Organization, Thiruvananthapuram 695 547, India

<sup>c</sup> Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai 400 076, India

### ARTICLE INFO

#### Article history:

Received 9 March 2017

Received in revised form 20 June 2017

Accepted 22 June 2017

Available online xxx

#### Keywords:

CALPHAD

Metastable phases

Phase separation

Spinodal decomposition

Yttrium silicates

### ABSTRACT

Yttrium monosilicate and disilicate are important materials for environmental barrier coatings. The two silicates were synthesized by sol-gel route and their phase selection upon calcination and thermal exposure was studied. First products of crystallization were the monosilicate and yttria. Amorphous silica precipitated out at 1300 °C as apatite phase. During prolonged high temperature treatment, up to 100 h at 1400 °C, the apatite disappeared and the disilicate appeared, only to disappear itself as the system approached equilibrium. Thermodynamic calculations performed using Thermo-Calc software show the presence of a metastable miscibility gaps in the amorphous (liquid) phase field. As a consequence, phase separation in the amorphous phase prior to crystallization is responsible for the formation of yttria-rich and silica-rich phases during crystallization. Multiple phase formation during both, yttrium monosilicate and disilicate synthesis is consistent with the presence of the amorphous phase miscibility gaps around the silicate compositions.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Yttrium silicates are materials of interest as environmental barrier coatings (EBCs) on ultra-high temperature ceramics [1–3]. These coatings protect Si-based non-oxide ceramics like SiC fiber reinforced SiC matrix composites against high velocity water vapor attack in applications such as hot sections of gas turbine engines. Silicon carbide possesses adequate oxidation resistance in static dry air at temperatures up to about 1400 °C as a protective silica scale is formed that prevents further rapid oxidation [4,5]. In the presence of water-vapor-laden high velocity gases, however, the silica is attacked by the water vapor to form silicic acid, mainly Si(OH)<sub>4</sub>, which is a gaseous species. The volatile loss of silica leads to recession (ablation) of the component surface [6–9]. The primary purpose of an EBC is to isolate the silicon based structural material from the high velocity water-vapor-laden gases. The coating itself needs to be impervious and resistant to the water vapor

attack. It should also have a good match of its coefficient of thermal expansion (CTE) with that of the substrate [1,2,10].

A few candidate EBC materials have been developed, starting with mullite (with or without zirconia), calcium aluminosilicate (CAS), barium strontium aluminosilicate (BSAS), Ta<sub>2</sub>O<sub>5</sub>, rare earth silicates (RE<sub>2</sub>SiO<sub>5</sub> and RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, where RE = Y, Sc or lanthanides) and rare earth phosphates like LaPO<sub>4</sub> or YPO<sub>4</sub> [2,11–13]. Recently, among the rare earth silicates, yttrium silicate has been studied extensively as an EBC material. Two stable yttrium silicates exist as intermediate phases in the yttria-silica system (Fig. 1), namely yttrium monosilicate, Y<sub>2</sub>SiO<sub>5</sub> (MS) and yttrium disilicate, Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (DS). The monosilicate was reported to be more stable in water vapor environment due to its lower silica activity when compared to the disilicate [3,14]. Rare-earth monosilicates are also interesting for other applications such as phosphors, gate high dielectrics and cathodoluminescent materials [15–17]. On the other hand, yttrium disilicate exhibits better CTE match with the underlying SiC, though it exhibits many polymorphic transformations. These attributes have inspired a multi-layer EBC architecture with DS as an inner layer and MS as the outer one.

Sol-gel synthesis is the primary route for preparing yttrium silicates. Obtaining phase-pure silicates, whether MS or DS, has been a synthesis challenge. Phase-pure MS can be synthesized only by cal-

\* Corresponding author.

E-mail address: [agandhi@iitb.ac.in](mailto:agandhi@iitb.ac.in) (A.S. Gandhi).

<sup>1</sup> Present Address: Institute of Materials, École Polytechnique Fédérale De Lausanne (EPFL), Switzerland.

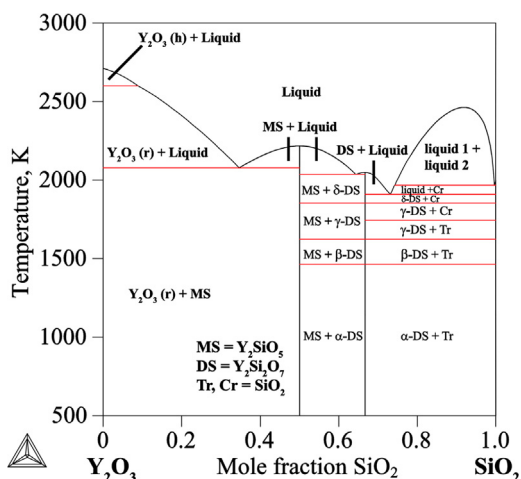


Fig. 1. Phase diagram of  $Y_2O_3 - SiO_2$  system calculated using Thermo-Calc<sup>®</sup> software using Gibbs energy functions from Mao et al. [32].

ination at temperatures of 1400 °C or higher, with long exposure times exceeding 4 h [18,19]. Impurity phases encountered during synthesis of MS usually consist of yttria, DS and apatite, though crystalline silica has sometimes been reported [20,21]. The impurity phases reported in DS synthesis primarily consist of crystalline silica (e.g. quartz or cristobalite), apatite and MS, with occasional appearance of yttria [22–24]. Focusing on MS synthesis, various processing routes apart from sol-gel synthesis have been explored, such as Czochralski crystal growth, solid-state reaction (sometimes combined with mechanical milling), hydrothermal synthesis, molten salt flux growth, solution combustion synthesis [18,25,26]. In all these studies, prolonged thermal exposure at temperatures higher than 1400 °C was required for obtaining phase-pure MS. Low temperature synthesis of phase-pure MS, as first and only product of crystallization, has not been reported. Deposition of EBC by plasma spraying involves rapid solidification of splats. It is observed from the literature that plasma sprayed coatings of MS composition are not single phase. The phase assemblage in such coatings comprises of different combinations like disilicate/silica, disilicate/monosilicate, monosilicate/rare-earth oxide [12,27–29]. It was unclear why multiple phases form in coatings with MS and DS composition. In order to explain the appearance of multiple phases in synthesis and processing of yttrium silicates, we have attempted to understand phase selection in yttrium monosilicate and disilicate synthesis by sol-gel experiments and thermodynamic assessment. Identification of miscibility gaps in the liquid phase field at sub-solidus temperatures and correlating the phase formation in sol-gel derived yttria-silica powders have led to an insight into this issue. The various stable and metastable phases observed in the yttria-silica system are summarized below, followed by the details of work done.

## 2. Phase stability in the yttria-silica system

Yttria has a cubic bixbyite structure, described as a defect fluorite structure. Silica with several polymorphs has quartz as the stable phase. Toropov and Bondar [30] reported three intermediate phases namely yttrium monosilicate, yttrium disilicate and apatite. Apatite has a molar ratio of  $Y_2O_3:SiO_2$  around 2:3 with molecular formula as  $Y_4Si_3O_{12}$  or  $Y_{4.67}(SiO_4)_3O$ . This phase is now believed to be a metastable phase which forms due to impurities from the crucibles or present intrinsically in the reagents or precursor/sol [31–33]. A revised quasibinary phase diagram of the  $Y_2O_3-SiO_2$  system (Fig. 1) calculated using Gibbs energy functions from Mao

et al. [32], shows only two intermediate phases, namely yttrium monosilicate and yttrium disilicate.

Yttrium monosilicate ( $Y_2SiO_5$ ) has two polymorphs X1 and X2 with a displacive transformation from X1 to X2. Nevertheless, the transformation is irreversible thereby X2 phase can be detected at room temperature. The crystal structures of these polymorphs differ in terms of the formula units per cell and cation coordination as detailed below. The low temperature polymorph (X1 phase) has space group symmetry of  $P2_1/c$  with two non-equivalent yttrium sites (Y1 and Y2). It has four formula units yielding 32 ions in the unit cell. The yttrium ion coordination numbers for Y1 and Y2 are 9 and 7, respectively. Furthermore, there are 1 and 3 non-bonded oxygen ions associated with  $Y^{3+}$  cation Y1 and Y2, respectively. The high temperature X2 polymorph has space group symmetry of  $C2/c$ . This structure has 8 formula units and 64 ions in the unit cell and two non-equivalent yttrium sites with coordination number of 7 and 6. There are two non-bonded oxygen ions for each yttrium site. Only one type of Si site is present in both the polymorphs. Generally,  $SiO_2$  is coordinated with four oxygen ions in the lattice which are also bound to either site of  $Y^{3+}$ . Overall, it can be concluded that during X1 to X2 transformations, the coordination number of Y1 site changes from 9 to 6.

## 3. Experimental procedure

In the present study, we have studied the sol-gel synthesis of MS and DS, with varying the catalyst nature and gelation conditions. Calcined powders were subjected to various thermal treatment schedules to understand the conditions that favor phase-pure synthesis. Metastable and stable thermodynamic assessment has been performed to show that a submerged miscibility gap in the liquid/amorphous phase field explains multiple phase formation in MS and DS synthesis.

### 3.1. Synthesis

Yttrium nitrate hexahydrate (Alfa Aesar, 99.99%) and tetraethyl orthosilicate (TEOS, Sigma Aldrich, 98%) were used as precursors to synthesize yttrium monosilicate and yttrium disilicate. The precursors were dissolved in ethyl alcohol to prepare 1M solution separately. Both the solutions were mixed together in desired proportions and concentrated HCl (1 wt.% of the solution) was added in the case of acid catalysis. The molar ratio of  $Y_2O_3:SiO_2$  in the solution was maintained to be 1:1 and 1:2 for  $Y_2SiO_5$  and  $Y_2Si_2O_7$ , respectively. In base catalysis, the amount of ammonia solution was separately varied between 2 wt.% and 16 wt.% of the solution. Each such solution was stirred at room temperature for 24 h. Later, the sol was introduced into an air-circulating oven at 70 °C till gelation was observed. After gelation, the xerogel was ground and then calcined in a muffle furnace (Carbolite, Model HTF 17/3) at 1400 °C for 2 h. In this study, the effect of the acid or base catalyst to the phase selection in monosilicates was studied for three different conditions by adding 1 wt.% HCl, 2 and 16 wt.% of ammonia solution respectively. For comparison, solid-state route was adopted by grinding  $Y_2O_3$  and  $SiO_2$  powders with 1:1 ratio and calcining at 1400 °C for 2 h.

Thermogravimetric (TG) and differential thermal analysis (DTA) was performed on the xerogel at a heating rate of 10 °C/min from room temperature to 1100 °C in flowing argon. The temperature which showed maximum weight loss was chosen as the start temperature for calcination and phase evolution studies on the xerogel.

### 3.2. Heat treatments

The gel derived from the acid catalyzed sol was selected for further studies. To understand crystallization and further phase evolution in the calcined powders, the gel was progressively heat

Download English Version:

<https://daneshyari.com/en/article/5440364>

Download Persian Version:

<https://daneshyari.com/article/5440364>

[Daneshyari.com](https://daneshyari.com)