

## Combustion synthesis and photoluminescence study of silicate biomaterials

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**Abstract.** Silicate based bioceramics are promising candidates as biomaterials for tissue engineering. The combustion synthesis method provides control on the morphology and particle size of the synthesized material. This paper discusses the combustion synthesis of akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7$ ), which has been shown to have good *in vitro* and *in vivo* bioactivities by earlier studies. Both  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  have akermanite structure.  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  were prepared using urea and ammonium nitrate. The combustion synthesis using urea and ammonium nitrate was found to be cost effective and efficient method of synthesis. The photoluminescence study of  $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  shows host specific intense emission of  $\text{Eu}^{2+}$ .

**Keywords.** Biomaterials; silicates; akermanite; combustion synthesis; photoluminescence.

### 1. Introduction

It is essential to develop biocompatible, bioactive, bioresorbable and durable materials for orthopaedic and dental implants, that are capable of bearing high stress and loads, and that invoke positive cellular and genetic responses for the rapid repair, modification, regeneration and maintenance of the affected tissue in human body (Cerruti and Sahai 2006). Silicate-based bioceramics, including silicate bioglass 45S5 (Hench 1991; Radev *et al* 2009), wollastonite ( $\text{CaSiO}_3$ ) (Liu *et al* 2004; Wu *et al* 2007; Xue *et al* 2007), akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) (Radev *et al* 2009), diopside ( $\text{Ca}_2\text{MgSi}_2\text{O}_6$ ) (Iwata *et al* 2004; Wu and Chang 2007) and merwinite ( $\text{Ca}_3\text{MgSi}_2\text{O}_8$ ) (Ou *et al* 2008) ceramics have been shown to have excellent apatite forming abilities in simulated body fluids. Other studies showed that these silicate ceramics also possess good *in vivo* bioactivity (Hench 1998; Nonami and Tsutsumi 1999; Xu *et al* 2008; Huang *et al* 2009). *In vitro* and *in vivo* investigations of a calcium magnesium silicate ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) bioceramic for bone regeneration showed that akermanite extract promoted proliferation and osteogenic differentiation. These results suggest that akermanite might be a potential and attractive bioceramic for tissue engineering (Hongli *et al* 2006; Wu *et al* 2006; Liu *et al* 2008; Yan *et al* 2009). A bioactive, degradable, and cytocompatible akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) scaffold with high porosity (63.5–90.3%) and pore interconnectivity with a corresponding compressive strength between 1130 and 530 kPa has been reported (Wu *et al* 2005). Akermanite and wollastonite have also been studied for drug delivery (Dora *et al* 2008).

Most of the silicates have high melting points. Moreover, they can appear in crystalline as well as glassy form. Synthesis of silicates is rather tricky for these reasons. Conventionally, solid-state diffusion methods have been used for the synthesis of silicates. Akermanite ceramics prepared by sintering akermanite powder compacts at 1370°C for 6 h, is previously reported (Wu and Chang 2006). Pure akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) powders with polycrystalline particles having dimensions of 5–40  $\mu\text{m}$  were synthesized by sol-gel method (Wu and Chang 2004). The combustion synthesis as a preparation process to produce homogeneous, very fine crystalline, unagglomerated, multicomponent oxide ceramic powders without the intermediate decomposition and/or calcining steps has attracted a good deal of attention (Kingsley and Patil 1988; Kingsley *et al* 1990). The combustion synthesis is based on the exothermic reaction between fuel and oxidizer. The combustion process has several advantages over the other methods in terms of simplicity, cost-effectiveness, energy saving, purity and homogeneity. The combustion-derived powders have narrow size distribution with average agglomerate particle sizes in the range of 0.5–5  $\mu\text{m}$ . The fine particle nature of the combustion-derived powder is attributed to the low exothermicity of the combustion reaction and evolution of large amount of gases ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ), which help to dissipate the heat thereby preventing the oxides from sintering (Ekambaram and Patil 1995, 1997; Chandrappa *et al* 1999).

The luminescence properties of biomaterials may be useful in studying osteoblast adhesion and proliferation, host-biomaterial interaction, to observe the *in vivo* course biomaterial-associated infections. This luminescent material may be potentially applied in the drug delivery and disease therapy fields.

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## 2. Experimental

In this study  $(Ca_{2-x}Sr_x)MgSi_2O_7:Eu^{3+}$  with  $x$ -values 0, 0.5, 1.5 and 2 were synthesized by combustion method. The detailed description of the methods can be found in the original works of Patil and co-workers (Kingsley and Patil 1988; Kingsley *et al* 1990; Suresh *et al* 1991; Manoharan and Patil 1992; Ravindranathan *et al* 1993; Ekambaram and Patil 1995, 1997). Ingredients used were metal carbonates, silicic acid ( $SiO_2 \cdot xH_2O$ ) and dopant salts. The dopant europium concentration was 2 mol % of alkaline earth ion. An equivalent amount of  $Eu_2O_3$  was dissolved in 3M nitric acid for this purpose. Urea was used as a fuel and ammonium nitrate as oxidizer. Fuel to oxidizer ratio, optimized as described by Bhatkar *et al* (2002, 2007) was used. Details of the molar ratio of ingredients used in the synthesis of all compounds are given in table 1.

All constituents in stoichiometric proportions, along with fuel and oxidizer were mixed together and small quantity of double distilled water was added. The mixture on thoroughly mixing was transferred to a pre-heated furnace at  $500^\circ C$ . On rapid heating the mixture evaporated and ignited at  $450^\circ C$ , with the evolution of a large amount of gases, to yield silicates. Entire process was completed within a few minutes. The as-prepared phosphors did not show intense emission, probably the activator Eu was not incorporated in divalent form. The phosphors were reheated, in the reducing

atmosphere provided by heating in a closed box with charcoal, at  $900^\circ C$  for 1 h.

Photoluminescence (PL) spectra were recorded on a Hitachi F-4000 spectro-fluorimeter with a spectral slit width of 1.5 nm, at room temperature. To confirm the structure of the synthesized phosphors, powder photographs were obtained using Philips diffractometer, PW 1710.

## 3. Results and discussion

Akermanite belongs to the tetragonal crystal system with space group,  $P4_2m$ , where  $a = 7.8288$ ,  $c = 5.0052$ ,  $Z = 2$  and point group  $42m$ . It is optically transparent to translucent and colourless. The X-ray powder pattern is characterized by strong lines at 2.87 (100), 3.09 (30), 1.764 (30), 2.039 (20), 2.488 (18), 3.73 (14), 5.55 (12) (Swainson *et al* 1992). Both  $Ca_2MgSi_2O_7$  and  $Sr_2MgSi_2O_7$  have akermanite structure. In this type of structure there is one calcium or strontium site, which is coordinated by eight oxygen ions. The review of the data from the earlier studies (Blasse *et al* 1968; Poort *et al* 1997) on the nature of emission and the decay time for these phosphors and comparison with the results from this study, are summarized in table 2.

The PL properties of individual compounds are discussed below: Figure 1 shows the excitation spectra

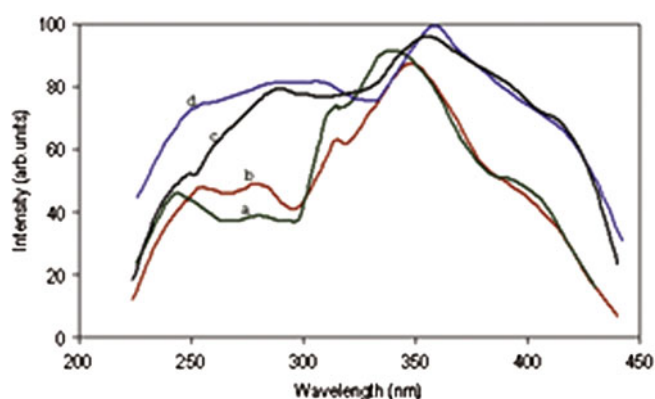
**Table 1.** Details of molar ratio of ingredients used in synthesis.

Sl. no.	Name of compound	Starting materials				
1	$Ca_2MgSi_2O_7:Eu^{2+}$ Mole ratio:->	$CaCO_3, Mg(NO_3)_2$ 1.96, 1	$SiO_2 \cdot xH_2O$ 2	$Eu(NO_3)_2$ 0.04	$NH_4NO_3$ 30	Urea 35
2	$Ca_{1.5}Sr_{0.5}MgSi_2O_7:Eu^{2+}$ Mole ratio:->	$CaCO_3, SrCO_3, Mg(NO_3)_2$ 1.46, 0.5, 1	$SiO_2 \cdot xH_2O$ 2	$Eu(NO_3)_2$ 0.04	$NH_4NO_3$ 30	Urea 35
3	$Ca_{0.5}Sr_{1.5}MgSi_2O_7:Eu^{2+}$ Mole ratio:->	$CaCO_3, SrCO_3, Mg(NO_3)_2$ 0.5, 1.46, 1	$SiO_2 \cdot xH_2O$ 2	$Eu(NO_3)_2$ 0.04	$NH_4NO_3$ 30	Urea 35
4	$Sr_2MgSi_2O_7:Eu^{2+}$ Mole ratio:->	$SrCO_3, Mg(NO_3)_2$ 1.96, 1	$SiO_2 \cdot xH_2O$ 2	$Eu(NO_3)_2$ 0.04	$NH_4NO_3$ 30	Urea 35

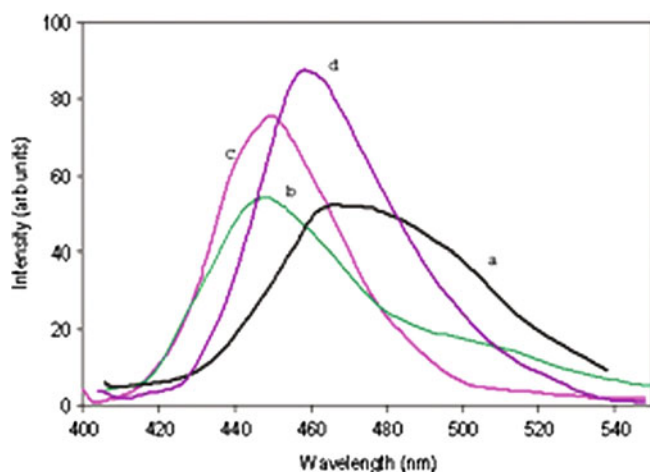
**Table 2.** Review of data from earlier studies and comparison with results from this study on nature of emission and decay time.

Sl. No.	Name of compound	Crystal structure	Emission peak (nm) <sup>b</sup>	Emission peak (nm) <sup>a</sup>	$T_{50}$ (K)	Decay time ( $\mu s$ )	Reference
1	$Ca_2MgSi_2O_7:Eu^{2+}$	Akermanite	535 545	475 bb	285 280	0.2 1.1	Blasse <i>et al</i> (1968) Poort <i>et al</i> (1997)
2	$Ca_{1.5}Sr_{0.5}MgSi_2O_7:Eu^{2+}$		525	448	280	1.0	Poort <i>et al</i> (1997)
3	$Ca_{0.5}Sr_{1.5}MgSi_2O_7:Eu^{2+}$		490	450	280	0.8	Poort <i>et al</i> (1997)
4	$Sr_2MgSi_2O_7:Eu^{2+}$	Akermanite	470 475	457	305 300	0.3 0.7	Blasse <i>et al</i> (1968) Poort <i>et al</i> (1997)

<sup>a</sup> This work for PL measurements at room temperature. <sup>b</sup> Literature values at 4.2 K

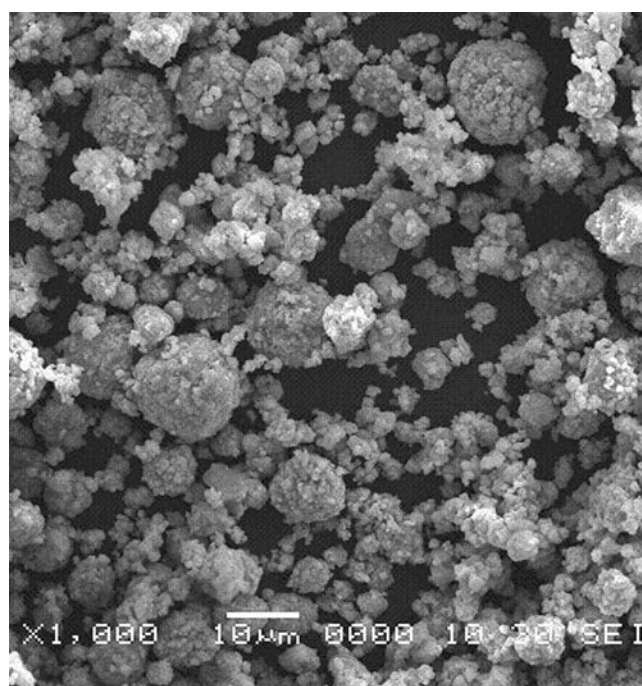


**Figure 1.** PL spectra for  $\text{Eu}^{2+}$  doped disilicate a.  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  excitation for 447 nm emission, b.  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{MgSi}_2\text{O}_7$  excitation for 448 nm emission, c.  $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{MgSi}_2\text{O}_7$  excitation for 478 nm emission and d.  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  excitation for 460 nm emission.

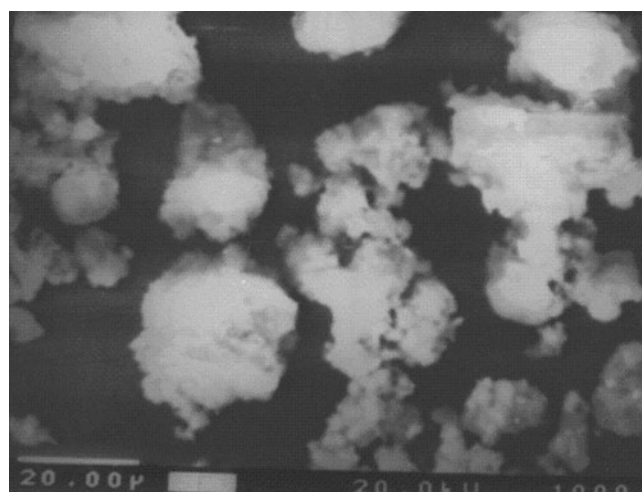


**Figure 2.** PL spectra for  $\text{Eu}^{2+}$  doped disilicate a.  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  emission for 385 nm excitation, b.  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{MgSi}_2\text{O}_7$  emission for 385 nm excitation, c.  $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{MgSi}_2\text{O}_7$  emission for 385 nm excitation and d.  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  emission for 385 nm excitation.

for  $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ,  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ,  $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ , and  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ . The emission spectra are shown in figure 2. Efficient excitation by 385 nm was observed for  $\text{Eu}^{2+}$  doped disilicates as seen from figure 1. The emission spectrum of  $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  (curve a), is a broad band at 475 nm.  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  (curve b) exhibits blue emission around 448 nm. Emission in  $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  (curve g) peaks at 450 nm. Emission in  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  (curve h) peaks at around 457 nm. Excitation spectrum of all the samples (curves a–d) shows considerable intensity at 385 nm. At room temperature the intensity of emission, except for  $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$  is considerably quenched, which is consistent with the literature data. The luminescence process of  $\text{Eu}^{2+}$ -activated phosphor is characterized by the  $4f_6 \ ^5d \rightarrow 4f_7$  transition of  $\text{Eu}^{2+}$  acting as an activator centre. The absorption and emission due to



**Figure 3.** SEM image of combustion synthesized material without calcinations.



**Figure 4.** SEM image of combustion synthesized material heated at  $900^\circ\text{C}$ .

the transition between  $4f_7$  and  $4f_6 \ ^5d$  states of  $\text{Eu}^{2+}$  strongly depend on host material, cations replaceable by  $\text{Eu}^{2+}$  in the host matrix and the crystal field acting on  $\text{Eu}^{2+}$ .

The morphology and size of the prepared materials were determined from SEM studies. Figure 3 shows a typical image of the combustion synthesized material. The precursor powders had spherical-like shape and micron size. It also shows agglomerated grains which might be due to the residence time of the powder inside a combustion furnace. The morphology of the powder heated at a temperature of  $900^\circ\text{C}$

is shown in figure 4. The particles form a cluster and the particle size increases with heating.

#### 4. Conclusions

Both  $\text{Ca}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}$  and  $\text{Sr}_2\text{MgSi}_2\text{O}_7: \text{Eu}^{2+}$  have akermanite structures. The combustion synthesis using urea and ammonium nitrate is an easy, time saving and cost effective method for the synthesis. The photoluminescence study of these materials show the strong emission of  $\text{Eu}^{2+}$  in alkaline earth silicates which agrees well with the literature. The biocompatibility of the akermanite has already been reported by many researchers. The luminescence properties of these biomaterials may be useful in their use as biomarkers and in the controlled drug delivery.

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