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Non-hydrolytic sol-gel processing of chloride precursors loaded at forsterite stoichiometry

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ABSTRACT

This paper for the first time investigates the sol-gel reaction of magnesium chloride and silicon tetrachloride, directed at the forsterite (Mg_2SiO_4) stoichiometry, using dry ethanol and glacial acetic acid as the solvent and chelating agent, respectively. The synthesized particles before and after calcination were characterized by transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy mapping, X-ray diffraction and Fourier transform infrared spectroscopy. According to the results, the calcined nanoparticles showed a magnesia/forsterite structure along with silicon depletion, despite loading the forsterite stoichiometry. On the other hand, silicon-acetoxy bonds were detected in the xerogel (before calcination) as a result of the chelation reaction, albeit with a relatively uniform distribution of the essential elements. Since no non-alcoholyzed silicon-chlorine bond was detected in the xerogel, the development of the calcined structure was explained by the deficient sol-gel condensation and subsequent evaporation of silicon tetraacetate. It was inferred that the excessive amount of hydrogen chloride as the coproduct of the ethanolysis and chelation reactions of the precursors inhibits the condensation step, as confirmed by a supplementary test in an exaggerated circumstance. In conclusion, the silicon-containing species acts like a limiting reagent in the sol-gel condensation of forsterite using the chloride precursors and acetic acid chelator, in spite of loading the related stoichiometry.

1. Introduction

Forsterite is a magnesium silicate with the chemical formula Mg_2SiO_4 and orthorhombic crystal structure. This ceramic has a low electrical conductivity and high melting point (1890 °C), which makes it a suitable material for electrical insulation even at high temperatures. Also, it has good refractory properties for high-temperature applications, due to its high melting point, low thermal expansion, elevated chemical stability, and great insulation properties [1]. From the biomedical viewpoint, forsterite contains ions that are released in biological environments, leading to the development of a hydroxy-carbonate apatite layer with a positive effect on bone calcification. Moreover, forsterite shows good biocompatibility, bioactivity, biodegradability and, more importantly, improved mechanical properties (fracture toughness) compared to hydroxyapatite [2]. In this regard, nanocrystalline forsterite has superior mechanical and bioactivity behaviors compared with coarse-sized forsterite [3,4]. Among the methods developed for the synthesis of nanocrystalline forsterite, the sol-gel process provides a highly homogeneous mixture of initial components, reduced crystallization temperature, and controllable morphology and phase composition, due to molecular-level mixing of the precursors.

There are a number of reports in the literature on the sol-gel synthesis of forsterite, where most of them have used tetraethyl orthosilicate (TEOS) as the silicon precursor and salts like $Mg(NO_3)_2$, $Mg(CH_3COO)_2$, and $Mg(OCH_3)_2$ as the magnesium source. In the sol-gel synthesis of multi-component silicate systems, the different rates of hydrolysis and condensation between/among precursors pose a challenge. This can result in a chemical inhomogeneity of the gel, leading to a higher crystallization

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temperature and undesirable phases. Several approaches have been used to overcome this limitation, such as a slow addition of water, partial pre-hydrolysis of silicon alkoxides, and chemical modification by chelating agents [5]. Among them, ethanolic sol-gel processing of TEOS with magnesium methoxide, acetate or nitrate precursors using acetic acid as the chelating agent is known as a routine procedure for forsterite synthesis [5–9]. Nevertheless, the type of sol-gel precursors is a variable affecting the product characteristics. Despite the lower cost and more gelation rate of silicon tetrachloride ($SiCl_4$) compared to TEOS [10], to our knowledge, little work has been focused on using $SiCl_4$ as the silicon source to synthesize multi-component silicates. Alternatively, chloride precursors have been successfully used to synthesize other multi-component ceramics, for example zirconium titanate [11–20]. This work aims to study the non-hydrolytic sol-gel reaction of magnesium chloride and silicon tetrachloride loaded at the forsterite stoichiometry using ethanol as the solvent and acetic acid as the chelating agent, for the first time.

2. Experimental procedure

The used processing procedure was similar to that reported in Refs. [5–9] in which albeit TEOS and magnesium methoxide ($Mg(OCH_3)_2$) were precursors. However, in the current work, other precursors (chlorides) as a sol-gel variable were tested. Anhydrous magnesium chloride ($MgCl_2$, Merck, Germany, >98%), silicon tetrachloride ($SiCl_4$, Merck, Germany, >99%), dry ethanol (C_2H_5OH, Merck, Germany, 100%), and glacial acetic acid (CH_3COOH, Merck, Germany, 100%) were used as starting materials. Typically, 1.6 gr $MgCl_2$ was dissolved in 30 ml ethanol and 2 ml acetic acid by using a magnetic stirrer. After complete dissolution, the proper amount of $SiCl_4$ (the molar ratio of Si:Mg was 1:2 based on the forsterite stoichiometry) was introduced dropwise to the above solution and stirred for 2 h. The resultant clear sol was aged at room temperature for 48 h and then dried at 80 °C for 6 h, giving a white xerogel. Afterward, an amount of the obtained xerogel was calcined at 800 °C for 2 h to proceed crystallization and develop forsterite. Additionally, in order to confirm the justification presented for the above calcined structure, a new sample was synthesized similar to the above procedure, only with this difference that 60 μL hydrochloric acid solution (HCl, Merck, Germany, 37%) was added to the sol as well as the acetic acid addition.

The xerogel and calcined powders were characterized by transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy mapping (TEM/XMAP, FEI Titan 80-300, 200 kV), X-ray diffraction (XRD, Bruker AXS, Cu Kα radiation) and Fourier transform infrared spectroscopy (FTIR, Bruker Vector 22). For the TEM studies, a small content of the samples was dispersed in water, ultrasonicated for 10 min and then dropped on a copper grid. For the powder XRD analysis, a scan step size of 0.02° and scan step time of 4 s were used. Also, a wavenumber range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1} was used for the FTIR experiments.

3. Results and discussion

Fig. 1a and b shows the TEM micrograph of the xerogel powder synthesized without the HCl solution, where both bright-field and dark-field images were represented for a better contrast and easier recognition. As can be seen, the xerogel is composed of nanoparticles with a relatively irregular shape, a size distribution of 10–50 nm, and a mean size of 20 nm. Since the sol-gel process is conducted at a liquid phase and low temperature, ionic rearrangements required to obtain stable crystalline phases do not occur during processing. Thus, sol-gel derived products generally

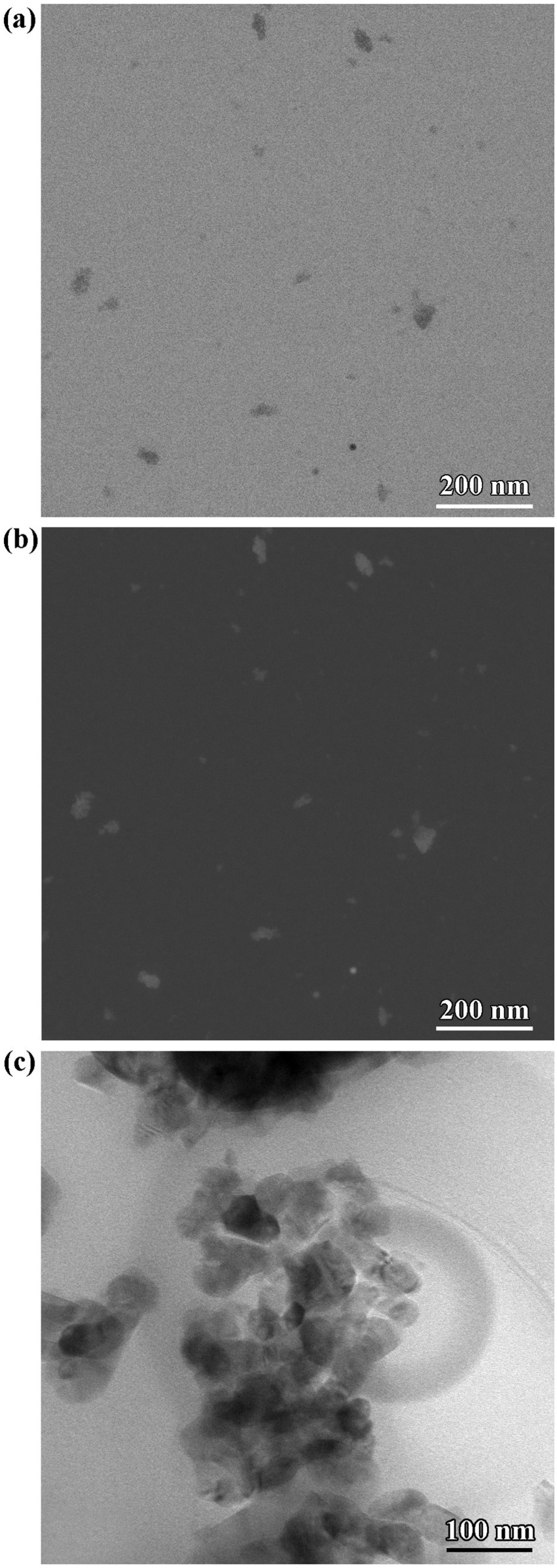

Fig. 1. TEM micrograph of the xerogel powder synthesized without the HCl addition: bright-field (a) and dark-field (b), and the powder calcined at 800 °C for 2 h (c).