SYNTHESIS OF SiO_2, ENSTATITE ($MgSiO_3$), AND CORDIERITE ($Mg_2Al_4Si_5O_{18}$) FROM ISOPROPANOL AND ETHANOL SOLUTIONS

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Abstract

A chemical procedure for the synthesis of monosized SiO_2, $MgSiO_3$ (Enstatite), and $Mg_2Al_4Si_5O_{18}$ (Cordierite) powders is described. It uses metal nitrates and TEOS (tetraethylorthosilicate; $[Si(OC_2H_5)_4]$) as the starting materials. The metal nitrates (Mg and/or Al) were dissolved in water in stoichiometrically desired proportions. The precipitation of glass precursors was carried out in isopropyl alcohol (or ethyl alcohol)/water/ammonium hydroxide mixtures at room temperature, following the addition of metal nitrates. The pH values of the solutions were adjusted via controlled dilute-NH_4OH additions. Spherical powders of less than 1 μm median diameter were produced, therefore their grinding or milling was unnecessary for preparing thick films or green tapes. The crystallization characteristics of solution-synthesized enstatite and cordierite samples were investigated by powder X-ray diffraction. The morphological properties of the synthesized powders were determined by scanning electron microscopy.

1. Introduction

Fumed Silica (SiO_2 glass) has many technological applications due to its excellent optical, electrical, and thermal properties. However, traditional melt-based methods of processing are objectionable due to the high temperatures required (~ 2000°C). Sol-gel methods [1-15] have been used to produce porous, high specific surface area shapes of amorphous SiO_2. Subsequently, these bodies can be fully densified by sintering (viscous flow mechanism) at relatively low temperatures, such as 1000°C [9, 11, 14].

Sol-gel processing techniques for preparing porous SiO_2 bodies are often divided into two general methods. In one case (method I), colloidal dispersions (i.e., sols) of fine SiO_2 particles are prepared and subsequently destabilized, or gelled, by chemical and/or thermal treatments [2, 3]. The gel is a semirigid, open, three-dimensional network of particles which contains large amounts of interstitial liquid. In method II, organometallic compounds are hydrolyzed and polymerized [4-15]. Gelation occurs as growing polymeric species agglomerate and crosslink to form an extensive, three-dimensional network (which again contains large amounts of interstitial liquid). In contrast to sol-gel method I, processing via hydrolysis and condensation polymerization of organometallic compounds (e.g., tetraethylorthosilicate, tetramethylorthosilicate) generally results in bodies with very fine porosity and high specific surface area (as high as ~900 m^2/g) [4-9, 11]. Consequently, full densification is often achieved at lower temperatures (i.e., in the range 700 to 1000°C).

Spherical hydrous silica particles with narrow size distribution were previously produced by Stober *et al.* [15] via the hydrolysis/condensation method. Under conditions of constant stirring at room temperature, TEOS (tetraethylorthosilicate) was added to a solution of reagent-grade ethanol and concentrated ammonium hydroxide solution. The

TEOS underwent hydrolysis/condensation reaction, forming (poly)silicic acid. Within minutes, precipitation of uniform spherical particles occurred. By controlling the reactant concentrations, average particle diameters in the range ≈ 0.2 to 0.6 μm could be produced [15].

Cordierite ($Mg_2Al_4Si_5O_{18}$) is mainly used in glass-ceramic compositions utilized in multilayer electronic circuit substrates and boards, ceramic sound-insulating boards, ceramic filters for separating solids from fluids, kiln furniture, thermal insulation material applications requiring controlled porosity, temperature-resistant catalysis systems for the removal of nitrogen oxides from the exhaust gases, the manufacture of low coefficient of thermal expansion, and thermal shock resistant ceramics, low-expansion honeycomb ceramics manufacture for catalytic converters and diesel exhaust gas filters, microwave absorbing heating elements, electromagnetic wave absorbers, fiber-reinforced ceramic composites, mullite-cordierite composite ceramics for semiconductor devices, photosensitive electrically insulating paste manufacture, ultrafiltration membranes, ceramic heat exchangers, thermoelectric conversion materials, and multilayer coatings with ceramic top layer on metal articles such as on the heads of motor pistons. Enstatite ($MgSiO_3$), on the other hand, being a binary compound of the MgO-SiO_2 system has been a heavily encountered phase of the traditional, Mg-containing aluminosilicate ceramics. Enstatite is used, in recent years, in the manufacture of dental glass ceramics and inorganic fibers.

The synthesis of Cordierite ($Mg_2Al_4Si_5O_{18}$), from "*organic*" solutions by the alcoholic sol-gel method, has been attempted by Chowdhry *et al.* [16] and Douy [17]. In these studies, Cordierite has been synthesized from Mg- and Al-nitrates, together with TEOS (as the Si-Alkoxide source), either using H_2O (aqueous) or ethanol (alcoholic route) as the solvent, and in the presence of "polyacrylamide" (in aqueous route) or "poly(2-hydroxyethyl metacrylate)" (in the alcoholic route) as the organic gelation agent. The synthesis of Enstatite ($MgSiO_3$), to our knowledge, has not previously been attempted by the method of TEOS hydrolysis/condensation technique.

The present work first focusses on the synthesis of monosized SiO_2 powders by the Stober *et al.* [15] recipe, and then, the chemical preparation of Cordierite and Enstatite (from the nitrates of cations) fine powders, by the TEOS hydrolysis/condensation route, without using any organic gelation agents. The present work, in a sense, may be considered as an attempt towards the "modification" of the original "*Stober-recipe*" (used for the synthesis of pure SiO_2) to obtain the sub-micron, homogeneous and high-phase purity powders of Cordierite and Enstatite.

2. Experimental Procedure

Pure and monosized SiO_2 powders were synthesized according to the Stober *et al.* [15] and Sacks *et al.* [13] formulations. Reagent-grade *Isopropanol* or *Ethanol* (Merck, Germany) were used as the solvent. TEOS (*tetraethlyorthosilicate*) used was also reagent-grade (Merck, Germany). The precipitation runs were performed in glass labware, on a magnetic stirrer plate, at room temperature. Concentrated (≈ 30 wt% NH_3) *ammonium hydroxide* solutions were used to adjust the pH values. After precipitation, powders were centrifuged and washed with distilled water and dried in an oven at 95°C, overnight. Subsequently, powders were calcined on α-alumina plates or dishes in a loose-stack

(uncompacted) arrangement for 12 to 24 hours at T = 500 to 1200°C (stagnant air atmosphere).

Cordierite ($Mg_2Al_4Si_5O_{18}$) and Enstatite ($MgSiO_3$) powders were synthesized in the same manner, by the necessary additions of the stoichiometric amounts of Mg-nitrate and/or Al-nitrate solutions of proper strength. No organic gelation agent was used in the preparation of these binary and ternary oxides. The precipitates were recovered from the mother liquors as described above.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku, DMax/B diffractometer using monochromatic FeKα radiation and a step size of 0.03° 2θ at a count time of 1 second. Scanning electron microscopy (SEM; JEOL-JSM 6400) was also used to characterize powders. The powder samples were sputter coated with an approximately 25 nm-thick layer of gold-palladium alloy prior to observations in the microscope. Energy dispersive X-ray spectroscopy (EDXS; Kevex, USA) analysis were carried out on the samples to perform a semi-quantitative analysis on the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to about ± 3 wt%.

3. Results and Discussion

(A) Synthesis of SiO_2 Spheres

Pure SiO_2 were synthesized by the hydrolysis/condensation reaction of TEOS in the presence of ammonium hydroxide, in aqueous solutions, at room temperature. Two alcoholic components were tried; namely, ethanol and isopropanol. No significant difference was observed between these alcohols in terms of their influence on the particle morphology. Amorphous SiO_2 spheres with an average particle size of 250 nm (with quite a narrow particle size distribution) were produced. Figure 1 shows the typical XRD spectra of pure SiO_2 powders heated in a stagnant air atmosphere over the temperature range of 600 to 1050°C. Cristobalite gradually began to crystallize out at about 900°C (and up) in these powders. The particle morphologies of the produced SiO_2 spheres were depicted in the SEM micrographs of Figure 2. It was, hereby, confirmed that the Stober *et al.* [15] recipe, for the preparation of sub-micron SiO_2 spheres, works well.

(B) Synthesis of Enstatite ($MgSiO_3$)

The synthesis of Enstatite has been achieved by a slight modification in the Stober *et al.* technique. The stoichiometric amount of Mg^{2+} was added in the form of a Mg-nitrate solution. The rest of the experimental parameters and conditions were not changed. The recovered precursors (from the mother liquor) of $MgSiO_3$ were amorphous, and they started to crystallize out the Enstatite phase at about 1000°C. Figure 3 shows the typical XRD pattern of the precursor powders after they have been heated at 1100°C for 20 hours, in a stagnant air atmosphere. The XRD pattern of the single phase $MgSiO_3$ depicted in Figure 3 conformed to the JCPDS PDF 11-273, 19-768, 35-610, 19-769, and 22-714.

The particle morphology of the synthesized $MgSiO_3$ powders was shown in the SEM micrographs of Figure 4. The samples were heated at 500°C for 12 hours prior to observations in the microscope. Both of the depicted micrographs do belong to the same

Figure 1. XRD spect
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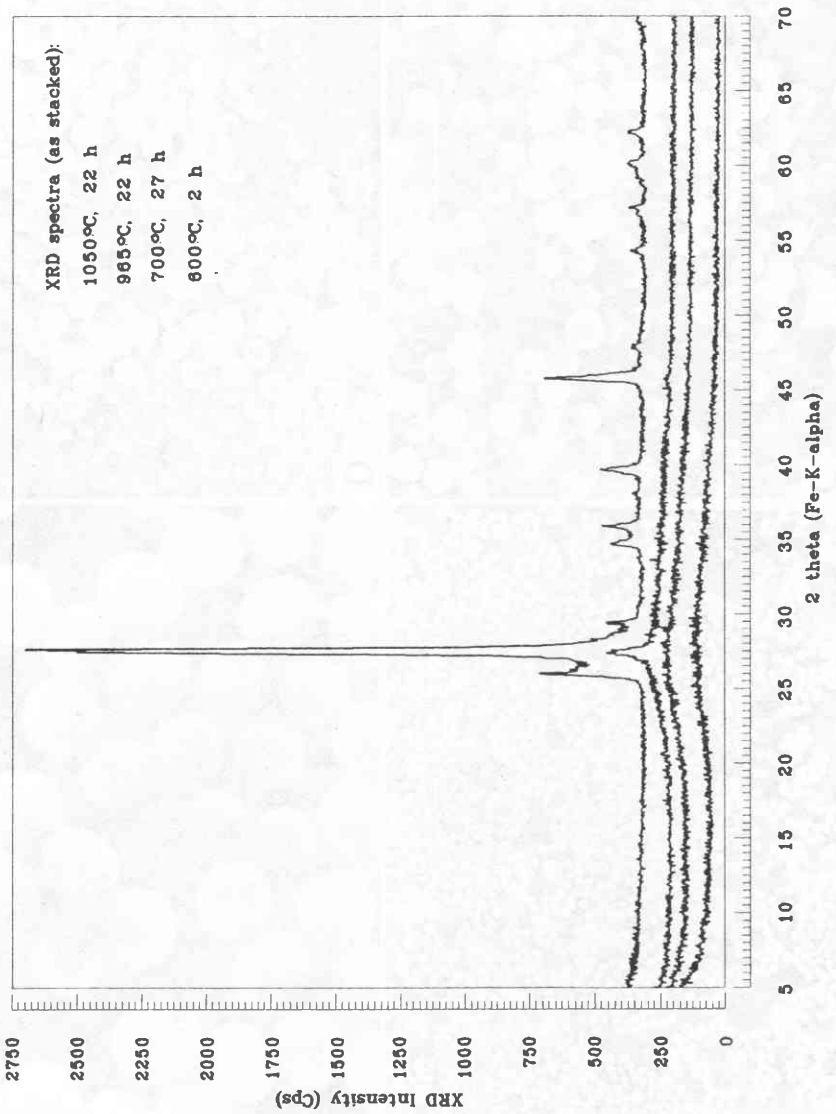

Figure 1. XRD spectra of pure SiO_2 spheres synthesized via TEOS hydrolysis/condensation route (*solvent*: ethyl alcohol, calcined in air)

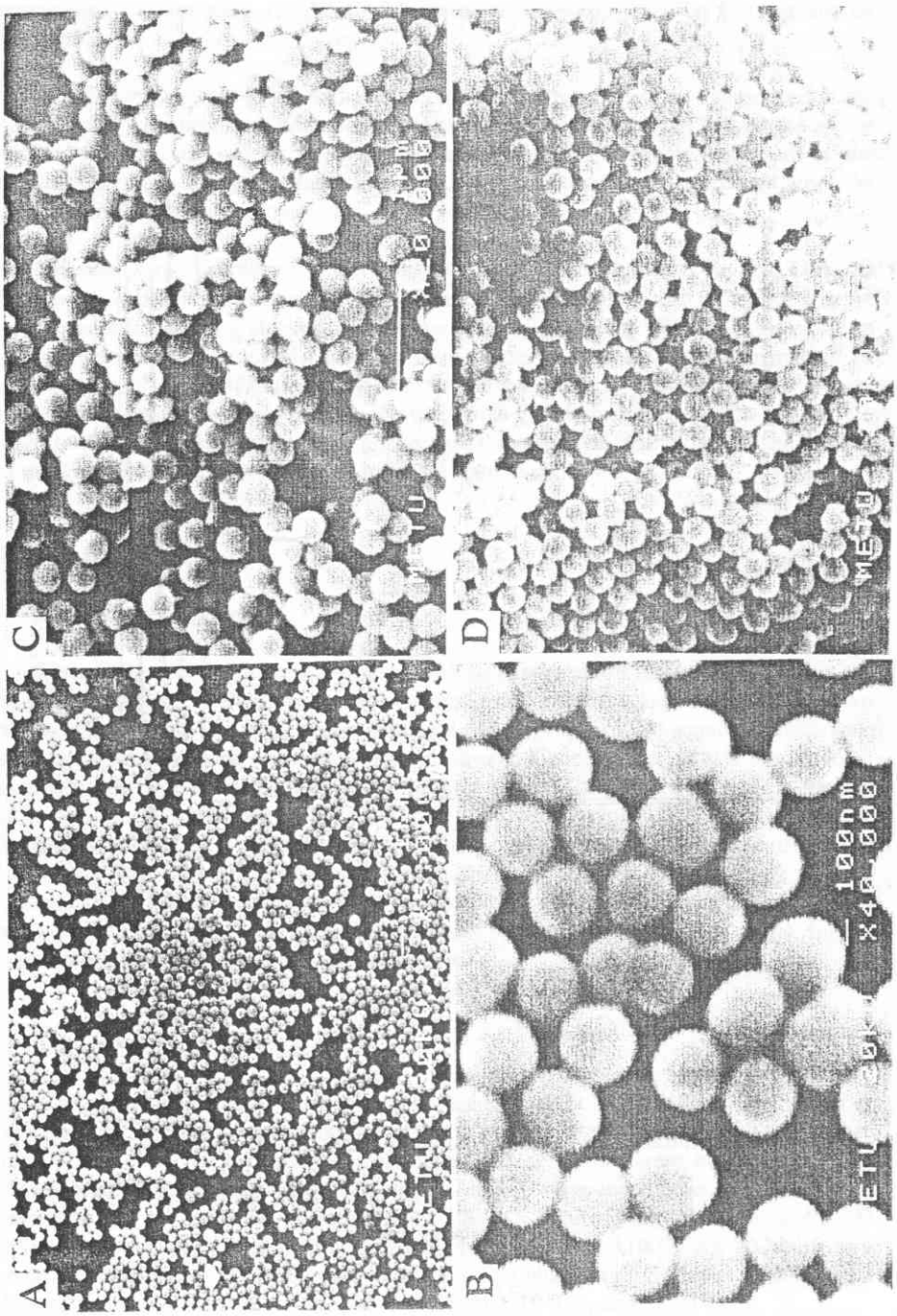

Figure 2. SEM micrographs of pure SiO_2 spheres (as recovered from the solutions) (*A & B:* Ethanol, *C & D:* Isopropanol)

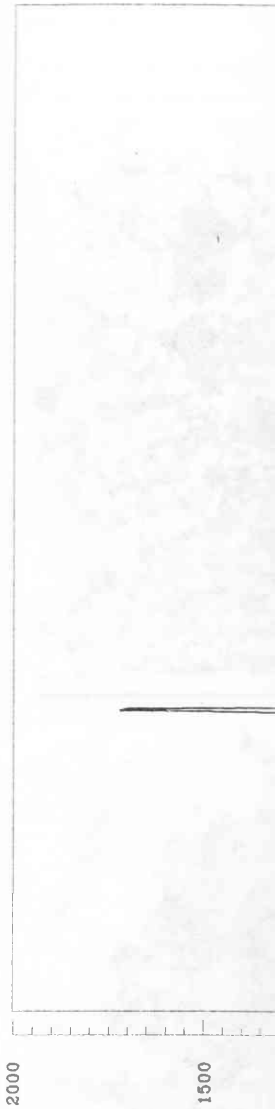

Figure 3. Typical XRD s
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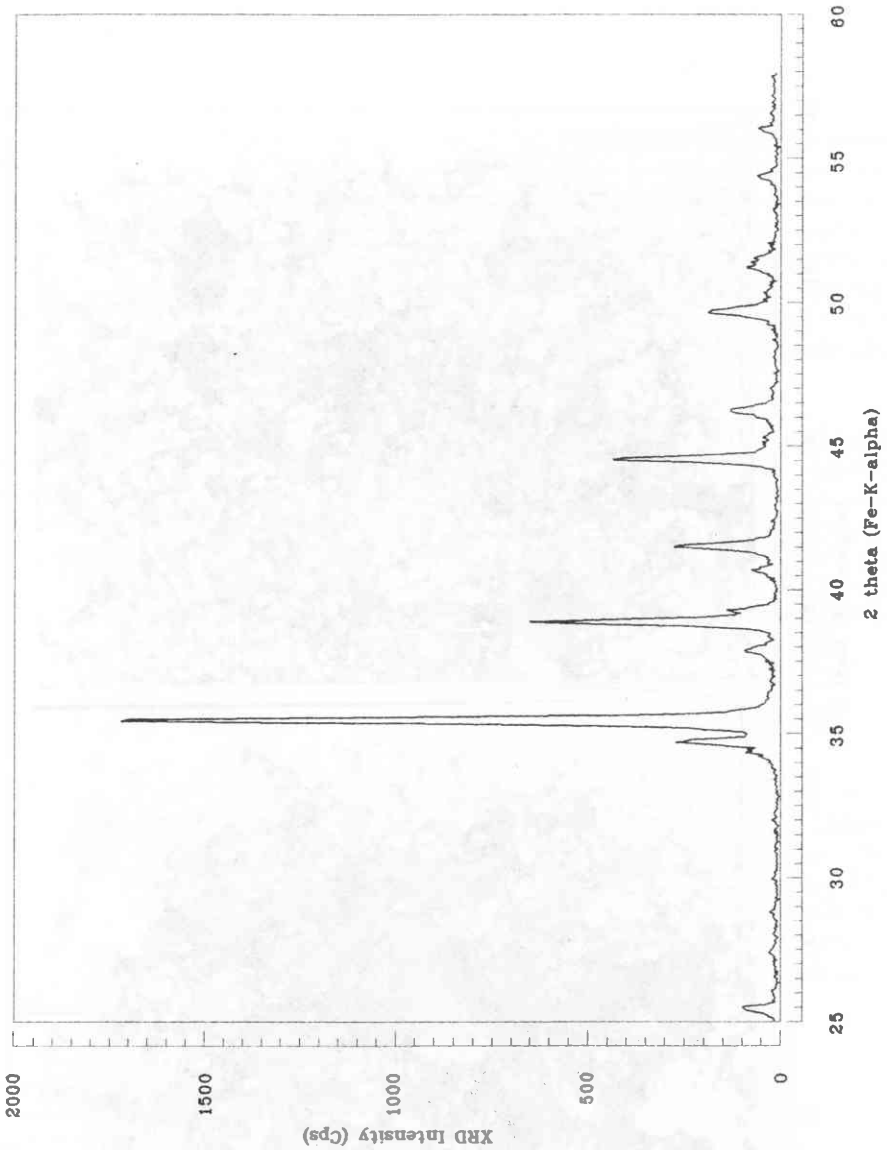

Figure 3. Typical XRD spectra of the synthesized Enstatite ($MgSiO_3$) powders (*After calcination at 1100°C, in a stagnant air atmosphere, for 20 hours*)

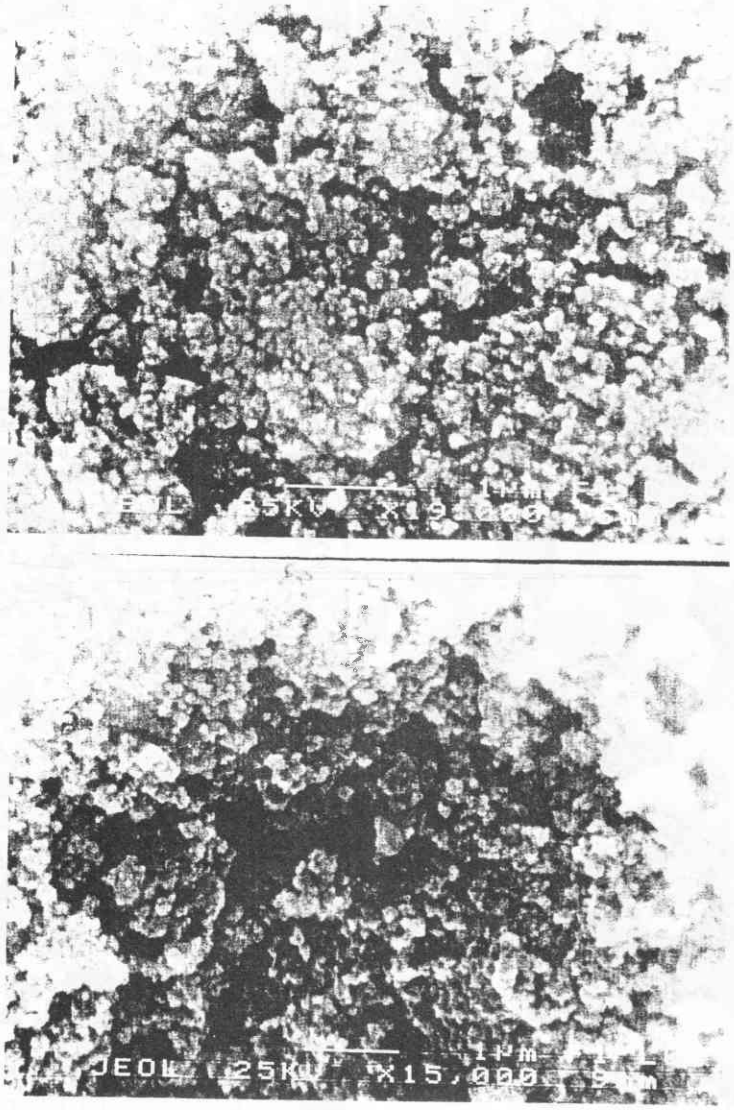

Figure 4. SEM micrographs of pure Enstatite ($MgSiO_3$) powders calcined at 500°C

Figure 5. Typical XRD s
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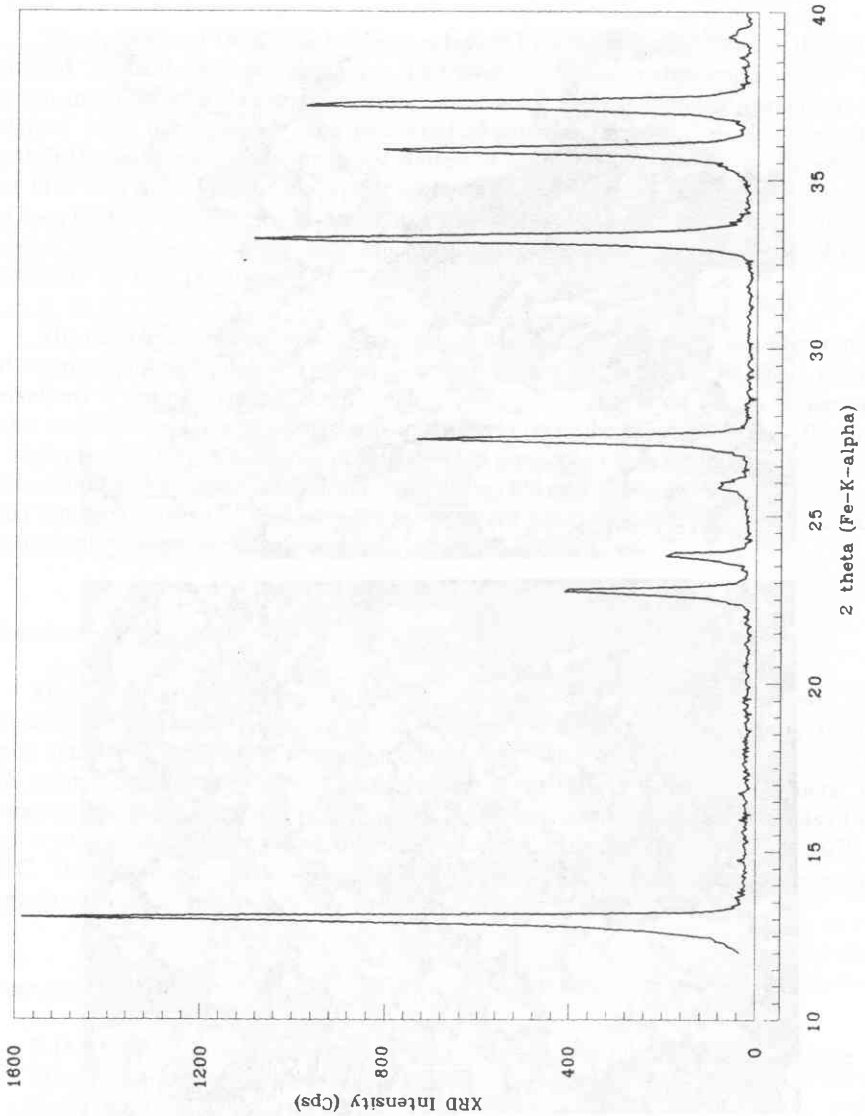

Figure 5. Typical XRD spectra of the synthesized Cordierite ($Mg_2Al_4Si_5O_{18}$) powders (*After calcination at 1100°C, in a stagnant air atmosphere, for 20 hours*)

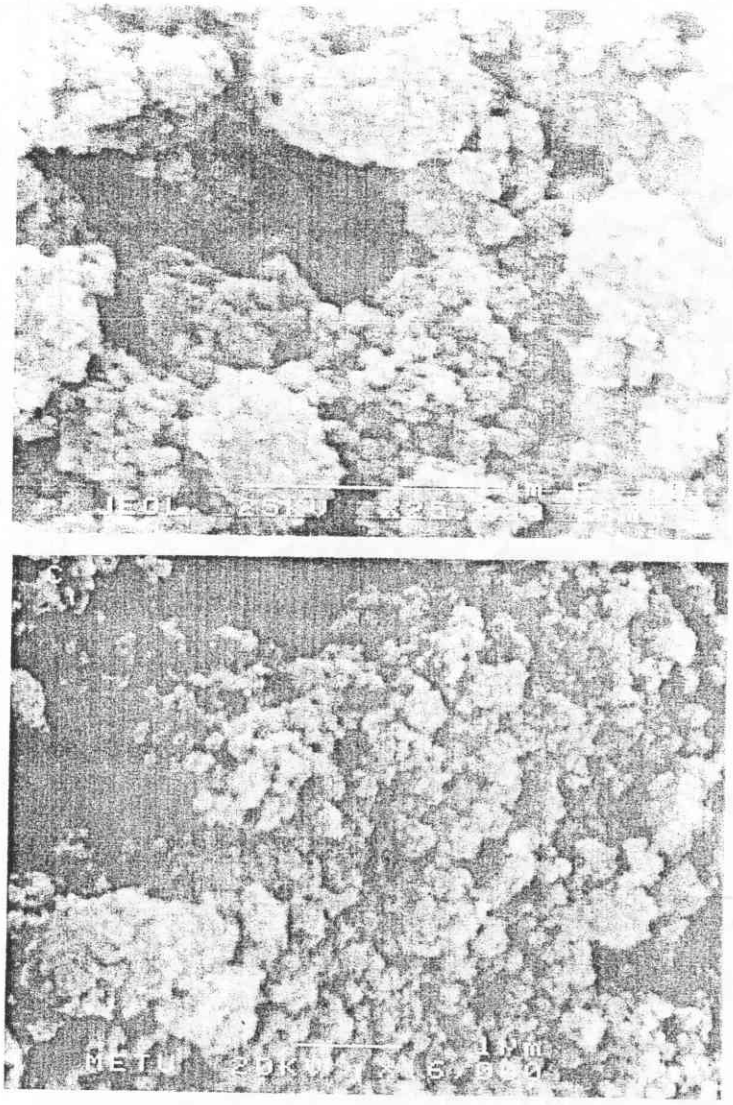

Figure 6. SEM micrographs of pure Cordierite ($Mg_2Al_4Si_5O_{18}$) powders calcined at 500°C

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4. Conclusions

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powder sample. The average particle size was seen to be in the range of 70 to 100 nm in our high phase purity Enstatite powders. The presence of a significant amount of agglomeration in the powder body suggests that the cation concentrations were not yet at their optimum values (for the desired monodispersed powder morphology), and this point warrants further research on the employed synthesis route.

(C) Synthesis of Cordierite ($Mg_2Al_4Si_5O_{18}$)

The synthesis of Cordierite has been achieved by a slight modification in the above-mentioned "Enstatite synthesis" technique. This time, the stoichiometric amount of Al^{3+} was added in the form of a Al-nitrate solution. The rest of the experimental parameters and conditions were not changed. The recovered precursors (from the mother liquor) of $Mg_2Al_4Si_5O_{18}$ were amorphous, and they started to crystallize out the Cordierite phase at about 1100°C. Figure 5 shows the typical XRD pattern of the precursor powders after they have been heated at 1100°C for 20 hours, in a stagnant air atmosphere. The XRD pattern of the single phase (mostly α-Cordierite) $Mg_2Al_4Si_5O_{18}$ depicted in Figure 5 conformed to the JCPDS PDF 12-303, 13-293, and 13-294.

The particle morphology of the synthesized $Mg_2Al_4Si_5O_{18}$ powders was shown in the SEM micrographs of Figure 6. The samples were heated at 500°C for 12 hours prior to observations in the microscope. Both of the depicted micrographs do belong to the same powder sample. The average particle size was seen to be in the range of 80 to 100 nm in our high-phase purity Cordierite powders. The presence of a significant amount of agglomeration in the powder body again suggests that the cation concentrations were not yet at their optimum values (for the desired monodispersed powder morphology), and this point warrants further research on the employed synthesis route.

4. Conclusions

High purity and homogeneity SiO_2, Enstatite and Cordierite powders were synthesized by the hydrolysis/condensation reaction of TEOS in highly basic, organic gelation agent-free, solutions at room temperature. Mg^{2+} and Al^{3+} were introduced into the TEOS solutions in the form of nitrates to prepare Enstatite and Cordierite powders. The precursors were amorphous, and in the case of binary and ternary oxide compounds of this study, crystallization was observed to commence in the temperature range of 1050 to 1100°C. The sintering properties of these powders will be the subject of further research of our group.

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CHEMICAL SYNTH
($PbZrO_3$) BY HOMO

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1. Introduction

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