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Synthesis of eucryptite spheres

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Abstract Eucryptite spheres with average diameters in the range 40–60 μm were synthesized using a newly developed sol-emulsion-gel approach. Unlike the conventional method, emulsions were prepared with aqueous powder suspensions. With this scheme, a large-scale production of eucryptite spheres, from suspensions with a solid content of 50–60wt%, is readily straightforward. We found that emulsions are formed in a narrow synthesis range determined by the large number of experimental parameters such as the composition of the suspension, the type/amount of the organic solvent and of the surfactant. Although the formation of eucryptite spheres is sensitive to a small variation in these parameters, we have established optimal synthesis conditions for their formation.

Introduction

The hexagonal aluminosilicate β-eucryptite ($LiAlSiO_4$) has remarkable thermal-expansion properties, with coefficients that are extremely anisotropic ($\alpha_a \sim 8.6 \times 10^{-6}$ deg^{-1}; $\alpha_c \sim -18.4 \times 10^{-6}$ deg^{-1}) and almost independent of the temperature in the range of 300–1,400 K. Moreover, its negative thermal expansion characteristics are well described in the literature [1–3]. In ceramic industry, these materials are very important because they are widely used in high anti-thermal shock applications, electronic devices and automotive applications (catalyst supports) [4]. Generally, functional materials with spherical particle shapes are essentially attractive because of their specific properties (e.g. excellent flow properties). In recent years, the emulsion method has been successfully used for the synthesis of spherical mixed oxides among which include: magnesium aluminate “$MgAl_2O_4$” [5], chromium titanium oxide “$Cr_{2-x}Ti_xO_3$” [6] and barium titanate “$BaTiO_3$” [7]. The vast majority of these recent contributions actually involve water-in-oil (w/o)-type emulsion [5–8].

The principle of the w/o emulsion process is to disperse an aqueous sol (“water phase”), prepared from aqueous salts solutions and/or alkoxides, into an organic solvent (“oil phase”) of low dielectric constant. The sol solution can be stabilized and well dispersed to form liquid droplets by adding an appropriate surfactant. Afterwards, a suitable gelling agent is used for the hardening of the sol droplets and gel spheres are produced. During the sintering step, the decomposition of organic species is associated with an important mass loss. Since the resulting shrinkage enhances the cracking of the spheres, the use of aqueous powder suspension provides a promising route to produce materials with spherical particles.

Our focus here is to find out suitable constraints and parameters for the preparation of eucryptite spheres from the aqueous suspensions of $LiAlSiO_4$ powders. For this purpose, the study of the influence of several factors such as the nature of the suspension, the reactant amounts and the temperature is required. In doing so, we establish the optimal synthesis conditions required for the formation of eucryptite spheres.

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Experimental work

Principle

Scheme 1 presents our experimental procedure based on the sol-emulsion-gel method, involving basically four main steps. The aqueous powder suspension was prepared by dispersing the pre-synthesized eucryptite powder in an aqueous additive solution and the oil phase was obtained by mixing the organic liquid with a surfactant (step 1). Under continuous stirring (step 2), the emulsion was formed by dispersing the aqueous powder suspension inside the oil phase. In step 3, the solidification of the emulsified droplets into solid particles was performed using a gelling agent (e.g. precipitation of hydroxides utilizing TEA) or by removal of water (e.g. dropwise addition of the emulsion in a hot oil bath or using a suitable dehydrating agent). The last step based on the conversion of the precursor suspension into spherical particles was performed inside the furnace (step 4).

Chemicals

Eucryptite powders ($LiAlSiO_4$) pre-synthesized at 800 °C and 1,100 °C using the conventional ceramic method are the starting powders (details of preparation given below). The selected additives are magnesium nitrate hexahydrate (Merk; 98%) and poly(acryl)acid (PAA) (Aldrich; 60 wt% solution in water, the average Mw is 2000). Heptane (Roth; density: 0.700) and mineral oil (Sigma-Aldrich; density: 0.862) are examined as organic liquids. Span60 (Aldrich) and Span80 (Merck) are the selected surfactants. The gelling and the dehydrating agents are triethylamine (TEA) (Fulka; 99.5 %) and ethanol, respectively.

To synthesize eucryptite powders ($LiAlSiO_4$), adequate amounts of reagent-grade Al_2O_3, SiO_2 and Li_2CO_3 were first mixed and heated at 800 °C for 4 hours. The resulting mixture was milled with ethanol in a planetary ball-mill (Pulverisette 5, Fritsch GMBH; Si_3N_4 mill jars and balls). According to the XRD analysis results, the powder obtained at 800 °C (powder E1) is a mixture of oxides and a very small amount of β-eucryptite. Finally, by increasing the thermal treatment up to 1,100 °C (3 h, powder E2), the entire diffraction peaks match very well with the pattern of a single crystalline β-$LiAlSiO_4$ phase (PDF, 026–0840). The presence of some traces of amorphous silica is materialized by a broad maximum in 2θ in the range 10°–20°.

Preparation of aqueous suspensions

Additive solutions were chosen among diluted PAA (0.2–1 wt%) and concentrated (0.5–2 M) Mg-nitrate aqueous solutions. Since the solid content influences the stability and the formation of emulsions, suspensions with different mass ratio powder/aqueous phase (P/A) value of 40:60, 50:50, 60:40 and 65:35 were investigated (Table 1). As a function of the desired composition, a specific mass of $LiAlSiO_4$ powder was mixed with an appropriate amount of additive solution and ball-milled for 17–20 h. From the large composition of suspensions recorded here, those prepared using the 2 M concentrated Mg-nitrate and the 0.3 wt% PAA aqueous solutions were the most appropriate ones. In PAA solution, stable suspensions containing up to $\sim$70 wt% of eucryptite powders were successfully prepared. However using Mg-nitrate solution as aqueous phase, more than 60 wt% of eucryptite led to the formation of less stable suspensions. The composition and characteristics of some of the stable suspensions are presented in Table 1.

Scheme 1 Experimental procedure used for the preparation of eucryptite spheres

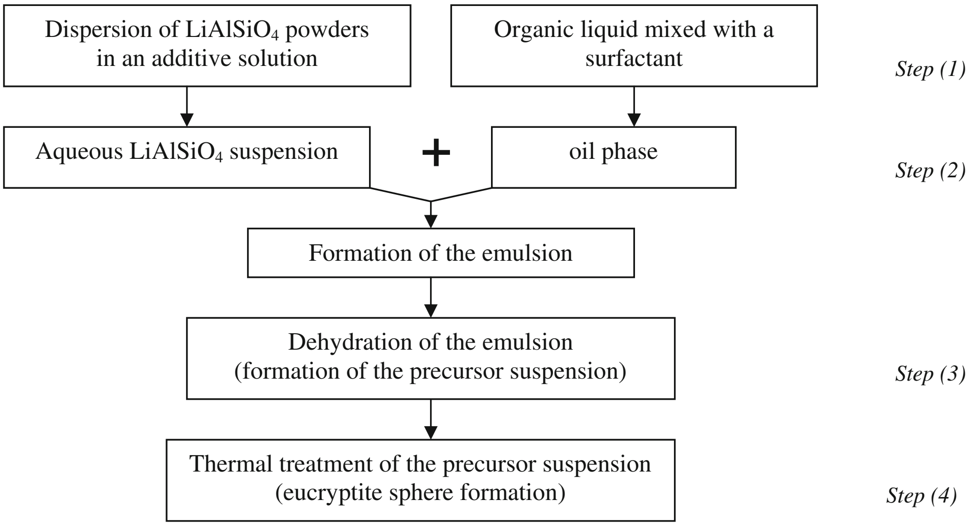

Table 1 Composition and characterizations of some $LiAlSiO_4$ suspensions (starting material: powder E2)

Designation of suspensions	Composition of suspensions			Characteristics of suspensions					
	Aqueous phase	P/A	Additive content (mg/g of E2)	pH	Particle size (μm)			Viscosity	
					D_{10}	D_{50}	D_{90}	Flow type	η (mPa.s)
M50	Mg-nitrate	50:50	512.8	6.76	2.16	4.01	6.12	P	*
M60		60:40	341.9	6.52	2.91	6.38	11.02	P	*
P50	PAA	50:50	3.0	12.05	1.83	3.10	6.20	N	19
P60		60:40	2.0	12.50	1.80	3.10	5.81	N	31
P65		65:35	1.6	11.68	2.04	5.06	9.22	N	15

P/A: mass ratio between the $LiAlSiO_4$ powder (E2) and the aqueous phase

* Variation of η with the shear rate (see Fig. 1); N is Newtonian, P is non Newtonian (Pseudoplastic)

Preparation of water-in-oil (w/o) emulsions

An emulsion can be defined as a kinetically stable dispersion of two immiscible liquids, stabilized by an interfacial film of surfactants. The surfactant reduces the interface tension between an oil phase and a water phase and enables them to be mixed and emulsified [9]. Practically, the emulsion type (water-in-oil (w/o) or oil-in-water (o/w) emulsions) is predicted by the HLB value of the surfactant. Surfactants with low HLB values (in the range of 3–6) tend to form stable w/o emulsions while those with high HLB values ($\approx$8–18) produce o/w emulsions [10].

In the present study, the water-in-oil (w/o) emulsion was formed at room temperature by dispersing the water phase into the oil phase, under hand shaking or constant stirring (800–1,200 rpm). As surfactant, we have selected Span60 and Span80 with HLB value of 4.7 and 4.3, respectively. The oil phase was obtained by mixing a little amount of surfactant (2–10 wt%) into the selected organic solvent (heptane, mineral oil) while the water phases were the suspensions prepared as described in Sect. "Preparation of aqueous suspensions". For the optimization of the emulsification conditions, the mass ratio between the aqueous suspension and the organic liquid was varied between 1:3 and 1:5. As observed using the conventional method based on the use of sols as water phase [11–13], the emulsification of the aqueous powder suspension was also completed within few minutes. Table 2 presents the characteristics of some emulsions prepared, under hand shaking, with Span80.

Formation and thermal treatment of the precursor suspensions

Precursor suspensions are referred to the particles resulting from the solidification of emulsified droplets. Their formation was performed following two main methods: (a) the removal of water from the droplets by dropwise addition of the emulsion in a hot bath of an organic solvent [11] and (b) the solidification of droplets under stirring by the addition of a precipitating agent (e.g. TEA) or by extraction of water using a suitable dehydrating liquid (e.g. alcohols) [8, 14]. Several trials using TEA and ethanol failed because of the destruction of droplets during the requested processes of centrifugation/filtration. The optimum solidification of droplets was attained by the dropwise addition of the emulsion in a mineral oil bath which was kept in the temperature range 120–140 °C. Note that, temperatures below 120 °C and above 140 °C enable the coalescence of droplets. The dehydrated emulsion named "precursor suspension" was recovered by decantation of the floating mineral oil. Afterwards, the rest of the oil was separated from the solid spheres through the thermal treatment of the precursor suspension between 25 and 700 °C under controlled heating rate (2–5 °C/min) and atmosphere (air/N_2). The hardening of resulting soft spheres was achieved at 1,300 °C ($\sim$30 min).

Characterization techniques

Measurements of particles of various suspensions and powders were performed based on laser diffraction combined with polarisation intensity scattering (Beckman Coulter LS13320 PIDS). The viscosity of suspensions was measured at 25 °C using a rheometer RHEOTEST RN 4 and the pH measurements were performed with a pH-meter (EcoSense pH10). Emulsions and precursor suspensions were examined with a light microscope (ZEISS). Scanning electron microscope (SEM) images were obtained using a ZEISS Digital SEM DSM 962. The weight loss occurring during the thermal treatment of the precursor suspension was registered with the help of a thermoanalyser combined to the furnace (HTM REETZ). The phase composition of synthesized powders was determined by the powder X-ray diffraction, performed on a diffractometer using CuKα radiation.

Table 2 Characteristics of emulsions and precursor suspensions (starting powder: E2; surfactant: Span80)

Sample N°	Suspensions	Span80 (wt%)	Light microscopy results	
			Emulsions	Precursor suspensions
S1	M40	5	Well-dispersed droplets	Spheres, few irregular particles
S2	M50	3–6	Well-dispersed droplets	Well-dispersed microspheres
S3	M60	5	Well-dispersed droplets	Spheres, few irregular particles
S4	P40	2–8	Unstable droplets	⊗
S5	P50	2–5	Unstable droplets	⊗
S6	P60	2–4	Coalescence	⊗
S7	P60	5–10	Well-dispersed droplets	Well-dispersed microspheres
S8	P65	10	Droplets, few fine particles	Spheres, few irregular particles

⊗, fine particles or agglomerates; wt% of span80: with respect to the mass of mineral oil

Results and discussions

Formation and characterization of aqueous suspensions

In what follows, suspensions of $LiAlSiO_4$ in magnesium nitrate and in poly(acryl)acid solutions are referred to $Mg(NO_3)_2-$ and PAA-suspensions, respectively. As expected, the pH of investigated suspensions varies with the chemical composition of the aqueous phase. When the aqueous phase is the PAA solution (pH = 3.8), $LiAlSiO_4$ powders lead to the formation of basic suspensions with pH values in the range 11.6–12.5. This observation is explained by the ion exchange processes such as $Li^+ \rightarrow H^+$ occurring on the eucryptite powder. On the other hand, the chemical processes occurring within the "$LiAlSiO_4$ powder-$Mg(NO_3)_2$" system, e.g. the formation of magnesium hydroxy-species and the ion exchange processes $Li^+ \rightarrow Mg^{2+}$, determine the pH value of the $Mg(NO_3)_2-$suspensions. One sees clearly that registered pH values of 6.5–6.8 are relatively closer to that of the Mg-nitrate solution (pH = 5.6).

For the suspensions listed in Table 1 it is clearly seen that the average size of particles (D_{50}) varies in the narrow range 3.0–6.4 μm. For constant $LiAlSiO_4$ content, the average particle size (D_{50}) of the PAA-suspension is lower than that of the $Mg(NO_3)_2-$suspension. An increase of the particle size of the $Mg(NO_3)_2-$suspension with the increase of the $LiAlSiO_4$ content is observed. However, in the case of the PAA-suspension an obvious increase in the size of particle occurs only above 60 wt% of $LiAlSiO_4$ powders. These observations result mainly from the chemical processes occurring between the eucryptite powder and the aqueous phase. For instance, the formation of Mg-hydroxy-species within the $Mg(NO_3)_2-$suspension enhances the easy formation of microaggregrates of eucryptite particles consequently leading to an increase in the particle sizes. The rheological behaviour of investigated suspensions is presented in Table 1. In particular, the viscosity of $Mg(NO_3)_2-$suspensions as function of the shear rate is displayed in Fig. 1. Suspensions prepared in PAA solution exhibit a Newtonian flow while a pseudoplastic flow is observed when the $Mg(NO_3)_2$ solution is the aqueous phase. For the $Mg(NO_3)_2-$suspensions, high registered particle sizes and the large dependence of the viscosity on the shear rate support the presence of a network structure (Table 1). As the shear rate increases, this effect becomes less marked, suggesting that any particle-particle interaction is relatively weak and likely to breakdown at high shear rates (Fig. 1). On the other hand, the increase of the solid content of the suspension results in more particle-particle interactions and an increase in resistance to the flow. In the case of the PAA-suspension, an uncommon behaviour is observed. The viscosity increases with the increasing amount of $LiAlSiO_4$ powder reaches a maximum value of 31 mPa.s at 60 wt% of $LiAlSiO_4$ powder and then decreases for further increase of the solid content. Size distributions data show that the increase of the $LiAlSiO_4$ content above 60 wt% leads to the formation of PAA-suspensions made of relatively large

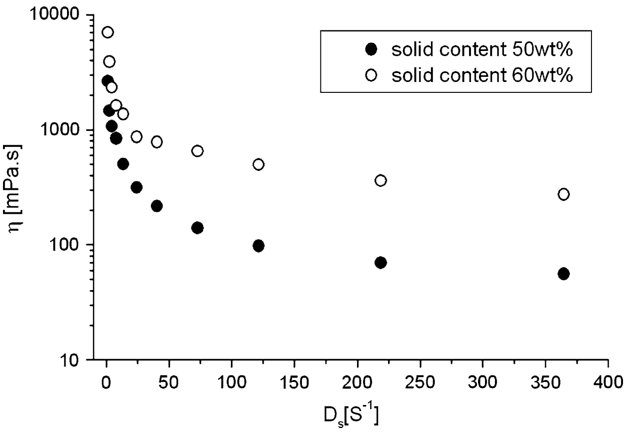

Fig. 1 Viscosity curves of eucryptite suspensions prepared with Mg-nitrate solution

particles (Table 1). From that, the particle-particle interactions are reduced and the suspensions with a lower viscosity are formed.

Preparation of water-in-oil (w/o) emulsions

Using Span60 and Span80 as surfactants, w/o emulsions prepared with heptane show a pronounced coalescence. However in mineral oil, well-dispersed droplets were obtained when convenient synthesis parameters were selected. The difference in the emulsion stability for mineral oil and heptane is attributed to the difference between the viscosities of these two reagents. Because of its high viscosity, mineral oil is much more efficient than heptane in keeping the stable emulsion and in minimizing the phase separation. This result points out the importance of the type of the organic solvent on the stability of emulsions. In particular, the variation of the size of emulsified droplets with the concentration of surfactant in the organic phase was not significant. We found in general that the influence of the synthesis parameters on the formation of stable and well-dispersed w/o emulsions is mostly similar to the observation commonly made using the conventional procedure [5–8].

By keeping the above-mentioned factors in consideration, it was possible to form w/o emulsions from several aqueous suspensions of $LiAlSiO_4$ powders. Using mineral oil as organic solvent, the mass ratio suspension-to-mineral oil (S/MO) in the range 1:3–1:4 was found to be more effective. Smaller amounts of the mineral oil yielded larger droplets. By increasing the amount of the mineral oil, uniform microspheres with much smaller diameters were obtained. The larger the density difference between the water and the organic phase, the easier the formation of more droplets, since the shear stresses stimulated their break up [13]. Table 2 presents the characteristics of emulsions obtained for a mass ratio S/MO value of 1:3.23. One sees that for each of the investigated suspensions, a critical weight ratio $LiAlSiO_4$ powder-to-aqueous phase (P/A) was required to obtain well-dispersed droplets. Starting from the PAA-suspension, a solid content less or above 60 wt% was not effective for the formation of stable emulsions. This influence was relatively limited when the $Mg(NO_3)_2$-suspension was used. The maximum solid loading required for the formation of stable emulsions with $Mg(NO_3)_2$ and PAA suspensions were 50 wt% and 60 wt%, respectively. This discrepancy is related to the difference within the characteristics (particle size distribution, the viscosity) of the different suspensions (Table 1). It is important to note that, suitable suspensions are not necessarily those with relatively high solids loading and a relatively low viscosity. If it was the case, the suspension P65 ($\eta = 15$ mPa.s) should be the most appropriate one. From a general point of view, the powder suspensions used for the preparation of the w/o emulsion should be optimized in terms of solid loading, aqueous phase and the chemical used as additive. Besides, the compatibility between the composition of the suspension and that of the continuous phase should not be neglected. From the above investigations, Span80 was found to be the most appropriate surfactant. Its amount in the range 5–10 wt% (with respect to the mass of mineral oil) was sufficient for the formation of suitable emulsions. Using the Span60, some trials led to the formation of well-dispersed droplets. This is the case of the emulsion prepared by dispersing the suspension P40 inside a continuous phase made of 5 wt% Span60 in mineral oil. In Table 2, it is clearly seen that for the same suspension composition, optimized emulsification conditions are not achieved with the Span80. These aspects among several others suggest the necessity to choose proper experimental parameters for a particular emulsion system. Moreover it has been established that like the suspensions prepared from a single $LiAlSiO_4$ phase (powder E2) those prepared from the mixture of oxides (powder E1) also give stable emulsion, but under different conditions (e.g. amount of surfactant).

Formation of spherical particles from the precursor suspension

Preparation of the precursor suspension

Among the procedures applied for the conversion of emulsified droplets in solid particles, best results were obtained by dropwise addition of the emulsion in a hot mineral oil bath (Sect. "Formation and thermal treatment of the precursor suspensions"). From a general point of view it has been found that, emulsions prepared under inappropriate reaction conditions were unstable during the dehydration processes. This remains true even when the emulsion is made of the well-dispersed droplets that can be stable during several days/months. These observations result mainly from the incompatibility between the reaction conditions. Because of the large number of experimental parameters, such behaviour cannot be easily avoided. Consequently, for the investigated emulsion systems, precursor suspensions suitable for further thermal investigations were obtained under a narrow range of the synthesis conditions. The Table 2 presents an example of results obtained for a selected mass ratio suspension-to-mineral oil (S/MO) value of 1:3.23.

Thermal treatment of the precursor suspension

The thermal decomposition of precursor suspensions was followed under inert atmosphere (Argon). Figure 2 shows a typical example of registered curves. It can be seen that the decomposition occurs in two main steps. During the first step (25–180 °C), the complete dehydration of the precursor suspension occurs and leads to a negligible mass loss of ~2%. In the second step (180–550 °C), the organic constituents (mineral oil, additives and surfactants) are evaporated. Due to the superimposition of the different decomposition processes, the mass loss of ~13% is released once. Remarkably, the yellowish precursor suspension changes into a dark powder made of soft spheres. The amount of carbon/carbon species responsible for this change of coloration is too small to be detected on the XRD pattern. Through further thermal treatment, the variation of the particle shapes as function of the composition of the surrounding atmosphere becomes remarkable. For instance, eucryptite powders prepared above 1,100 °C in presence of air (white colour) are aggregated, while under N_2 atmosphere, the formation of a thin film of the remaining carbon on the particles surface (powder with a grey colour) prevents the aggregation. From these results, it turns out that particle-particle interactions are much more controlled under inert atmosphere than in air.

The XRD patterns of samples prepared at 1,300 °C (N_2) from PAA-precursors show typical expected diffraction peaks (Fig. 3). Identified phases, β-$LiAlSiO_4$ (crystalline) and SiO_2 (amorphous), are similar to those of the starting powder E2 but their respective amounts change slightly. Despite this fact, resulting spheres of β-$LiAlSiO_4$ have a purity degree greater than 90%. On the other hand when $Mg(NO_3)_2$ is the selected additive, particles with less than 70% of β-$LiAlSiO_4$ are obtained. The secondary phases (e.g. $MgAl_2O_4$) which change in function of the synthesis conditions are formed from intermediate reactions occurring between the amorphous SiO_2 and the decomposition products of $Mg(NO_3)_2$. It turns out that, PAA is the most effective additive required for the formation of relatively pure spheres of β-$LiAlSiO_4$.

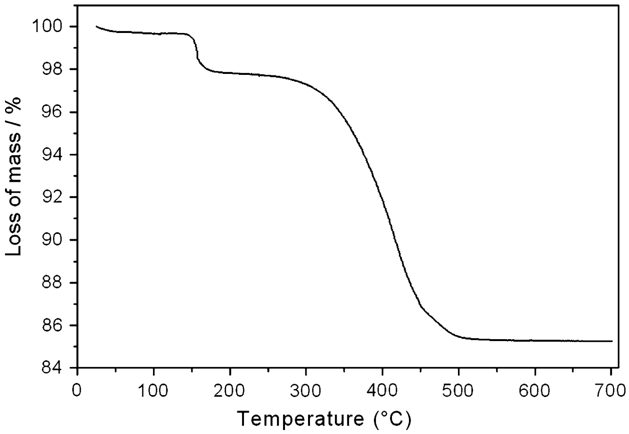

Fig. 2 Thermal decomposition of the precursor suspension under Argon (S7, 10 wt% of Span80; heating rate:3 °C/min)

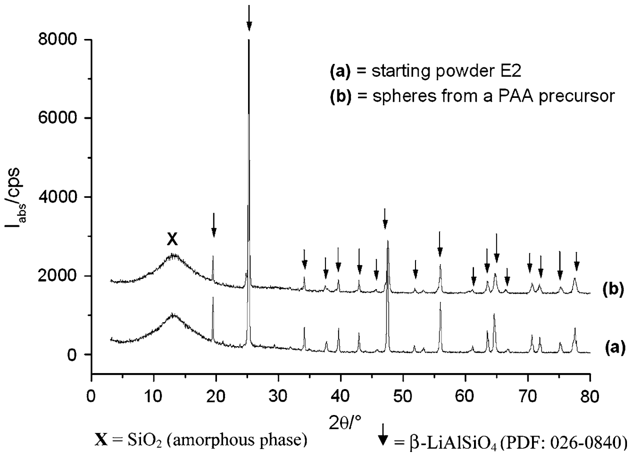

Fig. 3 XRD patterns of (**a**) β-$LiAlSiO_4$ powders prepared for 3 h at 1,100 °C in air (starting powder E2) and of (**b**) β-$LiAlSiO_4$ spheres obtained after thermal treatment of the PAA-precursor suspension (S11) under N_2 at 1,300 °C for 30 min

The morphology of eucryptite particles obtained from the PAA- and $Mg(NO_3)_2$-precursor suspensions is shown on Figs. 4 and 5. Porous and well-spherical particles, prepared from PAA-precursor suspensions, are clearly identified (Fig. 4). However, dense irregular particles, prepared from the $Mg(NO_3)_2$-precursor suspensions, show a significant aggregation (Fig. 5). This demonstrates that the type of chemical additive used for the preparation of the suspension is essential for the formation of eucryptite spheres. The size distribution of eucryptite particles is given in Table 3. Starting from the PAA-suspension (P60), 6 wt% of Span80 in mineral oil is effective for the formation of eucryptite spheres. However, optimal synthesis conditions are achieved through subsequent increase of the amount of Span80, up to ~10 wt%. A comparison between the recorded D_{10}, D_{50} and D_{90} values (S10 and S11) confirms this point of view. On the other hand, maintaining the other synthesis parameters constant, eucryptite spheres prepared from the mixture of oxides (powder E1) were larger (D_{50} = 57.71 µm, S12) than those obtained (D_{50} = 42.70 µm, S11) using a single $LiAlSiO_4$ phase (powder E2). This result shows the importance of the type of the starting powder on the particle size of resulting spheres.

Conclusion

The present work demonstrates that aqueous powder suspensions can be used for the sol-emulsion-gel process. We were able to provide optimal synthesis conditions to

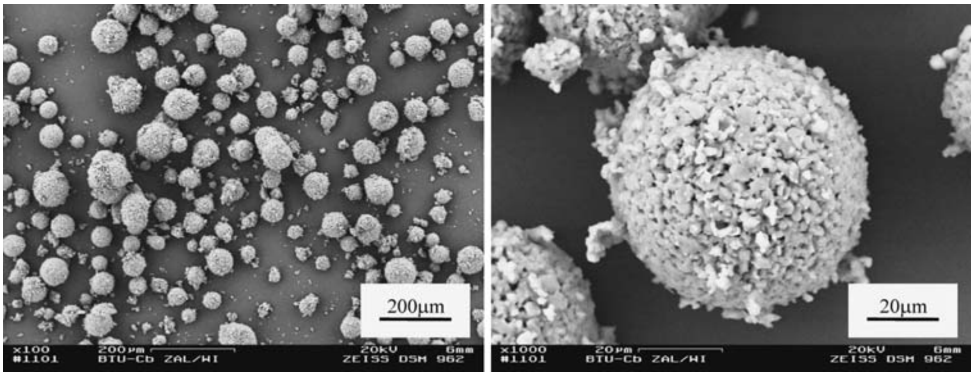

Fig. 4 SEM pictures of eucryptite particles obtained at 1,300 °C (N_2) from a PAA suspension (S11; Surfactant: 10%Span80)

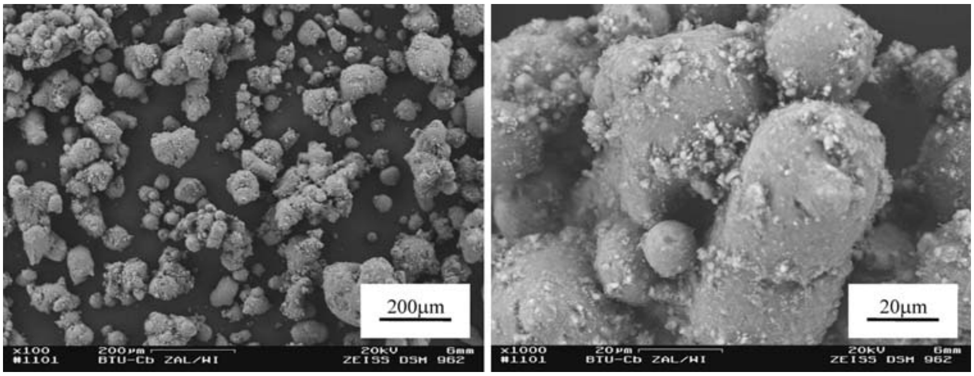

Fig. 5 SEM pictures of eucryptite particles obtained at 1,300 °C (N_2) from a $Mg(NO_3)_2$-suspension (Surfactant: 10%Span80)

Table 3 Particle size distribution of eucryptite spheres prepared at 1,300 °C

Sample N°	Suspensions	Span80 (wt%)	Particle size (µm)		
			D_{10}	D_{50}	D_{90}
S9	M50	10	5.81	37.19	70.63
S10	P60	6	9.10	53.34	82.13
S11	P60	10	5.11	42.70	71.91
S12	P60*	10	8.00	57.71	131.30

* Prepared starting from the powder E1; wt% of Span80: with respect to the mass of mineral oil

produce eucryptite spheres with average diameters in the range 40–60 µm. The key step is the determination of the characteristics of the suspension (solids loading, particle size, pH and composition of the aqueous phase) enabling the formation of a well-dispersed emulsion from an oil phase with a specific composition (type and amount of the organic solvent and of the surfactant). By adjusting the emulsification parameters (characteristics of the suspension, composition of the continuous phase) and the sintering conditions (temperature and composition of the surrounding atmosphere), the shape of eucryptite particles were systematically controlled. For example, when mineral oil is the organic liquid and Span80 the surfactant, a PAA-suspension with a high solid loading of 60 wt% yields eucryptite porous spheres with average diameters of 42.70 µm. It is interesting to note that our synthesis scheme can be easily adapted to other metal oxides. The broad variation of the size of the spheres could make them useful for different applications.

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