Synthesis and thermal properties of silicon oxycarbide/spodumene materials

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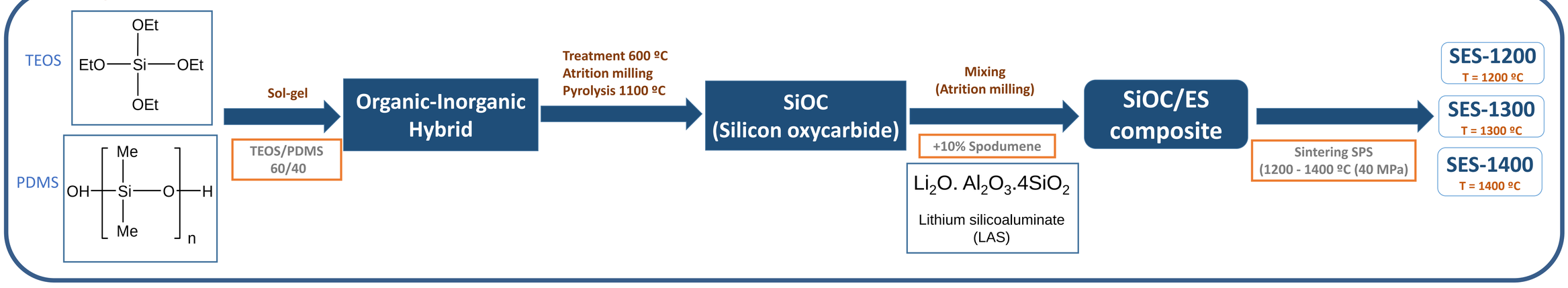
ABSTRACT

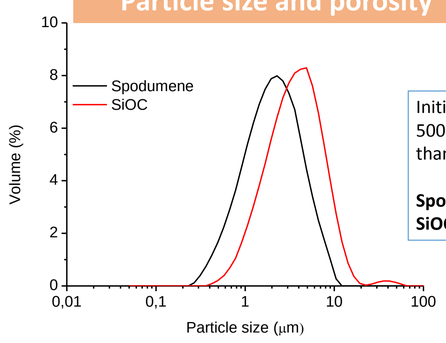
Lithium silicoaluminates (LAS: $Li_2O.Al_2O_3.SiO_2$) have very low or negative coefficients of thermal expansion (CDT), which makes them very interesting materials from a technological and industrial point of view to improve the thermal shock resistance of ceramic and glassy materials. LAS are found in natural minerals such as eucryptite, spodumene and petalite, but only the last two are commercially available. Spodumene (S) is used as a source of LAS. On the other hand, oxycarbide glasses (SiOC) have a SiO_2 matrix where part of the oxygen has been replaced by carbon, and also contain a carbon phase homogeneously embedded within this Si-O-C matrix. The great advantage of these materials is that, depending on the precursors, synthesis-processing conditions, pyrolysis temperature and the addition of reinforcing materials, the properties of the final materials can be pre-designed and materials with specific characteristics can be obtained depending on the application. In this work, dense SiOC/S composite materials have been developed using the unconventional spark plasma sintering technique. The maximum sintering temperature used was the liquidus temperature of the spodumene (1400 ºC). The thermal properties of these materials have been characterised. The thermal conductivity of the material increases from 1.41 to 2.14 $Wm^{-1}K^{-1}$ for materials without and with spodumene, probably due to the presence of lithium. These SiOC/S materials show low CDTs ranging from 0.1 to 4.5 $x10^{-6}$ K^{-1}, increasing with sintering temperature. During sintering, the SiOC/S material undergoes several transformations. At 1200 ºC the S is transformed into petalite and at higher temperatures the crystallisation of quartz-cristobalite is observed, which justifies the increase of the CDT.

Experimental Procedure



RESULTS:

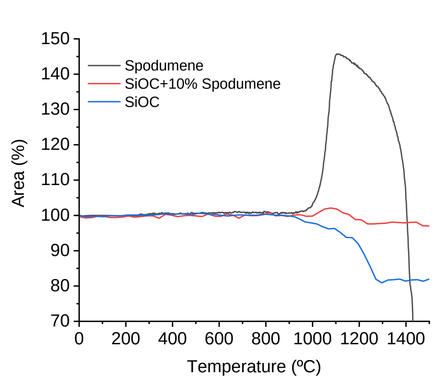
Particle size and porosity

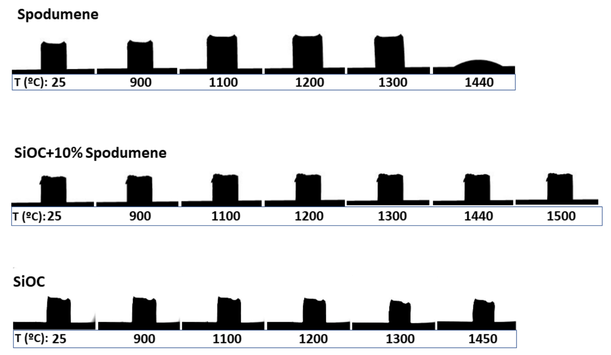


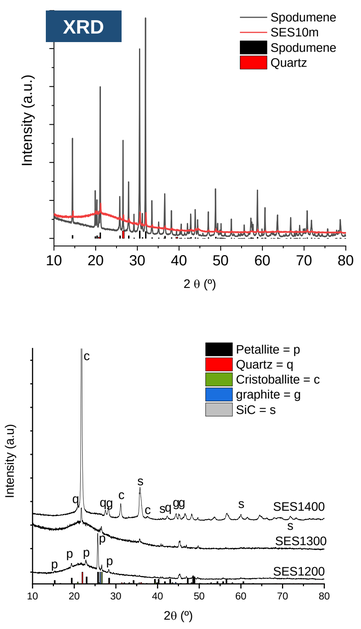
Initially, spodumene displays a coarse particle size (< 500 µm) which is reduced up to the same size range than SiOC powders.

Spodumene d_{50} = 1,91 µm
SiOC d_{50} = 3,42 µm

Hot stage microscopy







After sintering the SiOC/ES composites reach a proper densification with a porosity values very low.

Spodumene:
900-1100 ºC, expansion (≈ 45%) α to β transformation
1100-1440 ºC contraction (76%) until reach the flowing point at 1440 ºC

SiOC:
From 900 to 1200 ºC contraction
Sintering up to 1300 ºC and then a horizontal plateau (crystallization)

SiOC + 10 % Spodumene:
1000 ºC the mixture expands (2%) and then at 1100 ºC contracts (3%)
The sintering occurs from 1200 to 1440 ºC reaching a plateau (crystallization)

The sintering temperature is reached 100 ºC before by the fluxing properties of lithia present in spodumene.

SiOC:
1)Phase separation: SiOC → SiO_2 + SiC + C_{free}
2) Crystallization: SiC + C_{free}

SiOC + Spodumene:
Spodumene can experience tranformation and crystallizations depending on compositon and temperature.

Structural evolution: XRD and FT-IR

Initial Composition:
Spodumene ~ 94%, quartz ~ 1% and feldspar ~ 1%
Chemical composition:
Li_2O = 7.2 %, Al_2O_3 = 25,0 %, SiO_2 = 62.5 %, Fe_2O_3 = 0.12%, Na_2O = 0,35%, K_2O = 0.3%, P_2O_5 = 0.25% and CaO = 0.10%.

Spodumene: spodumene and quartz.

The SiOC +10% spodumene mixture shows additionally a broad halo ≈ 22 º related to vitreous silica derived materials.

SiOC/ES composites:
SES1200: The spodumene is transformed in petallite.

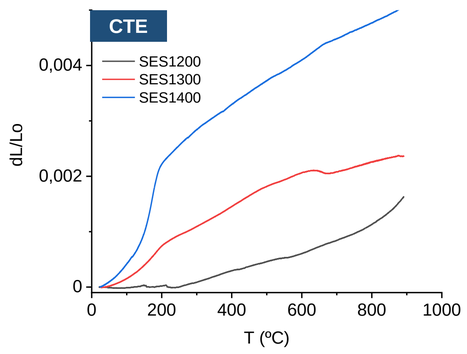
SES1300-SES1400:
Increasing with the sintering temperature appears the peaks related to β-SiC, quartz and cristoballite.

Spodumene:
Si-O-Si (1126,1087, 1027 and 462 cm^{-1})
Si-O-Al (916 cm^{-1})
AlO_6 groups (860, 640 and 592, 536 cm^{-1})
LIO_4 (536 cm^{-1})

SiOC+10% spodumene:
SiOC (1092, 812 and 468 cm^{-1})
Spodumene bands are slighly observed (916, 639 and 588 cm^{-1})

SiOC/ES composites:
- The SiOC bands move towards higher wavenumbers indicating the densification and strengthening of the silica network.
- The bands sharpen with sintering temperature indicating a high degree of crystallinity.
- The phase separation and carbothermal reduction produce both amorphous (880 cm^{-1}) and β-SiC (792 cm^{-1}).
- **SES1400** shows the presence of cristobalite (616 cm^{-1})

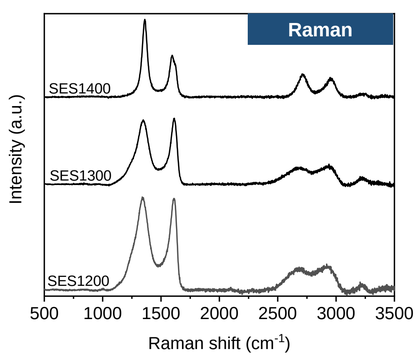
Thermal properties: Coefficient of thermal expansion (CTE) and thermal conductivity



	CTE ($x10^{-6}$ (K^{-1})	K ($Wm^{-1}k^{-1}$)	C (%)	L_a (nm)
SES1200	0,13-1,9	1,28	7,6	4,4
SES1300	3,29	1,58	7,31	4,5
SES1400	4,51	2,14	7,35	2,4

C(%) slighly decreases with sintering temperature
C_{free} phase experiences a rearregement increasing its ordering degree but reducing its domain size (L_a).
Both parameters indicate the beginning of the carbothermal reduction of silica

$SiO_2 + 3C_{free} \rightarrow SiC + CO_x(g)$



CTE and K increase with sintering temperature

SiOC/ES composites display different CTE at low at high temperature.

SES1200 displays very promising values of CTE due to the formation of petallite (0,3 x 10^{-6} K^{-1}):
$\alpha_{25\text{-}200}$ ($x10^{-6}$ K^{-1}) = 0,13
$\alpha_{200\text{-}800}$ ($x10^{-6}$ K^{-1}) = 1,9

K increases due to the increase of C_{free} ordering, the formation of new crystalline SiC and probably to the presence of lithia.

CONCLUSIONS

Bulk highly dense silicon oxycarbide/spodumene composites have been obtained employing spark plasma sintering at relatively low temperature (1200-1400 ºC). At 1200 the spodumene is transformed into petalite. At higher temperatures, especially noticeable at 1400 ºC, the phase separation of SiOC (into SiO_2, SiC and C), carbothermal reduction of SiO_2 (with the formation of SiC) and crystallization of cristobalite are observed.

SES1200 displays very promising values of CTE (0,13-1,9 x 10^{-6} K^{-1}) due to the crystallization of petallite. The K increases with the sintering tempeature up to 2,14 $Wm^{-1}k^{-1}$ as consequence of the crystallization of C_{free} SiC and probably by the presence of lithia.