

TEMPERATURE-RELATED DEHYDRATION AND STRUCTURAL DEVELOPMENT
OF SOL-GEL PREPARED TYPE I MULLITE PRECURSORS

by

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Mullite is an important compound in the field of advanced ceramics. For the preparation of ultrafine and pure precursor powders, the sol-gel route is a convenient method. Mullite precursors are characterized by different crystallization paths [1]. Type I precursors are non-crystalline up to 900°C and crystallize to mullite above this temperature. Precursor type II consists of weakly crystalline pseudo-boehmite and an amorphous silica-rich phase; mullite formation starts at temperatures $\geq 1200^\circ\text{C}$. Type III precursors are amorphous up to 900°C and crystallization of γ -alumina with SiO_2 -rich amorphous phase is observed above this temperature; crystallization of mullite occurs above 1200°C.

Two sol-gel derived precursors for stoichiometric mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), synthesized by slow hydrolysis methods, were investigated by FTIR spectroscopy, thermogravimetry and determination of the analytical water content. Precursor A was prepared by use of aluminium nitrate and tetraethoxysilane (TEOS) as starting materials, precursor B was synthesized from aluminium sec.-butoxide and TEOS. The 150°C-dried precursor powders (as-prepared) were heat-treated in 100°C steps in the range from 200 to 1000°C. Due to their crystallization behaviour, both samples correspond to type I precursors.

The IR absorption bands of the H_2O (5160 cm^{-1}) and (Si, Al)-OH (4540 cm^{-1}) combination mode, the (H_2O , OH) stretching modes (3430 cm^{-1}) and the H_2O bending modes (1635 cm^{-1}) were used to monitor the temperature-dependent dehydration behaviour. Molecular water as well as OH groups are present in the as-prepared powders and in the heat-treated precursor phases. Precursor A shows a continuous loss of H_2O molecules and OH groups in the temperature range from as-prepared to 600°C, where most of H_2O and OH is released. Further dehydration occurs in the temperature step from 800 to 900°C. In precursor B the OH group content remains almost constant up to 500°C and is continuously reduced above this temperature. H_2O molecules are continuously removed over the whole temperature range. At 900°C both precursors show only minor amounts of H_2O and OH.

The IR spectra of the heat-treated samples in the range of lattice vibrations ($1400 - 400 \text{ cm}^{-1}$) show the structural changes of the precursor phases. The spectrum of the as-prepared sample of precursor A is characterized by two main band groups, located in the regions $1250 - 850 \text{ cm}^{-1}$ and $780 - 500 \text{ cm}^{-1}$. With increasing temperature up to 600°C the low-energy band is splitted in two bands, which continuously change in their relative intensity, and the high-energy band shifts to higher wavenumbers. The absorption bands of the samples heat-treated between 600 and 900°C show only slight changes. Precursor A additionally exhibits a strong absorption band at around 1400 cm^{-1} in the as-prepared sample, attributed to nitrate, which continuously vanishes up to 500°C . The temperature-related changes of the absorption bands of precursor B up to 800°C are less significant than for precursor A. Between 800 and 900°C remarkable changes of the spectrum are observed and the band pattern becomes very similar to that of precursor A. The IR spectra of the 1000°C -samples of both precursors closely match that of an alumina-rich mullite.

References

- [1] SCHNEIDER, H. et al. (1993): Mullite precursor phases. - J. Europ. Ceram. Soc. 11: 87-94