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Dehydration and structural development of mullite precursors: an FTIR spectroscopic study

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Abstract

Mullite type, I and III precursors were prepared by a sol-gel process using tetraethoxysilane and aluminum sec.-butoxide as starting materials. The precursors were treated by 15 h heating steps in intervals of 100°C from 200 to 1000°C. Type III precursors are characterised by a more discontinuous decrease of the analytical water content compared to that of type I precursors. The FTIR powder spectra of the preheated precursors show weak absorption bands at 5160 and 4540 cm^{-1} which are due to H_2O and OH combination modes, thus proving the presence of both, H_2O molecules and OH groups as structural components of the precursors. (H_2O, OH) stretching modes are centered at around 3430 cm^{-1} and H_2O bending modes at 1635 cm^{-1}. The deconvolution of the stretching mode bands reveals non-bridging and bridging H_2O molecules and OH groups. Close similarities in the pattern of the 1400–400 cm^{-1} vibrational region between type I and III precursors exist up to preheating temperatures of 800°C. Significant differences are evident at temperatures of 900°C, where the spectrum of the type III precursor still corresponds to that at 800°C, while the type I precursor reveals a spectrum with features present in the spectrum of mullite. Bands centered around 1110 and 1010 cm^{-1} are assigned to Si–O stretching vibrations of the SiO_4 tetrahedral units and are strongly shifted in 900°C treated type I precursors to higher wavenumbers. This band shift is a strong indication for an increasing degree of network condensation and for changes in the Si–O distances to tetrahedra dimensions similar to those of mullite. A significant absorption around 860 cm^{-1} is assigned to Al–O stretching modes of AlO_4 tetrahedral units, a band around 570 cm^{-1} is assigned to Al–O stretching vibrations of AlO_6 octahedral units. A slightly decreasing intensity of this band with increasing preheating temperatures, along with a strongly increasing intensity of the 860 cm^{-1} band demonstrates a clear preference of Al for a four-fold coordinated structural position in the precursors preheated at high temperatures. This process is correlated to the dehydration process occurring in the medium- to high-temperature field of network condensation starting at around 400°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mullite; Precursors; Sol-gel processes

1. Introduction

Mullite is a widely used engineering material in ceramics. The sol-gel synthesis of high-purity and ultrafine mullite precursor powders is of increasing importance for optical, electronical, and high-temperature structural applications.[1] Since the crystallisation paths of the precursor powders significantly influence the properties of ceramics, detailed knowledge on the temperature dependent structural development of the precursors is of high importance.

Three main types of mullite precursor synthesis by sol-gel routes were discerned.[2,3] Using admixtures of tetraethoxysilane, TEOS, and aluminum sec.-butoxide, $Al(OBu^s)_3$, as starting materials, type I mullite precursors are produced by slow air humidity hydrolysis, type II precursors by rapid hydrolysis with excess H_2O under strongly basic conditions ($pH > 10$), and type III precursors by rapid hydrolysis under moderately basic conditions ($pH < 10$). Type I and III precursors remain non-crystalline from room temperature up to 900°C. Above this temperature type I precursors crystallise to alumina-rich mullite, while type III precursors transform to γ-Al_2O_3. In both cases a silica-rich amorphous phase is coexisting with the crystalline phases, though in different amounts. Mullite formation in type III precursors is observed at temperatures of 1200°C. Type II precursors consist of a non-crystalline SiO_2-rich phase and poorly crystalline pseudo-boehmite, transforming to γ-Al_2O_3 at 350°C, and mullite crystallisation occurs above 1200°C. Since type II precursors contain no detectable amounts of non-crystalline precursor phases comparable with those of type I and III precursors, type II precursors are not the subject of the present study.

The aim of this paper is to provide a model for the temperature dependent structural development of type I

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and III precursors, considering the extensive dehydration process with respect to a better understanding of the temperature related physical properties of advanced mullite ceramics.

2. Experimental

2.1. Sample preparation

The mullite precursor phases were prepared by using TEOS, $Si(OC_2H_5)_4$ (Merck, 800658) and $Al(OBu^s)_3$, $Al(OC_4H_9)_3$ (Merck, 820054) as starting materials.[2] Both metal alkoxides were admixed in proportions corresponding to stoichiometric $3Al_2O_3{\cdot}2SiO_2$ mullite. For the preparation of type I precursors the admixed metal alkoxides were diluted with isopropanol (Merck, 109634). After homogenisation, the mixture was allowed to hydrolise only by air contact in a glove box at a relative humidity of about 40%. After a period of 10 days the solution gelled. For the preparation of type III precursors, TEOS was mixed with an appropriate portion of isopropanol and water under basic conditions (pH = 10). The prehydrolised TEOS solution was mixed with $Al(OBu^s)_3$, diluted in isopropanol, and the mixed solutions gelled immediately. The resulting gels of both precursor types were dried at 150°C for 15 h ("as-prepared" precursor), then powdered by dry short-time hand grinding in an agate mortar and differently treated by 15 h heating steps at temperatures of 200, 300, 400, 500, 600, 700, 800, 900 and 1000°C. X-ray diffractometry proved all samples preheated up to temperatures of 900°C to be non-crystalline. The X-ray powder data were collected on a Philips X'pert diffractometer, equipped with a Cu tube, a graphite monochromator, and a scintillation counter.

2.2. Analytical water and weight-loss determination

The analytical water content of the as-prepared precursors and of the preheated precursors was determined with a modified DuPont moisture evolution analyser (MEA) 903 H working on the basis of water electrolysis.[4] The water content of ultrapure $Mg(OH)_2$ (Merck, 5870) was used for standardisation of the MEA. Each preheated precursor sample (3.5–5.0 mg) was annealed at a rate of 500°C min^{-1} to 970°C and held at this maximum temperature for 60 min. The water evolved was taken as the total analytical H_2O^+ content of the preheated precursor samples. The mean error of the values amounts to ±0.5 wt.%.

For the weight-loss determination a Mettler thermobalance TG 50 equipped with a TA 4000 thermo analyses system was used. Each preheated precursor sample (17–24 mg) was annealed at a heating rate of 5°C min^{-1} to 1000°C.[5]

2.3. FTIR spectroscopy

Because of a more effective sample handling with respect to a dry atmosphere, KBr micropellets with a sample/KBr weight ratio of 0.0025 were produced for the FTIR powder measurements. A sample/KBr weight ratio of 0.05 was exclusively used for measurements in the near-IR region of the H_2O and OH combination modes. Both, powdered samples and KBr were dried at 110°C for 2 h prior to pressing.

FTIR powder spectra were recorded from 5500 to 400 cm^{-1} by means of the Perkin-Elmer FTIR spectrometer 1760 X equipped with a TGS detector and a CsI microfocus accessory. Background and sample spectra were obtained from 64 scans each with a nominal resolution of 4 cm^{-1}. The spectra were deconvoluted into single Gaussian-shaped absorption bands using the program PeakFit (Jandel Scientific). The data handling was managed by the program IRDM (Perkin-Elmer).

3. Results

3.1. Absorption features assigned to structural water

As evident from Fig. 1, the analytical water contents determined by MEA are in good agreement with the thermogravimetrically determined weight-losses of the

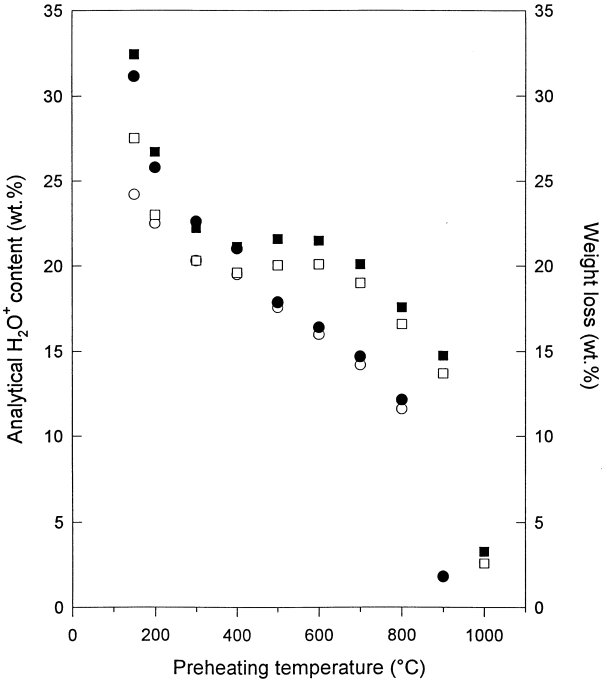

Fig. 1. Analytical H_2O^+ contents determined by MEA (open symbols) and weight-losses determined by TG (full symbols) for mullite precursors type I (symbol: circle)[6] and type III (symbol: square), as-prepared (150°C dried) and preheated at temperatures from 200 to 1000°C in intervals of 100°C.

precursor samples. Compared to the H_2O^+ contents, the weight-loss values of the precursors preheated up to 400°C are significantly higher. This is apparently due to the additional decomposition of the organic starting materials. The differences in the analytical H_2O^+ contents of the as-prepared samples roughly amount to 7 wt.% for type I and to 5 wt.% for type III precursors. The temperature-dependent dehydration of precursor type I was already described in detail.[6] Type III precusors are characterised by a more discontinuous decrease of the analytical water content compared to that of type I precursors. At preheating temperatures of 900°C, the type I precursor contains only 1.8 wt.% H_2O^+, while the type III precursor contains 13.7 wt.%. At 1000°C non-crystalline type III precursors still contain essential amounts of water which is evident from the total analytical H_2O^+ content of 2.6 wt.% (Fig. 1).

The FTIR powder spectra of the preheated precursor samples in the region of the H_2O and (Si,Al)–OH combination modes consist of two weak bands centered around 5160 and 4540 cm^{-1} and prove the presence of both, H_2O molecules and OH groups as structural components of the precursors. The upper part of Fig. 2 shows the integral absorbances of the 5160 cm^{-1} H_2O combination bands of type III precursors. Compared to type I precursors,[6] type III precursors show a more slight and continuous decrease of the H_2O absorbances with practically constant values between 500 and 700°C, and a further strong decrease at 1000°C. The equivalent diagram of the (Si,Al)–OH combination mode at 4540 cm^{-1} in the lower part of Fig. 2 shows a continuous decrease of the OH absorbances up to 900°C, followed by a strong decrease at 1000°C. Consequently the OH/H_2O ratio of type III precursors is continuously increasing over the whole range of preheating temperatures. This is in contrast to type I precursors which show a strong increase of the OH/H_2O ratio up to 600°C and an apparent recombination of OH groups to H_2O molecules above 600°C.[6] It is important to note that in type III precursors essential amounts of H_2O molecules and OH groups are still present at preheating temperatures of 1000°C.

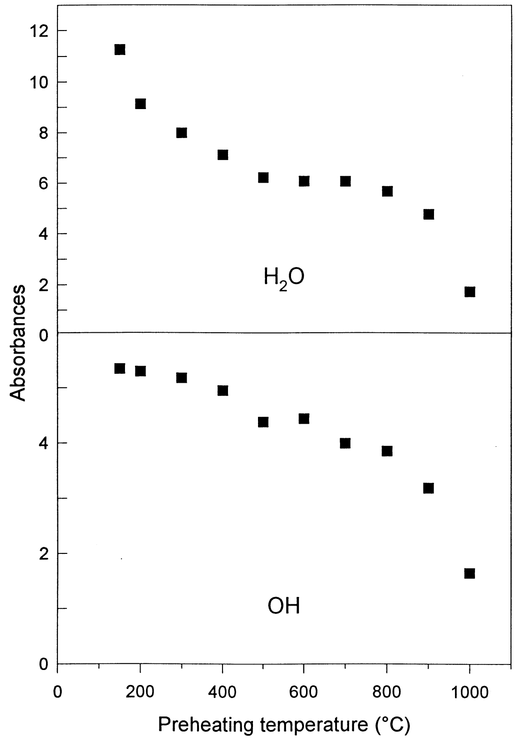

Fig. 2. Integral absorbance values of as-prepared and preheated mullite precursors type III (symbol: full square) for the H_2O combination band centered at 5160 cm^{-1} (upper part) and for the (Si,Al)–OH combination band centered at 4540 cm^{-1} (lower part).

The great difference in the band intensities between the stretching modes of OH groups and H_2O molecules centered around 3430 cm^{-1} and the bending mode of H_2O molecules centered around 1635 cm^{-1} is in agreement with the presence of both, H_2O and OH. The absorbances of the H_2O bending vibration are closely correlated to the absorbances of the H_2O combination mode. On the basis of the model for the structural (H_2O,OH) incorporation developed for type I precursors showing four fitted bands,[6] the deconvolution of the absorption in the (H_2O,OH) stretching vibrational region of type III precursors also reveals four bands signed with I, II, III and IV. The corresponding wavenumber values are listed in Table 1. As shown in Fig. 3, these reasonable band positions are best observed as

Table 1
Band positions (in cm^{-1}) derived from deconvoluted absorptions in the OH stretching and lattice vibrational region and band assignment for type I and III mullite precursors from as-prepared samples (as-prep) and samples preheated at 900°C (stretch: stretching vibration, bend: bending vibration)

Band no.	Band position				Band assignment[a]
	Type I		Type III		
	as-prep	900°C	as-prep	900°C	
I	3588	3534	3574	3580	OH stretch
II	3435	3426	3434	3434	H_2O stretch
III	3220	3135	3228	3217	OH stretch
IV	2999	2908	3000	3000	H_2O stretch
V	1104	1166	1117	1135	Si–O stretch (SiO_4)
VI	1005	1068	1014	1028	Si–O stretch (SiO_4)
VII	858	843	863	868	Al–O stretch (AlO_4)
VIII	702	673	711	721	T–O–T bend + Al-OH bend
IX	567	547	576	571	Al–O stretch (AlO_6)
X	441	437	449	450	O–Si–O bend (SiO_4)

[a] In mullite, bands at 1168, 1131, 1107 and 988 cm^{-1} are assigned to Si–O stretch (SiO_4), at 909 and 828 cm^{-1} to Al–O stretch (AlO_4), at 737 cm^{-1} to T–O–T bend (TO_4), at 620 cm^{-1} to O–Al–O bend (AlO_4), at 578 cm^{-1} to Al–O stretch (AlO_6), and at 482 cm^{-1} to O–Si–O bend (SiO_4) and Al–O–Al bend (AlO_6).[9]

maxima and shoulders in the spectrum of 900°C pretreated type I precursors. The four fitted bands are assigned to two different types of H_2O molecules and two different types of OH groups. Since most of the water in the as-prepared and high-T pretreated precursors is present as H_2O molecules, the strong band II around 3435 cm^{-1} is assigned to the stretching vibration of one type of H_2O molecules. The weaker band I around 3580 cm^{-1}, also strikingly present in the high-T pretreated type I precursor, is assigned to the stretching vibration of one type of OH groups. In precursors preheated at lower temperatures, H_2O and OH should be present in more comparable amounts; consequently the relatively strong band III around 3225 cm^{-1} is attributed to a second type of OH and the weak band IV around 3000 cm^{-1} to a second type of H_2O. Significant differences are evident in the (H_2O,OH) absorption pattern of type I and type III precursors preheated at 900°C (Fig. 3). While the absorption features of the 900°C treated type III precursor are similar to those of the as-prepared precursor, the 900°C treated type I precursor reveals significant changes in its absorption pattern compared to the as-prepared phase. The bands of the type I precursor show a slight but significant shift to lower wavenumbers at a preheating temperature of 900°C.

3.2. Absorption features assigned to lattice vibrations

Close similarities exist in the pattern of the FTIR powder spectra in the 1400–400 cm^{-1} vibrational region between type I and type III precursors up to preheating temperatures of 800°C. Significant differences are evident at preheating temperatures of 900°C, where the spectrum of the type III precursor still corresponds to that of the 800°C spectrum, while the type I precursor reveals a spectrum with features also present in the spectrum of mullite (Figs. 4 and 5). At temperatures of 1000°C, type I precursors are transformed to mullite which shows its characteristic absorption bands in the 1200–1100, 1000–700 and 650–400 cm^{-1} region.[7–9] The spectrum of type III precursors preheated at 1000°C resembles that of 900°C treated type I precursors but is strongly influenced by absorptions due to the presence of γ-Al_2O_3 with maxima in the 800–550 cm^{-1} range and probably also by the amorphous SiO_2-rich phase with band maxima around 1110 and 470 cm^{-1}. However,

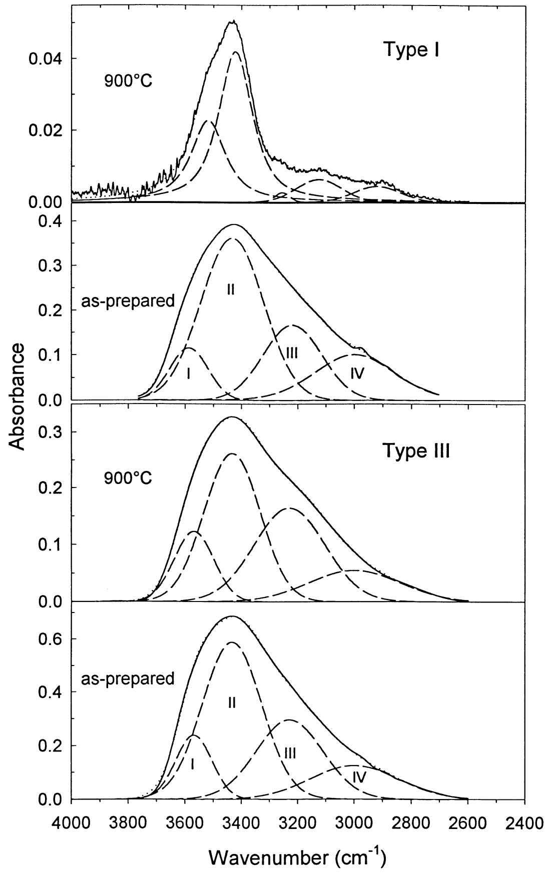

Fig. 3. FTIR spectra in the (H_2O,OH) stretching vibrational region of as-prepared and 900°C treated type I and III mullite precursors. The spectra are deconvoluted into four (I–IV) single Gaussian-shaped bands. For band positions see Table 1. Note the different absorbance scales.

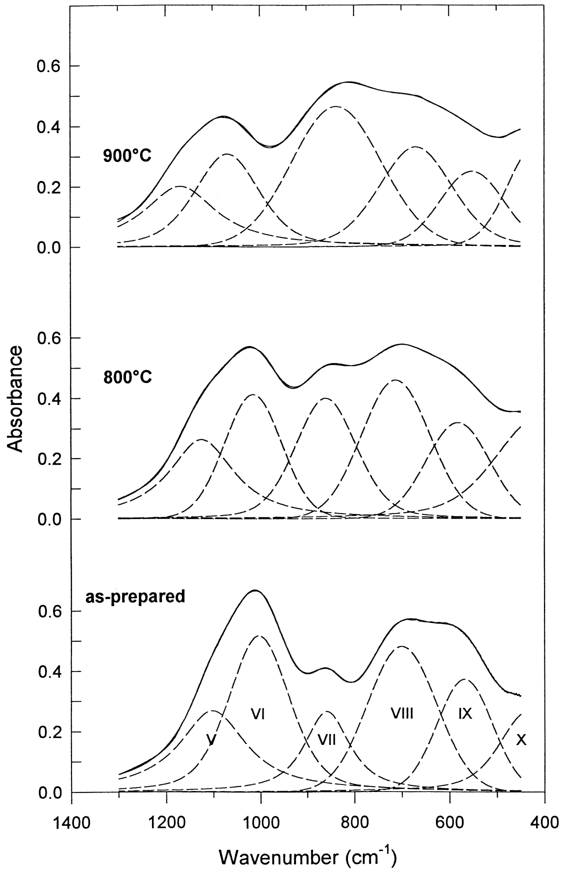

Fig. 4. FTIR spectra in the lattice vibrational region of mullite precursors type I, as-prepared and preheated at 800 and 900°C. The spectra are deconvoluted into six (V–X) single Gaussian-shaped bands. For band positions see Table 1.

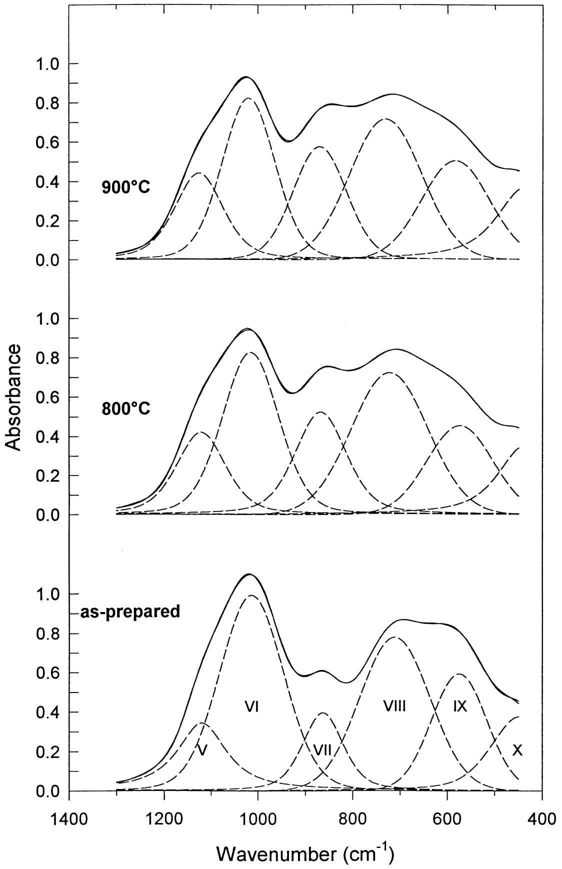

Fig. 5. FTIR spectra in the lattice vibrational region of mullite precursors type III, as-prepared and preheated at 800 and 900°C. The spectra are deconvoluted into six (V–X) single Gaussian-shaped bands. For band positions see Table 1.

essential amounts of non-crystalline phase must be present in the type III precursor. Starting with wavenumber values observed as maxima and shoulders in the spectra of the as-prepared precursors, the deconvolution of the absorptions reveals six fitted bands with halfwidths of about 150 cm^{-1}. The wavenumber position of the bands of the as-prepared samples signed with V, VI, VII, VIII, IX and X and of samples preheated at 900°C are summarised in Table 1. The spectra of the deconvoluted absorptions of the as-prepared precursors and the precursors preheated at 800 and 900°C are represented in Figs. 4 and 5. For the bands V and VI around 1110 and 1010 cm^{-1} a weak and continuous increase of the wavenumber with increasing preheating temperatures up to 800°C with an abrupt increase of the wavenumber at 900°C is evident from Fig. 6. For type I precursors, bands VII, VIII, and IX show a slight decrease of the wavenumber at preheating temperatures of 900°C (Table 1). The spectra of both precursor types are characterised by a strong increase of the intensity of the band VII around 860 cm^{-1} with increasing preheating temperatures up to 900°C. Apparently the bands VIII and IX around 705 and 570 cm^{-1} are decreasing in intensity with increasing temperature.

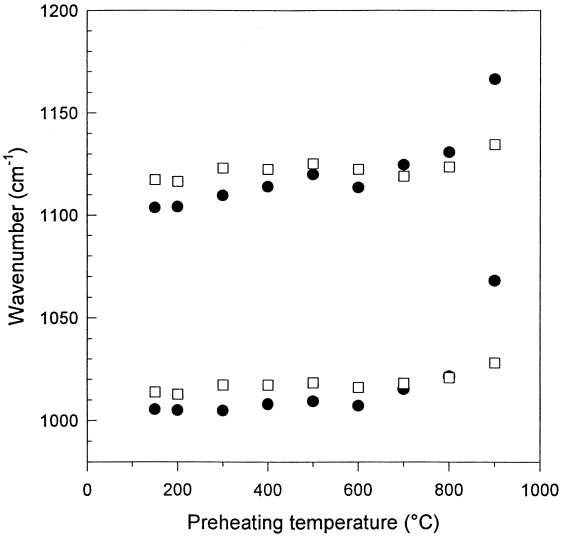

Fig. 6. Diagram relating the preheating temperature and the wavenumber position for Si–O stretching bands of mullite precursors type I (symbol: full circle) and type III (symbol: open square).

4. Discussion

In type I precursors, preheated up to 600°C the OH/H_2O ratio increases continuously with increasing preheating temperature. Above 600°C molecular H_2O is the dominating component of type I precursors, indicating a recombination of OH groups to H_2O molecules. The formation of H_2O molecules represents an initial stage to the complete dehydration of the type I precursor phases. It has been proposed,[6] that some of this "recombination-produced" H_2O is trapped in newly formed closed micropores, leading to an increase of the vapour pressure. Above 800°C opening of micropores due to microfracturing does occur, and as a consequence, H_2O evaporates. This is in contrast to the dehydration behaviour of type III precursors which show a slight and continuous increase of the OH/H_2O ratio up to only about 400°C, followed by a nearly constant to slightly decreasing OH/H_2O ratio. However, also at 1000°C, type III compositions contain essential amounts of structural OH groups and H_2O molecules.

On the basis of a diagram relating OH stretching band positions and O–H...O distances,[10] bridging and non-bridging H_2O molecules and OH groups are discernable in both mullite precursor types. The deconvolution of the broad and strong absorption in the (H_2O,OH) stretching vibrational region reveals four bands attributed to two types of H_2O and two types of OH. The high-energy OH band position I and H_2O band positions II require practically no hydrogen bonding, whereas the OH band position III and the H_2O band position IV require strong hydrogen bonding with O–H...O distances of about 2.7 and 2.65 Å, respectively. A similar scheme of H_2O and OH bridging is also described in glasses.[11] The (H_2O,OH) spectra of the precursors, preheated at high temperatures, are dominated by the band II around 3435 cm^{-1} assigned to the stretching vibration of non-hydrogen bonded H_2O. At preheating temperatures of 900°C, non-hydrogen bonded H_2O and OH are the stable forms of water present in type I precursors. Type III precursors contain essentially higher amounts of non-hydrogen bonded H_2O and OH in addition to strongly hydrogen bonded OH also present at preheating temperatures above 900°C.

Type I and III mullite precursors up to 800°C display very similar vibrations in the 1400–400 cm^{-1} region (Figs. 4 and 5). This should be interpreted in terms of similar Al–O–Si structural arrangements in both types of precursors. This is of interest, taking into account the different transformation behaviour of both precursors. The bands in the 1400–400 cm^{-1} vibrational region centered around 1110 (band V) and 1010 cm^{-1} (VI) are assigned to Si–O stretching vibrations of the SiO_4 tetrahedral units. These two bands are strongly shifted in 900°C treated type I precursors to higher wavenumbers (Fig. 6). The position of these two bands is close to the position of the Si–O stretching bands in mullite at around 1170, 1130 and 990 cm^{-1}.[9] Though there is clear XRD evidence that the 900°C treated type I material is still completely X-ray amorphous, this band shift is a strong indication for an increasing degree of network condensation and for changes in the Si–O distances in the 900°C treated precursor to SiO_4 tetrahedra dimensions similar to those occurring in mullite, characterised by one short T(Si,Al)–O distance of about 1.667 Å.[12] In type III precursors no striking changes in the band positions are observable up to 900°C. A slight shift to higher wavenumbers is evident in samples preheated to 1000°C. Band X centered around 445 cm^{-1} is assigned to O–Si–O bending modes of the tetrahedral units. The significant absorption centered around 860 cm^{-1} (band VII) is assigned to Al–O stretching modes of tetrahedral AlO_4 units. The increasing intensity of this band in both precursor types with increasing preheating temperature indicates a strong increase of AlO_4 tetrahedra present as structural units in precursors preheated at higher temperatures. The band IX around 570 cm^{-1} is assigned to Al-O stretching vibrations of AlO_6 octahedral units. The slightly decreasing intensity of this band with increasing preheating temperatures, along with the strongly increasing intensity of the 860 cm^{-1} band (VII) demonstrates a clear preference of Al for a four-fold coordinated structural position in the precursors preheated at high temperatures. The strong band VIII located at 705 cm^{-1} is primarily assigned to the (Si,Al)–O–(Si,Al) bending modes of the tetrahedral network. This assignment is in agreement with the proposed T–O–T bending mode for the band at 737 cm^{-1} in mullite.[9] Under this assumption, the low wavenumber would be indicative for relatively low (Si,Al)–O–(Si,Al) angles within the tetrahedral network. It is highly probable that this band is overlapped by Al–OH bending modes also occurring in this energy region. This interpretation explains the relatively weak intensity of band VIII in the 900°C treated type I precursor with its very low water content, compared to the relatively strong intensity of this band in the equivalent type III precursor with its essentially higher water content. There is no structural reason for the different (OH, H_2O) content in type III precursors. Probably the microstructure and related different surface properties have a controlling influence.

It can be concluded that in the low-temperature state of the heat treated precursors, AlO_6 octahedra are the dominating structural units and that with increasing temperature AlO_4 tetrahedra become more dominant. This process is correlated to the dehydration process occurring in the medium- to high-temperature field of network condensation starting at around 400°C and indicates an inhibiting role of H_2O and OH for the formation of AlO_4 units. The preferred occurrence of AlO_6 octahedra in low-, and AlO_4 tetrahedra in high-temperature treated precursors is supported by results of NMR investigations.[13,14] The corresponding Al–O stretching vibrations in mullite are centered at 909 and 828 cm^{-1} for AlO_4 tetrahedral units and at 578 cm^{-1} for AlO_6 octahedral units.[9] The band assigned to the AlO_6 octahedra is a striking feature of the mullite spectrum. Apparently the crystallisation of mullite is related to newly formed AlO_6 octahedra, whereas SiO_4 and AlO_4 tetrahedra are available structural units. Detailed FTIR and ^{27}Al NMR study in short temperature steps, starting e.g. at 800°C, may provide more information to clarify whether there exists a more-step ordering process prior to mullite crystallisation. It is evident that structural changes in type I precursors occur at significantly lower temperatures as in type III precursors. This different behaviour is essentially determined by the strong retainment of H_2O and OH in type III precursors in the 400–700°C temperature range.

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