Synthesis and photoluminescence properties of nanostructured mullite/ α - Al_2O_3

O. Khatim^a, T.H.N. Nguyen^a, M. Amamra^a, L. Museur^b, A. Khodan^c, A. Kanaev^{a,*}

^a Laboratoire des Sciences des Procédés et des Matériaux, CNRS, Université Paris 13, Sorbonne Paris Cité, 93430 Villetaneuse, France

^b Laboratoire de Physique des Lasers, CNRS UMR 7538, Institut Galilée, Université Paris 13, 93430 Villetaneuse, France

^c A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, 31, Leninski Prospect, 119991 Moscow, Russia

Received 17 December 2013; received in revised form 1 March 2014; accepted 2 March 2014

Available online 31 March 2014

Abstract

Phase transformation of α - Al_2O_3 to mullite was observed by correlated X-ray diffraction and low-temperature (7 K) time- and energy-resolved photoluminescence methods. The aluminosilicate solids with different Si:Al ratios were prepared after thermal treatment (1400 °C) of ultraporous alumina (UPA) monoliths impregnated with vapour of silica precursors at room temperature. The initial dispersion of Si is homogeneous on a size-scale of 5 nm raw UPA fibres, which grow in size during the thermal treatment stage up to ~50–100 nm. Three phases were resolved in the considered $\text{SiO}_2/\text{Al}_2\text{O}_3$ system: silica, α - Al_2O_3 and their interaction product 2:1 mullite ($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$). The 2:1 mullite mass increases and α - Al_2O_3 mass decreases with an increase of the initial silica content. At the SiO_2 content in the initial system above 20 mol.%, the phase transformation to 2:1 mullite is complete and no α - Al_2O_3 was observed. No mullite phases with either lower or higher Si content were observed. The fundamental absorption onset energy 7.55 eV of 2:1 mullite was measured. © 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Nanostructured materials; Alumina (α - Al_2O_3); Mullite; Phase transition; Luminescence

1. Introduction

Mullite is an important ceramic material of great technological interest. It is used as a refractory material providing high-temperature strength, thermal shock resistance, excellent thermal stability, chemical resistance, resistance to abrasion and good electrical resistivity [1,2]. The observed mullites are stable alumina–silica oxygen-deficient compounds with stoichiometry ranging from a silica-rich 3:2 ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) to an alumina-rich 2:1 ($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) phase, the general formula of which can be presented as $\text{Al}_{(4+14x)/3}[\text{Al}_{8/3}\text{Si}_2]_{1-x}\text{O}_{10-x}\otimes_x$ with $\otimes$ representing an oxygen vacancy [3]. Consequently, the mullite stability domain generally spans over 20–30 mol.% Si.

Most often, mullite forms composites associated with α alumina. Its stability is suggested to depend on the presence of α -phase Al_2O_3 and an appropriate phase diagram has to consider the experimental conditions and method of synthesis. In particular, the formation mechanism and kinetics depend on the spatial scale (molecular, nano, micro), at which the precursor silica and alumina components are mixed. Studies of the material behaviour in nonequilibrium conditions and those directed to achieve phase-pure mullite monoliths are in progress. In this context, experimental and theoretical data about formation kinetics in relation to electronic properties of mullites are of real interest.

At the same time, studies of the electronic band structure of mullites are rare. A theoretical study of the electronic structure and spectroscopic properties of selected aluminosilicate polymorphs andalusite, sillimanite and kyanite was performed using a density functional theory

* Corresponding author.

E-mail address: andreikanaev@lspm.cnrs.fr (A. Kanaev).

(DFT)-based orthogonalized linear combination of atomic orbitals (OLCAO) method [4]. It has been shown that these direct band gap solids have interband energies of, respectively, 5.05, 5.21 and 5.80 eV. Mullites with partially occupied sites make theoretical calculation a formidable task. Aryal et al. [5,6] have recently presented a detailed theoretical investigation of the structural and electronic properties of different mullite phases $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $4\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $9\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, corresponding to $x = 0.25$, 0.40, 0.67 and 0.842, respectively. The results presented for the mullite phases and two end members, sillimanite ($x = 0$) and Al_2O_3 ($x = 1$), have indicated the direct band gap solids at the Brillouin zone centre Γ with the band gap energy decreasing from 5.19 eV ($x = 0$) to 3.00 eV ($x = 1$) with the increase of alumina content (x). Moreover, this decrease is almost linear in the range of $0 \leq x \leq 0.67$ with band gap energies of 4.4 and 3.95 eV, respectively, for the most studied 3:2 and 2:1 mullites. This behaviour is explained by the conduction band (CB) bottom variations due to the presence of oxygen vacancies and distortions in the Al/Si tetrahedra. Although the calculated band gap energies by this method are generally underestimated, the obtained trend is expected to reflect the reality.

To our knowledge, there is almost no experimental information concerning the electronic band structure or energies of mullite phases available so far that permit the comparison. The only band gap energy 7.7 ± 0.2 eV of 2:1 mullite single crystal has been reported by Büchner and Guse [7] in the 1970s based on electron energy loss measurements and Kramers–Kronig analysis of dielectric tensor components. These results have shown a distinct anisotropic electronic structure of the mullite.

In the present communication we report on the synthesis of mullite from monolithic nanostructured hydrated amorphous alumina and analysis of structural and low-temperature time- and energy-resolved photoluminescence properties of the obtained mixed mullite/ α -alumina solids. The solids with different Si:Al ratios were prepared after thermal treatment of ultraporous alumina (UPA) monoliths impregnated with vapour of silica precursors. We observe the α - Al_2O_3 to mullite transformation based on correlated X-ray diffraction (XRD) and photoluminescence analyses.

2. Experiment

Various precursors (mixtures of solids, sols and salt) and preparation methods (sintering of mechanically mixed powders, hydrothermal treatment and chemical vapour deposition) can be used to synthesise mullite ceramics. In the present work, we have used ultraporous alumina treated with trimethylethoxysilane (TMES: $(\text{CH}_3)_3\text{Si}-\text{C}_2\text{H}_5\text{O}$) or tetraethoxysilane (TEOS: $\text{Si}(\text{OC}_2\text{H}_5)_4$) vapour at room temperature followed by thermal treatment at 1400 °C. The TMES molecule, because of one –OH terminal group, permits the monolayer coverage of UPA fibres up to the

elemental ratio Si:Al ≈ 0.05 , while the TEOS molecule possessing two oppositely positioned –OH groups permits the multilayer UPA fibres coverage and the attainment of a considerably larger elemental Si:Al ratio.

2.1. Material preparation

The raw UPA samples were grown at room temperature, in humid atmosphere, by oxidation of laminated aluminium plates through a liquid mercury–silver layer [8,9]. The growth rate of these UPA monoliths is $\sim 1 \text{ cm h}^{-1}$. The obtained samples have a high porosity of $\sim 99\%$ and a specific surface area of $\sim 300 \text{ m}^2 \text{ g}^{-1}$. The product is a hydrated amorphous alumina containing 40–43 wt.% of water. The microstructure consists of tangled hydrated alumina fibers with a diameter of about 5 nm. The thermal treatment of raw UPA results in fibre growth accompanied by the specific area decrease. At the same time, the crystallization of γ , θ and α alumina takes place respectively at 870, 1100 and 1200 °C. The characteristic size of alumina fibres and specific area of these polymorphs constitute 7 nm and $150 \text{ m}^2 \text{ g}^{-1}$ (γ), 10 nm and $100 \text{ m}^2 \text{ g}^{-1}$ (θ) and 250 nm and $10 \text{ m}^2 \text{ g}^{-1}$ (α). The impregnation of Si species TMES and TEOS modify this phase behaviour and increase the transition temperatures. For example, TMES vapour impregnation until UPA structure saturation (which corresponds to the monolayer molecular coverage) brings $\sim 6 \text{ wt.}\%$ Si inside UPA in form of amorphous silica (after thermal treatment), which delays the α polymorph appearance until almost 1400 °C instead of 1200 °C without silica addition.

The temperature of the mullite appearance almost corresponds to that of α phase Al_2O_3 . In this work we exposed the raw UPA impregnated with different amounts of Si to 1400 °C for 18 h. After this treatment, α alumina and mullite are formed depending on the Si/Al molar ratio. A complementary series with different time of thermal treatment showed that the phase transformation almost terminates after 8 h and no further modifications take place after this time.

2.2. Material characterization

The nanoscale morphology of the prepared samples was characterized by high-resolution transmission electron microscopy (HRTEM) using a JEOL2011 operated at 200 keV with a LaB_6 emission source of electrons. Element maps (Ti) of the samples were obtained using energy filtered transmission electron microscopy (EFTEM) with a Gatan Imaging Filter 2000 system connected to the microscope. The energy and spatial resolutions of the system were, respectively, 1 eV and 1 nm.

The elemental analysis has been performed using a Leica S440 scanning electron microscope equipped with Bruker systems for energy-dispersive X-ray spectroscopy (EDS). The accelerating voltage for electrons was fixed at 15 kV and the beam current at 2 nA. The analysis method used

is a semi-quantitative one. The error of measurements is $\sim 1\%$.

The structural characterization of samples was performed by the XRD method on an INEL XRG 3000 installation using a Cu K_α ($\lambda = 1.5418 \text{ \AA}$) radiation source.

The luminescence properties of the samples were studied using the VUV synchrotron radiation (SR) source of the DORIS storage ring at HASYLAB (DESY, Hamburg). The facility of the SUPERLUMI station used in the experiments is described in detail elsewhere [10]. Briefly, samples were cooled down to 8 K and irradiated by monochromatized SR ($\Delta\lambda = 3.3 \text{ \AA}$) under high vacuum ($\sim 10^{-9}$ mbar). The measurements of luminescence spectra were carried out using a visible 0.275 m ARC Spectra Pro-300i monochromator equipped with a CCD detector cooled with liquid nitrogen or an R6358P photomultiplier (Hamamatsu) operating in the photon-counting mode. The pulse structure of SR (130 ps, 10 MHz repetition rate) enables time-resolved luminescence analysis at a time scale of 100 ns with sub-nanosecond temporal resolution. Spectra were recorded within a time gate $\Delta\tau$ delayed after the SR excitation pulse. Typically two time gates were used simultaneously: a fast one of $\Delta\tau_1 = 1\text{--}4$ ns and a slow one of $\Delta\tau_2 = 25\text{--}100$ ns. Complementary luminescence decay curves were measured at fixed excitation and luminescence photon energies. The recorded excitation spectra were corrected for the primary monochromator reflectivity (using sodium salicylate phosphor) and SR current.

3. Results and discussion

The elemental kinetics of Si impregnation into raw UPA matrices by using TEOS vapour at room temperature is shown in Fig. 1. Interestingly, the deposition process is saturated at Si/Al = 25 mol.%, while the grafted TEOS molecule has free hydroxyl groups available for further condensation of a new molecular layer. The process saturation cannot be explained by filling of the available pore

volume, since 99% void space of UPA is capable of receiving a much larger TEOS mass. The saturation may be due to the condensation reaction between two hydroxyls of grafted TEOS molecules, which terminates the deposition process.

In the general case, the filling of surface sites can be represented by the expression

$$N = \sum_{i=0,1,2,\dots} A_i e^{-t/\tau_i} \quad (1)$$

where A_i and τ_i are number densities and deposition time constants of the i th site. Since the fit of the experimental points by Eq. (1) with $i = 1$ was not satisfactory, we concluded that at least two different sites receive the TEOS molecules. The fits of the experimental data with $i = 2$ is presented in Fig. 1 by a solid line. It shows that the short-lived exponents with $t < 1$ h (not resolved) accounts for Si/Al $\approx 5\%$ and the dominant long-lived exponent has a characteristic deposition time of $\tau \approx 13$ h. We tentatively attribute the fast component to the TEOS condensation with surface hydroxyls of raw UPA and the slow one to the condensation between grafted and free TEOS molecules. In support of this assignment, we have carried out the deposition process of a TMES molecule possessing one terminal hydroxyl and capable of forming a monolayer coating; the measured Si content at this process saturation resulted in Si/Al = 5 mol.%, which is in agreement with that of the fast TEOS component.

The thermal treatment at 1400°C of UPA impregnated with TEOS until a deep saturation (25 mol.% Si according to Fig. 1 results in pure mullite phase, the XRD pattern of which is shown in Fig. 2a. At the same time in the absence of Si impregnation, pure α -phase alumina has been observed after the thermal treatment, the XRD pattern of which is shown in Fig. 2b. The TEM image of mullite crystals is shown in Fig. 3. Their characteristics size is ~ 100 nm, which is smaller than that of α alumina obtained in similar experimental conditions.

The temperature of the mullite appearance corresponds to that of α phase Al_2O_3 and the transformed mullite content is expected to depend on Si loading. In order to investigate this effect, we have performed a series of XRD measurements of samples prepared with different Si content. The relative intensities of the mullite (120 and 210) and α - Al_2O_3 (012) peaks were analysed. As Fig. 4 shows, the mullite peak intensity increases sharply when the Si content increases above 12.5 mol.%. The main conclusion is that both α - Al_2O_3 and mullite phases coexist at the Si content below 20 mol.%. Above this point, the material is of the pure mullite phase. We tentatively assign the synthesized mullite to the alumina-rich 2:1 ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) phase.

The luminescence spectra of UPA impregnated with TMES until 5 mol.% Si and thermally treated at 1400°C for 18 h are shown in Fig. 5a. Although little mullite is formed in these conditions, these spectra serve to be a reference point for the mullite formation series. The observed ultraviolet UV–visible band at 300 nm has been previously assigned to partially compensated anion vacancies, F^+

Fig. 1. Si content in ultraporous Al_2O_3 as a function of the impregnation time of TEOS vapour (20°C).

Fig. 2. XRD patterns ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$) of crystallographic phases mullite (a) and α (b) obtained after thermal treatment (1400 °C/18 h) of ultraporous Al_2O_3 with Si content of 25 mol.% (a) and 0% (b).

Fig. 3. TEM image of mullite crystals obtained after TEOS vapour (20 °C) impregnation of UPA for 168 h and subsequent thermal treatment at 1400 °C for 18 h.

centers, while the visible emission band at 450 nm has been assigned in nanosized alumina to the F centre formed by oxygen vacancies trapping one (F^+) and two (F) electrons, respectively [11]. Moreover, self-trapped excitons produced indirectly, e.g. by the recombination of free and trapped charges, contribute to the UV emission. Besides the UV–visible bands shown in Fig. 5a, a VUV band at 170 nm appears in the luminescence spectra, which belongs to self-trapped excitons in $\alpha\text{-Al}_2\text{O}_3$ [12]. The luminescence excitation spectra of the VUV, UV and visible emission bands are shown in Fig. 5b. The first two clearly show a signature of the interband transitions in the energy range

above the fundamental absorption onset at 132.47 nm ($E_g = 9.36 \text{ eV}$), which is in agreement with literature data [12]. In contrast, the visible band excitation does not show up the interband transitions and is related to the defect structure of the material.

We remark that the VUV band (170 nm) strongly weakens compared to pure UPA(α), while the UV (300 nm) intensifies. The intensified component of the UV band has long decay time ($\geq 1 \mu\text{s}$). At the same time, the short-lived (nanosecond) component of the UV band weakens. In agreement with Ref. [11] and our recent analysis of pure UPA samples [13], this short-lived component can be

Fig. 4. Evolution of 012 (α) and 120/210 (mullite) crystallographic peak intensities ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$) as a function of TEOS impregnation time: 1 h (a), 5 h (b), 7 h (c), 8 h (d), 14 h (e) and 168 h (f). Thermal treatment was conducted at 1400°C for 18 h.

Fig. 5. UV–visible luminescence spectra (a) and excitation spectra (b) of TMES-treated ultraporous Al_2O_3 . The excitations are dominated by slow luminescence decay, except for the sharp intense peak at 135.84 nm (lum. 170 nm) and a weak band at 192 nm (lum. 300 nm). *Denotes the second order of SR scattering (a).

assigned to F^+ centres. It contributes to the luminescence excitation spectra with several symmetry-split absorption bands between 4 and 6 eV [11].

Our measurements (Fig. 5) show only a weak contribution to the excitation of the long-lived UV band (peaking at 300 nm) below E_g , which permits assigning it to a self-trapped exciton. In contrast, at the excitation energy 6.20 eV (200 nm), another short-lived UV band appears with the maximum at 310 nm, which can be assigned to F^+ centres [13]. Moreover, one can suppose that the VUV (170 nm) band belongs to excitons localized in the surface layer, since it is affected by the deposited silica. The VUV band weakening can be related to the preferential localization of excitons on bulk defects, the emission of which is at 300 nm.

The luminescence spectra of the UPA impregnated with TEOS permitted higher Si loadings are shown in Fig. 6. In these conditions, both $\alpha\text{-Al}_2\text{O}_3$ and mullite coexist. At excitation above the fundamental absorption onset of $\alpha\text{-Al}_2\text{O}_3$, the VUV band (170 nm) disappears, while the UV (300 nm) weakens progressively with Si addition. This emission disappears at the critical Si concentration $C_{\text{Si}}^* \geq 16 \text{ mol.}\%$. In agreement with our XRD analysis, we relate this effect to the complete transformation of $\alpha\text{-Al}_2\text{O}_3$ to mullite. The inspection of the near-infrared (IR) spectral range shows another emission, which appears non-regularly in our UPA solids. This near-IR luminescence also strongly intensifies after TMES impregnation, which suggests a similar mechanism to that leading to the UV band intensification. Accordingly, this luminescence comes from bulk sites, which are preferentially excited after silica deposition on the UPA surface. With more addition of Si (after TEOS impregnation) the near-IR band weakens; however, it does

Fig. 6. UV-visible luminescence spectra ($\lambda_{\text{exc}} = 130$ nm) of TEOS-treated ultraporous Al_2O_3 during 1 h (a), 3 h (b), 5 h (c), 8 h (d) and 14 h (e). Thermal treatment was conducted at 1400 °C for 18 h.

not disappear like the UV one. Moreover, its band shape modifies during Si impregnation for 8 h (see Fig. 6c and d).

Optical properties of oxide solids are influenced by metal ions, which can appear in quantities below 0.1 wt.%. Ions with an incomplete 3d shell (Ti^{3+} , Cr^{3+} , V^{3+} , Mn^{4+} , Fe^{3+} , Ni^{3+}) substitute for Al^{3+} ions in the $\alpha\text{-Al}_2\text{O}_3$ lattice, providing a strong absorption between 6 and 7 eV [14]. Because of a high sensitivity, the luminescence method is capable of observing traces of metal ions [15,16].

The main impurities of our crystalline alumina are Si, S, K, Na, Fe, P and Ca, which together amount to $\sim 10^{-3}$ wt.%; the contamination by other impurities is below 10^{-4} wt.% [17]. In particular, Cr is present at a very low level of below 10^{-5} wt.%. Despite this low content, fluorescence methods permit us to observe near-IR luminescence of Cr^{3+} ions at concentrations as low as 10^{-7} wt.% [18].

The transition-metal ions Cr^{3+} preferentially occupy substitutional sites of octahedrally coordinated Al^{3+} (which is a case of both $\alpha\text{-Al}_2\text{O}_3$ and mullite structures) and their luminescence spectra in this configuration depend on local crystalline field strength. The radiative transitions originated from the same $^4\text{A}_2$ excited state terminate on the energetically lowest $^4\text{T}_2$ or ^2E states respectively in weak or strong field environments. The weak-field emission band due to the $^4\text{T}_2 \rightarrow ^4\text{A}_2$ transition typically centres between 700 and 800 nm, with a half-width-full maximum at

~ 100 nm, while strong-field emission spectra show sharp R lines due to the $^2\text{E} \rightarrow ^4\text{A}_2$ transition [15,19]. The spectral position of these lines sensitively depends on the environment. In particular, when the Al_2O_3 crystalline structure changes the doublet exhibits a shift [18,20–22]. The lines vanish when the crystalline structure is damaged [22]. Their spectral position depends on Cr^{3+} concentration and red shifts with its increase [21].

Our recorded IR luminescence spectra of both $\alpha\text{-Al}_2\text{O}_3$ and mullite phases correspond to the strong-field environment of chromium ions. The high resolution spectra of UPA samples impregnated with TEOS during 1 and 8 h, which, according to Fig. 1, correspond to the Si content of 6 and 16 mol.%, are shown in Fig. 7. At the lower Si content, the near-IR luminescence consists of two narrow peaks at 691.9 and 693.3 nm (a), while at the higher content, these lines disappear and other lines appear at 682.6 and 686.0 nm (b). According to previous studies [20], these doublets can be assigned to zero-phonon lines (R lines) of $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$ transitions of Cr^{3+} in a strong crystal field.

The doublet lines at 691.9 (R2) and 693.3 nm (R1) (Fig. 7a) in samples with low Si content < 16 mol.% are in excellent agreements with Cr^{3+} transitions in $\alpha\text{-Al}_2\text{O}_3$ reported by Snytnikov et al. [18]. The appearance of mullite phase modifies the Cr^{3+} environment, which may result in a spectral shift of the doublet. Indeed, at a Si concentration above $C_{\text{Si}} = 16$ mol.%, the doublet undergoes a blue shift to 682.6 and 686.0 nm, which corresponds to a $\theta\text{-Al}_2\text{O}_3$ environment [18]. It is known that silica treatment shifts the nucleation of $\alpha\text{-Al}_2\text{O}_3$ to temperatures considerably higher than 1250 °C, necessary for α phase appearance in pure UPA [9]. Indeed, we have found pure θ polymorph after the thermal treatment of TMES-treated UPA at 1400 °C during a relatively short time of 4 h. It can therefore be assumed that inclusions of θ phase exist in mullite in small quantities, which cannot be observed by XRD. At the same time, it seems unlikely that the Cr^{3+} emission originates from traces of θ phase rather than from still significantly present (~ 10 wt.%) α phase. More probable, the new lines position is explained by the mullite environment. The larger width of the shifted lines indicates a more disordered mullite structure compared to α alumina.

Earlier, the Cr^{3+} doublet at 694.3.0 and 692.7 nm was observed in luminescence of Si containing sillimanite Al_2SiO_5 phase and assumed to be connected to the micro-impurities of $\alpha\text{-Al}_2\text{O}_3$ [15]. In our work the doublet is observed at a different spectral position closer to that characteristic of the $\theta\text{-Al}_2\text{O}_3$ environment. Since α phase is strongly present in our Si-containing samples, the difference between the results of Ref. [15] and those of the present study can be rather attributed to different environments, which are respectively sillimanite and 2:1 mullite.

Because of a very low Cr^{3+} concentration in UPA samples, their direct excitation is of low efficiency. At the same time, the energy transfer from the host matrix to impurity centres is expected to be very efficient. This explains the

Fig. 7. High-resolution near-IR luminescence spectra of TEOS-treated ultraporous Al_2O_3 for 1 h (a) and 8 h (b). Thermal treatment was conducted at 1400 °C for 18 h.

relatively easy recording of the Cr^{3+} ions luminescence at the interband host matrix excitation in our experiments. In order to gain more information about the bandgap modification during $\alpha\text{-Al}_2\text{O}_3$ to mullite transformation, we have performed measurements of the excitation spectra

of Cr^{3+} near-IR luminescence at different Si content. The results are presented in Fig. 8.

The luminescence excitation spectra of $\alpha\text{-Al}_2\text{O}_3$ are dominated by the interband electronic transitions situated at $h\nu \geq E_g = 9.36$ eV (132.47 nm). Additionally, an excitation band appears at 7 eV (180 nm) with $\Delta_{\text{FWHM}} = 0.7$ eV, previously assigned to the electronic transition from $t_{1u}(\pi)/t_{2u}(\pi)$ nonbonding O-ligand orbitals to the $t_{2g}(\pi^*)/e_g(\sigma^*)$ antibonding orbital, localized on the Cr^{3+} ion [23]. When Si content in alumina increases, another continuum grows up at energies above 7.55 eV. At the same time, the $\alpha\text{-Al}_2\text{O}_3$ transitions weaken until a complete disappearance at Si concentrations above 20 mol.%, which corresponds to alumina-rich 2:1 mullite. In general, a luminescence excitation spectrum is a convolution of the absorption spectrum and spectral dependence of an energy transfer to the emitting state. The new excitation continuum in Fig. 8 reflects therefore (like that in pure $\alpha\text{-Al}_2\text{O}_3$) the fundamental absorption of a new material. Since the last point corresponds to pure mullite phase, we attribute the absorption onset at $E_g = 7.55$ eV to the bandgap energy of mullite phase. The obtained value is in good agreement with 7.7 ± 0.2 eV earlier reported by Büchner and Guse [7] for 2:1 mullite single crystal based on electron energy loss measurements and Kramers–Kronig analysis of dielectric tensor components.

The quantitative analysis of the mullite ratio can be obtained from both XRD and luminescence spectroscopy data. The first needs a normalization factor based on the knowledge of XRD peak sensitivities. The mullite molar ratios of the prepared samples were calculated from the XRD intensity data according to the equation:

$$F_m^{\text{XRD}} = \frac{I_{m120} + I_{m210}}{mI_{m120} + I_{m210} + 2.7 \cdot I_{\alpha 012}}$$

where I 's denote the respective mullite and α peaks areas. The normalization factor was estimated from the peak

Fig. 8. Excitation spectra of 690 nm luminescence of TEOS-treated ultraporous Al_2O_3 for 1 h (a), 3 h (b), 5 h (c) and 25 h (d). Thermal treatment was conducted at 1400 °C for 18 h.

Fig. 9. Mullite content onto ultraporous Al_2O_3 as a function of Si content derived from XRD (■) and luminescence analysis (▲).

areas of pure mullite and α phases. The mullite ratio obtained from luminescence excitation spectra was calculated from relative intensities (I) of the excitation bands of mullite and $\alpha\text{-Al}_2\text{O}_3$:

$$F_m^{\text{spec}} = \frac{I_m}{I_m + I_{\alpha\text{-Al}_2\text{O}_3}}$$

The mullite ratios extracted from XRD and luminescence experiments are shown in Fig. 9 vs. Si content in UPA samples.

An excellent agreement between the data extracted from XRD (F_m^{XRD}) and spectroscopy (F_m^{spec}) measurements can be seen for a Si content above 9 mol.%. Below this value, the XRD analysis indicates a small presence of mullite while spectroscopic data correspond to the pure α alumina. The origin of this disagreement is not yet clear. The experimental results indicate the mullite phase appearance at a Si content of 10 mol.% and the complete transformation to mullite in samples with more than 20 mol.% Si. This last Si content corresponds to the 2:1 mullite composition, which permits us to draw conclusions about the alumina-rich 2:1 ($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) phase formation. The Si content variation from 10 to 20 mol.% is accompanied by the intensification of both XRD lines of 2:1 mullite and absorption above 7.55 eV. Neither the XRD lines position nor the absorption threshold is changed. All these findings indicate that the phase transition from $\alpha\text{-Al}_2\text{O}_3$ to 2:1 mullite does not involve the total sample volume but propagates into the bulk with a phase-transformation reaction front. Accordingly, three phases can coexist in the considered $\text{SiO}_2/\text{Al}_2\text{O}_3$ system: $\alpha\text{-Al}_2\text{O}_3$, silica and their interaction product 2:1 mullite. The lowest Si content when the mullite appears may correspond to the thermodynamic equilibrium between surface mullite and bulk α alumina phases.

4. Conclusions

We have studied the transformation of $\alpha\text{-Al}_2\text{O}_3$ into mullite by correlated XRD and low-temperature (7 K) time- and energy-resolved photoluminescence methods.

The aluminosilicate solids with different Si:Al ratios were prepared after thermal treatment (1400 °C/18 h) of ultra-porous alumina monoliths impregnated with vapour of silica precursors TMES or TEOS at room temperature. The materials show up the near-IR luminescence of Cr^{3+} ions, the concentration of which in the material is below 10^{-5} wt.%. The zero-phonon doublet at 691.9 (R2) and 693.3 nm (R1) corresponds to ${}^2\text{E}_g\text{-}{}^4\text{A}_{2g}$ transitions of octahedrally coordinated Cr^{3+} ions in a strong crystal field of α alumina. This doublet spectral position shifts at the critical Si concentration $C_{\text{Si}} \geq 16$ mol.%, when mullite phase approaches saturation. The mullite ratio increases with Si content between 10 and 20 mol.%. The total $\alpha\text{-Al}_2\text{O}_3$ conversion above 20 mol.% of Si corresponds to 2:1 mullite ($2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$). We suggest that mullite and $\alpha\text{-Al}_2\text{O}_3$ domains coexist, while the mullite phase propagates into the material bulk at the silica addition. The fundamental absorption onset energy 7.55 eV of 2:1 mullite has been measured from the excitation spectra of Cr^{3+} near-IR luminescence. The XRD and luminescence measurements do not indicate the formation of other mullite polymorphs with either lower or higher Si content.

Acknowledgements

This work has been supported by the IHP-Contract CALIPSO 312284 (project DESY-I-20110047 EC) of the European Commission. ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l'Investissement d'Avenir) are gratefully acknowledged for their financial support of this work through Labex SEAM (Science and Engineering for Advanced Materials and devices) ANR 11 LABX 086, ANR 11 IDEX 05 02.

References

- [1] Aksay IA, Dabbs DM, Sarikaya M. *J Am Ceram Soc* 1991;74:2343.
- [2] Schneider H, Komarneni S. *Mullite*. Weinheim: Wiley; 2005.
- [3] Duval DJ, Risbud SH, Shackelford JF. *Mullite*. In: Shackelford JF, Doremus RH, editors. *Ceramic and glass materials: structure, properties and processing*. Berlin: Springer Verlag; 2008.
- [4] Aryal S, Rulis P, Ching W-Y. *Am Mineral* 2008;93:114.
- [5] Aryal S, Rulis P, Ching W-Y. *J Am Ceram Soc* 2012;95:2075.
- [6] Aryal SR. PhD thesis, University of Missouri-Kansas City; 2012.
- [7] Büchner U, Guse W. *Phys Status Solidi (b)* 1977;80:615.
- [8] Vignes J-L, Frappart C, di Costanzo T, Rouchaud J-C, Mazerolles L, Michel D. *J Mater Sci* 2008;43:1234.
- [9] di Costanzo T, Fomkin AA, Frappart C, Khodan AN, Kuznetsov DG, Mazerolles L, et al. *Mater Sci Forum* 2004;453–454:315.
- [10] Zimmerer G. *Nucl Instrum Methods Phys Res A* 1991;308:178.
- [11] Valbis J, Itoh N. *Rad Effects Defects Solids* 1991;116:171.
- [12] Kirm M, Zimmerer G, Feldbach E, Lushchik A, Lushchik Ch, Savikhin F. *Phys Rev B* 1999;60:502.
- [13] Museur L, Bouslama M, Amamra M, Kanaev A. *Phys Status Solidi RRL* 2013;7:1026.
- [14] Tippins HH. *Phys Rev B: Condens Matter* 1970;1:126.
- [15] Gaft M, Strek W, Nagli L, Panczer G, Rossman GR, Marciniak L. *J Lumin* 2012;132:2855.
- [16] Trinkler L, Berzina B, Jakimovica D, Grabis J, Steins I. *Opt Mater* 2011;33:817.

- [17] Scherban AP, Virich VD, Solopichin AD, Kovtun GP, Nguyen HN, Amamra M, et al. In: Proc EMRS 2014 spring conference, 26–30 May, Lille.
- [18] Snytnikov VN, Stoyanovskii VO, Ushakov VA, Parmon VN. *Kinet Catal* 2005;46:260.
- [19] Wojtowicz AJ, Lempicki A. *Phys Rev B* 1989;39:8695.
- [20] Wen Q, Lipkin DM, Clarke DR. *J Am Ceram Soc* 1998;81:3345.
- [21] Patra A, Tallman RE, Weinstein BA. *Opt Mater* 2005;27:1396.
- [22] Pan C, Chen S-Y, Shen P. *J Cryst Growth* 2008;310:699.
- [23] Tippins HH. *Phys Rev B* 1970;1:126.