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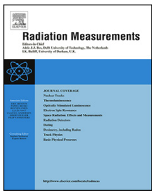

Luminescence study of alumina nanopowders prepared by various methods

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HIGHLIGHTS

- Combustion synthesized alumina is compared with phase pure one using luminescence.
- Excitonic excitation peak at 9.1 eV is shifted towards higher energies in nanopowders.
- Time resolved luminescence was used to identify nature of emission centres.

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ABSTRACT

Mixed nanopowders of transition alumina prepared by combustion synthesis and phase pure ultraporous α-alumina by oxidation method were investigated using low temperature time-resolved cathodoluminescence and photoluminescence spectroscopy under VUV-XUV excitation. In all samples along with the 7.6 eV emission of self-trapped excitons of α-alumina, luminescence bands due to F, F^+ centres with maxima at 3 and 3.8 eV and other UV–visible luminescence bands of intrinsic and extrinsic origin with varying intensity depending on sample preparation method and thermal treatment were studied. In alumina nanopowders the excitonic excitation peak at ~9.1 eV near fundamental absorption edge is shifted to the higher energies by 0.15 eV in comparison with the same feature in single crystals. The nanostructure of alumina is responsible for this shift.

1. Introduction

Aluminium oxide (Al_2O_3) is an important material for different optical and technological applications in the form of ceramics or single crystals, but there is a growing interest in nanostructured alumina, because of its large surface area being favourable for catalyst support and filtration. Significant research has been carried out on single crystals of α-Al_2O_3 using luminescence and other methods (see Kirm et al. (1999); Valbis and Itoh (1991) and references therein). Recently, various modification (incl. α-, θ-, γ-Al_2O_3) of phase pure ultra-porous alumina nanopowder (hereafter called as UPA) with the low impurity content was investigated using low temperature time-resolved luminescence spectroscopy (Museur et al., 2013).

Metastable aluminium oxide phases (e.g. δ-, θ-, κ- and γ-Al_2O_3) with the common name of transition alumina also exist in the nature. The latter phases have different crystal structure, electronic properties and have been significantly less studied, but such activities based on luminescence spectroscopy are rising (e.g. Kirm et al. (2010); Oja et al. (2013); Pustovarov et al. (2012); Trinkler et al. (2012)). Due to their thermochemical properties the preparation of pure phase samples is a real challenge and therefore metastable alumina samples typically contain multiple Al_2O_3-phases complicating identification of elementary processes in such mixtures. Depending on the preparation method often unintended impurities are introduced into alumina samples. In order to reduce influence of surface related effects (luminescence quenching etc.) the XUV and electron beam excitation is applied, methods which penetrate deeper into the samples prohibiting near-surface effects at fundamental absorption regime, which has to be considered in investigation of wide gap crystals (Lushchik et al., 1994). The main goal of this work is to enlighten electronic properties, relaxation of electronic excitations, identify phase and crystallite size specific features in luminescence of alumina samples prepared with different synthesis methods.

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2. Sample preparation, structural properties and experimental techniques

Nanostructured UPA was produced using oxidation of high purity aluminium (99.999%) through a liquid mercury and silver film, which leads to formation of highly porous (99%) macroscopic (cm dimensions), but nanostructured (tangled alumina fibres of 5 nm diameter) monoliths as described by Vignes et al. (2008). The further post-treatment at elevated temperatures (1200–1250 °C) results in nanostructured α-alumina with characteristic crystallite size of 200–300 nm as described in the paper by Museur et al. (2013). This method has advantage over combustion and solid state synthesis as amount of impurities is well controlled by using high purity aluminium and its impurity content is smaller in comparison with samples prepared by combustion synthesis.

Two samples were prepared using the combustion synthesis method analogous to Oja et al. (2013). The chemicals used in the synthesis of these samples were $Al(NO_3)_3 \cdot 9H_2O$ (for the ALO 1600 – Alfa Aesar, 99.999% and for the ALO 5050 – REAHIM, 99.99%) and urea (Alfa Aesar) as a fuel. Sample ALO 1600 was produced using stoichiometric mixture with fuel/nitrate molar ratio 5:2 whereas sample ALO 5050 was synthesised using fuel rich mixture which corresponds to a molar ratio of 25:4. According to Ianoş et al. (2009) fuel-rich synthesis gives lower combustion temperature and therefore different phase composition and higher specific surface area compared to stoichiometric synthesis. Burning out of residual carbon and phase composition adjustment is achieved by an annealing procedure resulting in an increase of crystallite size. Samples were annealed in air at 1600 °C for 5 h (ALO 1600) and at 1000 °C for 1 h (ALO 5050). After annealing procedure the sample ALO 1600 was white powder but sample ALO 5050 was still greyish powder indicating either presence of carbon or absorption of oxygen vacancies.

The phase composition and crystallite size of the samples were determined by powder X-ray diffraction (XRD) analysis and the obtained values are presented in Table 1. Sample ALO 5050 consists of several Al_2O_3 phases with different crystallite size, which is a general complication in studies of transition alumina whereas other studied samples were composed of α-Al_2O_3 phase. Analysis of the quantitative phase composition (using the Rietveld method, program FULLPROF) is not straight forward because of the overlap of XRD patterns from various phases are responsible for relatively large a few percent error bars on the obtained values. The γ-Al_2O_3 phase has only very broad diffraction lines referring to small crystallite size below 10 nm. Although there can be an a few nm error in absolute size, the crystallite size of α-Al_2O_3 is practically an order of magnitude larger (see Table 1). Crystallite size estimations were performed using the Scherrer equation.

Low temperature cathodoluminescence (CL) studies were performed in Tartu using a home-built setup equipped with VUV and UV–visible monochromators, pulsed electron gun (EGPS-3101, Kimball Physics) and multiscaler photon counter (MSA-300, Becker&Hickl GmbH) for accumulation of luminescence decay curves. It was possible to tune the energy of electrons (1–10 keV), pulse width of exciting electrons (δt) and interval between successive pulses (Δt). In the present study energy of 10 keV, δt = 100 ns and Δt = 200 μs were used.

Table 1
Phase composition of studied Al_2O_3 samples and estimated crystallite size based on the XRD analysis.

Sample name	Phase composition	Volume weighted crystallite size
Al_2O_3 1600	α-phase	α-phase ~180 nm
Al_2O_3 5050	α-phase (~40–50%) γ-phase (~50–60%)	α-phase ~80 nm γ-phase <10 nm
Al_2O_3 UPA	α -phase	α -phase ~200–300 nm

Time-resolved low temperature luminescence studies in VUV region up to 35 eV were carried out at the SUPERLUMI station (Zimmerer, 2007) and under XUV excitation (starting from 40 eV) at the beamline BW3 (Kirm et al., 2003) of HASYLAB at DESY (Hamburg, Germany). It is important to point out that emission spectra are not corrected to the transmission of detection system because of the extremely wide (1.5–8.5 eV) energy range used in studies. The shifts of the VUV luminescence peaks recorded at the CL-setup and at the BW3 are due to differences in the analysing channel (monochromator + detector). However, there are clearly sample specific features observable in the spectra (see Fig. 1).

3. Results and discussion

Fig. 1 demonstrates the time-integrated luminescence spectra recorded at 10 K and 78 K (LNT) at the BW3 (130 eV photons) and CL-setup (10 keV electrons), respectively. In both cases penetration depth (~50 nm for 130 eV photons and ~500 nm for 10 keV e-beam) is higher than near intrinsic absorption where corresponding penetration depth is 10 nm (absorption 10^{-6} cm^{-1}) in wide gap crystals. 130 eV photons are able to excite electrons from Al 2s (~118 eV) and 2p (~72 eV) core shells (see luminescence study by Kirm et al. (2003)). The self-trapped exciton (STE) emission at 7.6 eV is well pronounced for dominantly α-alumina containing samples (ALO 1600 and UPA) as expected. Ratio of UV/VUV emission intensities is in favour the former ones in ALO 5050 sample, where according to the XRD up to 50% of the sample contains small

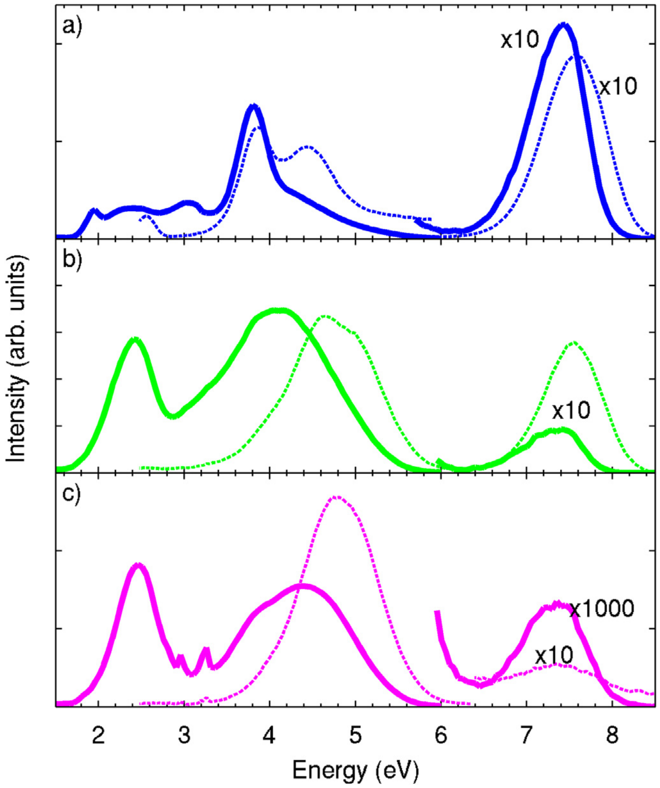

Fig. 1. TI emission spectra excited by 10 keV electrons (solid lines) at 78 K and 130 eV photons (dashed lines) at 10K. a) Blue – Al_2O_3 UPA; b) Green–Al_2O_3 1600; c) Magenta – Al_2O_3 5050. CL spectra were recorded with two monochromators. The range above 6 eV with the VUV instrument and below with the UV–visible spectrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)