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X-ray excited optical luminescence of metal oxide single crystals

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ABSTRACT

The X-ray excited optical luminescence response of sapphire (α -Al₂O₃), aluminium lanthanate (LaAlO₃), and magnesium oxide (MgO) were measured at room temperature as a function of incident photon energy in the range from 500 to 1000 eV. The luminescence yield varies weakly with energy above 600 eV and is dominated by the presence of the O K absorption edge in all cases and the La M_{2,3} edge for LaAlO₃. The emission spectra in the visible range measured at a fixed incidence X-ray photon energy of 1000 eV shows for LaAlO₃ a simple spectrum composed of two broad lines, a dominant sharp line for sapphire arising from Cr³⁺ impurities, and a complex spectrum for MgO, containing both broad and sharp spectral lines originating predominantly from impurities. SrTiO₃ and Nb-doped SrTiO₃ crystals were also measured and are found to have much smaller luminescence yields than the other materials investigated. Our results show that residual impurities that are inevitably present in high quality bulk crystals can be employed as colour centres for the detection of X-ray light in X-ray transmission spectroscopy.

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1. Introduction

The development of synchrotron light sources with tunable monochromatic X-ray beams has led to the establishment of new spectroscopic characterisation methods that have been instrumental to our understanding of the physical processes governing condensed matter at the nano and atomic scale. Magnetic X-ray absorption spectroscopy presents a striking example of the capabilities of synchrotron light to probe magnetism with element specificity, submonolayer sensitivity, sub-ns time resolution, and nanometre spatial resolution. These features are used in photoemission electron microscopy and scanning transmission X-ray microscopy (STXM) to image magnetic structures down to 15 nm resolution and to investigate magnetic dynamics down to the 100 ps regime [1–3].

We have recently proposed a development in STXM that uses the X-ray excited optical luminescence (XEOL) response of crystalline substrates as a method for measuring the X-ray transmission across thin films or buried layers deposited on a bulk crystal [4]. This method enables space- and energy-resolved electronic and magnetic spectroscopic characterisation of epitaxial and buried films, which often require a single crystalline template for growth. In this context, it is important to determine the XEOL yield of a wide number of single crystal substrates in order to determine their

suitability as integrated luminescence detectors for X-ray absorption measurements in scanning X-ray transmission microscopy.

Photoluminescence refers to the optical emission of photons upon excitation with an incoming photon [5]. In luminescence, electrons are excited from the valence to the conduction band, and the emission of light results from radiative transitions associated with electron-hole recombination. This process competes with non-radiative transitions, where the excess energy is transferred to the lattice via phonons or through Auger recombination processes [6]. Hence, the luminescence spectrum of a material depends strongly on the nature of the band gap (direct or indirect), the presence of charge traps (impurities, lattice defects, oxygen vacancies, or surface states), the density of excited carriers, the energy of the incident light, and temperature. Most optical luminescence studies are carried out using ultraviolet light to excite the system, although X-rays and electron beams (cathodeluminescence) are employed also. X-ray excited optical luminescence can be produced by direct excitation as well as by secondary processes, where high energy electrons, such as photoelectrons and Auger electrons, thermalise in the solid to produce additional secondary electrons and holes [5,7,8]. Besides its use for scintillation and fluorescence detectors for X-rays [9], XEOL has been explored as a technique to probe the X-ray absorption of materials as an alternative to the total electron yield or fluorescence detection [5,7,8,10–15], although the reliability of this method has been questioned on account of the complexity of the de-excitation process and the sensitivity of the luminescence spectra to extrinsic contributions, such as defects and impurities [7]. However, XEOL can be used as a valuable tool for

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X-ray detection when operating in energy ranges away from resonances, to guarantee linearity in the luminescence signal. In this work we study the X-ray induced luminescence of several widely used substrates employed for the growth of epitaxial films. We find that α -Al₂O₃ (sapphire), MgO, and LaAlO₃ have large luminescence yields in the visible light spectrum, with flat responses in the X-ray energy range from 600 to 1000 eV (where most *L* edges of the transition elements lie), except for LaAlO₃ due to the La M_{4,5} absorption lines at around 850 eV. The luminescence in MgO and sapphire are dominated by trace amounts of impurities present in the bulk crystal.

2. Experimental

The measurements reported here were carried out in the scanning X-ray transmission microscope installed at the PolLux beamline (Paul Scherrer Institut, Switzerland) [4,16]. The linearly polarised X-ray beam, set at normal incidence, is focused on the sample using a Fresnel zone plate (25 nm spot size), while the optical light transmitted through the sample is measured either with a CCD detector (Andor DV860DCS-BV) for the intensity versus incident X-ray energy scans, or using a visible light spectrometer (Ocean Optics USB2000 with a 600 lines/mm grating, 1.3 nm resolution at 500 nm) to determine the spectral response in the optical range (both detectors have a spectral response in the 340–1000 nm range). The luminescence data as a function of X-ray photon energy were taken as step-wise scans across a line on the sample (spanning 5–20 μ m) and the data presented here correspond to the line averages (varying between 20 and 40 scans). The incident X-ray beam intensity (of the order of 10⁷ photons/s) was subsequently measured with a Si photodetector and shows some reduction at the O K, Ti L₁ and Cr L_{2,3} absorption edges due to the adventitious presence of these elements in the X-ray optics [17]. The emission spectra were taken at a single spot on the sample; for each sample, measurements with and without the X-ray beam were recorded in order to remove the background and detector dark current contributions. All measurements reported here were carried out at room temperature. The probing depth of the X-rays varies between 0.2 and 1 μ m for the samples and energy range studied here (being shorter at lower energies) [18]. The samples consist of double side epi-polished single crystals of MgO(001), α -Al₂O₃(001), LaAlO₃(001), and 0.1 wt% Nb-doped and undoped SrTiO₃(001) (CrysTec GmbH) and were measured as received. The samples are 0.5 mm thick, hence they satisfy the condition for total X-ray absorption. Except for the conducting Nb-doped SrTiO₃, which presented a translucent dark greyish colour, all crystals were optically clear and transparent in appearance, while micrometric twins could be observed in the rhombohedral LaAlO₃ crystal. No changes in colouration are observed after exposure to the X-ray beam and no changes in the luminescence intensity are observed for consecutive measurements of the spectra, ruling out radiation damage in the samples or changes in colour centres.

3. Results and discussion

The X-ray induced optical luminescence as a function of incoming photon energy in the range from 500 to 1000 eV is shown in Fig. 1 for MgO, α -Al₂O₃, LaAlO₃, and Nb-doped SrTiO₃. The spectra have been normalised to the incident X-ray intensity by vertically shifting the latter in such a way that the dip in intensity observed at the Cr L_{2,3} edge, present in the incident beam, was absent in the normalised signal. (As we shall see below, the bulk MgO and α -Al₂O₃ crystals contain Cr impurities; however, these are expected to be present in trace amounts and to give a negligible contribution to the absorption signal.) Overall, one finds that the integrated

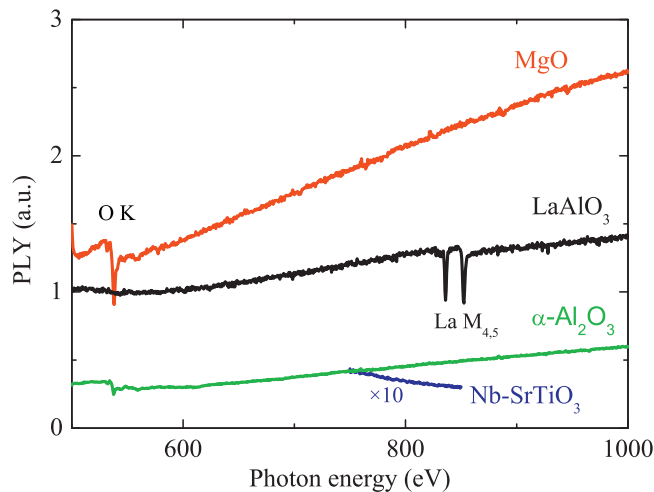


Fig. 1. Normalised X-ray induced optical luminescence yield (PLY) of MgO, α -Al₂O₃, LaAlO₃, and Nb-doped SrTiO₃ as a function of incident photon energy.

XEOL intensity does not vary strongly with energy in the range from 600 to 1000 eV, being of similar magnitude for MgO and LaAlO₃ and slightly smaller for sapphire. On the other hand, the XEOL efficiency of Nb-doped SrTiO₃ is over a factor of 10 smaller than that of α -Al₂O₃, while for undoped SrTiO₃ the luminescence signal was below the detection limit of our set-up. For the LaAlO₃ a noticeable reduction in luminescence is observed at the La_{4,5} absorption edges (852.4 and 836.2 eV, respectively). This can be explained by a sharp reduction in the scattering volume due to the much shorter absorption length at the resonances [19].

Fig. 2 shows the emission spectra of MgO, α -Al₂O₃, and LaAlO₃ measured at a fixed incidence X-ray energy (1000 eV) in the range from 1.20 to 3.65 eV. The spectra are strikingly different from each other: while sapphire displays a small number of sharp excitation lines, LaAlO₃ shows a broad peak and MgO a combination of both sharp lines superimposed on a set of broad peaks. The integrated spectral intensity is of the same order of magnitude for these samples, in agreement with the X-ray energy XEOL scans shown in Fig. 1, while all luminescence features are limited to the lower end

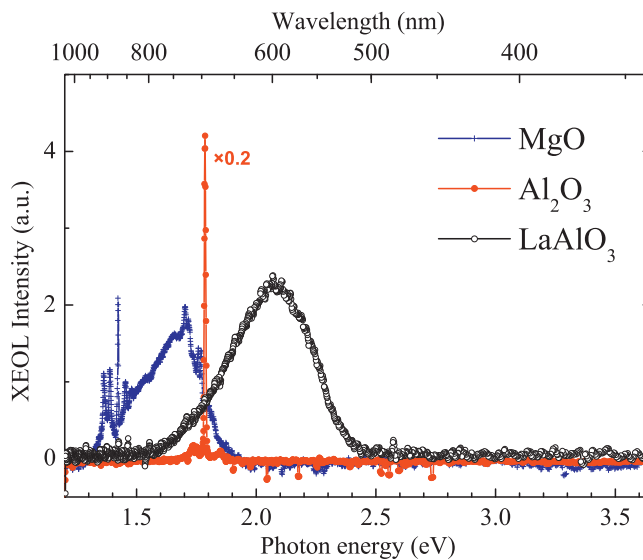


Fig. 2. Luminescence spectra of MgO, α -Al₂O₃, and LaAlO₃ at a fixed incident X-ray energy (1000 eV). The data were smoothed by a five-point averaging procedure (corresponding approximately to the energy resolution of the spectrometer of about 1.3 nm or 6 meV).

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