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Vibronic photoexcitation spectra of irradiated spinel $MgO{\cdot}nAl_2O_3\,(n = 2)$ at low temperatures

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ABSTRACT

A vibronic photoexcitation band at approximately 230 nm was found at 13 K in reactor neutron- and electron-irradiated magnesium aluminate spinel ($MgO \cdot nAl_2O_3$). Vibronic structure was found to be temperature dependent and became obscure at over 120 K. Huang–Rhys factor S and Debye temperature Θ_D were estimated from the temperature dependence of the 230 nm band by curve-fitting method using Debye approximation. Origin of the vibronic photoexcitation band was suggested as F center.

1. Introduction

Magnesium aluminate spinel ($MgO \cdot nAl_2O_3$) is an oxide with tolerance to irradiation. This material is a good candidate for some important applications in advanced fusion reactor technology such as window materials for radio frequency heating, insulating materials and liquid metal cooling system [1–3]. The crystal structure of the $MgO \cdot nAl_2O_3$ consists of a cubic cell with $Fd3m$ symmetry, containing a close-packed array of 32 oxygen atoms with cations in tetrahedral and octahedral interstices [4]. Relatively complex structure comparing to those of its constituent oxides MgO and α-Al_2O_3 makes the study of defect more difficult. Formation of both anion (F-type center) and cation (V-type center) vacancies is possible by neutron irradiation in spinel single crystals. Studies of irradiation induced point defects such as F- type centers in $MgO \cdot nAl_2O_3$ were reported for both stoichiometric and non-stoichiometric spinel crystals [4–8]. F-center absorption band shifts towards higher energies in non-stoichiometric spinel crystals because of lattice constant. This shift in absorption band is consistent with Mollvo–Ivey relation [6]. Vibronic F type centers at low temperatures were reported for MgO [9] and α-Al_2O_3 [10,11]. However, there is no report on the vibronic photoexcitation (PE) band in $MgO \cdot nAl_2O_3(n = 2)$ to the best of our knowledge. F-center excitation band in neutron-irradiated non-stoichiometric spinel has tail at higher energy region which falls below 6.2 eV or 200 nm. To measure the excitation spectra in the vacuum ultraviolet (VUV) range we have used synchrotron radiation light source.

In the present study, we used VUV spectroscopy to investigate the anion vacancies in neutron- and electron-irradiated $MgO \cdot nAl_2O_3$ single crystals. Vibronic F-center PE spectra of irradiated magnesium aluminate spinel were reported for the first time. Temperature dependent feature of the vibronic excitation band provided the information to estimate Huang–Rhys factor (electron–phonon coupling constant) and Debye temperature.

2. Experimental

Single crystals of undoped non-stoichiometric magnesium aluminate spinel ($MgO \cdot nAl_2O_3$)($n = 2$) grown by Czochralski method were provided by Furuuchi Chemical Co., Japan. The typical size of the samples was $7 \times 5 \times 1\ mm^3$. The samples were irradiated with reactor neutrons and electrons at low temperatures. Neutron bombardment was performed by using low-temperature loop (LTL) facility in Kyoto University Reactor Research Institute (KURRI) at 20 K. Total irradiation dose was $1.3 \times 10^{17}\ n/cm^2$, which corresponds to 6.9×10^{-5} displacement per atom (dpa) estimated by using the average displacement energy 52 eV [12]. Electron-irradiation was performed at liquid nitrogen temperature by using

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electron linear accelerator (KURRI-LINAC). The energy of electron beam was 30 MeV with fluence of 5.8×10^{18} e/cm^2 at a flux of 1.6×10^{14} e/cm$^2 \cdot$s.

Photoluminescence (PL) and PE spectra were measured using the VUV beamline 4B8 of the Beijing Synchrotron Radiation Facility (BSRF) in Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The electron energy of the storage ring was 2.5 GeV and the beam current was approximately 240–160 mA in measurement. PE and PL spectra were measured at temperatures 13–290 K. PE spectra were measured at wavelengths 125–350 nm and PL spectra were measured at wavelengths 330–700 nm. Seya-Namioka type grating monochromator (1200 L/mm) was used for measuring PE spectra and ACTON SP308 monochromator (1200 L/mm) was used to measure PL spectra. The spectral resolution of the system is 0.2 nm. The signal was detected by a Hamamatsu H8259-01 photon counting head. PE spectra were calibrated by using sodium salicylate signal.

3. Results

3.1. Room temperature PE and PL spectra

Fig. 1 shows the VUV–UV PE (left) and PL (right) spectra of irradiated and unirradiated spinel samples at room temperature (RT). Emission spectra were measured under the 219 nm. PE spectra were obtained by monitoring luminescence at 476 nm. Peak position of the PE band was found at approximately 210 nm in electron- and neutron-irradiated samples whereas the peak positions for the unirradiated sample found at approximately 190 nm. Emission peak was found at approximately 475 nm for electron- and neutron-irradiated samples. Unirradiated sample shows no obvious peak on the emission band. The emission peak at approximately 475 nm band shifted to 465 nm at low temperatures in electron- and neutron-irradiated samples (Fig. 3). Full-width half-maximum (FWHM) of emission spectra for both neutron and electron irradiated samples was found to be 124 and 119 nm at RT and 13 K, respectively.

Fig. 2 shows the extended PE spectrum of neutron-irradiated sample with FWHM of about 77 nm. The spectrum was fitted by Gaussian curve fitting. P1 (green dash)[1] and P2 (green) show the Gaussian curves calculated by fit multi-peaks method using Origin-Pro-8 program. Peak positions of the P1 and P2 bands were estimated to be 195 and 235 nm, respectively. The experimental curve (black line) is fitted well with the total fit (red line). PE spectrum of unirradiated sample (blue line) was represented for comparison.

3.2. PL and vibronic PE spectra at 13 K

Fig. 3 (left) shows the vibronic PE spectra of electron- (a), neutron-irradiated (b) and unirradiated (c) spinel samples obtained by monitoring luminescence at 380 nm. These spectra were measured at 13 K. Vibronic features appeared due to weak electron–phonon coupling at low temperatures. Peak position of the vibronic excitation band was at approximately 230 nm. Peak positions of the vibronic lines and the energy separations are listed in Table 1. Unirradiated sample shows no vibronic PE band. Emission spectra of electron- (a), neutron-irradiated (b) and unirradiated (c) spinel samples were also shown in Fig. 3 (right).

Fig. 4 shows the vibronic PE spectra of neutron-irradiated spinel monitored at various wavelengths on 465 nm emission band (Fig. 3). Intensity of the most intense line at 271.3 was higher than the broad excitation band when monitored at 380 nm. Intensity of

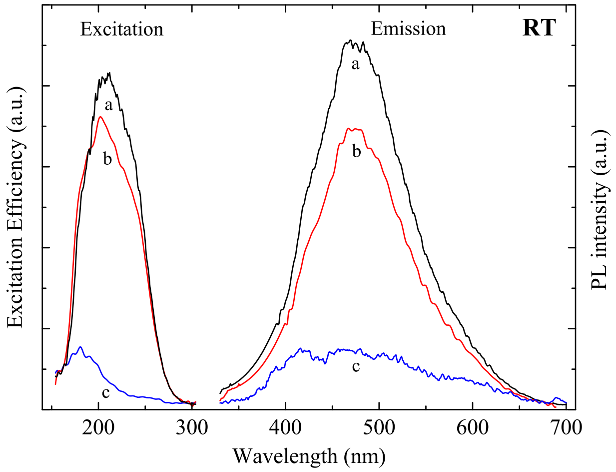

Fig. 1. VUV–UV photoexcitation (left) and photoluminescence (right) spectra of irradiated and unirradiated $MgO \cdot nAl_2O_3 (n = 2)$. Electron- (a), neutron-irradiated (b) and unirradiated (c) samples. Observation wavelength: 476 nm. Excitation wavelength: 219 nm.

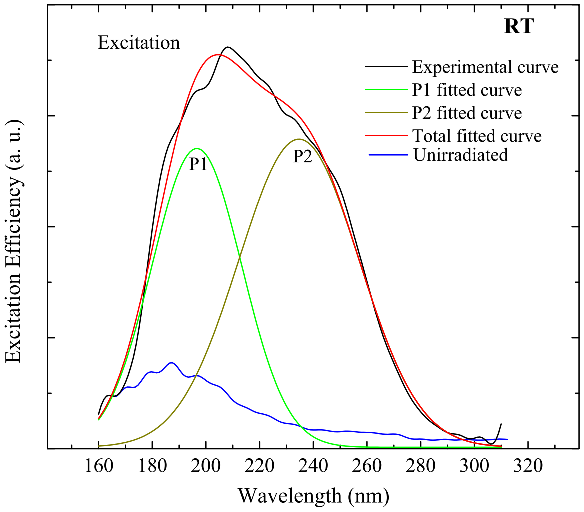

Fig. 2. Photoexcitation spectra of neutron-irradiated and unirradiated spinel samples at room temperature. Observation wavelength: 476 nm.

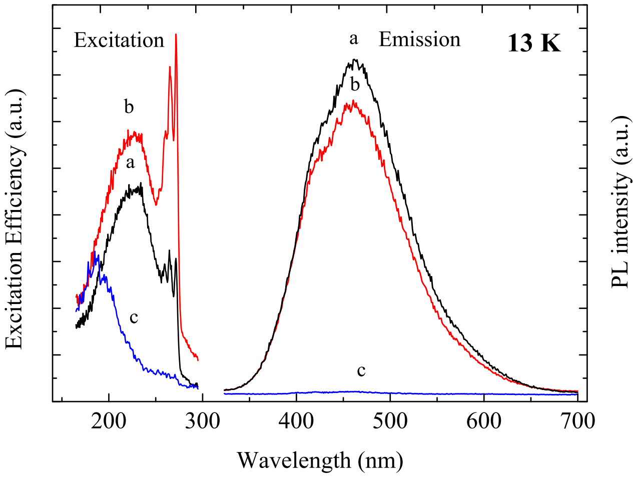

Fig. 3. Vibronic photoexcitation (left) and emission spectra of electron- (a), neutron-irradiated (b) and unirradiated (c) spinel samples at 13 K. Observation wavelength: 380 nm. Excitation wavelength: 240 nm.

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[1] For interpretation of color in Figs. 1–7, the reader is referred to the web version of this article.