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Monitoring F, F^+ and F_2^{2+} related intense defect emissions from nanocrystalline MgO

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ABSTRACT

MgO contains several oxygen defect related absorption peaks in the UV as well as in the visible region. The emission spectra are obtained at three different excitations, 6.02 eV (206 nm), 4.59 eV (270 nm) and 3.75 eV (330 nm) respectively. Each excitation results in an intense emission associated with F^+, F_2^{2+} and F-type oxygen defect centers. These intense defect emissions mostly appear in the UV and visible region of the energy spectrum. Since the emission peaks are associated with oxygen vacancies, annealing at 800 °C reduces the intensity of these peaks. The ratio of the emission intensity of F^+/F and F^+/F_2^{2+} decreases at 800 °C, whereas F/F_2^{2+} intensity ratio increases at 800 °C. It is anticipated that thermal conversion of F^+ and F_2^{2+} to F centers at 800 °C results in the enhancement of F/F_2^{2+} emission intensity ratio at high temperature.

1. Introduction

MgO is a wide band gap insulator with a bulk band gap of 7.8 eV. Because of its insulating nature MgO is used as an insulator for magnetic tunnel junction and as a substrate for the growth of high T_c superconductors [1–3]. Nanocrystalline MgO is useful in tetrahartz spectroscopy and in developing tetrahertz quasi optic components [4]. Nanocrystalline MgO exhibits unique absorption and luminescence properties on account of the presence of large numbers of atoms on the low coordination (C) sites including terraces (5C), edges (4C), corners (3C), etc. [5,6]. Defects present on these sites are easily excited on illumination with UV light. The major types of defects present in MgO are F centers or colour centers. These F centers are nothing but oxygen vacancies with trapped electrons. Removal of O^{2-} from MgO results in the formation of F^{2+} (oxygen vacancy without any electron), detachment of O^- results in the formation of F^+ (one trapped electron) and removal of neutral O atom forms F center (two trapped electrons) [7,8]. Chen, Williams and Sibley observed F^+ and F center related absorption peaks at 4.96 eV and 5.03 eV, respectively [9]. Nanocrystalline MgO contains several defect absorption peaks ranging from ultraviolet to infrared regions. These absorptions are related with bulk F, F^+, surface F, F^+ and F center aggregates [10]. These defects show response to different excitation energies, e.g. excitation with energy of 7 eV ionizes defects present on the surface and at the interface between nanocrystallites. Excitation with photon energy between 5 and 6 eV ionizes only low coordinated surface defects, whereas excitation with energy less than 5 eV generates excitons on the surface as well as on the interface [11]. Rosenblatt et al. [12]. observed F^+ and F center related emissions at 390 nm and 530 nm. Recently, Moon et al. [13] and Niu et al. [14] observed bright blue emission from MgO nanocrystallites. Zhang et al. observed green emission from MgO nanobelt and assigned this peak to oxygen vacancies [15]. Many of the applications of MgO are owing to the presence of these F centers. MgO is useful for tunable solid state lasers, since the F^+ centers present in it emits light in the visible region [16]. The F centers are reported to enhance the catalytic activity of MgO in the dehydrogenation of methane [17–19].

Herein, we report the luminescence properties of nanocrystalline MgO. Although there are few reports on the F center related emissions in nanocrystalline MgO, none of the reports have elaborately discussed the appearance of F, F or F_2^{2+} related emissions in nanoscale MgO. In order to understand the response of different defects to the incident light energy, MgO is excited with 6.02 eV (206 nm), 4.59 eV (270 nm) and 3.75 eV (330 nm) respectively. It is observed that the emission intensity of F, F^+ and F aggregates changes on changing the excitation energy. Moreover, effect of high temperature air annealing on the luminescence is studied and observed a reduction in the intensity of the defect emission peaks.

2. Synthesis details

2.1. Preparation of nanoscale MgO

The chemicals used for the preparation of MgO were magnesium nitrate hexahydrate (Merck, purity $\geq 99\%$) and sodium

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hydroxide, NaOH (Merck, purity $\geq 97\%$). Magnesium nitrate solution of 0.1 molar (M) was prepared in 100 mL double distilled water and stirred for 15 min, keeping the solution temperature at 50 °C. After 15 min 0.2 M NaOH solutions were added into it in the stirring condition. White precipitate appeared at the end of the stirring for 3 h. The precipitate was washed with double distilled water and ethanol respectively. For washing the solution was taken in a 50 mL centrifuge tube and centrifuged at 6000 rpm. After first washing with water the product at the bottom of the centrifuge tube was sonicated in ethanol and then again centrifuged. The process of washing was continued for 3 times first with water followed by ethanol. The product was kept in a hot air oven maintained at 80 °C. The sample became completely dry after 10 h. The powder was then kept in a tube furnace with an initially temperature of 25 °C. After putting the sample the furnace is switched on. The furnace temperature reached 600 °C at a heating rate of $\sim$0.2 s/degree. We kept the sample in the furnace for 3 h for annealing and after 3 h the furnace was switched off. The sample was kept inside until the furnace temperature reached 25 °C. The sample was then taken out of the furnace and kept in container. The sample was labeled Mg600.

2.2. Characterization details

The crystalline phase of MgO was monitored in a Bruker D 8 focus AXS X-ray diffractometer equipped with Cu $K\alpha$ radiation source ($\lambda = 0.154$ nm). The scanning range was 0.05°/s and the step size was 0.005°. Transmission electron microscope (TEM) images were obtained in JEOL-JEM 2100 transmission electron microscope at an operating voltage of 200 kV. Room temperature absorption spectra of the samples were obtained in Shimadzu 2450 UV–vis diffuse reflectance (DRS) spectrophotometer with $BaSO_4$ as the reference. Room temperature photoluminescence (PL) spectra were obtained in Perkin Elmer LS-55 spectrometer with Xenon light as the exciting source. The emission detector was R928 photomultiplier tube that could operate from 200 up to 900 nm and had the maximum anode and cathode sensitivity in and around 400 nm. The excitation and emission slits were fixed at 10 nm.

3. Results and discussion

3.1. Structural and morphological study

X-ray diffraction pattern of Mg600 is shown in Fig. 1. The diffraction pattern corresponds to the face centered cubic lattice of MgO having space group $Fm\bar{3}m(225)$ (JCPDS-89-7746). Mg600 contains a small peak at $2\theta = 58.69°$ corresponding to (1 1 0) peak of $Mg(OH)_2$ (JCPDS-860441). Presence of $Mg(OH)_2$ peak infers that the sample may contain hydrogen related impurities. These hydrogen related impurities could be formed when the –OH from $Mg(OH)_2$ interacts with oxygen vacancies present in MgO [20]. The possible role of hydrogen impurities on the emission of MgO will be discussed latter. The crystallite size is calculated using Scherrer's formula in the Eva software equipped with the X-ray diffractometer. The Scherrer's formula is $d = 0.9\lambda/\beta \cos\theta$, where d is the crystallite size, λ is the wavelength of X-ray radiation, β is the full width at half maximum and θ is the diffraction angle. We considered intense (2 0 0) diffraction peak for the determination of the crystallite size. The calculated crystallite size is 10.7 nm.

Transmission electron microscope images of Mg600 are shown in Fig. 2a and b. Fig. 2a shows that the particles are agglomerated and are of varied shape. Inset of Fig. 2a shows the histogram displaying size distribution of the nanoparticles with average size of 12 nm. The crystalline nature of the prepared nanoparticle is confirmed from the observation of the clear lattice planes in Fig. 2b and from the selected area electron diffraction (SAED) pattern shown in the inset of Fig. 2b.

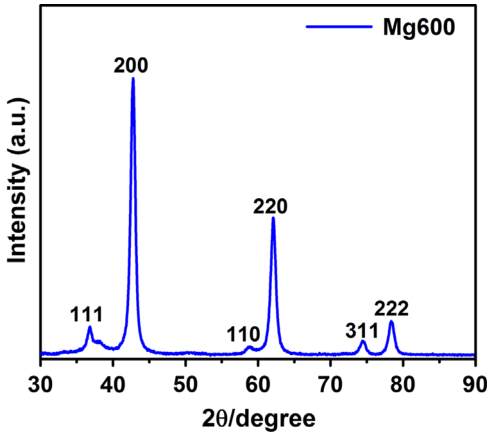

Fig. 1. X-ray diffraction pattern of nanocrystalline MgO.

3.2. UV–vis absorption study

Kubelka–Munk absorption plot and the corresponding reflectance spectra of Mg600 are shown in Fig. 3a and b. Kubelka–Munk absorption or $F(R)$ is obtained from reflectance R considering the equation, $F(R) = (1-R)^2/2R$, where R is reflectance of the sample. The lower spectral detection limit of the UV–vis spectrophotometer is 200 nm. Therefore, we could not detect any absorption or reflectance below 200 nm. The UV–vis spectral range from 280 to 700 nm are Gaussian fitted with fitting correctness, $r^2 = 0.9985$ (shown inset of Fig. 3a). For bulk MgO the absorption threshold could be seen at 7.7 eV in the UV region [5]. However, nanocrystalline MgO contains several absorption peaks in the UV and visible region. Those absorptions are due to the presence of defects and low coordinated cations and anions on the surface, interface, etc. [21,22]. The absorption at $\sim$200 nm (6.2 eV) involves excitation of 5 coordinated surface anions [5,23]. In the present study the observed absorption at 250 nm (4.96 eV) could be associated with bulk F or F^+ centers [9,10]. The absorption at 289 nm (4.29 eV) is owing to singlet to singlet $^1A_{1g}$ to ^1E transition of electrons present in the surface F_s center [24]. The other singlet to singlet $^1A_{1g}$ to $^1A_{1g}$ excitation of surface F_s center is observed at 405 nm (3.06 eV). These two singlet to singlet transitions of surface F_s center arises owing to crystal field splitting of the 2p states of oxygen defect on the surface [24]. The absorption peak at 652 nm (1.90 eV) involves singlet to triplet photoexcitation of electrons from ground $^1A_{1g}$ state to excited $^3A_{1g}$ state of surface F_s center [24]. The absorption peak at 365 nm (3.39 eV) is due to the surface F_s^+ center and involves $^2A_{1g}$ to $^2A_{1g}$ electronic transition [24]. The absorption peak at 324 nm (3.83 eV) is due to F_2^{2+} centers [25,26]. The dimmers or aggregates of F centers are formed by the pairing of the nearest F centers (F, F^+ or F^{2+}). Thus, depending on the number of trapped electrons by the paired oxygen vacancies these aggregates are referred as F_2 (with four electrons), F_2^+ (three electrons), F_2^{2+} (two electrons in two vacancies) respectively [12,14,26]. The absorption peak at 559 nm (2.21 eV) is likely due to V^- center [27–28]. V^- center consists of a single hole trapped oxygen ion adjacent to a magnesium vacancy having the configuration O^{2-}–[$Mg_{vacancy}$]–O^- [29]. The absorption at 444 nm (2.79 eV) is due to the transition of a four coordinated F center [30,31]. The absorption at 605 nm (2.05 eV) appears owing to 5-coordinated surface F_s^+ centers [32,33]. In the present discussion the notation corresponding to surface or bulk F or F^+ centers is provided based on the theoretical work by Illas et al. [24].