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Modification of the Structural and Optical Properties of Commercial ZnO Powder by Mechanical Activation

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Abstract:

Mechanical activation was used as a method for modification of the structural and optical properties of commercial ZnO powder. For this purpose zinc oxide powder was mechanically treated by grinding in a high-energy vibro-mill in a continual regime in air up to 300 minutes. Starting and modified ZnO samples were characterized using XRD, BET and TEM measurements. Optical properties of these samples were investigated by Raman and photoluminescence (PL) spectroscopy. The color of commercial ZnO powder was white while mechanically activated ZnO powder was dark yellow, indicating the presence of nonstoichiometry. In the Raman spectra of non-activated sample Raman modes of bulk ZnO were observed, while the spectra of modified samples point out structural and stoichiometric changes. The PL spectra of modified samples excited by 325 and 442 nm lines of a He-Cd laser show great difference with respect to the spectra of the original sample. This study confirms that change in the defect structure of the ZnO crystal lattice introduced by mechanical activation affects the optical properties of this material.

Keywords: Zinc Oxide, Mechanical Activation, Raman, Photoluminescence.

1. Introduction

Zinc oxide is greatly used for the production of materials and components for different applications due to its specific properties [1-3]. Thus, investigations of possible modifications of its properties are of both scientific and practical interest. Changes in properties as a consequence of mechanical activation, which is used most often in powder obtaining technologies, deserve special attention [4]. A complex analysis of activated powders is necessary and requires both a good knowledge of the nature of processes, which occur, and their mutual influences and complete information on the fine defect structure and the laws of its evolution.

ZnO is of great interest for photonic applications, and thus, the optical properties of different forms of ZnO (single crystal, thin films, powder, and nanostructures) have been

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extensively studied [5]. Among many other methods, Raman and photoluminescence (PL) spectroscopy are highly effective in optical characterization of this material.

In the present work we describe the influence of mechanical activation on the structural characteristics and Raman and PL spectra of commercial zinc oxide powder.

2. Experimental procedure

In these investigations a commercial zinc oxide powder (Kemika, p.a. 99.96 %) was used. The zinc oxide powder was mechanically activated by grinding in a vibro-mill with steel rings (type MN 954/3, KHD Humboldt Wedag AG) in a continual regime in air (the steel vessel volume was 500 cm³, and the quantity of powders was 200 g). The grinding time was 30 and 300 minutes and appropriate powder labels are ZnO(30) and ZnO(300), respectively.

The specific surface area of powder samples was measured by a nitrogen gas sorption analyzer (ASAP 2000 Micromeritics) using the BET method.

X-ray diffraction patterns of non-activated and activated powders were obtained using a Norelco-Philips PW-1050 diffractometer, with CuK_α radiation and a step scan mode of 0.02°/0.4s. Structural refinements were carried out using the Rietveld program Koalariet-Xfit [6].

Raman measurements were performed at room temperature in the backscattering geometry using the 442-nm line of a HeCd laser, Jobin-Yvon U1000 monochromator and a photomultiplier as a detector.

Photoluminescence (PL) spectra were excited by UV (325 nm) and visible (442 nm) lines of a HeCd laser using the same equipment as for the Raman measurements. PL spectra were measured in air at room temperature.

3. Results and discussion

3.1. Powder characterization

Mechanical activation induces physico-chemical changes in the material, which have a significant influence on materials properties and hence their application. It was determined that the starting powder had a specific surface area of 2.96 m²/g, presuming that the particles are of a spherical shape, the calculated equivalent diameter of powder particles was about 0.36 μm. The BET surface area of activated powders showed an increase from 3.78 to 5.92 m²/g for ZnO(30) and ZnO(300) samples, respectively. The increased surface area points to the process of particle breaking taking place during this stage of grinding (calculated equivalent diameters are 0.28 and 0.18 μm for ZnO(30) and ZnO(300) samples, respectively).

Fig. 1 shows the XRD patterns of the ZnO powders, the initial one and those subjected to mechanical activation. The XRD pattern of the starting powder exhibits sharp peaks of hexagonal ZnO (JCPDS PDF 36-1451). After 30 minutes of mechanical treatment intensities of all starting diffraction peaks are significantly lowered, and especially after 300 minutes of activation. The decrease of crystallinity that takes place in this type of powder processing is a consequence of defect formation and comminution of crystallite size causing broadening of the diffraction peaks. The calculated average sizes of ZnO crystallites, i.e. the regions of coherent scattering, were 190 nm for the non-activated powder sample and 106 and 44 nm for powder samples activated for 30 and 300 minutes, respectively.

The morphology of the particles and agglomerates and dispersivity of ZnO powders in different stages of mechanical activation were previously investigated by TEM and ED [7]. Based on these results, one can conclude that the starting, non-activated ZnO powder consists

of microcrystal particles, with dimensions from 0.1 to 1 μm and a high level of form anisotropy. Electron diffraction patterns of individual particles present a regular network of monocrystal reflections.

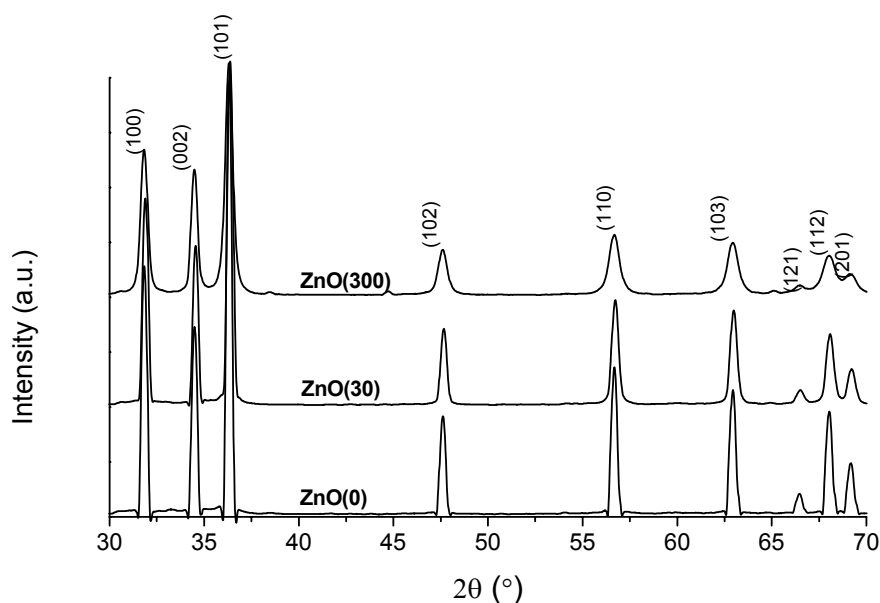


Fig. 1. X-ray diffraction patterns of the non-activated and activated ZnO powders.

After activation for 300 minutes a powder, which can be considered as a highly disperse mixture of small particles, is obtained. Most of these particles are in the form of aggregates, with dimensions of 0.3 - 0.1 μm . The ring-like ED patterns indicate that these aggregates have a polycrystalline structure. It was concluded that mechanical activation leads to the breaking-up of starting particles into fragments, which are very disordered.

3.2. Raman spectra

Raman spectrum taken on non-activated ZnO powder (labeled as ZnO(0)) is shown in Fig. 2. The observed first-order Raman modes were assigned on the basis of group theoretical analysis [8-10]: 100 (E_2^{low}), 383 ($A_1(\text{TO})$), 409 ($E_1(\text{TO})$), 438.4 (E_2^{high}), 543 ($A_1(\text{LO})$), 585 ($E_1(\text{LO})$), and 652 cm^{-1} (A_1). Additionally, several second-order Raman modes located at 331, 776, 984, 1112, and 1159 cm^{-1} were found. The presence of two additional modes (AMs) at 275 and 284 cm^{-1} was also observed. These AMs were related to intrinsic host lattice defects, which either become activated as vibrating complexes upon dopant incorporation in ZnO or exhibit lower structural quality of undoped ZnO films [11].

Raman spectra of ZnO powders after activation for 30 and 300 min are also presented in Fig. 2. Compared with the spectrum of non-activated powder, several obvious changes can be observed. First, in the low wave-number region only the 100, 438, 540 and 583 cm^{-1} peaks remained when the activation time increases, i.e. the grain size decreases to the nanometer scale. In addition, 987 and 1112 cm^{-1} modes seemed to be hidden behind the broad background, leading to an asymmetrical and broad 1153 cm^{-1} peak. Furthermore, the intensity of all observed vibrational modes decreases and their line shape become asymmetric, while a

mode shift to lower wave numbers with decreasing grain size was observed. Such changes have been usually attributed to the confinement of optical phonons by grain boundaries in nanosized powders [12]. However the redshift of E_2^{high} phonon mode can be also caused by the presence of intrinsic defects [13] in mechanically activated ZnO. Really, a drastic increase in the intensity ratio of the $E_1(\text{LO})$ peak to the E_2^{high} peak, points to defect formation [14] by mechanical activation. These conclusions are in accordance with the XRD changes.

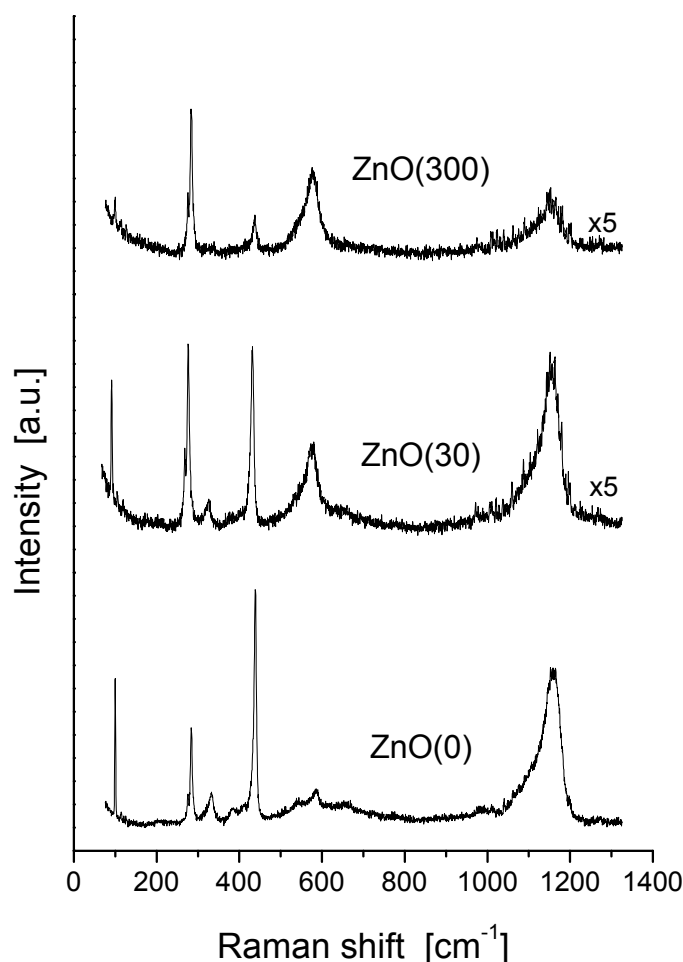


Fig. 2. Raman spectra of the non-activated (ZnO(0)) and ZnO powders activated for 30 and 300 min (ZnO(30) and ZnO(300)).

Furthermore, it was found that the electron-LO phonon coupling strength, determined by the ratio of second to first order Raman scattering cross section decreases with increasing activation time. These results will be helpful to understand the transport process and optical properties in ZnO materials [15].

3.2. Photoluminescence

Fig. 3a presents photoluminescence spectra of the three different ZnO powders excited by a 442 nm laser beam at room temperature. It is clearly seen that all PL spectra show a broad and structureless band in the orange spectral region, with a line width of about 130 nm (obtained by Gaussian fitting). With increasing activation time, the PL intensity

increases, followed by a slight increase of the PL band width while its central position varies around 600 nm. In spectra of ZnO(0) besides this broad PL band, a narrower one is observed at about 467 nm.

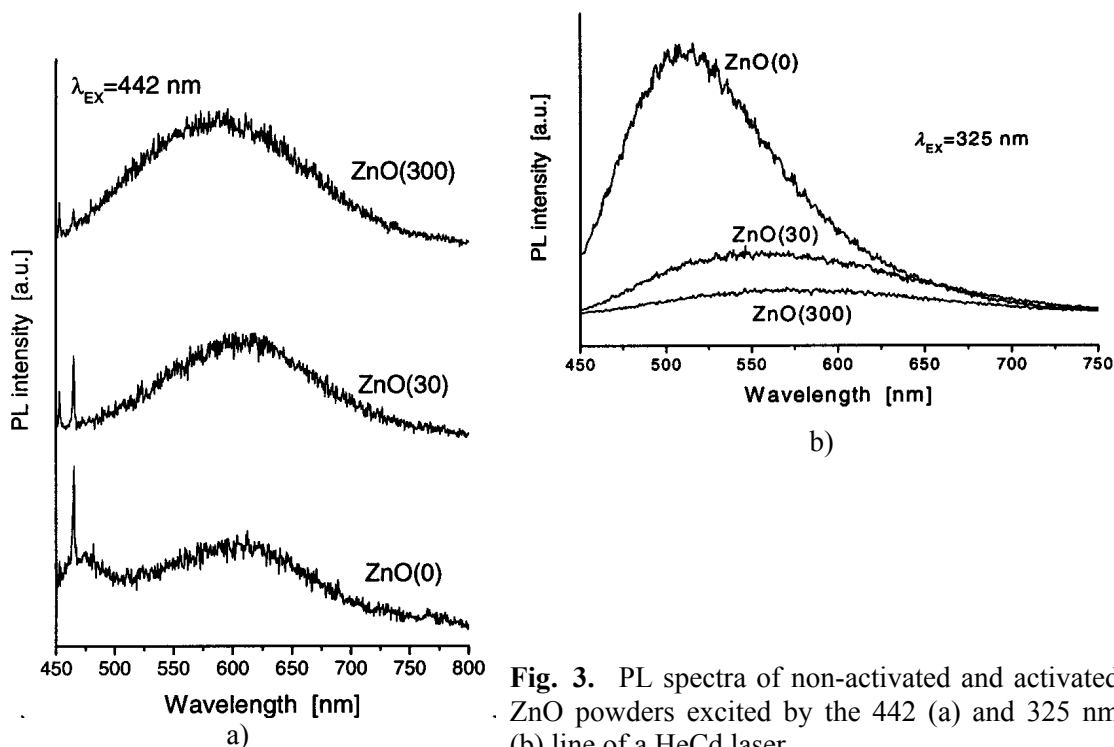


Fig. 3. PL spectra of non-activated and activated ZnO powders excited by the 442 (a) and 325 nm (b) line of a HeCd laser.

Since the PL emission maximum (at about 600 nm and 2.07 eV) is much lower than the band gap of ZnO (3.2 for bulk and 3.3 eV for nanocrystal), the visible emission cannot be ascribed to direct recombination of a conduction electron in the Zn 3*d* band and a hole in the O 2*p* valence band. This emission was attributed to electron transition, mediated by defect levels in the band gap, such as oxygen vacancies, Zn interstitials and so forth [12].

Fig. 3b presents PL spectra of the three ZnO powders excited by the UV line of a HeCd laser with a wavelength of 325 nm (photon energy of 3.81 eV). With increasing activation time, the PL intensity drastically decreases, while the line width increases with a shift of emission maximum towards longer wavelengths. It is obvious that all spectra can be decomposed into two PL bands, one in the green and another in the yellow (orange) region.

It is now quite commonly accepted that the green luminescence in ZnO arises from a radiative recombination involving an intrinsic defect center located at the surface [5]. A strong correlation has been observed between the green-emission intensity and the density of paramagnetic isolated oxygen vacancies in ZnO powders [16]. In addition, both the green PL efficiency and the isolated vacancy density are observed to peak as a function of free-carrier concentration, indicating that the singly ionized (paramagnetic) isolated oxygen vacancy could be the green luminescence center in ZnO. However, oxygen vacancy complexes, as specific defects, are not a green luminescence center in ZnO; they may in fact act as a quenching center. On the other hand, yellow luminescence was not sensitive to surface modifications of the nanostructures, hence it most likely originates from deep level defects in the bulk, not the surface. The deep level involved in to be yellow luminescence is likely interstitial oxygen.

4. Conclusions

Mechanical activation of ZnO powder causes a decrease in the intensity of Raman spectra as well as asymmetric line shape and redshift of some Raman modes. These changes can be attributed to the formation of intrinsic defects by mechanical activation of ZnO combined with the effects of optical phonon confinement in nanosized powders. It was also found that the electron-LO phonon coupling strength, determined by the ratio of second to first order Raman scattering cross sections, decreases with increasing activation time.

As a consequence of mechanical activation the intensity of the photoluminescence signal excited by visible light increases, whereas the PL excited by UV light decreases and shifts from the green to yellow spectral range. This allows us to conclude that oxygen vacancy complexes as well as oxygen and Zn interstitials become dominant defects in activated ZnO powders instead of isolated oxygen vacancies in non-activated powder.

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Садржај: Структурна и оптичка својства комерцијалног праха ZnO модификоване су коришћењем метода механичке активације. У ту сврху је цинк-оксидни прах механички третиран млевењем у високоенергетском вибротлину у континуалном режиму у ваздуху до 300 минута. Полазни и модификовани узорци ZnO карактерисани су методама рендгенске дифракције, трансмисионе електронске микроскопије и БЕТ мерења. Оптичка својства ових узорака испитивана су применом Раманове и фотолуминесцентне спектроскопије. Боја комерцијалног праха ZnO је бела, док механички активирани прахови постају тамножути, што указује на њихову нестехиометрију. У Рамановим спектрима неактивираниог узорка запажају се Раманови модови карактеристични за запремински ZnO, док спектри модификованих узорака указују на структурне и стехиометријске промене. Фотолуминесцентни спектри модификованих узорака, ексцитовани линијама He-Cd ласера таласне дужине 325 и 442 nm, показују велике разлике у односу на спектре оригиналног узорка. Ово истраживање потврђује да промене у дефектној структури кристалне решетке цинк-оксида уведене механичком активацијом значајно утичу на оптичка својства овог материјала.

Кључне речи: цинк-оксид, механичка активација, Раман фотолуминесценција.
