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Estimation of electron–phonon coupling and Urbach energy in group-I elements doped ZnO nanoparticles and thin films by sol–gel method

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ABSTRACT

Group-I (Li, Na, K & Cs) elements doped ZnO nanoparticles (NPs) and thin films were prepared using sol–gel method. XRD data and TEM images confirm the absence of any other secondary phase different from wurtzite type ZnO. Spherical shapes of grains are observed from the surfaces of doped ZnO films by atomic force microscope images (AFM) and presences of dopants are confirmed from energy dispersive X-ray spectra. The Raman active E_2 (high), E_2 (low), E_1 and A_1 (LO) modes are observed from both ZnO NPs and thin films. First-order longitudinal optical (LO) phonon is found to have contributions from direct band transition and localized excitons. Electron–phonon coupling, phonon lifetime and deformation energy of ZnO are calculated based on the effect of dopants with respect to the multiple Raman LO phonon scattering. Presence of localized interbands states in doped ZnO NPs and thin films are found from the Urbach energy calculations.

1. Introduction

Nanomaterials, especially metal oxides have received considerable attention over the last few years due to their distinguished performance and potential applications in various fields. Among these oxides, zinc oxide (ZnO) exhibits the most diverse and abundant configurations of nanostructures [1–3]. ZnO itself has normally a hexagonal wurtzite structure and it is well-known as an n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV [4]. Recently, much attention has been given focusing the modification of ZnO by doping with transition metals [5–8]. These studies demonstrated that the metals can change bandgap (E_g) of ZnO, and the dopants can control ZnO the grain size. P-type ZnO may be achieved by the substitution of group-I elements on 'Zn' site [9–11] and group-V elements on 'O' site [12–14], respectively. Group-I elements are better dopants materials than group-V elements in terms of the shallow accepter levels [15].Ungar et al. [16] investigated the electrical and luminescent properties of ZnO ceramics doped with Li, Na and Kushnirenko et al. [17] reported a comparative study of the effects of group-I elements on the structural and optical properties of the ZnO nanoparticles.

Raman spectroscopy is a versatile technique for fast and nondestructive study of dopant incorporation, particularly when impurity induced modes can be traced back to individual constituents and their concentration, as demonstrated for example with Mg and As in hexagonal and cubic GaN [18]. Ni et al. [19] use Raman spectroscopy to investigate the vibrational properties of Li-doped ZnO films to get insight into the effect of substitutional Li atoms in the crystal structure of ZnO. Majumdar et al. [20] studied the structural properties of Li doped ZnO thin films using Raman spectroscopy. We reported the broadening of longitudinal optical phonon in Na and Mg codoped ZnO thin films [21] and a detailed Raman study is carried out in Cs doped ZnO thin films [22]. The electron–phonon coupling is an important aspect in semiconductor materials due its significant influence on the optical and electrical properties, such as the energy relaxation rate of excited carriers and phonon reproduction of excitons in the luminescence [23]. In a simple situation, the radial electric field of the ionic nuclei in the crystal results in Coulomb interaction with the exciton and the strength of such an exciton–phonon coupling will be enhanced if the wavelength of the phonon vibration is comparable to the spatial extent of the exciton [24–29].

Structural and optical constant of undoped and doped ZnO nanoparticles and thin films were extensively studied. In this regard, we focus electron–phonon coupling and Urbach energy calculations. Structural disorder in the materials could be characterized by the slope of Urbach tail or Urbach energy. The

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value could also be used to evaluate defect concentration in the nano materials. Urbach energy values of the films increase with Mn incorporation and its change inversely with the optical band gaps were reported [30]. This increase leads to a redistribution of states, from band to tail and tail to tail transitions and in turn, a decrease in the optical gap occurs due to the broadening of the Urbach tail. These results are related to the optical band gap and Urbach tail which are in agreement with those reported for doped ZnO with different kind of impurities like Al, F, Er, Ta, Co, In and Sn [31–35]. In this paper, we discuss the electron–phonon coupling and phonon lifetime from Raman spectroscopy. Also the interband states from Urbach energy for group-I (Li, Na, K and Cs) doped ZnO nanoparticles and thin films using sol–gel method.

2. Experimental procedure

The ZnO nanoparticles is prepared by simple sol–gel method using zinc acetate dihydrate, potassium hydroxides and alkaline metal (Li, Na, K and Cs) chlorides used as a starting precursors. All the chemicals are purchased from Sigma–Aldrich with 99% purity. The doping of Li, Na, K and Cs is fixed at 5 mol.% (both NPs and thin films) with respect to zinc for comparative study purpose. Zinc acetate dihydrate is dissolved in distil water with the 0.2 M concentration. The solution is then kept under constant stirring at room temperature using magnetic stirrer for one hour. During the stirring time 1 M of potassium hydroxide solution is added drop by drop touching the walls of the vessel. After completion of the

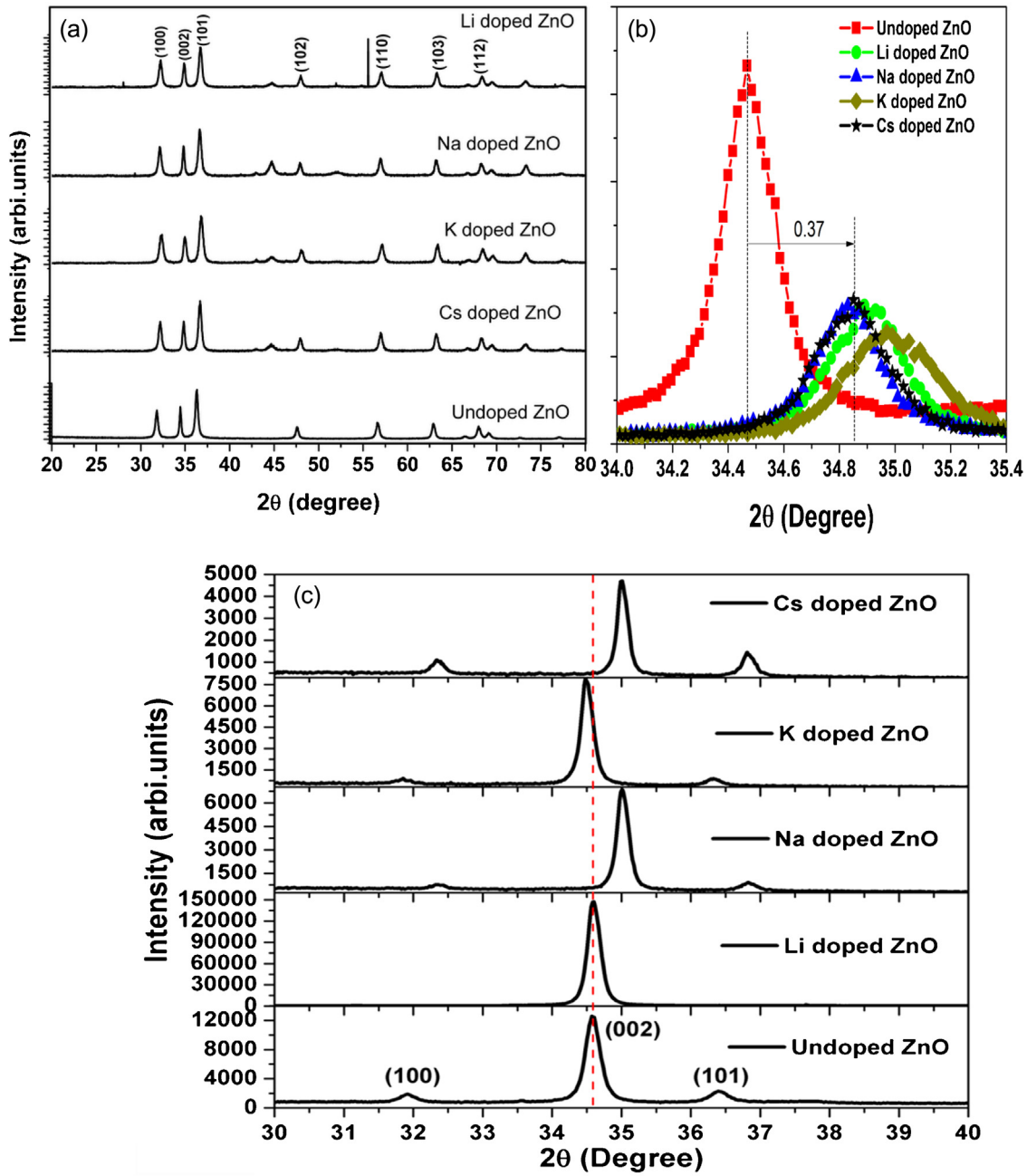

Fig. 1. XRD patterns of (a) Nanoparticles, (b) Shift of (101) plane in nanoparticles, (c) XRD patterns of thin films.