Physica E 83 (2016) 389–397

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Synthesis and characterization of magnesium oxide nanocrystallites and probing the vacancy-type defects through positron annihilation studies

Anjan Das [a,*], Atis Chandra Mandal [b], Soma Roy [c], Pendem Prashanth [c,1], Sk Izaz Ahamed [c,2], Subhrasmita Kar [c,2], Mithun S. Prasad [c,2], P.M.G. Nambissan [c]

[a] Department of Physics, A.P.C. Roy Government College, Siliguri, Darjeeling 734010, West Bengal, India
[b] Department of Physics, University of Burdwan, Golapbag, Burdwan 713104, West Bengal, India
[c] Applied Nuclear Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

HIGHLIGHTS

- Identification of stages of PsH complex formation and vacancy clustering.
- First use of positron annihilation spectroscopy for the investigation of these phenomena.
- Satisfactory explanation to the changes in band gap in samples of different crystallite sizes.

ARTICLE INFO

Article history:
Received 19 September 2015
Received in revised form
12 March 2016
Accepted 17 March 2016
Available online 18 March 2016

Keywords:
Defects
Nanocrystals
Magnesium oxide
Optical absorption
Positron annihilation
Vacancy clusters

ABSTRACT

Magnesium oxide nanocrystallites exhibit certain abnormal characteristics when compared to those of other wide band gap oxide semiconductors in the sense they are most prone to water absorption and formation of a hydroxide layer on the surface. The problem can be rectified by heating and pure nanocrystallites can be synthesized with controllable sizes. Inevitably the defect properties are distinctly divided between two stages, the one with the hydroxide layer (region I) and the other after the removal of the layer by annealing (region II). The lattice parameters, the optical band gap and even the positron annihilation characteristics are conspicuous by their distinct behavior in the two stages of the surface configurations of nanoparticles. While region I was specific with the formation of positronium-hydrogen complexes that drastically altered the defect-specific positron lifetimes, pick-off annihilation of ortho-positronium atoms marked region II. The vacancy clusters within the nanocrystallites also trapped positrons. They agglomerated due to the effect of the higher temperatures and resulted in the growth of the nanocrystallites. The coincidence Doppler broadening spectroscopic measurements supported these findings and all the more indicated the trapping of positrons additionally into the neutral divacancies and negatively charged trivacancies. This is apart from the Mg^{2+} monovacancies which acted as the dominant trapping centers for positrons.

1. Introduction

Nanoscale metal oxides possess excellent optical, electrical, electronic and special chemical properties [1] and therefore are useful in many advanced technologies. Magnesium oxide (MgO) is used in catalysis, toxic waste remediation, antibacterial materials, refractory material industries, paints and superconductor products [2,3]. It has attracted much attention due to its wide band gap, variously reported in the range 4.19–6.60 eV, and also due to its favorable properties as a catalyst in important chemical reactions [4]. MgO is a very suitable candidate for insulation applications due to its low heat capacity and high melting point [5].

Various kinds of fabrication techniques have been proposed for the synthesis of MgO nanocrystallites such as chemical vapor deposition [6], laser ablation [7], solvent mixed spray pyrolysis technique [8], hydrothermal method [9], sol–gel method [10], co-precipitation method [11] and thermal decomposition of

* Corresponding author.
E-mail address: anjan802002@yahoo.co.in (A. Das).
[1] On leave from and presently at National Institute of Technology, Calicut, Kerala 673601, India
[2] On leave from and presently at Indian Institute of Science Education and Research, Mohanpur, West Bengal 741246, India

http://dx.doi.org/10.1016/j.physe.2016.03.032
1386-9477/

hydroxide or carbonate [12]. Sol–gel process is the most promising, economical and convenient method of production of uniformly crystallized MgO nanocrystallites. We also adopted the sol–gel route of synthesis for obtaining fine MgO nanocrystallites in this work. Different characterization tools like X-ray diffraction and high resolution transmission electron microscopy (HRTEM) have been used to determine the size, morphology and crystal structure of the synthesized nanocrystallites. Further, Ultra-violet and visible light absorption spectroscopy is used to determine the optical band gap of the samples. Besides all these, it should be mentioned that structural defects like vacancies and their complexes have important roles in tailoring the properties of the semiconductor nanocrystalline materials. It often turns out to be an absolute necessity to characterize and monitor their dynamics and interaction at various stages of the experimental sequence with as much precision and meticulousness as possible. In this context, positron annihilation spectroscopy (PAS) is carried out as part of the present work to gather information on them and the variations of the different positron annihilation parameters are monitored with the changes in crystallite sizes, especially since finite size effects are reportedly more prominent and measurable at very low nanocrystallite sizes [13].

2. Experimental details

2.1. Synthesis of MgO nanocrystallites

To synthesize the MgO nanocrystallites by aqueous sol-gel method, magnesium nitrate tetrahydrate ($Mg(NO_3)_2 \cdot 4H_2O$) was used as precursor. First, double distilled water and ethanol were mixed in the ratio 2:1 in a beaker. The requisite amount of $Mg(NO_3)_2 \cdot 4H_2O$ was added with the solution to make its concentration 0.2 M. The solution was vigorously stirred for one hour with a magnetic stirrer. A clear solution was obtained. The solution was then heated at 80 °C to evaporate the excess ethanol. The gel so obtained was dried at 120 °C to obtain a dried white powder. The powder was separated into several parts and each was annealed at a different temperature to obtain samples of the desired crystallite sizes.

2.2. Characterization and optical absorption measurements

X-ray diffraction patterns of the samples were recorded with Bruker D8 Advance diffractometer at 40 kV and 40 mA and which used Cu Kα ($\lambda = 1.5406$ Å) radiation. All the samples were scanned from $2\theta = 20$–$115°$ with a scanning speed of 2° per minute. For optical absorption studies, the required amounts of the nanoparticulate samples were dissolved in absolute ethanol with the help of an ultrasonicator and examined using a PerkinElmer UV–vis–NIR spectrophotometer (Lambda 750). High resolution transmission electron microscopy (HRTEM) images were taken with a JEOL (Model JEM 2200FS) microscope operating at 200 kV.

2.3. Positron annihilation studies

The samples are then studied by positron annihilation techniques. Positron lifetime and coincidence Doppler broadening measurements are carried out using a 10 μCi strong ^{22}Na source. The source is deposited in solution form and dried on a very thin (~ 2 mg cm^{-2}) and well-annealed Ni foil whose extended portion is folded to cover the source deposition. The source in this form is kept immersed in the powdered sample taken in a glass tube. The glass tube is continuously evacuated to avoid air and/or absorbed gases in between the crystallites and the powder settled down under its own weight. Thus the source and sample had been always kept in moisture-free conditions. The powdered sample covered the source from all sides sufficiently in thickness to ensure positron annihilation within it and no positrons reached the walls of the glass tube. The positron lifetime spectrometer used for the measurements is a standard slow-fast gamma-gamma coincidence set up with a time resolution of 170 ps (full width at half maximum). For coincidence Doppler broadening spectroscopic (CDBS) measurements, two high pure germanium (HPGe) detectors of energy resolution 1.27 and 1.33 keV at 0.511 MeV are used. About 3×10^6 counts were collected under each positron lifetime spectrum. In CDBS measurements, about $(2–3) \times 10^7$ coincidence events were obtained under the two-parameter spectrum. Further details are given afterwards.

3. Results and discussion

3.1. X-ray diffraction and HRTEM

The XRD patterns of some of the samples are shown in Fig. 1. The prominent peaks of the X-ray diffraction patterns, especially those of the samples of relatively larger crystallite sizes, could be indexed as those of face-centered cubic phase of MgO with space group Fm-3m (ICDD reference pattern no. 01-087-0651). These peaks, common to all the samples, are assigned to (111), (200), (220), (311) and (222) reflections. Peaks corresponding to any other phase are either absent or below the limits of detection, which indicated the high purity of the samples. The exception was the case of the sample with the lowest crystallite size and it showed additional peaks coming out from a surface layer of

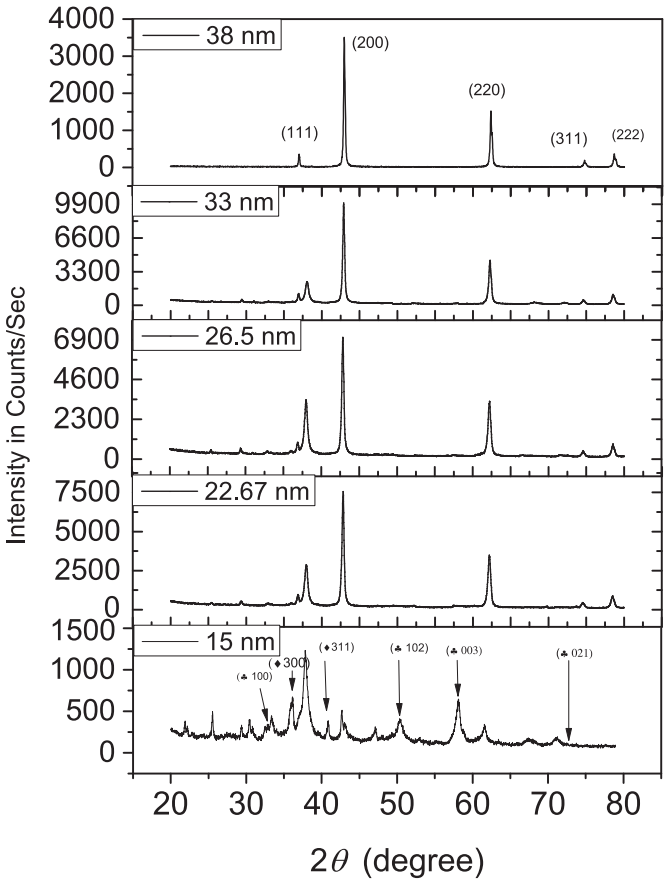

Fig. 1. The XRD patterns of some of the MgO nanocrystalline samples. MgO peaks have been indexed at the top panel. The bottom panel shows some major peaks of $Mg(NO_3)_2$ and $Mg(OH)_2$ indicated with ♦ and ♣ respectively for 15 nm sample.