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Synthesis, luminescence and micro-Raman study of $In_2Ge_2O_7$ nanobelts and nanowires

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ABSTRACT

Indium germanate ($In_2Ge_2O_7$) nanobelts and nano- and microwires have been synthesized by a thermal evaporation–deposition method and their luminescence properties have been investigated. High-resolution transmission electron microscopy shows the growth direction of the nanobelts. Cathodoluminescence in the scanning electron microscope and photoluminescence show the existence of a broad complex emission band with several components in the range 1.70–2.80 eV and a band at 3.20–3.30 eV. Comparison of the observed luminescence with the luminescence of GeO_2 suggests that some of the components are related to the presence of Ge_2O_7 groups in the germanate crystal structure and not to the sheets of InO_6 octahedra of the structure. Waveguiding behaviour of $In_2Ge_2O_7$ nano- and microwires has been demonstrated under excitation with 325 nm light. Raman spectra of the nanobelts have characteristic peaks which could enable to correlate specific Raman features with the presence of $In_2Ge_2O_7$ and to use this technique for indium germanate assessment.

1. Introduction

Germanates constitute a group of ternary oxides with several properties of interest in the fields of catalysis, sensing, optical and electro-optical applications and others. In particular, indium germanate, $In_2Ge_2O_7$ has been increasingly investigated and first principles studies regarding electronic structure and optical properties have been recently reported [1,2]. As in the case of other oxides, nanostructured germanates, mainly indium or zinc germanates, have been synthesized and investigated in the past years. In particular, indium germanate ($In_2Ge_2O_7$) nanobelts [3–5], microtubes [6], semi-nanotubes [7] and nanowires [4,8–10] grown by thermal evaporation methods or by a solvothermal route [11] have been reported. Previous reports on $In_2Ge_2O_7$ low dimensional structures deal mainly with their synthesis, morphology and structural characterization while optical properties were to a much lesser extent studied. In particular, there are only few data on the luminescence behaviour of these micro- or nanostructures, which appear to depend on the experimental conditions. Nanobelts show a photoluminescence (PL) peak at about 3.00 eV (410 nm) under excitation with 260 nm light [3], nanowires show a broad PL band centred at 2.50 eV when excited with a 325 nm He–Cd laser [8] and the cathodoluminescence (CL) spectra of microtubes [6] in the scanning electron microscope (SEM) consist of a band with maximum at 2.21 eV (560 nm). Also PL emission of $In_2Ge_2O_7$ powders was reported [12] to have a maximum at about 2.03 eV (610 nm) by λ_{exc} = 272 nm. The dispersion of luminescence results suggests that the main luminescence band of $In_2Ge_2O_7$ is a complex band involving several recombination paths. In this work, $In_2Ge_2O_7$ nanowires and nanobelts have been grown by a thermal evaporation method, their luminescence has been investigated by CL and PL, and spectral deconvolution techniques have been used to resolve the different components. GeO_2 and In_2O_3 nano- and microwires have been demonstrated to show good waveguiding behaviour [13,14]. The compound $In_2Ge_2O_7$ with a refractive index of about 1.65 [15] should also be a material suitable for waveguiding. For this reason, waveguiding of single nanobelts has been studied under laser beam excitation. The optical behaviour of the structures has been also investigated by micro-Raman spectroscopy and a relationship between Raman features and the $In_2Ge_2O_7$ nanostructures has been found.

2. Experimental details

The starting material for the growth of the $In_2Ge_2O_7$ nanostructures was a mixture of In_2O_3 (Strem Chemicals, 99.999% purity) Ge (Alpha Aesar, 99.999% purity) and carbon (Sigma Aldrich) powders with atomic ratio of 2:1:2. The powder mixture was prepared

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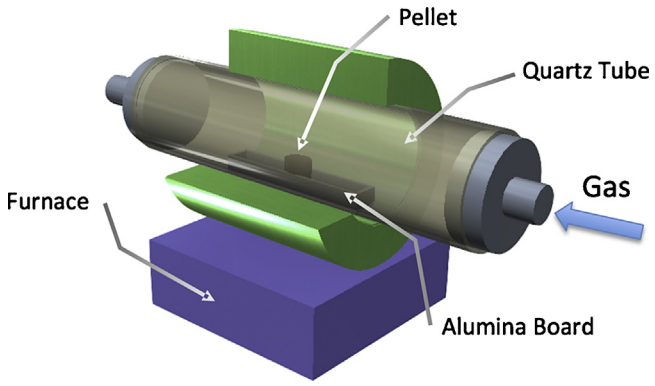

Fig. 1. Schematic of the experimental set up for the growth of nanostructures.

by milling in a centrifugal ball mill (Retsch S100) with 20 mm agate balls. The mixture was then compacted under a compressive load to form disc-shaped pellets of about 10 mm diameter and 4 mm thickness. The samples were then annealed under argon flow in a horizontal tube furnace at 800 °C for 8 hours. During the thermal treatment, different $In_2Ge_2O_7$ micro- and nanostructures grow on the pellet surface by an evaporation–deposition process in which the pellet surface acts as source and as substrate. Since the furnace was not sealed for high vacuum conditions gas flow is slightly oxidizing. This catalyst free method has been previously used to grow small dimensional structures of a number of oxides such as In_2O_3 [16,17] or GeO_2 [18,19]. Fig. 1 shows a schematic of the synthesis experimental set up. Grazing incidence X-ray diffraction (XRD) study was performed with a Philips X'Pert MRD Pro diffractometer. For the XRD measurements the structures were gently detached from the pellet and placed on a silicon substrate. The morphology and size of the structures grown on the pellet surface were investigated with a Leica 440 and a FEI Inspect SEM. Energy dispersive spectroscopy (EDS) was performed with a Bruker AXS Quantax system in a Leica 440 SEM and with an Oxford Inca system in a JEOL2100 TEM. CL measurements were carried out in a Hitachi 2500-S SEM with a Hamamatsu R928 photomultiplier or a PMA-12 charge-coupled device camera. Transmission electron microscopy (TEM) was performed with a Jeol JEM 2100 and a Jeol JEM 3000F TEM. The TEM samples were prepared by removing bundles of nanostructures from the surface of the pellet with a high precision microgripper mounted on a micropositioner and placing them on a TEM copper grid coated with a holey carbon film. For PL, waveguiding and Raman spectroscopy investigations a Horiba Jobin-Ybon LabRam Hr800 confocal microscope with a 325 nm He–Cd laser was used.

3. Results and discussion

After the thermal treatment the pellet appears completely covered with a high density of nanobelts and nano- and microwires as Fig. 2(a) and (b) shows. The structures show a certain alignment along the direction of gas flow and their density markedly depends on flow, so that more isolated structures grow under low flow conditions (Fig. 2(c)). In this case structures can be more readily separated which is of interest to perform experiments on single nanobelts or wires.

The structural analysis of ribbons and wires was first carried out by complementary XRD and EDS measurements. XRD pattern recorded on the pellets by grazing incidence (Fig. 3) shows peaks with a perfect match with the values of monoclinic $In_2Ge_2O_7$ (ICSD 01-082-0846).

The structure of the nanobelts was further assessed by selected area electron diffraction (SAED) measurements in TEM. Fig. 4(a)

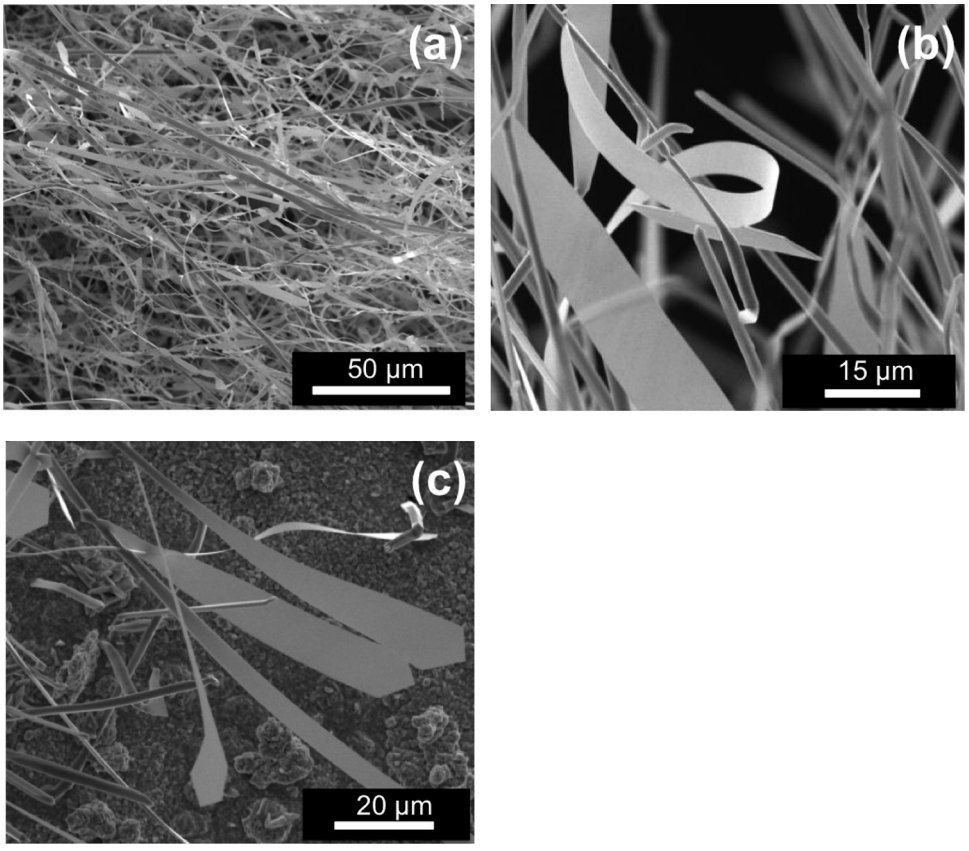

Fig. 2. (a) SEM images of (a) a high density of nanobelts and wires covering the substrate surface, (b) belts and wires at higher magnification and (c) isolated belts and wires grown under low gas flow.