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2008 J. Phys. D: Appl. Phys. 41 155408

(http://iopscience.iop.org/0022-3727/41/15/155408)

J. Phys. D: Appl. Phys. **41** (2008) 155408 (4pp) doi:10.1088/0022-3727/41/15/155408

Characterizations of single-phased cubic $Mg_{0.5}Zn_{0.5}O$ prepared at high pressure and high temperature

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Received 6 January 2008, in final form 24 April 2008
Published 9 July 2008
Online at stacks.iop.org/JPhysD/41/155408

Abstract
We report the preparation of a single-phased cubic $Mg_{0.5}Zn_{0.5}O$ semiconductor at high pressure and high temperature(HPHT) in this paper. Phase separation that was frequently observed in $Mg_{0.5}Zn_{0.5}O$ alloys at a normal pressure was avoided in our case. The formation of the single-phased $Mg_{0.5}Zn_{0.5}O$ resulted from the HPHT applied during the preparation process. The $Mg_{0.5}Zn_{0.5}O$ has a maximum absorption at about 265 nm and a sharp absorption edge at about 300 nm. The single-phased $Mg_{0.5}Zn_{0.5}O$ with an abrupt absorption edge obtained in this paper is of significance in realizing high-performance ultraviolet photodetectors based on MgZnO.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to its potential application in ultraviolet detectors, $Mg_xZn_{1-x}O$ has been extensively studied in recent years [1]. Quite a lot of publications have focused on the preparation and characterizations of $Mg_xZn_{1-x}O$ alloy material [2–8]. At a normal pressure ZnO usually crystallizes in the hexagonal structure while MgO in the cubic one. Therefore, phase separation occurs frequently in MgZnO alloys. It is reported that $Mg_xZn_{1-x}O$ remains single hexagonal phase when $0 < x < 0.36$, hexagonal and cubic MgZnO mixed phase when $0.36 < x < 0.62$ and single cubic phase when $x > 0.62$ [2]. It is difficult to obtain a single-phased MgZnO alloy with the Mg component lying between 0.36 and 0.62 at a normal pressure due to phase separation. It is reported that the mixed phase in MgZnO will show two absorption maxima and degrade the responsivity and rejection ratio of photodetectors made from this material. Therefore, the application of MgZnO alloys in photodetectors is severely hampered by the phase separation. Obtaining single-phased MgZnO alloys with the Mg component lying between 0.36 and 0.62 is of great importance and significance in realizing photodetectors operating in the solar blind spectrum range (220 nm–280 nm) [9]. It is documented that ZnO can crystallize in the cubic structure at a high pressure [10]. Therefore, the high pressure synthesis technique may be favourable for the formation of single-phased cubic MgZnO with high Mg content.

In this paper, $Mg_{0.5}Zn_{0.5}O$ has been obtained using the high pressure and high temperature (HPHT) preparation method. Structural characterizations show that the alloy is crystallized in single-phased cubic structures instead of mixed phase. The optical properties and phase diagram of the alloy are also studied.

2. Experiments

The experiment was carried out in a Chinese-style cubic high pressure apparatus with the model of SPD 6 × 1200; a schematic illustration of this apparatus can be found in figure 1, in which a six-fold anvil was used to apply high pressure to the samples. The precursors used were 99.99% ZnO and 99.99% MgO. ZnO and MgO were mixed with an atomic ratio of 1 : 1 and pre-pressed into a disc shape. The mixture was sintered at 1100 °C to get rid of the adsorbed water. Then it was put into the high pressure apparatus to be treated at HPHT. The pressure

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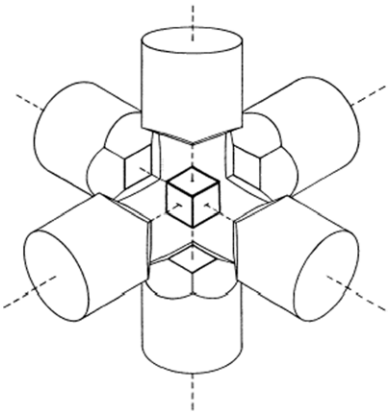

Figure 1. Schematic diagram of the reaction cell of the Chinese-type cubic HPHT apparatus used in this experiment (SPD 6 × 1200).

in the apparatus was kept at 5 GPa and the temperature at 1800 °C during the HPHT preparation process. The duration of the HPHT treatment is 20 min. In order to release the remnant stress, the as-prepared sample was annealed at 400 °C in air for 1 h. For comparison pure ZnO and MgO were also treated under the same conditions as references.

X-ray diffraction (XRD) was used to analyse the crystal structure, and the 0.15406 nm line of $CuK_{\alpha 1}$ was used as the radiation source. An optical microscope and a scanning electron microscope (SEM) were used to characterize the surface morphology. The composition of the samples was determined by an energy dispersive x-ray spectrometer (EDS). An F4500 spectrometer was used to measure the absorption spectra of the samples.

3. Results and discussion

Figures 2(*a*) and (*b*) show the XRD spectra of HPHT prepared MgO and ZnO samples and (*c*) and (*d*) those of the MgO and ZnO mixture before and after the HPHT preparation, respectively. In this figure, the miller indices shown in parentheses can be indexed to hexagonal phases, while those not in parentheses to the cubic ones. As shown in the figure, MgO and ZnO keep their own original cubic and hexagonal phase after the treatment. It has been reported that ZnO will change from hexagonal to cubic structure when being applied pressure larger than 15 GPa, while MgO keeps cubic structure [11]. Therefore it is rational that ZnO retains its original hexagonal structure after the HPHT process. According to the data shown in figures 2(*c*) and (*d*), the mixture of ZnO and MgO before the HPHT process has a mixed phase of cubic MgO and hexagonal ZnO, while after being processed at 5 GPa and 1800 °C for 20 min, the mixture turns into a single-phased cubic structure.

Figure 3 shows the EDS data of the ZnO and MgO mixed sample after the HPHT process. The atomic proportion of Mg in the sample is 50.16%, which is almost identical to the proportion of the precursor mixture (0.5 : 0.5). Usually, when the Mg content in $Mg_xZn_{1-x}O$ lies between 0.36 and 0.62, the phase of $Mg_xZn_{1-x}O$ will split into hexagonal $Mg_xZn_{1-x}O$ with a lower content of MgO and cubic $Mg_xZn_{1-x}O$ with a

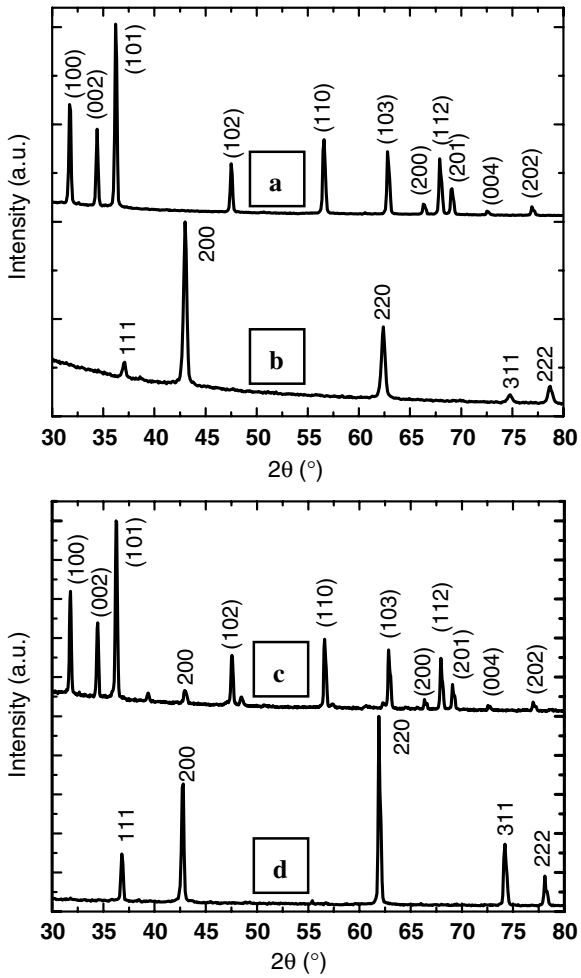

Figure 2. XRD spectra of as-prepared MgO (*a*) and ZnO (*b*); (*c*) and (*d*) are XRD spectra of the ZnO and MgO mixed sample before and after being processed at 5 GPa, 1800 °C for 20 min. Note that the miller indices shown in parentheses are from the hexagonal structure, while those without parentheses are from the cubic structure.

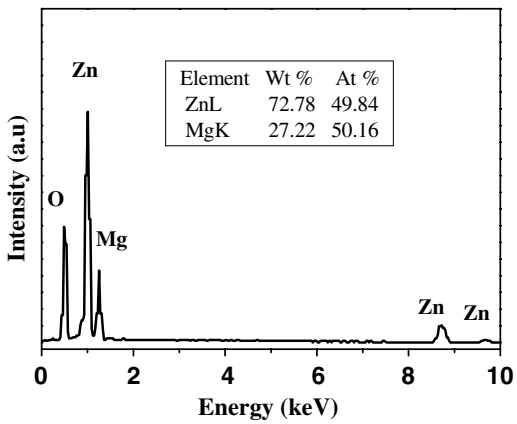

Figure 3. The EDS spectrum of the mixture of ZnO and MgO prepared at 5 GPa, 1800 °C.

higher content of MgO, and it is difficult to form single cubic or hexagonal phased $Mg_xZn_{1-x}O$ [12]. Figure 2(*c*) shows that the phase separation in $Mg_xZn_{1-x}O$ can be avoided at HPHT. According to the XRD data, the lattice parameter of Mg–Zn–O is 0.4239 nm, which is nearly the mean value of the lattice

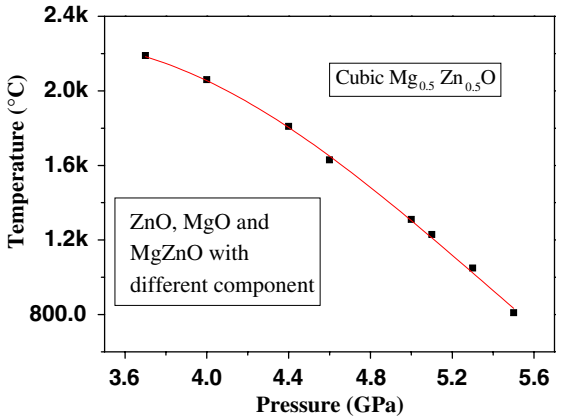

Figure 4. The phase diagram of $Mg_{0.5}Zn_{0.5}O$ obtained from our HPHT experiment.

constants of cubic ZnO (0.4280 nm) and MgO (0.4200 nm). We can deduce from these results that a single-phased cubic $Mg_{0.5}Zn_{0.5}O$ sample has been obtained in our experiment.

In order to study the influence of pressure and temperature on the formation of single cubic phased $Mg_{0.5}Zn_{0.5}O$, a series of experiments have been carried out at different pressures and different temperatures and then the schematic phase diagram of the $Mg_{0.5}Zn_{0.5}O$ alloy is illustrated, as shown in figure 4. The balanced line between the pure cubic phase and the mixed phase is shown by the solid line. The pressure and temperature region to form a single cubic phase is above the balanced line, and phase separation will occur in the region below the balanced line. As seen from the figure, the HPHT preparation conditions we used (5 GPa, 1800 °C) lie above the solid line, which is the reason why a single-phased cubic structure was obtained in our experiment.

The morphology of the ZnO, MgO and $Zn_{0.5}Mg_{0.5}O$ samples prepared at HPHT can be found in figure 5. From figure 5(*a*) one can see that MgO has been sintered to a ceram-like material after the treatment. ZnO changes from initial powder to polycrystal and its colour changes from white to light yellow. Further experimental results show that the colour of ZnO deepens with the increase in the processing pressure and temperature, which means that when the pressure and temperature are increased, more defects are created in ZnO. Figures 5(*c*) and (*d*) show the optical microscope and SEM images of the $Mg_{0.5}Zn_{0.5}O$ sample. We can see from the images that the sample surface is granular, and the granularity of the sample is about 30 μm.

Figures 6(a) and (b) show the absorption spectrum of ZnO prepared at 5 GPa and 1800 °C. By comparing curves (a) and (b), one can find that the band-edge blueshifts after the treatment. The blueshift is thought to be due to the compression stress applied to the ZnO sample [13]. Figure 6(c) shows the absorption spectrum of $Mg_{0.5}Zn_{0.5}O$ prepared at 5 GPa and 1800 °C for 20 min. We can see from the figure that the absorption edge blueshifts compared with ZnO, which implies that the band gap of $Mg_{0.5}Zn_{0.5}O$ is widened because of Mg incorporation. Furthermore, the absorption edge of the as-prepared $Mg_{0.5}Zn_{0.5}O$ has a very gentle slope, which may be caused by the defects and stress in the material. The

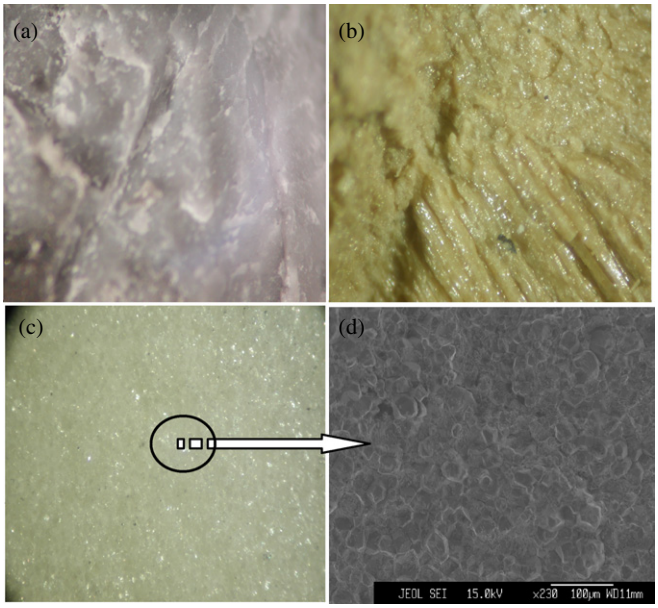

Figure 5. (Colour online) The optical microscope images of MgO (*a*) and ZnO (*b*); (*c*) and (*d*) are optical microscope and SEM images of $Mg_{0.5}Zn_{0.5}O$ prepared at 5 GPa, 1800 °C.

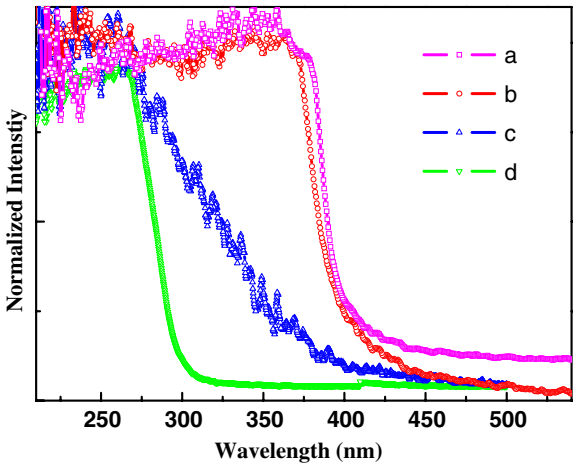

Figure 6. (a) The absorption spectra of precursor ZnO, (b) ZnO prepared at HPHT, (c) $Mg_{0.5}Zn_{0.5}O$ prepared at HPHT, (d) the absorption spectrum of $Mg_{0.5}Zn_{0.5}O$ first processed at HPHT then annealed at 400 °C for 1 h.

absorption edge becomes very abrupt after the sample is further annealed at 400 °C for 1 h, as shown in figure 6(d). Based on the experimental data in figure 6(d) and the relationship between the absorption coefficient and band gap, we can make out that the band-edge absorption central wavelength is at about 265 nm (4.68 eV), which lies in the solar blind spectrum range (220–280 nm). The abrupt absorption edge in the solar blind range obtained from our HPHT prepared $Mg_{0.5}Zn_{0.5}O$ sample reveals that HPHT may be a promising route to single-phased cubic $Mg_{0.5}Zn_{0.5}O$ for application in solar blind photo detectors.

4. Conclusion

In summary, single-phased cubic $Mg_{0.5}Zn_{0.5}O$ was prepared at 5 GPa, 1800 °C. The formation of the single cubic phase can be

attributed to the tendency of ZnO to assume a cubic structure at high pressure. After being further annealed at 400 °C, high-quality $Mg_{0.5}Zn_{0.5}O$ with an abrupt absorption edge centred at 265 nm was obtained. The results given in this paper may provide a promising route to single-phased $Mg_{0.5}Zn_{0.5}O$ for application in high-performance solar blind photodetectors.

Acknowledgments

This work is supported by the Key Project of National Natural Science Foundation of China (No 50532050), the '973' Program (No 2006CB604906), the Innovation Project of CAS and the National Natural Science Foundation of China under Grant Nos 60776011, 10774132 and 10674133.

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