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From monoclinic $Mg_2B_2O_5$ nanowires to triclinic $Mg_2B_2O_5$:Eu nanorods

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ABSTRACT

In this paper we report on the synthesis of single-crystal $Mg_2B_2O_5$ nanowires by heating the precursor powder made of disodium tetraborate decahydrate and magnesium chloride dihydrate at 850^0C. The as-received nanowires possess smooth surface with diameters varying between 25 and 40 nm. Also $Mg_2B_2O_5$ nanorods doped with Eu were synthesized by firing a mixture powder of the above obtained $Mg_2B_2O_5$ nanowires and Eu_2O_3 in air atmosphere. The as synthesized $Mg_2B_2O_5$:Eu nanorods have diameters varying between 110 and 130 nm. The structural and compositional characteristics of the as-synthesized products have been investigated by XRD, SEM, TEM, EDX, and SAED techniques. Photoluminescence investigations reveal that both Eu^{+3} and Eu^{+2} can coexist in $Mg_2B_2O_5$ nanorods. Eu^2 display a violet emission beak at 412 nm and Eu^{3+} display broad emissions centered at 538 and 615 nm.

Introduction

It is well-known that the reduction of microstructure size of crystalline materials into nanometer size can dramatically result in modification of their optical and electronic properties due to their high surface ratio to volume and quantum size effect. One dimensional (1D) nanostructures such as nanowires/nanorods and nanotubes are critical and important work directed toward understanding the fundamental physical concepts and their potential applications[1-3]. The rare earth elements (RE)-doped nanosize materials are found to be interesting for photoluminescence properties. The europium (Eu) among rare earth elements has been used as an activator in the red phosphors because of its strong red emission. Also, Eu can display two valence states: trivalent ($Eu^{3+}$and divalent (Eu^{2+}). Eu^{3+}ion is supersensitive to the evolution of its surroundings [4-6]. In addition, Eu^{3+}ion is also observed as phonon sideband on high energy side of $^7F_0$ - $^5D_2$ transition, due to the local structures coordinating Eu^{3+}ion [7]. Therefore, on the basis of aforementioned futures, Eu^{3+}ion ought to be a good probe and favorable for the investigation of the local structure. Compared with the linear spectrum of $Eu^{3+}$the emission and absorption spectra of Eu^{2+} ion usually consist of broad bands and the luminescence is very strongly dependent on the host lattice, which is quite different from the Eu^{3+}ion. Eu^{+2} ion is usually employed in fluorescent lamps, plasma display systems, and UV-emitting phosphors.

Moreover, most of host materials selected for red phosphors can be doped by remarkably small amount of europium due to concentration quenching. Recently, the researches on the synthesis and optical properties of rare-earth ion doped one-dimensional nanomaterials have been investigated, which exhibiting significant luminescent properties [8,9]. Borate systems have proved to be potential candidates for aforementioned applications [10-12]. Magnesium borate ($Mg_2B_2O_5$) material, besides its excellent features based on their excellent mechanical properties, chemical inertness, low thermal expansion coefficient, excellent mechanical properties, attractive thermal properties, thermo-luminescent properties, and good antiwear behavior [13-16] is a suitable host material for high efficiently optical materials. Magnesium borates with 1D structure, such as nanorods [17–19], nanowires [20–21], nanobelts [22], nanotubes [23] have been reported. Varieties of the previous methods expose some disadvantages such as irregular fragments-like morphology observed at their ends [20], agglomerates impurities existing at the surface of the one-dimensional nanostructure could be seen [20, 21, 23] as well as byproducts [20,22,23]. Thus, developing a simple, cost-effective and sustainable for synthesizing of highly nanowires/nanorods method has been of scientific and technological interest. In this work, we present simple and low cost method to synthesis such monoclinic $Mg_2B_2O_5$ nanowires. As well as the photoluminescence properties of $Mg_2B_2O_5$:Eu (Eu^{3+}/ Eu^{2+}) nanorods have been investigated. The route used in this report may be useful to explore the possibilities of commercial application of the single-phase magnesium borate nanostructures.

Excremental

Two steps were adapted to synthesis $Mg_2B_2O_5$:Eu nanorods. First, $Mg_2B_2O_5$ nanowires have been synthesis as follow: In beaker A, an aqueous solution was prepared by dissolving 2.1 gm of magnesium chloride dihydrate into 30 ml of deionized water and then an appropriate amount of ammonia ($NH_3{\cdot}H_2O$) was added as drop wise to this solution to adjust the pH as 9, resulting in a milk white solution. Under continues stirring, in another beaker B, 3.8 gm of disodium tetraborate decahydrate dissolved into 100 ml of deionized water. The 30 ml of solution A was carefully injected as drop wise into solution B. An appropriate amount ~ 1.2 gm of an organic additive ($C_6H_8O_7.H_2O$) was dissolved in the above mixture solution. The organic additive worked as a chelating agent in the reaction. The resulting solution was stirred at 120 °C for 5 h in a digital hot plate. Finally, the precursor powder of magnesium borate was got and used as initial reactant. When the alumina tube held in a traditional resistance-heating furnace was heated to 400 °C, alumina boat contained the precursor powder was quickly pushed to the central of the tube, then the system was rapidly heated to 850 °C as optimal degree and kept at this temperature for 210 minutes. High-purity argon was adopted as a protecting

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medium at a constant flow rate of 30 standard cubic centimeters per minute (sccm). Then the furnace was cooled down to room temperature as the natural process. After that, the as-obtained solid powder was filtered and washed several times with hot distilled water to remove the possibly impurities remaining in the final products, and finally dried at 60 °C in air.

Second, in order to investigate the photoluminescence properties of magnesium borate the as- obtained $Mg_2B_2O_5$ nanowires and Eu_2O_3 were used as starting materials. Stoichiometries amounts of as-synthesized $Mg_2B_2O_5$ nanowires and Eu_2O_3 together were carefully mixed and grounded in an agate mortar (1/7Eu from the total amount of $Mg_2B_2O_5$ nanowires powder). The mixture was situated into alumina tube and fired at 930 °C for 3 hours in air atmosphere. After cooling process : The products were analyzed by means of x-ray diffraction (XRD, D/MAX-rB, Cu *K* radiation). The overview of the sample morphology was identified by scanning electron microscopy (SEM, JEOL JSM-6700F), equipped with the system of energy-dispersive X-ray (EDX) analysis. The excitation and emission spectra were recorded with a Hitachi F-4500 fluorescence spectrometer at room temperature

Results and discussion

Figure 1a presents the XRD patterns of the sample fabricated by heating the precursor powder made from magnesium chloride dehydrate and disodium tetraborate decahydrate at temperature 850 °C. As can be seen all diffraction beaks can be indexed to a monoclinic structure $Mg_2B_2O_5$ with lattice parameter of a = 1.2314 , b = 0.3116, c = 0.9206 nm and with β = 104.25°. This result is in good agreement with the standard bulk values of $Mg_2B_2O_5$ lattice parameters within experimental errors (a= 1.231, b = 0.3120 and c = 0.9205 in the JCPDS Card no: 16-0168). It should be noted that no diffraction peaks from other phases have been observed indicating a high purity of as-obtained product.

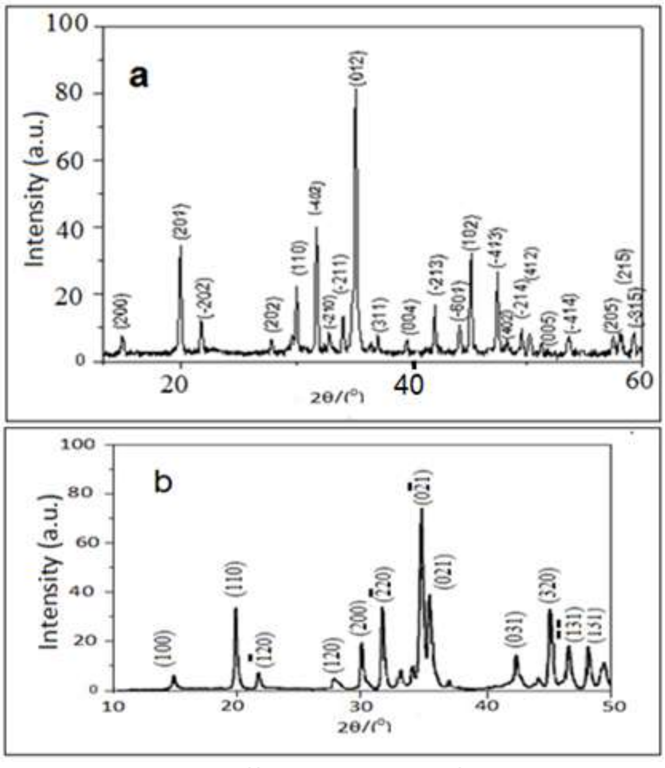

Figure 1. X-ray diffraction pattern of as-synthesized products (a) $Mg_2B_2O_5$ and (b) $Mg_2B_2O_5$:Eu.

Figure 2a shows the morphology of the $Mg_2B_2O_5$ product synthesized at a reaction temperature of 850 °C within reaction time of 210 min. The low-magnification SEM image display the overview of the nanostructures in abundant form which agglomerated into large amount of uniform nanowires with smooth surface. No impurities could be detected on the surface of the nanowires of as-synthesized product, established high purity of the product. The nanowires possess slighter diameter ranging between 25 and 40 nm and lengths of several micrometers. Furthermore, the SEM confirmed high aspect ratio of the as-synthesized nanowires. A typical EDX spectrum was conducted for element constituents of the specimen shown in Figure 2b, suggesting that the nanowire was made of Mg , B, and O elements. Transmission electron microscopy (TEM) was also employed to study the structure and the morphology of the as-synthesized $Mg_2B_2O_5$ nanostructures. Figure 2c exhibits a typical TEM morphology of the synthesized $Mg_2B_2O_5$ nanowires, establishing that the nanowires of $Mg_2B_2O_5$ possess smooth surface and almost are uniform in diameters, along their extension. Indicated in Figure 2d is the magnified TEM image of an individual $Mg_2B_2O_5$ nanowire and the corresponding selected area electron diffraction (SAED) pattern. The SAED pattern is shown in the upper-right inset of Figure 2d, exhibiting a single crystalline nature of these pure nanowires with the lattice constant consistent with XRD analyses presented above. The preferred growth axis for magnesium borate $Mg_2B_2O_5$ nanowires is elongated along [001].

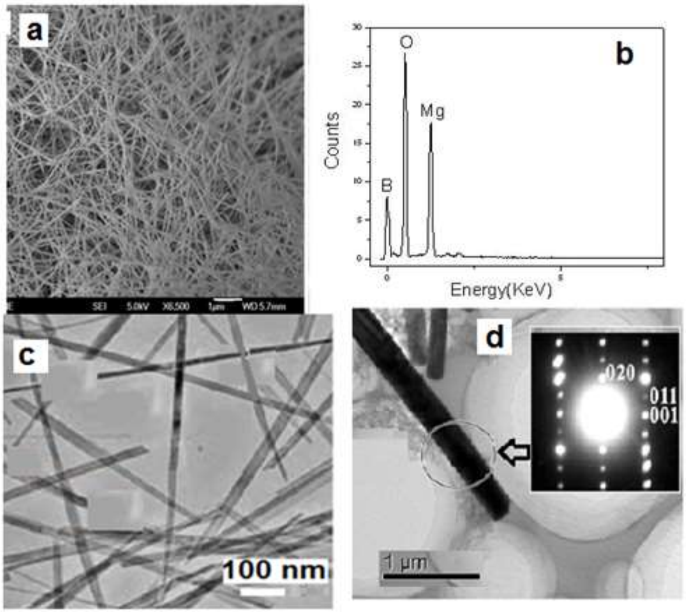

Figure 2. (a) Low-magnification SEM image showing a large amount of $Mg_2B_2O_5$ nanowires; (b) the corresponding EDX spectrum; (C) TEM image establishing smooth morphology of $Mg_2B_2O_5$ nanowires; (d) an individual nanowire of $Mg_2B_2O_5$ and (inset) the corresponding SAED pattern.

Figure 1b shows XRD pattern of the sample fabricated by calcining the mixture powder prepared from as-synthesized $Mg_2B_2O_5$ nanowires and Eu_2O_3 at 930 °C in air conditions. All diffractions peaks could be signed to a triclinic structure $Mg_2B_2O_5$. The result in agreement with the standard diffraction peaks (JCPDS Card no: 15-537). This phase differs from the ones obtained before doping Eu, which indexed as monoclinic structure as shown in Figure 1a. No X-ray reflection corresponding to any other crystal phase was observed.

Scanning electron microscopy (SEM) image (Fig. 3a) shows the general morphology of as synthesized $Mg_2B_2O_5$:Eu nanostructures obtained by fired the same as-received $Mg_2B_2O_5$ nanowires shown in Fig. 2a,c. As can be clearly seen, the as-received of $Mg_2B_2O_5$:Eu nanostructures are abundant of like-nanorods, possess diameters vary between 110 and 130 nm . This result (nanorods) are relatively shorter in lengths and larger in diameters compared to $Mg_2B_2O_5$ nanowires (Fig. 1a), and this is maybe due to the high temperature used for fabricating such $Mg_2B_2O_5$:Eu nanorods. Also, some dark contrast can be seen (indicated by the arrows) , this maybe ascribe to the effect induced by the Eu doping. Figure 3b shows the Energy dispersive X-ray (EDX) microanalysis of the chemical composition determines that the doped Eu with respect to the composition $Mg_2B_2O_5$. Thus is a clearly evidence that the rare earth ions are doped into the phase.

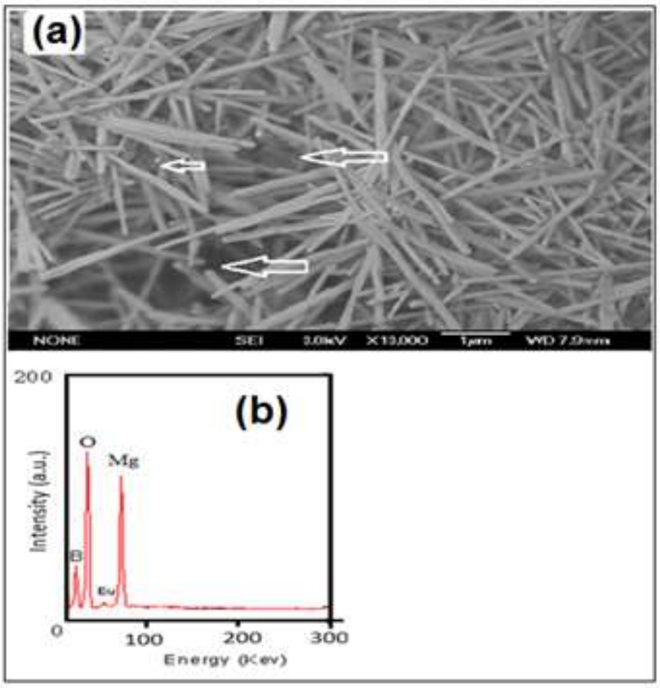

Figure 3. (a) SEM image showing a general morphology of $Mg_2B_2O_5$:Eu nanorods; (b) the corresponding EDX spectrum

The photoluminescence properties was carrying out in order to study the excitation and the emission spectra of as-synthesized $Mg_2B_2O_5$:Eu nanorods. As can be seen the excitation spectrum (Fig. 4a), exhibits a broad band centered at 257 nm related to the charge transfer (CT) transition from 2p orbital of O^{-2} ions to the orbital of Eu^{3+} ions. The position of CT band usually depends upon the length of Eu–O bond. The larger of Eu–O the strength of bond is, whereas the shorter the location of CT bond position is [24,25].

The sample $Mg_2B_2O_5$:Eu nanorods exhibits a violet region emission band, centered at 412 nm (Fig. 4b). The beak is assigned to the allowed transitions $4f^6 5d^1 \rightarrow 4f^7 d^0$ of Eu^{2+} ion. In addition, its emission can also be occurred in the green region of the visible spectrum [26, 27]. Therefore**,** it could be possible and uncomplicated to observe two weak emissions band at 538 and 615 nm respectively (Fig. b). These two emission bands correspond to intra-configuration $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions interior on Eu^{3+} ion respectively [28]. The semi-weak broad emission near 538 nm is due to the magnetic dipole transition owning $^5D_0 \rightarrow {}^7F_1$ states, leading to the green light emitted by the resulting material $Mg_2B_2O_5$:Eu nanorods. Whereas, the other weak emission centered at 615 is due to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, which leading to the orange light . The emission from higher energy level of Eu^{3+} ions ($^5D_1$, $^5D_2$) was difficult to detected since the multi-phonon from higher exited level might has high probability. Therefore, only $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions for $Eu^{3+}$are observed in the emission spectra for our synthesized sample $Mg_2B_2O_5$:Eu nanorods. The overview results lead us to the suggestion that both divalent (Eu^{2+}) and trivalent (Eu^{3+}) states can coexist in as-synthesize $Mg_2B_2O_5$ nanorods after hearing process. The existents of the weak Eu^{3+} emission band shows that the reduction process was incomplete although of that it can be account as a good evidence of the efficient reduction $Eu^{3+} \rightarrow Eu^{2+}$ process. The Eu^{2+} emission is intense enough to find important industrial applications in, for example the tricolor low pressure mercury florescence lamps.

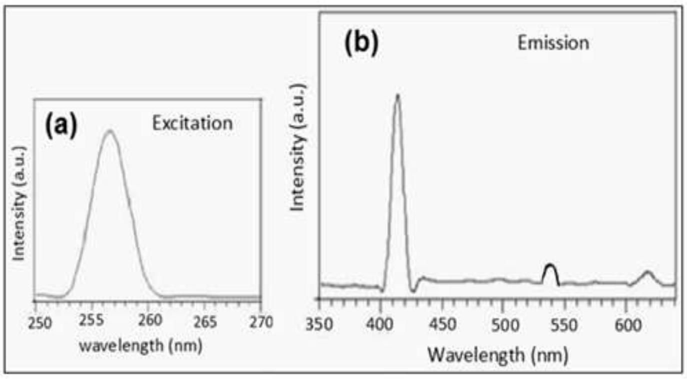

Figure 4. (a) **Excitation and (b) emission spectrum of $Mg_2B_2O_5$:Eu nanorods**

Conclusion

In summary, uniform $Mg_2B_2O_5$ nanowires were successfully synthesized by directly heating the precursor powder of disodium tetraborate and magnesium chloride dihydrate at 850 ^{0}C. Also $Mg_2B_2O_5$: Eu nanorods has been fabricated by calcining the as-prepared $Mg_2B_2O_5$ nanowires and Eu_2O_3 in air at 930 ^{0}C. The characterization of ID nanostructure through SEM and TEM show that the nanowires made of $Mg_2B_2O_5$ possess a diameter of 25-40 nm, whereas nanorods composed of $Mg_2B_2O_5$:Eu possess a diameter of 110 -130 nm. $Mg_2B_2O_5$:Eu nanorods exhibits emission spectrum regions, Eu^{2+} display a violet emission centered at 412 nm and Eu^{3+} display two week broad emissions centered at 538 and 615 nm respectively. The nanorod materials reported here might find application in green or orange phosphors as well as in UV-emitting phosphors.

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