Journal of Achievements in Materials and Manufacturing Engineering

VOLUME 48
ISSUE 1
September
2011

Synthesis and characteristics of optical properties of crystalline $YAl_3(BO_3)_4$:Cr,Ce

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Received 16.07.2011; published in revised form 01.09.2011

Properties

ABSTRACT

Purpose: The purpose of this study is to explore the possibility of conrol the grain size of YAB nanopowder and to investigate the optimum amount of dopant cerium or chromium ions in the matrix of YAB for luminescent intensity.

Design/methodology/approach: Nanocrystalline samples of YAB were prepared by sol-gel method and calcination at 1273 K. The structure and morphology of nanopowders were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and aerodynamic aerosol aerodynamic methods. Fluorescent intensity was measured by Fourier transform infrared (FTIR) and intersection of three-dimensional matrix (EM-EX) methods.

Findings: It was confirmed that the mean size of the obtained particles depended on the chain length of the precursor polimer used for reaction. The luminescence of YAB doped with cerium and chromium ions was measured.

Research limitations/implications: The results can be used in order to further develop sol-gel technology to obtain pure and doped YAB nanopowder.

Originality/value: Single phase crystalline YAB synthesis was developed. The measurements XRD confirmed that doping of YAB with some of RE or TM ions favours the formation of additional phase YBO_3, having the orgonic structure.

Keywords: Sol-gel method; Nanoparticles; Fluorescence

Reference to this paper should be given in the following way:
I. Cieślik, J. Żmija, A. Majchrowski, M. Pępczyńska, P. Morawiak, M. Włodarski, Synthesis and characteristic of optical properties of crystalline $YAl_3(BO_3)_4$:Cr,Ce, Journal of Achievements in Materials and Manufacturing Engineering 48/1 (2011) 24-28.

1. Introduction

Developing optoelectronics forces the use of new materials with improved different physicochemical properties. New functional materials that fulfil various functions arise great interest. Especially oxide materials, doped with rare earth (RE) and transition (TM) metals, are interesting due to their optical properties. Materials with good luminescent properties, having broad optical transparency and long fluorescence lifetimes are needed [1].

Particularly borates, possessing the structure of trigonal huntite derivative $YAl_3(BO_3)_4$ (YAB) have been extensively studied recently [2, 3]. Borates can be doped with RE and TM metal ions. Boron in oxides can exist in the form of trigonal planar configuration with oxygen BO_3 or tetrahedral coordination BO_4, which lead to creation of poliborate rings [4, 5]. It gives the opportunity to form many different structures with different combinations of cations. Moreover, the borate crystals such as: $YAl_3(BO_3)_4$, BiB_3O_5 [6], $LaSc_3(BO_3)_4$ [3] are transparent from

UV to IR range [6]. Doping them with active ions gives the possibility to obtain different spectra characteristics. Borates are used in tunable laser applications [7]. Doping them with active ions gives the possibility to obtain different spectra characteristic.

Moreover, YAB crystals belong to trigonal space group R32. YAB is a non-linear optical crystal with excellent properties for infrared laser emission under diode pumping as well as for self-frequency doubling laser (SFD) [6, 8]. One promising way to enhance nonlinear optical properties of YAB is to form the composites containing YAB crystallites embedded into polymer matrices [9-11].

Chromium of cerium-doped YAB crystals are active material which can generate laser radiation. Depending on the dopant used one may receive the different laser wavelengths. Dopants of chromium and cerium generate radiation which is safe for eyes (from 425 nm to 675 nm). This is one of the reasons for interest in these materials. YAB is an excellent matrices due to its thermal, chemical and physical stability. Brenier et al. [6] showed that YAB has high non-linear optical coefficients, high optical quality, high mechanical strength, good thermal conductivity, chemical stability as well as lack of photorefractive damage.

Borates mentioned earlier in form of powders are mainly used as luminescent agents in devices such as: fluorescent lamps, X-ray detector systems, lasers or in plasma display panels [13]. Purity and size of grains affects the borates properties. The influence of the amount of the dopant and the grain size on the optical properties of $REAl_3(BO_3)_4$, RE=Y, Gd were studied in Ref. [12]. Conventionally the combustion synthesis is conducted at high temperatures. The combustion method causes formation of defects and inhomogeneities even though it is carried out with stoichiometric amounts of reactants. As to conduct the reactions at lower temperatures one can use a solution method for example sol-gel reaction [14].

YAB matrices doped with cerium ions is considered as promising materials to be used in detectors or scintillators [15], which is due to the fact that YAB is a compound containing the largest number of boron among the ortoborates.

In the present work various polymerizing agents were used. The purity and the size of nanoparticles depend on many factors the limitations of which are: temperature during the formation of crystals and the amount of deionized water applied to precursors dissolution. The temperature and time of pyrolysis affect the phase purity and the size of the prepared crystals.

Nanopowder samples of YAB pure and doped with cerium or chromium ions have been obtained by the Pechini method. This method is useful in producing numerous nanocrystalline materials for optoelectronic applications. Pechini reaction is a modification of sol-gel method. In general, the sol-gel process involves the transition of the system from a liquid sol into a solid gel phase. The method is extremely simple to perform which makes it more attractive than other methods. It is also a method of controlling particles size from micro- to nano-size.

It was reported that two other phases namely YBO_3 and $Al_{18}B_4O_{33}$, were formed during synthesis of doped YAB powders [16]. In our research, formation only of the former phase YBO_3, was observed detected.

Cell parameters of the prepared powders were estimated by X-ray powder diffraction and scanning electron microscope. The optical properties were characterized using the absorption and emission spectrophotometers. According to the results the influence of the technological procedure details as well as optical properties are presented and discussed.

2. Experimental

The YAB matrices doped with chromium and cerium ions were obtained by means of the modified sol-gel method. The inorganic precursors were dissolved in water and acid to form the sol medium. The first phase of the process based on the polyesterification reaction. At this stage branched chains of linear polymers are formed. Edetic acid, mannitol, sorbitol, citric acid, and ethylene glycol were used as polymerizing agents to prepare matrices of YAB. Mannitol and citric acid solutions were obtained by dissolving in water (the molar ratio of the citric acid to mannitol was 1:1), then solutions were mixed using a magnetic stirrer and heated at 60ºC in air atmosphere for one and half hour. Citric acid, salicylic acid and mannitol were used as polymerizing agents to prepare matrices of YAB. Created polyester is a dispersing agent that lowers the reaction temperature and prevents particle agglomeration as well as excessive growth of crystallites.

High purity yttrium oxide, hydrate of aluminium nitrate, and cerium or chromium oxide powders were used as metal precursors. Boric acid was a source of boron. Boric acid and hydrate of aluminium nitrate were dissolved in distilled water under stirring and heating in order to obtain clear solution. The nitric acid solution of yttrium oxide was put into mixture of citric acid and mannitol with simultaneous increase of temperature up to 80ºC and kept in furnace for one hour. Then, it was mixed in water the solution of boron acid and aluminium precursor. creating a complex. In the next stage oxides of metals (chromium oxide and cerium oxide) were dissolved in concentrated nitric acid. After complete homogenization these solutions were added to the mixture of polymer solution with boron matrix. Thus prepared mixture was left in a quartz crucible for several hours at 90ºC in order to concentrate the solution, and the transition from sol to gel occurred. After receiving the gel the temperature increased up to 300ºC and kept in crucible for four hours. The resulting sample was subjected to pyrolysis at 1000ºC under a cover. Then it was cooled and milled in an agate mortar.

Before testing the samples under a scanning electron microscope (SEM), they were suspended in the polymer in order to reduce the undesirable effect of agglomeration.

3. Results and discussion

3.1. X-ray investigation and morphology of $YAl_3(BO_3)_4$

Analyse of nanocrystaline phases was made by X-ray diffraction (XRD) using the Brucker D8 Discover with Cu K ά radiation at the wave length λ = 1.54060 Å. The typical X-ray powder diffraction pattern is shown in Fig. 1. All crystalline diagrams show the diffraction lines corresponding to the structure of YAB. The observed powder XRD patterns of YAB have only one phase having a hexagonal structure with R 32 space group.

Unfortunately, doping of YAB with chromium or cerium ions favours the formation of additional phase YBO_3 (Fig. 2).

To investigate the grain size and boundaries of YAB matrices, we used scanning electron microscopy (SEM Phenom – Vega Tescan, FEI). Results are shown in Figs. 3a and 3b. Main drawback of sol-gel method is formation of agglomerates that are clearly visible in Fig. 3a.

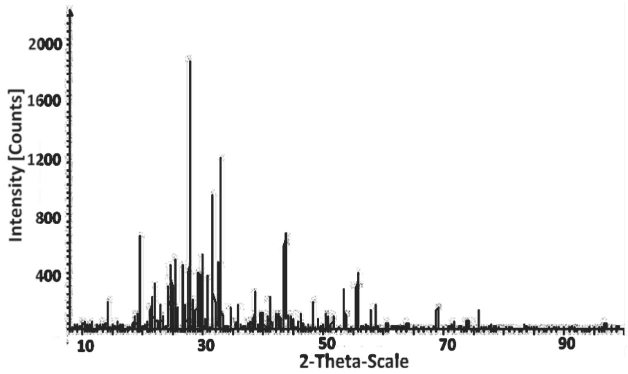


Fig. 1. X-ray diffractions pattern of $YAl_3(BO_3)_4$ powder samples

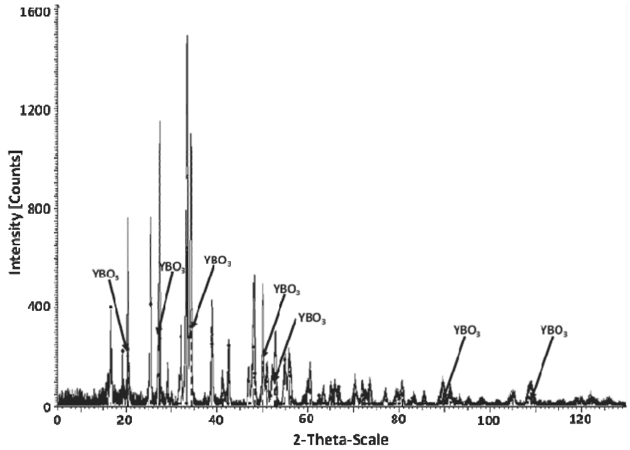


Fig. 2. X-ray diffractions pattern of $YAl_3(BO_3)_4$ powder doped of RE ions

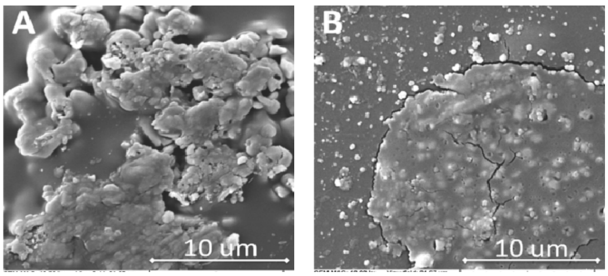
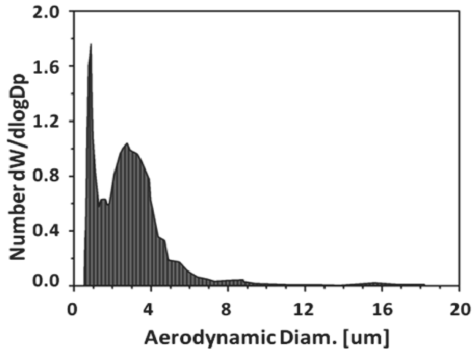


Fig. 3. Scanning electron microscopy images (SEM) of YAB nanopowder: a) nanopowder sample and b) nanopowder suspended in a polymer

Because of that we dispersed a sample in a certain polymer and then put in on a glass plate. After drying, a thin film was received and examined using a scanning electron microscope giving more clear photos (Fig. 3b). To confirm the grain size another measurement was performed. The study was conducted using aerodynamic aerosol analyser method (UVAPS 3314).

The results are shown in Figs. 4a and 4b. The particle size distribution was also measured. The Fig. 4a shows the particles distribution of YAB obtained with use of edetic acid (EDTA) and mannitol, while Fig. 4b shows the distribution of particles for sample of YAB obtained for citric acid and mannitol. Maximum particle size depends on used polymer precursors Fig. 4a shows the maximum at about 500 nm, while Fig. 4b shows the maximum at 3 µm.

a)



b)

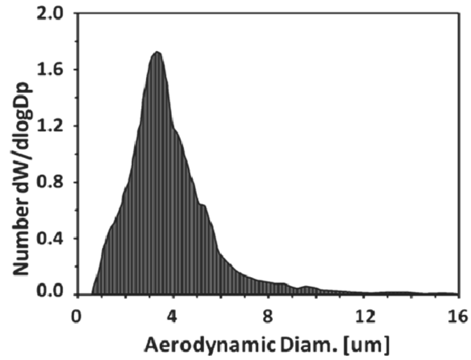


Fig. 4. a) Schematic distribution of the aerodynamic particle YAB undoped obtained on the edetic acid; b) schematic distribution of the aerodynamic diameter particle YAB powder undoped obtained on the citric acid

3.2. Spectral characteristics of YAB doped with cerium and chromium ions

Emission and excited spectra, of doped YAB samples are presented in Figs. 5-8. We used the Edinburgh LS 900 spectrofluorometer (Xenon lamp 450W) for two different samples of YAB doped with cerium and with chromium. The other source of the exciting light was the He-Cd laser (442 nm, 30 mW, Omnichrome). Measurements were made at room temperature to observe visible emission. The samples of YAB:Cr^{3+} and YAB:Ce^{3+} contained 1 at.% of dopants.

Figure 5 shows the emission spectrum for YAB:Cr^{3+} powder excited with laser (442 nm – dotted line) and xenon lamp (415 nm – line). Very narrow and intense peaks can be observed. The maximum emission spectrum exists at 690 nm (observed for YAB:Cr^{3+}). Emission spectrum obtained with the laser is visibly sharper and has separated peaks. Therefore, further studies presented in this paper. Experiment was also conducted for samples of YAB doped with cerium (Fig. 6) and the results were very similar.

However, for samples of YAB:Ce^{3+} (Fig. 6) peaks are wider maximum is located at 578 nm. To compare the results the single crystals of YAB doped with chromium ions were also measured.

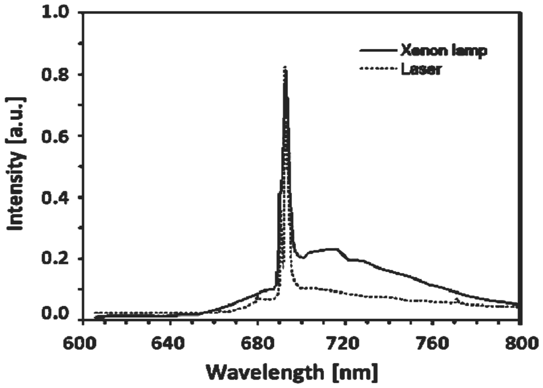


Fig. 5. Emission spectrum nanocrystaline of $YAl_3(BO_3)_4$:Cr^{3+} excited xenon lamp and laser

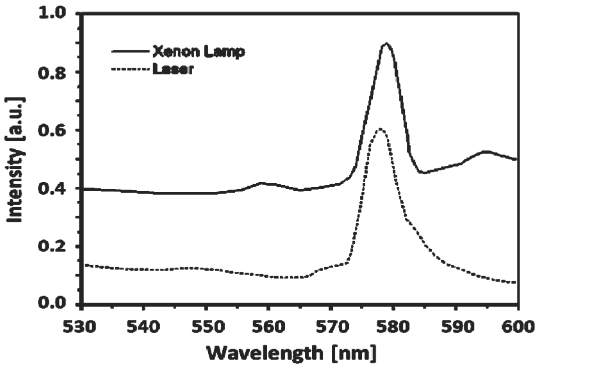


Fig. 6. Emission spectrum nanocrystaline of $YAl_3(BO_3)_4$:Ce^{3+} excited xenon lamp and laser

Comparative emission spectra of nanocrystals (Fig. 7a) and single crystal (Fig. 7b) of YAB:Cr^{3+} were prepared. The maximum emission peaks for both samples are located at the wavelength of about 685 nm.

a) b)

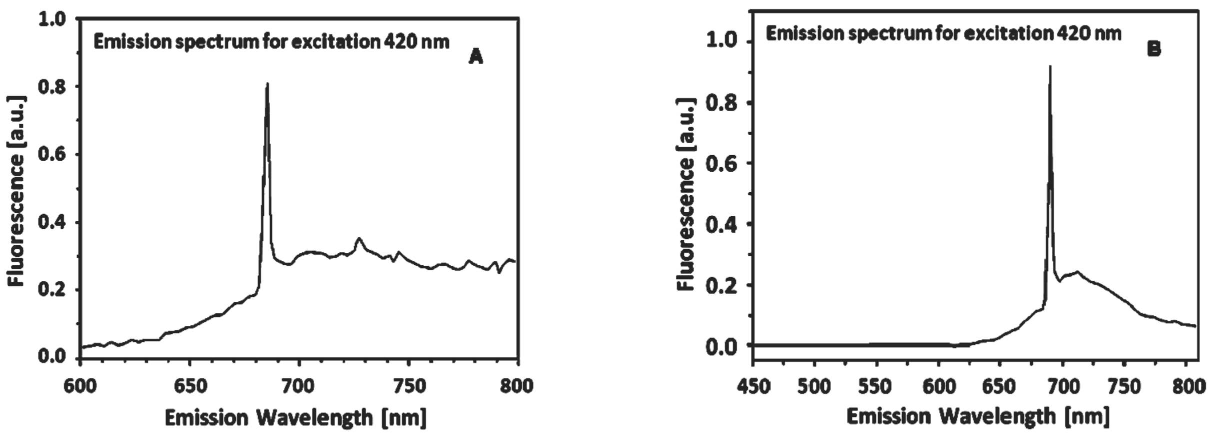


Fig. 7. Emission spectrum of a) YAB:Cr^{3+}1at. % nanopowder; b) YAB:Cr^{3+} 1at.% monocrystal

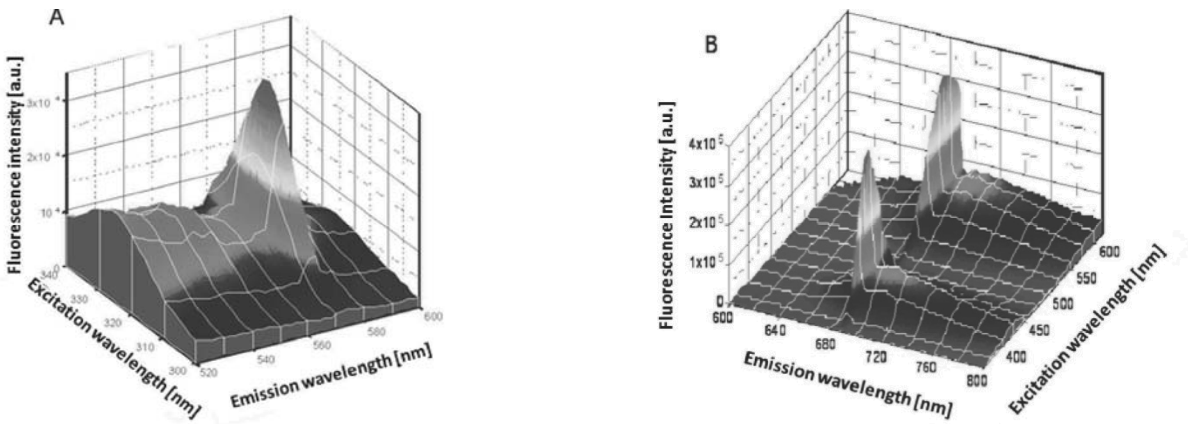


Fig. 8. Three-dimensional excitation emission characteristics a) of YAB: Cr^{3+}1 at.% nanopowder; b) of YAB:Ce^{3+}1at.% nanopowder

The emission intensity for single crystal sample of $YAB:Cr^{3+}$ (Fig. 7b) is higher than for nanocrystal of $YAB:Cr^{3+}$. It is important to remember that between the micrometer and nanometer values of grain there will be differences in light emission intensity. Yan et al. [16] showed that the submicrometer nanopowders are characterized by higher luminescent intensities than nanometer size powders. In fact the submicron particles show higher intensities than the nano particles and probably reduction of the light intensity is caused by the energy traps formation at nanoparticles.

A nanoparticle $YAB:Cr^{3+}$ shows stronger luminescence than $YAB:Ce^{3+}$ cerium ions what is probably dependent on the preparation of the samples. Cerium ions were introduced into the matrices in the form of Ce^{4+}ions and subsequently reduced to Ce^{3+} in the reducing atmosphere. It is most likely that not all the cerium ions were reduced to Ce^{3+}.

For both samples three-dimensional excitation emission (EM-EX) characteristics were measured which are shown in Figs. 8a and 8b. The characteristic plot was obtained by the intersection of three-dimensional matrices of EM-EX. Horizontal lines connect the points with the same emission intensity. The strongest fluorescence in the samples was obtained after excitation with the visible light for of nanocrystalline $YAB:Cr^{3+}$and YAB: Ce^{3+} (around 430 nm and 580 nm) respectively. Reduction of the luminescence intensity is a result of miniaturization of the crystal size which has much larger area, energy traps and more defects than a single crystal.

4. Conclusions

The sol-gel technology opens a route for obtaining of particles with sizes depending on the dispersion medium. Although the reaction is homogeneous and pure phase of borates may cause many problems. It is related to the fact that the reaction conditions favour the formation of second phase YBO_3. This is due to the complexity of the chemistry of borates [16]. The particle size distribution is wide and repeatable. The longer chains polymers were used, the smaller grains could be obtained.

The spectral characteristics for a nanocrystalline of $YAB:Ce^{3+}$, single crystal and nanocrystalline of $YAB:Cr^{+3}$ were presented. The fluorescence intensity for a single crystal is much larger than for nanocrystallines. However, matrices of YAB powder doped with the chromium ions show stronger luminescence than YAB doped with chromium ions. The oxidation state of the cerium ions introduced into the matrices has an influence on the luminescence intensity.

The characterized technology seems to be proper and competitive with conventional methods of obtaining a single crystal on the industrial scale which is very difficult.

Acknowledgements

This paper has been done in 2011 year under financial support of the Polish Ministry of Sciences and Higher Education, Key project POIG. 01.03.01-14-016/08 “New Photonic Materials and their Advanced Applications” and the WAT University Grant PBS 23 827.

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