Studies on Structural, optical and Magnetic properties of Yttrium Aluminum Bromate (YAB) Nanomaterials, prepared at high annealing temperature

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Abstract. In this research, we present structural, photo-luminescence and magnetic properties of the Yttrium Aluminum Borate (YAB) nanomaterial, synthesized by low-cost Sol-gel method in high temperature range. X-ray diffraction (XRD) analysis, shows that crystal structure of YAB is of nanometric size ranging between 38 nm to 47 nm for the annealing temperature above 900°C. Photoluminescence property shows that YAB gives intense Blue light emission in the visible region. High-temperature annealing was found to increase the grain size and enhance the blue luminescence. Vibrating Sample Magnetometer (VSM) shows that coercivity increases while Magnetization and retentivity decreases for YAB nanomaterials for the temperature above 900 degree Celsius. Prepared YAB materials may be useful for LED or related devices.

Keywords: YAB, Chemical method, Nanomaterials, Optical, Magnetic.

1. INTRODUCTION

Yttrium Aluminum Borate, YAl₃(BO₃)₄ (YAB) has been cynosure of intense continuous research among scientist and researchers because of its wide application in various fields of science and technology. Rhombohedral Crystal structure of YAB shows that it belongs to a family of double borate and exhibits a layered structure with a hexagonal lattice within each layer [1]. The yttrium ion is coordinated with six oxygen atoms in a trigonal prismatic site with D₃ symmetry. Aluminum ions occupy the octahedral site (Oh-symmetry). The metal ion is coordinated to three oxygen atoms from the borate top and bottom layers, where the two triangles are slightly rotated against each other. The boron atoms are occupying the C₃ and C₂ symmetry via planar triangular because of the presence of two distinct borate groups such as BO₄ and BO₆ respectively. The shapes of B(1)O₃ and B(2)O₃ atomic groups are equilateral and isosceles triangles respectively[2].YAB lattice provides suitable sites for rare-earth or transition metal ions doping [3]. The lattice parameters of YAB crystal are = b = 9.295 Å, c = 7.243 Å, a = g = 90° and b = 120°. YAB melts incongruently at 1280°C and decomposes into YBO₃ and AlBO₃ [4]. Therefore, it cannot be crystallized from stoichiometric melts.
Fig 1. (a). Yttrium Aluminum Borate YAl₃(BO₃)₄ (YAB) crystal structure (b) Primitive unit cell, (c). Brillouin zone [5]

This borate based YAB is Non Linear optics (NLO) Material having a lot of good properties such as large NLO coefficient, moderate birefringence and good physical and chemical stability. Because of these properties, it can be applicable for products related to national security and defense, data processing, ultrafast optical communication, data storage, optical limiting, logic devices, optical switching, image transmission, and optical computing [6]. The applications can be made in the UV region (260nm to 400 nm) as well as in the visible region (400 nm to 480nm) that are equally important and useful in the various areas of science and technology [7]. The development of the fourth harmonic generation of an Nd-based laser at 266 nm with an average power of 5.05 W was an excellent instance for application of YAB as potential NLO material for UV applications. Other reports suggest that it can also be made as host material for Lasers with cut-off wavelength 300 nm. In the visible region (from 400nm to 700nm wavelength), this borate based YAB also showed efficient performance in both display and lighting applications. This is because it possesses some peculiar physical and chemical properties as compared with other borates. For instance, it has wide optical transparency even towards the short UV range, high optical damage threshold, good thermal & chemical stability, high decomposition temperature (1235°C) and non-hygrosopicity [8]. In addition, YAB showed high coloring index having high refractive index. Therefore, for the LED Light emission, YAB is used as phosphor which may be preferred over the CE³⁺ doped Yttrium Aluminum garnet (YAG) phosphor because YAG has low coloring effect which may damage retina of the eye when anyone sees over the LED Light; As a result, it may damage biological clock of the healthy human being, animal and plant, Also YAG is a lanthanide having low availability in the biosphere. Therefore, study of YAB on high annealing temperature (above 900 degree) is presented in this research, because we have already presented our analysis on the low annealing temperature (below 900 degree) and we got exhilarating result [9].
2. MATERIAL AND METHODS

YAB material was synthesized with Sol-gel auto combustion method (polymeric precursor method). Analytical AR grade chemical having assay greater than 99% were chosen since they have least content of impurity element. The sample was made with combinations of YAB (Yttrium Aluminum Borate) in the proportionate ratio (stoichiometric Ratio) of 1:3:4 for Yttrium, Aluminum, and Borate respectively. For this, 3.4698g/mole of Yttrium Nitrate, 11.2539 g/mole of aluminum Nitrate and 2.4732g/mole of boric acid and 5.7636g/mole of citric acid were taken for material synthesis. Geiger Muller machine was used for weighing synthesis material. Three beakers were taken for this purpose. In the first beaker, aqueous solution of Yttrium Nitrate (3.4697 g/mole), Aluminum Nitrate (11.2530g/mole) and Citric Acid (5.7649g/mole) were mixed in deionized water. In the second beaker, Boric Acid (2.4732g/mole) were dissolved in water. These two solutions of beaker were stirred for some time for complete mixing of making it complete liquid. Then in the third beaker, both beaker solutions were mixed and stirred for some time. Then the sample was placed under reflux for 2 hours for magnetic heating. As a result, gel was formed. Then formed GEL was kept under micro-oven at 90 degree for 12 hrs. All water was evaporated from gel and amorphous solid powder was formed. This solid powder was crushed in mortar pistol, and then complete sample of (around 7gm) powder was formed. Around 1.2 gm of the first sample was kept under heating treatment in muffle furnace for annealing at 900 degree and 1000 degree for four hours. The whole sol-gel process of preparation is shown as graphical abstract in Fig 2.
3. RESULT & DISCUSSION

3.1 XRD analysis:
The XRD analysis were performed for as prepared borate nanomaterial annealed at high temperature of 1000°C using X-ray diffractometer [Model: Bruker D8 Advance, Germany] as shown in figure 3 (a-b). The XRD were analysed using CuKα radiation having wavelength $\lambda=1.5406$ Å in the range of diffraction angle of range between 10°-90°. The analysis shows that at high annealing temperature, pure phase hexagonal symmetry material was formed having all the characteristics peaks. This high annealing temperature is so chosen because during literature review, it was found that other research group has already worked above temperature of 1150 °C for synthesis of borate nanomaterial [10]. The prepared nanomaterial was perfectly indexed with the earlier researcher work having hkl values (002), (010), (012), (110), (014), (112) etc. [11] The sample annealed at 900°C have indexed to pure phase borate nanomaterial [ICDD: 98-002-7931]. The space group found to P63/mmc and space group number 194 and symmetry of material is hexagonal structure. Similarly similar parameters were also evaluated for sample annealed at 1000°C and parameters are reference code is [ICDD: 98-0101-9264]. The space group found to P63/mmc and space group number 194 and symmetry of material is hexagonal structure. Similarly similar parameters were also evaluated for sample annealed at 1000°C and parameters are reference code is [ICDD: 98-0101-9264]. Further structural parameters were evaluated like lattice parameter, cell volume etc. for the pure phase prepared YAB nanomaterial and shown in table-1.

Table 1. Structural parameter analysis

| Materials | Cell parameter | XRD Density (g/cm$^3$) | Cell Volume(cm$^3$) | Crystallite Size |
|-----------|----------------|------------------------|---------------------|-----------------|
|           | a (Å)          | b (Å)                  | c (Å)               |                 |
| YAB 900   | 3.7960         | 3.7960                 | 8.8150              | 4.46            | 38.45 nm |
| YAB 1000  | 3.7780         | 3.7780                 | 8.8140              | 4.50            | 47.67 nm |

The crystallite size was evaluated using Scherer’s formulae and it was found to be approximate 38.45 nm and 47.67 nm [12]. Further detail analysis of crystallite size and lattice strain was calculated using Williamson-Hall plot and it was found to increase from 34.12 nm to 44.78 nm but strain found to decrease from $4.65\times10^{-3}$ to $1.7\times10^{-3}$ as shown in figure 4 (a-b). Thus from above result we conclude that pure phase Yttrium aluminium borate nanoparticles can also be prepared at below 1100°C temperature as in our reported work.

Figure 3(a-b). XRD spectra of YAB annealed at 900°C-1000°C
3.2. FTIR analysis:
The FTIR analysis were carried out to analyse the stretching and de-stretching of functional group present in the prepared material at nanoscale. The Fig 5 shows the FTIR spectrum of Yttrium aluminium borate nanomaterial, synthesized at different annealing temperature. The FTIR spectrum regions of YAB nanomaterial were further shortened to 1600-400 wavenumber (cm\(^{-1}\)) to evaluate the detailed study of functional group. The wavenumber occurring at 461 cm\(^{-1}\), 542 cm\(^{-1}\), 614 cm\(^{-1}\) correspond to the stretching of Y-O (yttrium-Oxygen). Further the vibrations around 707 cm\(^{-1}\), 776 cm\(^{-1}\), lies for the stretching of Al-O (aluminium-oxygen), the wavenumbers at 869, 918, 1064 cm\(^{-1}\), corresponds to the formation of YBO\(_3\) stretching [13-14]. The other stretching have been all illustrated in table 2.

| Sl. No | Wavenumber (cm\(^{-1}\)) | Functional Group |
|-------|--------------------------|------------------|
| 1.    | 1414                     | B-O              |
| 2.    | 1252-1355                | B-O              |
| 3.    | 500                      | B-O-B            |

Thus from data observed from table-2, it can be stated that pure phase yttrium aluminium borate nanoparticles have been successfully synthesized.
3.3 Photoluminescence Measurement (PL)

The Fig 6 shows the PL spectra of yttrium aluminium borate having annealed at temperatures 900°C and 1000°C for 4 hrs respectively. The prominent emission peaks were observed in the range of 405 nm, 435 nm and 457 nm having excitation of radiation of wavelength 365 nm. Further among the characteristics peaks, the most intense peak were noticed to be in the range of 405 nm which may corresponds to the intrinsic defect in the crystal lattice. The characteristic peak occurring at wavelength 435 nm generally corresponds to recombination of electron as other research group have also reported this sort of properties [15]. This property leads to creation of defects and vacancies of oxygen which can be used in variety of applications, which is common in material having tetrahedral and octahedral sites. Lastly the peak occurred in range of 457 nm correspond to blue emission having 3d^5-3d^4 electronic state [16]. The Pl spectra for the materials are almost same but intensity of peaks are higher for material prepared at higher temperature showing size dependent property of Pl emission was observed. The most important highlights of this research is that, all the emission radiation are in visible range, which may support for its applications for LED and related devices [8].

Figure 6. PI spectra of YAB nanoparticle annealed at 900°C and 1000°C temperature.
3.4 Magnetic Measurement:
Magnetic properties of YAB nanomaterial were evaluated using Lakeshore 7400 Vibrating Sample Magnetometer which is been shown in fig 7 (a-b). The measurement was made at room temperature having applied field up to 20000 Oe. The plot shows that with increase in applied field magnetization decreases before acquiring a saturation value. The material shows slight diamagnetic behavior at annealing temperature below 1000°C but after further increase in annealing temperature the behavior of the nanomaterial changes to paramagnetic behavior. This sort of change in properties of nanomaterial may be considered due to low annealing temperature, structural parameters, phase formation and other factors as well. If by the increase of annealing temperature, their paramagnetic behaviors persist then we can say that high annealing temperature YAB nanomaterial should be preferred over low annealing temperature nanomaterial for LED application or any other electrical or photoluminescent material application. At 5000 Oe applied field the magnetization increases for sample annealed at 900°C while at 1000°C, magnetization versus applied field response are different. Such anomalous change may be studied in detail, which is our future research problem. These findings may be the course of future investigation.

![Figure 7 (a-b). Magnetization versus applied field plot of YAB nanoparticle annealed at 900°C and 1000°C temperature.](image)

3.5 Optical Properties (Energy band evaluations)
Indirect band gap energy were evaluate for the prepared YAB nanoparticle, which is been depicted in Fig 8 (a-b) using simple Tauc equation, is given below.

\[
\alpha \cdot h \nu = B \cdot (h \nu - E_g)^n
\]

(12)

Where, constants have usual meaning discussed in earlier research work. We assumed \( n=0.5 \) for the evaluation of indirect band gap. The juncture of the slope of \( (\alpha h \nu)^2 \) versus photo energy \( (h \nu) \) plot, horizontal axis estimates the data of direct band gap, and the juncture of the slope of \( (\alpha h \nu)^{0.5} \) versus \( h \nu \) provides the indirect band gap as in our case. The indirect band gap was found to be 1.33 eV -1.28 eV for sample annealed for 900°C-1000°C. The result shows that band gap is a function of crystallite size which is also explained by bras model of effective mass [17]. Further the calculated band gap is low as compared to ferrite nanoparticles.

\[
E_g^* \approx E_{g}^{bulk} + \frac{\hbar^2 \beta^2}{2e \epsilon_r} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \frac{1.8e^2}{4\hbar \epsilon_0}
\]

Symbol having usual meanings.
This result shows that the observed band gap is very close to energy band gap of GaAs nanomaterial used in the Light Emitting Diode (LED) application, having band energy gap 1.441 ev [18]. If YAB is doped with any transition element like chromium and manganese, then energy band gap of the doped YAB may show better result (white light emission from present deep blue light emission) for which further study and test is required. Increasing or decreasing band gap may play significant role in the production of white LED emission with a low cost synthesis method. Thus the present research finding suggest that prepared YAB materials at Nanoscale may be useful as optical nanomaterials for its applications in LED or related devices.

4. CONCLUSIONS

YAB as optical nanomaterial were prepared successfully using low cost technique. The XRD measurement confirms the formation of pure phase having crystal size ranging between 38 nm to 47 nm at annealing temperature 900-1000 degree for 4 hrs. Williamson-hall plot was used to calculate crystallite size and strain. Magnetic property showed paramagnetic and diamagnetic behavior of the sample under different annealing temperature. We further found that this material possesses luminescent properties in visible range and has shown blue light emission. This material may be a suitable candidate for LED application and related devices. As we increase annealing temperature, particle size is increased but color of nanomaterial remains the same (blue in color). Therefore, we can conclude that doped YAB with transition metal like chromium, manganese or any other may produce white light in a different band gap for which further study and analysis is required to produce lanthanide free warm white light emission. The prepared material may be useful in optical, electronic devices though magnetic behavior may favors for its multifunctional behavior.

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REFERENCES

[1] Peterson GA, Keszler DA, Reynolds TA: Int J Inorganic Mat 2000, 2:101.
[2] Hisashi Yoshida, Kazuhiro Fujikawa, Hiroaki Toyoshima, Shinta Watanabe, Kazuyoshi Ogasawara
   Luminescence properties of YAl$_3$(BO$_3$)$_4$ substituted with Sc$^{3+}$ ions phys. stat. sol. (a) 203, No. 11,
   2701 – 2704 (2006) / DOI 10.1002/pssa.200669563
[3] Akhmetov SF, Akhmetova GL, Kovalenko VS, Leonuyk NI, Pashkova AV: Soviet-Phys Dokl 1978, 23:107
[4] Majchrowski, A., Jaroszewicz, L.R., Cieslik, I. et al. YAl$_3$(BO$_3$)$_4$:TM (TM = Mn, Co, Cr) nanocrystals
   synthesis for laser operated nonlinear optics. J Mater Sci: Mater Electron 24, 1485–1489 (2013).
[5] Reshak, A.H., Auluck, S., Majchrowski, A. et al. Optical second harmonic generation in YAB crystal,
   PMC Phys B 1, 8 (2008) Doi: 10.1186/1754-0429-1-8.
[6] M. Fiebig, J. Phys. D 38, R123 (2005).
[7] S. W. Cheong and M. Mostovoy, Nature Mater. 6, 13 (2007).
[8] Bungal Chima Jamaleiah, Shaik Nayab Rasool, Journal of Molecular Structure 1097 (2015) 161–165.
[9] Bibhuti Bikramaditya, Rakesh Kumar Singh, Nishant Kumar, Material Today Proceedings Accepted
   [Manuscript ID: D-21-05776]
[10] J. Madarasz, E. Beregi, J. Szatitsz, I. Földvari, G. Pokol, J. Therm. Anal. Calorm. 64 (2001) 1059–
    1065.
[11] H. Yang, Z. Ren, Y. Cui, L. Yu, S. Feng, J. Mater. Sci. 41 (2006) 4133–4136.
[12] Nishant Kumar, Rakesh Kumar Singh, Harendra Satyapal, Journal of Materials Science: Materials in
    Electronics (2020) 31:9231–9241.
[13] L.J.Q. Maia, A. Ibanez, L. Ortega, V.R. Mastelaro, A.C. Hernandes, J. Nanopart. Res. 10 (2008) 1251–
    1262.
[14] E. Beregi, A. Watterich, L. Kovacs, J. Madarasz, Vib. Spectrosc. 22 (2000) 169–173.
[15] Makkiyyu Abdullahi Musa, Raba’ah Syahidah Azis, Nurul Huda Osman, Jumiah Hassan, Results in
    Physics 7 (2017) 1135–1142
[16] C. Li, G. Fang, Q. Fu, F. Su, G. Li, X. Wu, X. Zhao, J. Cryst. Growth 292 (2006) 19-25.
[17] An Investigation of TiO2-ZnFe2O4 Nanocomposites for Visible Light Photo catalysis by Jeremy
    Wade, A thesis submitted to Department of Electrical Engineering; College of Engineering,
    University of South Florida, March 24, 2005.
[18] T.E Schlesinger. In Encyclopedia of Material: Science and Technology, 2001.