



SYNTHESIS AND OPTICAL PROPERTIES OF Yb³⁺ doped Li₃Ba₂La₃(MoO₄)₈

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ABSTRACT

Yb³⁺ doped Li₃Ba₂La₃(MoO₄)₈ phosphor was synthesized by combustion method. A pure phase was confirmed by X-ray diffraction pattern. SEM provides the information relating topological features, morphology, phase distribution and crystal structure. Photoluminescence spectra were measured which helps to understand the efficient energy transfer from host to Yb³⁺ ions. An investigation suggests that Yb³⁺ doped Li₃Ba₂La₃(MoO₄)₈ material may regard as potential solid-state laser crystal.

Keywords: SEM, spectral properties, energy transfer, crystal structure.

I. INTRODUCTION

With the rapid progress of high power diode laser, the Yb³⁺ doped laser material has been attracted great interesting [1]. Trivalent ytterbium (Yb³⁺) has only two manifolds in the 4f shell, that is, a ²F_{7/2}ground state and a ²F_{5/2} excited state, with an energy difference between the states of ~10 000 cm⁻¹. In comparison with Nd³⁺ active ion, a typical emission for Yb³⁺ activated phosphors features a fine-structure spectral shape owing to the Stark splitting of the two Yb³⁺manifolds. This simple and unique energy-level structure endows Yb³⁺ with several fascinating optical properties, including no absorption in the visible range, strong absorption near 980 nm (well-suited for InGaAs diode laser emission), and intense emission at 950–1150 nm (²F_{5/2}→²F_{7/2} transition; in the Short Wave Infra Red range i.e. SWIR)[2].

More recently, a new series of disordered Molybdates compounds Li₃Ba₂RE₃(MoO₄)₈ (RE = La-Lu, Y), which belong to the monoclinic system, with the space group C2/c, have emerged as new kinds of laser materials, especially in tunable and ultrafast laser domains [3-10]. The structure of Li₃Ba₂RE₃(MoO₄)₈ can be considered to be derived from the scheelite structure, in which the Ca²⁺ sites are occupied by a statistical mixture of 25% Ba²⁺, 37.5% Li⁺, and 37.5% RE³⁺. Previously, the laser performance of Nd³⁺ doped Li₃Ba₂Gd₃(MoO₄)₈ was reported as a laser material [5,6]. Recently, the spectroscopic properties and laser operations of Yb³⁺ doped Li₃Ba₂Gd₃(MoO₄)₈ and Li₃Ba₂Y₃(MoO₄)₈ were reported[7,8,11]. Li₃Ba₂La₃(MoO₄)₈ crystal is another member of Li₃Ba₂Ln₃(MoO₄)₈ (Ln = La–Lu, Y) family. In present work, the studies are exploring a new Yb³⁺-doped laser host crystal, this paper reports the synthesis and spectroscopic properties of Yb³⁺-doped Li₃Ba₂La₃(MoO₄)₈.

II. METHODS AND MATERIALS

Li₃Ba₂La₃(MoO₄)₈: Yb³⁺(5%) phosphors were synthesized by Combustion reaction. A stoichiometric amount of LiNO₃ (99.9%), Barium Nitrate Ba(NO₃)₂(99.99%), and Ammonium Molybdate (NH₄)₂Mo₇O₂₄ ·4H₂O (99.99%) taken in a mortar pestle. Then various amount equimolar mixture of Urea (NH₂CONH₂) was added to it. Weighing was done on highly precise meter pan balance having accuracy up to four digits. Then Ytterbium Oxide Yb₂O₃ (99.99%) according to molar concentration 5 m% dissolved in Con.HNO₃ was added and heating on magnetic

stirrer to prepare Ytterbium Nitrate then the whole constituent was crushed about 2 hours until pasty mass was formed as most nitrate and urea are hygroscopic and absorb moisture during mixing. The absorption of moisture is not undesirable, on contrary; it helps to form a homogeneous mixture. This mixture was transferred to china crucible and placed in a furnace maintained at temperature 750°C. The mixture is formed in the form of foam with an evolution of gases tremendously. A flame was observed. At the completion of the reaction, the china crucible was removed from the furnace and this sample was crushed in mortar pestle to obtain Yb activated $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} (5%) phosphor of which PL, XRD and SEM characterization were taken.

RESULTS AND DISCUSSION

Fig.1. exhibits the XRD pattern for $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} (5%) phosphor samples prepared by combustion synthesis at room

temperature. **Fig. 2** shows XRD pattern of $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{MoO}_4)_8$ (No. JCPDS 77- 0830) which was used as a reference as to the best of our knowledge no reference for Yb^{3+} compound has been published yet. It can be seen that diffraction peaks of the as-prepared phosphor are consistent with standard data of $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{MoO}_4)_8$ (No. JCPDS 77- 0830). The peaks in the XRD spectra are sharp and intense proving that a highly crystalline single-phase of $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$ phosphors with the monoclinic structure of space group C2/c was successfully synthesized by combustion synthesis is benefits for high luminescence.[12] The particle size of the product is calculated from a strong peak (131) according to the Debye-Scherrer's equation,

$$D = 0.89 \lambda / \beta \cos \theta$$

Where D is the average grain size, λ represents Cu K α wavelength 0.1542 nm and β is the half-width at a full maximum of the peak at Bragg's angle θ .

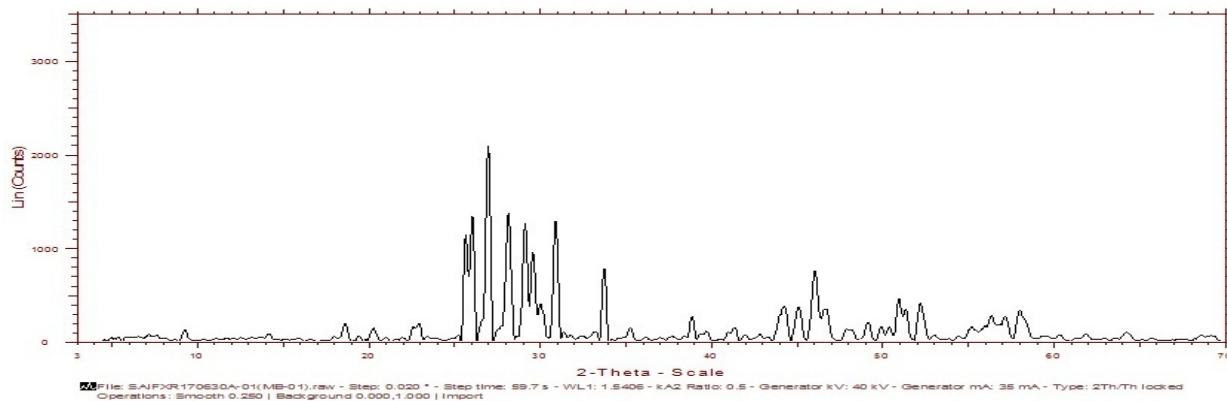


Fig. 1. X- ray diffraction for $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} (5%) phosphor

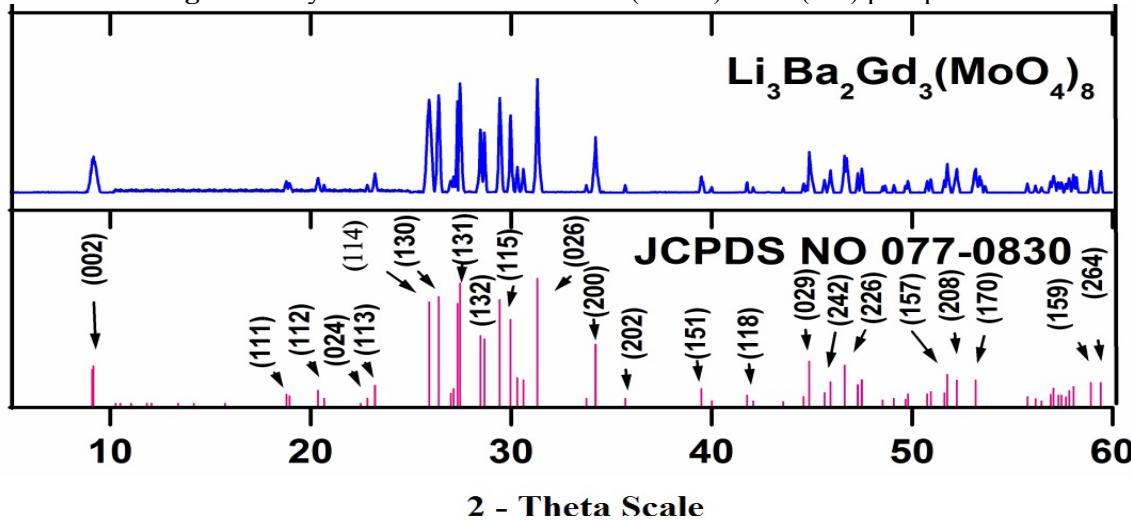


Fig.2. X-ray diffraction pattern of $\text{Li}_3\text{Ba}_2\text{Gd}_3(\text{MoO}_4)_8$ (No. JCPDS 77- 0830)

The morphology of the $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} (5%) phosphor powder was inspected by taking SEM pictures. The obtained SEM images are depicted in **Fig.3**. The phosphor contains well-crystallized particles with small ball morphology. The morphologies show rather large agglomerated particles (2–5 μm) with irregular shape and surrounded

by smaller particles. The obtained relatively large particles at rather low sintering temperature can be explained by high Li content in the structure, which promotes particle growth [7, 13, and 14]. The particle morphology and low melting point of Molybdates are suitable for laser ceramics preparations

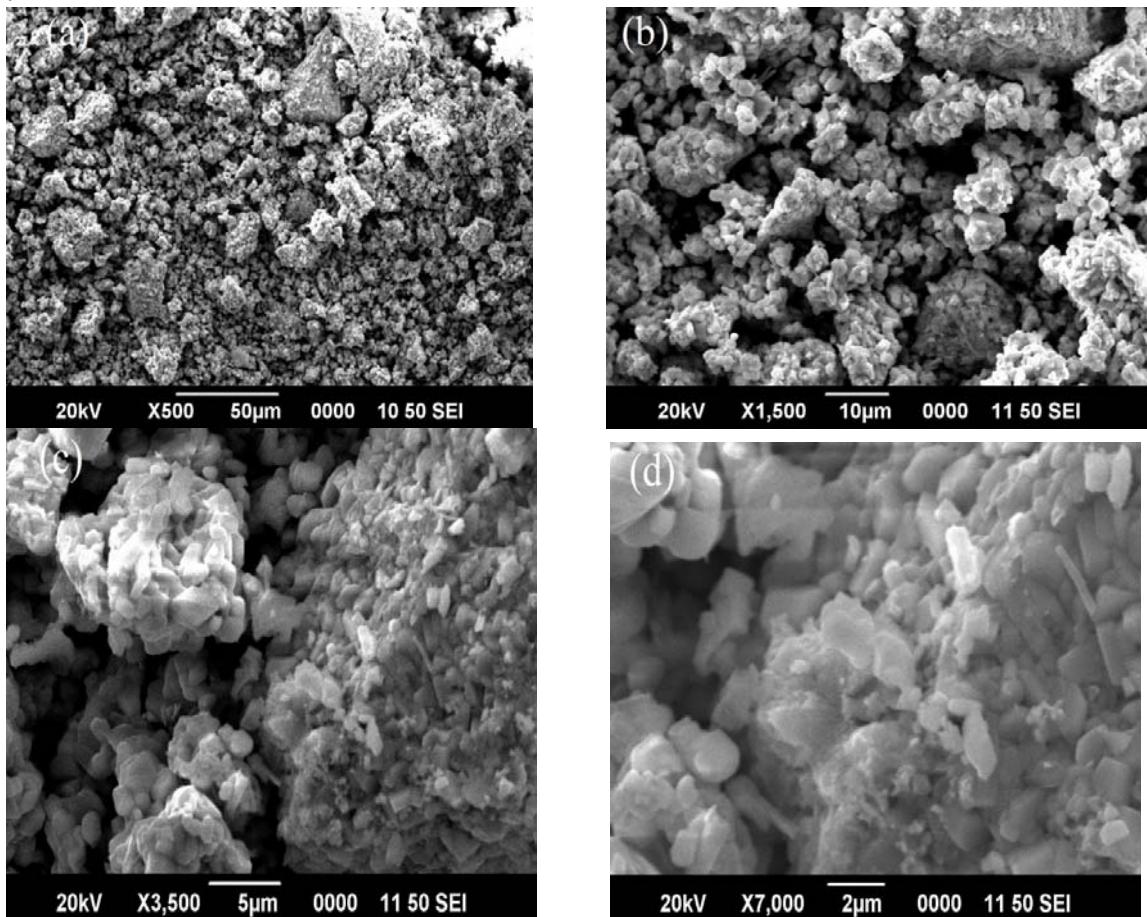


Fig3. SEM pictures of $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} (5%) phosphor under magnification of (a) $\times 500$ and (b) $\times 1,500$; (c) $\times 3,500$ and (d) $\times 7,000$

Fig. 4.(a) shows the excitation spectrum (monitoring 985 nm emission) covers only the UV spectral region from 200 to 400 nm (200 nm is the measurement limit of our spectrofluorometer). It can be seen clearly that the excitation spectrum consists of a strong and broadband from 200 to 400 nm with a maximum at about 297 nm and this is the charge-transfer band (CTB) ascribed to the host. The band located between 200 and 400 nm can be attributed to the charge transfer (CT) from $[\text{MoO}_4]^{2-}$ groups to Yb^{3+} . The high-energy side (<250 nm) of the excitation spectrum may be assigned to the fundamental absorption edge of the host, while the excitation shoulder on the

low-energy side (250–400 nm) is attributed to the absorption of Charge transfers, which can efficiently transfer excitation energy to the $^2\text{F}_{5/2}$ emitting states, followed by the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition.

Fig. 4. (b) shows the normalized photoluminescence emission of $\text{Li}_3\text{Ba}_2\text{La}_3(\text{MoO}_4)_8$: Yb^{3+} phosphor at room temperature. Under the excitation of 300 nm light, the material exhibits a broad and intense photoluminescence extending from 900 to 1100, featuring a fine spectral structure with four peaks at 969 nm, 985 nm, 1001 nm and 1018 nm which correspond to different optical transitions between the Stark levels of

the $^2F_{5/2}$ and $^2F_{7/2}$ states. The emission bands centered at 969 nm, 985 nm, 1001 nm and 1018 nm corresponds to the (0)-(2'), (0)-(1'), (0)-(0') and (1)-(0') transitions respectively, where number (0) and (1) (in the order of increasing energy) are labeled as sublevels of the $^2F_{7/2}$ ground state and number(0'), (1') and(2') are labeled as sublevels of $^2F_{5/2}$ excited state respectively[10,15]. The disordered crystalline environment of Yb³⁺ is reflected in a broad zero-line absorption, F (0) → F (0'), with a full width at half maximum of FWHM=19 cm⁻¹.

The sequence of Yb³⁺ energy levels has been established as $^2F_{7/2}=0$, 223, 353, 460 cm⁻¹, and $^2F_{5/2}=10248$, 10413 and 10634 cm⁻¹. This gives a ratio of the partition functions of the upper and lower Yb³⁺ multiplets close to unity. The energy levels of Li₃Ba₂La₃(MoO₄)₈: Yb³⁺crystal is very similar to that of Yb³⁺: Li₃Ba₂Gd₃(MoO₄)₈ crystal [6]. With reference available, it can be seen that absorption and emission cross section larger for Li₃Ba₂La₃(MoO₄)₈: Yb³⁺ [11].

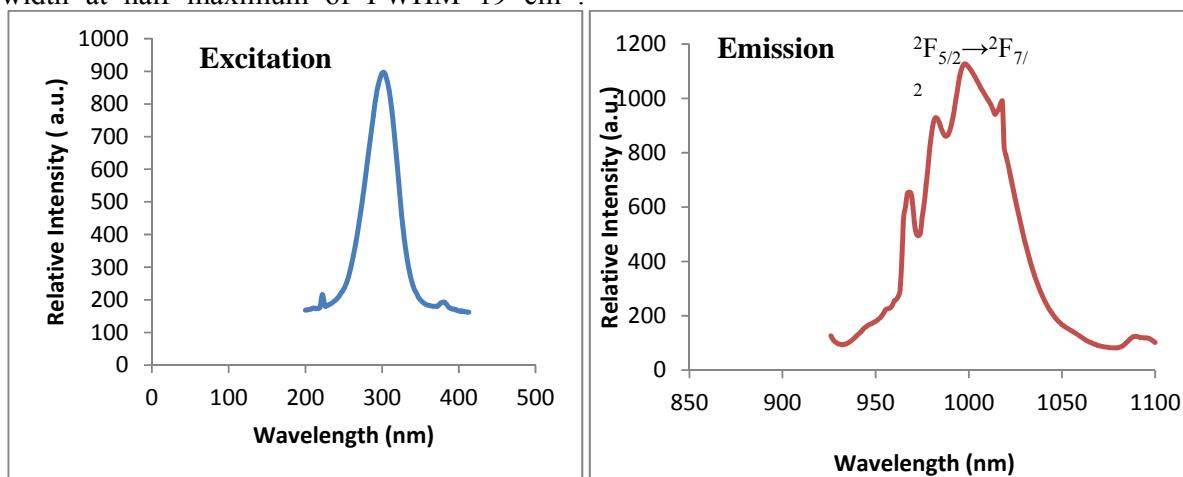


Fig. 4. Excitation (left) and emission (right) spectra of Li₃Ba₂La₃(MoO₄)₈: Yb³⁺(5%) phosphor.

IV. CONCLUSIONS

Li₃Ba₂La₃(MoO₄)₈: Yb³⁺(5%) phosphors were synthesized by Combustion reaction. It can be seen that diffraction peaks of the as-prepared phosphor are consistent with standard data of Li₃Ba₂Gd₃(MoO₄)₈ (No. JCPDS 77- 0830). The band located between 200 and 400 nm can be attributed to the charge transfer (CT) from [MoO₄]²⁻ groups to Yb³⁺. The energy levels of Li₃Ba₂La₃(MoO₄)₈: Yb³⁺crystal is very similar to that of Yb³⁺: Li₃Ba₂Gd₃(MoO₄)₈crystal. It can be seen that absorption and emission cross section larger for Li₃Ba₂La₃(MoO₄)₈: Yb³⁺, Therefore, this phosphor is a promising candidate for the application as a potential solid-state laser similarly for laser ceramics preparations.

V. REFERENCES

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