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Infrared to infrared upconversion emission in Pr^{3+}/Yb^{3+} co-doped La_2O_3 and $La(OH)_3$ nano-phosphors: A comparative study

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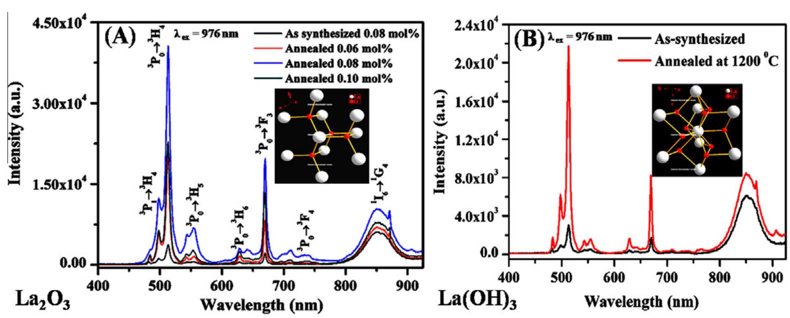
HIGHLIGHTS

- Yb^{3+}, Pr^{3+} co-doped La_2O_3 and $La(OH)_3$ nano-phosphors have been synthesized through solution combustion.
- The structural morphologies are seen to be different in two cases.
- Broad intense infrared emission observed on 976 nm laser excitation.
- Emission intensity enhances on annealing in all cases.
- $La(OH)_3$ is less toxic compared to La_2O_3 and is biocompatible.

GRAPHICAL ABSTRACT



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ABSTRACT

The Pr^{3+}/Yb^{3+} co-doped La_2O_3 and $La(OH)_3$ nano-phosphors have been synthesized through solution combustion method. The structure and morphology of the samples have been studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The physical and optical properties of the samples have been measured and compared. A broad intense infrared emission centered at 850 nm due to $^1I_6 \rightarrow {}^1G_4$ transition along with sharp green emission centerd at 513 nm due to $^3P_0 \rightarrow {}^3H_4$ transition are observed on excitation with 976 nm laser. The emission intensity of Pr^{3+} is optimized with concentration and it is maximum at 0.08 mol%. The annealed samples are found to be more crystalline and emit larger photoluminescence due to removal of quenching centers. The power dependent study of green upconversion emission indicates the involvement of two photons. The phosphor in $La(OH)_3$ phase is more stable though the photoluminescence emission is slightly weak. $La(OH)_3$ is less toxic compared to La_2O_3 and is biocompatible. It generates more heat and can be used in biothermal treatment.

Introduction

Rare earth doped nano-phosphors are noble luminescent materials due to its fascinating optical characteristics. These materials have potential applications in various fields such as display devices, cathode ray tubes, televisions, medical diagnostics and markers [1–11]. The rare earth ions in triply ionized state have large number of meta-stable long lived excited states, which play important role in these applications. They give efficient up and downconversion emissions due to 4f–4f and 4f5d–4f electronic transitions. Most of the earlier work based on upconversion process report a conversion of infrared light to visible or visible to ultraviolet (UV) light [12–18]. Only in few reports the upconversion in infrared to infrared regions have been observed [12,16,19]. Infrared to infrared upconversion emission have been studied by the several workers [20–22]. Since the study on infrared to infrared upconversion is very limited, therefore, it needs further attention.

The Pr^{3+} ion has distinguished features of transitions in blue [12–14,16,23,24], green [12,13,17,18,23], red [4,12,15,25,26] and infrared regions [12,16,19], which are strongly host dependent.

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In fact, Pr^{3+} ion is known for its strong blue emission but in special cases strong green, red and infrared emissions have also been observed. Pr^{3+} ion absorbs infrared 976 nm radiation weakly, which results poor fluorescence emission intensity. However, the presence of Yb^{3+} traces enhances the emission intensity significantly [12–18]. This occurs because the Yb^{3+} has very large absorption cross section for 976 nm radiation, which easily transfers the absorbed energy to Pr^{3+} ions through different channels.

Another part of a phosphor is the host material, which also plays an important role in strong upconversion emissions. Normally smaller the phonon frequency of host material larger will be the upconversion emission intensity. The luminescence spectrum of Pr^{3+} ion has been reported by different worker in various hosts [12–19,23–29]. Thus, Choi et al. have reported the luminescence properties of $SrTiO_3$:Pr^{3+}, Al^{3+} phosphor prepared by glycolate method and compared the photoluminescence efficiency of this with the same phosphor prepared using other synthesis routes [15]. Bluiett et al. have reported the energy transfer mechanisms in Yb, Pr:KPb_2Cl_5 for mid-infrared laser applications [28]. They have discussed the direct energy transfer between $Yb^{3+} \rightarrow Pr^{3+}$ and, $Yb^{3+} \rightarrow Yb^{3+}$ energy migration to distant Pr^{3+} ions, which is highly sensitive to donor and acceptor ions concentration. The concentration dependent near infrared quantum cutting in $NaYF_4$:Pr^{3+}, Yb^{3+} phosphor has been studied by Chen et al. [29]. They have demonstrated its application as a downconverting layer, which is placed on the crystalline solar cell panels to dissipate the thermal loss.

Recently, Li et al. have studied the synthesis and luminescence properties of Ho^{3+} ions in La_2O_3 and $La(OH)_3$ hosts and reported the formation of nano-rods in these host materials [30]. It was marked that La_2O_3 is a suitable host with phonon frequency ($\sim$400 cm^{-1}), which gives very intense emission when an activator is doped into it. However, La_2O_3 is highly hygroscopic in nature and it absorbs the moisture from environment at room temperature and finally converts to $La(OH)_3$. It is, therefore, always a point of confusion about the phase of the host when one uses La_2O_3 as host. $La(OH)_3$ has also been reported as a good host and has wide applications in various fields such as superconductive, electrode, ceramic, catalyst and sorbent materials [31–33]. This motivated us to take La_2O_3 as well as $La(OH)_3$ as host materials separately and to study their comparative structural and optical properties in detail. We observe broad infrared and sharp green emissions when Pr^{3+} and Yb^{3+} ions are co-doped in the two host materials.

In this article, we report Pr^{3+}/Yb^{3+} co-doped La_2O_3 and $La(OH)_3$ nano-phosphors synthesized through solution combustion method. The XRD and TEM measurements have been carried out in order to understand their structural and morphological properties. The FTIR spectra of the annealed samples show the vibrational features in two cases. The photoluminescence spectra of the as-synthesized and the annealed samples have been measured using 976 nm laser excitation and compared to each other. A broad intense infrared to infrared upconversion emission has been observed along with sharp green and red emissions in two cases. A power dependence study has been performed to identify the number of photons involved in the upconversion process. The emissions thus observed are discussed using schematic energy level diagram.

Experimental

The Pr^{3+}/Yb^{3+} co-doped nano-phosphor samples were synthesized through solution combustion method. La_2O_3, Yb_2O_3 and Pr_6O_{11} were used as starting materials and urea was used as the reducing agent/organic fuel for combustion. The compositions used were:

$$(100 - x - y)La_2O_3 + xYb_2O_3 + yPr_6O_{11}$$

where x was fixed at 3.0 mol% while y was made to vary as 0.06, 0.08 and 0.10 mol%. The starting materials were taken in their stoichiometric ratios and dissolved in 5 ml of nitric acid. The solution was then diluted using de-ionized water. Urea was then added to it and stirred in a beaker at 60 °C to get a homogeneous transparent solution with no visible residue. As the water content in the solution was reduced, the solution turned into a transparent gel. The gel thus obtained was placed in a closed furnace maintained at a fixed temperature ($\sim$700 °C) for combustion. During combustion lots of gases (CO_2, N_2, etc.) were released from the gel material as a result of exothermic reaction.

The white fluffy powder thus obtained was grinded into fine powder. This is termed as the as-synthesized sample. These macroscopic particles are composed of large number of tiny agglomerated nano-crystals. The as-synthesized sample was taken in batches and annealed at higher temperatures. The samples annealed at high temperatures resulted the removal of optical quenching centers and an increase in particle size, which enhance the fluorescence intensity. The powder was found to give broad infrared and sharp green emissions. The same sample was left at room temperature for 1 day. As a result, La_2O_3 absorbed moisture from atmosphere and converted into $La(OH)_3$.

$$La_2O_3 + 3H_2O \rightarrow 2La(OH)_3$$

The fluorescence intensity of Pr^{3+} in this condition was found to be reduced slightly. The structure of the samples in two cases was found to be different from each other. The XRD measurements confirmed that the host in the second case is $La(OH)_3$ instead of La_2O_3.

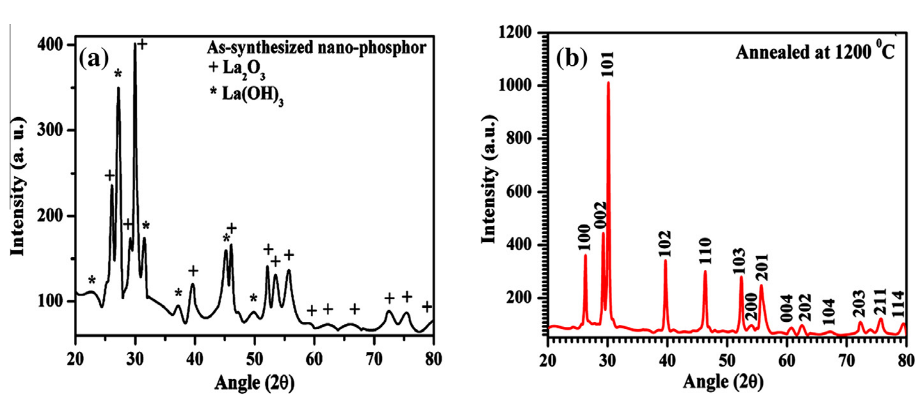

Fig. 1. XRD patterns of the (a) as-synthesized and (b) annealed (at 1200 °C/5 h) Pr^{3+}/Yb^{3+} co-doped La_2O_3 nano-phosphor samples.