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Original Article

Single step thermal treatment synthesis and characterization of lithium tetraborate nanophosphor

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ABSTRACT

This study includes the synthesis of nano-sized lithium tetraborate by an innovative single step thermal treatment method and characterization of the products. The heating temperature for the synthesis was varied between 200 and 850 °C with the retention time of 2 h. Polyvinyl pyrrolidone (PVP) with different concentrations was used as surfactant. Characterization of the samples was achieved by thermogravimetric analysis (TGA), derivative thermogravimetry analysis (DTG), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM) techniques and UV–vis spectroscopy. Thermal analysis of initial solution allowed the optimization of the heat treatment program and showed that the thermal stability of samples is started at 460 °C. FT-IR, XRD and TEM results proved the formation of pure nano-crystalline lithium tetraborate at temperature between 460 and 750 °C. Furthermore, the band gap investigation was performed using UV–vis spectra in the presence of different concentrations of PVP and in variety of calcination temperatures. The estimated optical bandgap was found to be between 5.2 and 6.2 eV.

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1. Introduction

Lithium tetraborate (LTB) has been a scientific focus since 1960s by its courtesy of the thermoluminescence property and potential application as versatile radiation detectors and dosimeters. In addition to X-ray and γ-ray radiation, lithium borate based dosimeters have an additional advantage of being sensitive to neutron radiation due to the presence of ^{6}Li and ^{10}B nuclei with large capture cross-sections for thermal neutrons [1–3]. Moreover, lithium tetraborate is an acousto-optical and optoelectronic material widely used in surface acoustic wave apparatuses, in sensor sectors and in laser technology owing to its non-linear optical characteristics in the ultraviolet region and its transparency down to 160 nm [1,4,5].

Even though, LTB was studied as an interesting material over the few past decades, the topic is open for extensive research to obtain this material in nano-scale size. The ultrafine structures containing 10^{-9} m grain size or an average phase are categorized as nanostructured materials (NSMs) [6]. At the moment, in a wider context of the phrase, any material that having grains or clusters less than 100 nm, or layers or filaments of that dimension, can be characterized as "nanostructured" [7]. The consideration to these substances has been motivated by the concept that, containing the small size of particle, grain, or phase and the high surface-to-volume ratio, these materials are assumed to display unrivaled optical, mechanical, magnetic, and electronic properties [8]. The properties of NSMs related to the consecutive four widespread microstructural features; (1) ultrafine grain size and size distribution (<100 nm), (2) the chemical compound of the fundamental phases, (3) the existence of interfaces, more particularly, grain boundaries, heterophase interfaces, or the free surface, and (4) interplay between the basic domains. The existence and interaction of these four features principally assign the unique properties of NSMs.

In nanoscale materials, a diversity of size-related factors can be integrated by controlling the sizes of the basic components during synthetic procedure [9].

Since, nanoparticles are small and thermodynamically tend to minimize their energy by formation of agglomerates in order to reach stable state, wherein the surface to volume ratio is minimized [10], so it is very important to prevent the nanoparticles from aggregation with other nanoparticles to make use of their properties in nanoscale. There are several capping materials for avoiding agglomeration such as organic ligand or inorganic surfactant reagents that can be used during synthesis process. Different types of polymers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyvinyl chloride (PVC) can be effectively applied to stabilize nanoparticles. Besides the type of the stabilizer as capping material, its concentration has also an important impact on their stability during their synthesis procedure [11]. Other important factors of a polymer to act as a good capping material are their molecular weight, their ability to produce large chain ions in solution, and their solubility in water [12].

The present study reports synthesis of LTB nanophosphors by innovative single step thermal treatment method in the presence of PVP (MW = 58,000) as a capping agent. Regarding the thermal method selected for synthesizing nanoparticles, thermal stability of the sample was considered. So, the influence of the PVP concentration and various calcination temperatures on the thermal stability, phase transition, size, morphology and optical bandgap of LTB nanophosphor are investigated.

2. Experimental

The starting materials for synthesis of LTB nanoparticles was lithium carbonate (Li_2CO_3) and boric acid (H_3BO_3) as lithium and boron sources respectively, and PVP (MW = 58,000) as a surfactant agent. Lithium carbonate, boric acid, and PVP were purchased from Sigma–Aldrich. All chemicals are analytical grade products and used without further purification.

In a typical preparation, 0.0058 mol of lithium carbonate and 0.024 mol of boric acid were added to 20 ml deionized water including PVP. In order to find the optimum concentration of PVP, a variety of its molar ratios of 0.009, 0.018, and 0.027 were examined. The master mixture was stirred for 1 h at 60 °C. To control the structure and size of nanoparticles, the stoichiometry and solubility of the precursors were considered [13]. The solution had a pH of 8.09 measured by means of a glass electrode. To achieve homogenous and monodisperse nanoparticles the temperature was optimized through the main stages of the synthesis process. The final solution was assigned to slow separation nucleation based on single step thermal treatment method, which is basically credited of Pechini method [14]. Besides particle size and morphology control, this method leads to a more precise stoichiometry [14–16]. Before the heat treatment, no precipitation was observed. The solution was sintered at different temperatures from 200 to 850 °C for 2 h to let the removing of organic content, crystallization of nanoparticles, and determining the optimum sintering temperature. The obtained solid cake was ground and sieved through 200 and 100 micron mesh to reduce the particle sizes close to the crystalline sizes.

The characterizations of the prepared LTB nanoparticles were conducted using various techniques to explore parameters of interest. Thermal analysis of LTB was investigated by thermogravimetric analysis (TGA), derivative thermogravimetry analysis (DTG) and differential scanning calorimetry (DSC) using a Perkin Elmer Thermal Analyzer model TGA7/DTA7 and a Mettler-Toledo DSC 822e model differential scanning calorimeter in the presence of N_2 with 10 °C/min heating rate from room temperature to 1000 °C to optimize the heat treatment program and determine the thermal stability of samples. Fourier transform infrared spectroscopy (FT-IR) was used to study the chemical composition of calcined samples at different temperatures using Perkin Elmer Spectrum 1650. The crystal phase and cell parameters of prepared samples were determined by X-ray diffraction (XRD) technique using Shimadzu 6000 diffractometer utilizing Cu Kα (0.154 nm) radiation. The morphology and average particle size of the nanocrystalline powder were evaluated using transmission electron microscopy (TEM) by JEOL 2010F UHR operating at an accelerating voltage of 200 kV. The average size and size distribution of nanoparticles were determined by Java-based image processing program image J. The optical properties of