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Studies on terbium doped apatite phosphors prepared by precipitation under microwave conditions

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ABSTRACT

In this study we present our first attempts to obtain silicate apatite phosphors by precipitation with NaOH under microwave conditions. Y and La precursors fired at different temperatures (800 °C÷1400 °C) led to phosphors with hexagonal apatite structure belonging to the space group $P_{63/m}$ and with crystallites size up to 105 nm. The structure and chemical composition of samples were evaluated based on FTIR, XRD and ICP-OES while the morphology, surface state and porosity were revealed using SEM and BET investigations. The impact of the firing temperature on the purity phase, crystalline order degree, crystallites size and luminescent properties of the apatite phosphors are discussed. It was found that the nature of rare earth (Y^{3+} or La^{3+}) same as the incorporation degree of activator (Tb^{3+}) is responsible for the apatites green - turquoise emission. ICP-OES measurements show that the Tb^{3+} amount incorporated in the apatite lattice increase with firing temperature and is lower in La-phosphors compared with Y-phosphors. The $^5D_4$–$^7F_5$ transition observed in the green spectral domain was dominant in Y- phosphors while $^5D_3$-$^7F_{6,5,4}$ transitions from blue spectral region was dominant in La-phosphors. The chromatic coordinates shifts from green to turquoise with firing temperature and depends on the excitation radiation, indicating the applicative potential of these phosphors in display screens for solid-state lighting applications.

1. Introduction

Compounds belonging to the apatite structural family are more and more researched as effective host lattice due to their chemical and thermal stability. Apatite compounds crystallizes in hexagonal system (space group $P63/m$, $Z = 2$) with general chemical formula of $A_{10}[XO_4]_6Z_2$. In this formulation, A represents divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}); XO_4 is a tetrahedral group (where X = P, V, As, Si, Ge) and Z can be a variety of anions (Cl^-, F^-, O^{2-}, OH^-) [1–3]. Rare earth (La^{3+}, Y^{3+}, Gd^{3+}) or alkali metal ions (Na^+, K^+, Li^+) also can occupy the A site with isomorphic substitution [4–6]. With such a wide range of substitutional possibilities, there is a great potential to design new phosphors and to optimize their luminescent properties. The substitution of elements in the apatite structure, usually alter the coordination environments of the activators, changing the photoluminescent properties [7]. Recently, a large variety of new apatite compositions have been obtained by cationic substitution either at A site or X site of which we mention: $NaY_9(SiO_4)_6O_2$ [8], $Ca_5La_5(SiO_4)_3(PO_4)_3O_2$ [9], $Sr_3LaNa(PO_4)_2SiO_4$ [10] or $Sr_2La_8(SiO_4)_6O_2$ [11]. The doping of apatite host lattices with rare earths (Eu, Tb, Ce, Dy) and/or transitional ions (Bi, Mn) generate luminescence that can be changed from red [12], blue [13], green [14] to pinks, turquoises or whites tones [15,16]. As a result, apatite type phosphors become good candidates in display devices and white-light emitting diodes (WLEDs) for solid-state lighting applications [16,17].

Preparation of micro or nanostructured apatite materials to fulfill the technical requirements imposed by the applicative domain (i.e. high crystallinity degree, phase purity, spherical morphology, uniform particle size, high luminescence) is not an easy task. A rigorous control of the synthesis parameters (i.e. pH, reagents concentrations, reaction time, temperature etc) is needed in order to obtain phosphors with desired composition and targeted properties [17–19]. Moreover, choosing an appropriate method can significantly determine the morphology, structure and optical properties of material. For example, microrod, microfiber and microbelt like apatites were prepared by sol-gel or electrospinning [9,20].

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The most commonly used method for the synthesis of micro-sized apatites (~5–20 μm) is the solid state reaction even if it requires high temperature (>1500 °C), long processing time (>10 h), reducing firing atmosphere, repeated milling and washing stages [21–23]. In addition, this method does not allow controlling the uniformity of the particles and the phase purity of the final product. Several other low-temperature synthesis methods were suggested as alternatives to high-temperature solid state reaction, such as: precipitation, hydrothermal, Pechini, or sol–gel [24–27]. The literature survey revealed limited information regarding the synthesis of silicate apatite phosphors by precipitation technique. Most of the studies are focused on silicate apatites as electrolytic material in solid oxide fuel cell (SOFC) [28–30]. For example, Yang and co-authors describes the synthesis of un-doped lanthanum silicates by co-precipitation with ammonia in presence of polyethylene glycol as dispersant to prevent particle agglomeration [28]. A carbonate precipitation combined with an azeotropic distillation process was reported by Yao and co-workers [29]. Recently, a novel co-precipitation method, based on chemical reaction between La(NO$_3$)$_3$ and Na$_2$SiO$_3$ was reported to synthesize apatite type lanthanum silicates for SOFC [30]. Literature does not report the use of microwave for the synthesis of silicate apatite phosphors although the use of microwave radiation for synthesis of inorganic compounds increased rapidly over the past years. Several interesting reviews on microwave-assisted synthesis of materials have been published [31–33].

In this paper, our aim is to synthesis, for the first time, apatite type phosphors using the microwave irradiation during the entire process of precipitation (formation of precipitate and maturation) in order to bring improvements on the structural and luminescent characteristics of apatite powders. Microwave irradiation can have a positive impact on the morpho - structural and luminescent characteristics of the apatite, providing high heating rates, selective heating, higher yields and reduced secondary reactions.

The novelty of this study brings together the advantages of both microwave irradiation and simultaneous addition of reagents with a controlled flow during the precipitation which is important with respect to the quality of the precursor and the final product. New aspects regarding the effect of firing temperature, nature of rare earth (Y^{3+}, La^{3+}) and incorporation degree of activator (Tb^{3+}) on morpho - structural and luminescent properties of phosphors were discussed in detail.

2. Material and methods

2.1. Materials

The synthesis of yttrium silicate apatite phosphors was done by precipitation under microwave conditions. The starting materials used for the phosphor synthesis are: nitric acid (65% Alfa Aesar); yttrium oxide (99.9%, Alfa Aesar), lanthanum oxide (99.9%, Alfa Aesar), calcium nitrate tetrahydrate (99.0%, Alfa Aesar), tetra ethilortosilicate (97% Alfa Aesar) as components for host lattice, terbium nitrate penta-hydrate (99.998%, Alfa Aesar) as activator sources; and sodium hydroxide (98%, Lachema) as precipitating agent. The amount of reactants was calculated to obtain phosphors with general formula $Ca_2RE_{7.88}Tb_{0.12}(SiO_4)_6O_2$ (RE = Y or La).

2.2. Synthesis procedure

The synthesis of apatite phosphors was accomplished through three stages namely: (1) precipitation of precursors, (2) thermal treatment of precursors and (3) conditioning of the fired mixture.

For start, metallic nitrate solution was prepared by dissolving proper amounts of Y_2O_3 or La_2O_3 in nitric acid followed by addition of calcium and terbium nitrates salts in order to achieve a molar

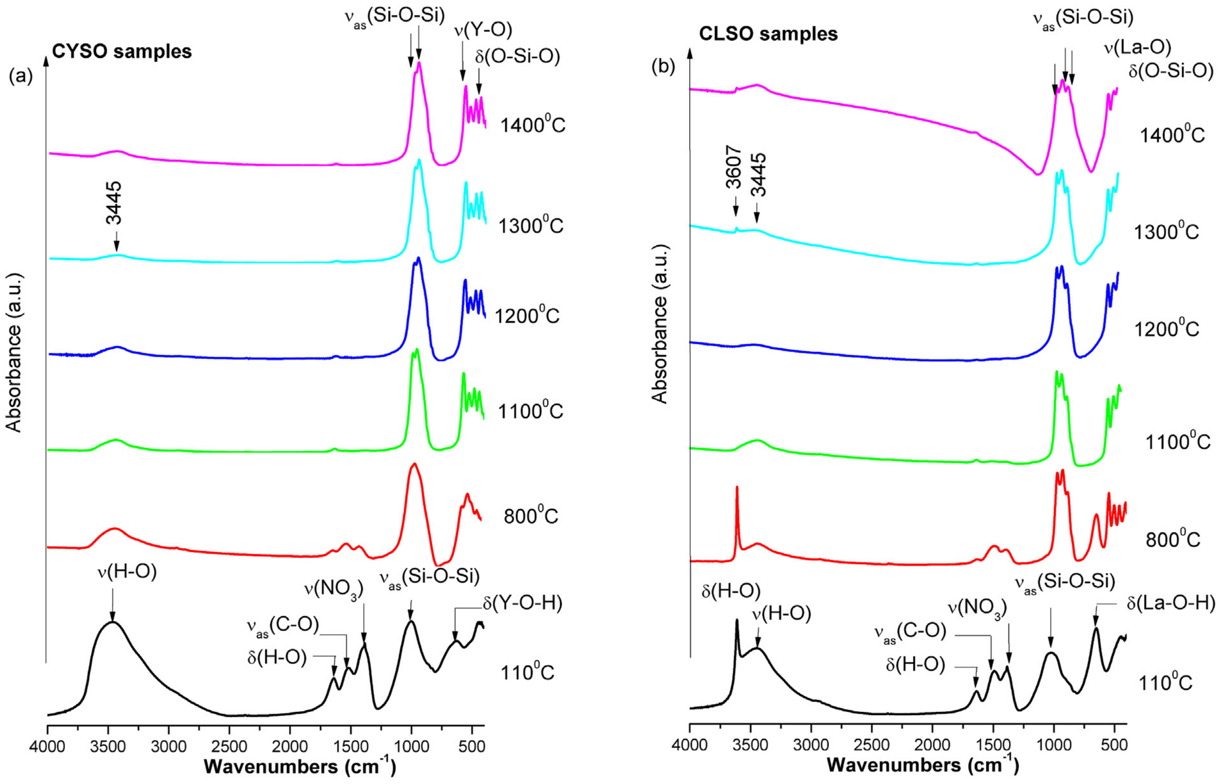

Fig. 1. FTIR spectra of CYSO (a) and CLSO (b) samples fired at different firing temperatures.