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Investigation of oxygen vacancy and photoluminescence in calcium tungstate nanophosphors with different particle sizes

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ABSTRACT

Calcium tungstate ($CaWO_4$) nanophosphors with the particle sizes from 35 to 90 nm were synthesized by a hydrothermal process through exactly controlling the pre-treated conditions. The influence of particle size on oxygen vacancy and photoluminescence properties in $CaWO_4$ nanophosphors was investigated and discussed. The crystal structure of the $CaWO_4$ nanophosphors presented a certain level of distortion due to the high concentration of oxygen vacancy. Under 350 nm excitation, a clear green emission aroused by oxygen vacancy was observed. The possible luminescence processes for the matrix and oxygen vacancy were proposed. The luminescence spectra of the nanophosphors revealed that the emission and absorption intensity aroused by oxygen vacancy were both enhanced when the size is decreased. On the basis of the above results, the essential relationship between particle size and oxygen vacancy in $CaWO_4$ nanophosphors was concluded that the concentration of oxygen vacancy could be increased by reducing its size, which was further confirmed by decay lifetimes.

1. Introduction

Nanoscaled phosphors are very attractive for applications in cathode luminescence ray tube, optical windows, and solid-state lighting. Compared with the bulk ones, nanophosphors could present unique optical characteristics. These natures are mainly caused by quantum effects which are derived from the decreasing number of allowable quantum states in the small particles. For example, nanophosphors represent higher quantum efficiency, longer lifetime, and higher quenching concentration than those of the bulk materials [1–3]. In addition, nanophosphors exhibit advantages in terms of the application that they are specially employed to acquire miniature luminescence devices and high resolution display equipments [4–7].

Alkaline metal tungstates and molybdates of scheelite-like structures have attracted particular attention due to their extensive applications in fundamental and applied sciences [8–13]. Among these alkaline metal based matrices, calcium tungstate ($CaWO_4$) is the most conspicuous because it has practical applications as laser host materials in quantum electronics and acintillators in medical devices [14–16]. In the structure of $CaWO_4$, there are some intrinsic defects which could cause additional absorptions and dramatically affect the optical properties of the crystal [17,18]. Many researchers have synthesized nanoscaled $CaWO_4$ phosphor and investigated its luminescence properties [19–21]. However, the research about the intrinsic defects in the structure of $CaWO_4$ nanophosphor was not involved in the above references [19–21]. In other nanosized systems, such as ZnO, CeO_2, the intrinsic defects (especially the oxygen vacancy) in these nanophosphors have been widely investigated and decent results have been acquired [22,23]. Therefore, clearly understanding the relation between defects and size is critical for the further study of $CaWO_4$ nanophosphor.

So far, many wet chemical methods, such as sol–gel processes, electrochemical method, precipitation method and hydrothermal reactions, have been employed to synthesize tungstate or molybdate [24–30]. Hydrothermal reaction is considered to be the most promising route to prepare nanomaterials due to its low crystallization temperature, controllable morphology of products, and high degree of precipitation, which could reduce the content of metal ions in effluents and be beneficial to environmental protection [31,32]. Herein, in this work, we adopted the

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hydrothermal method to synthesize $CaWO_4$ nanophosphor. Furthermore, $CaWO_4$ with various particle sizes from 35 to 90 nm were achieved through the control of reaction conditions. The photoluminescence properties of these nanophosphors associated with the size and oxygen vacancy were investigated and discussed.

2. Experimental

2.1. Materials

Analytical grade sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$), calcium chloride ($CaCl_2$), citric acid, and cetyltrimethylammonium bromide (CTAB) were purchased from the Shanghai Chemical Reagent Company and used as received without further purification. The reaction was carried out in a 30 mL capacity Teflon-lined stainless steel autoclave in an oven.

2.2. Synthesis

The nanophosphors were synthesized through a hydrothermal process with exactly controlling the concentration of surfactant CTAB. Here we give the preparation of sample 1 (S1) as an example. First, 0.0018 mol $Na_2WO_4{\cdot}2H_2O$ was dissolved in 25.0 mL deionized water. Then, 0.0018 mol $CaCl_2$ and 0.0054 mol CTAB were added in the solution at the same time. The solution was ceaselessly stirred for 1 h at room temperature. The resultant precursor suspension was then transferred into a Teflon-lined stainless steel autoclave and treated at 150 °C for 12 h. For the preparation of sample 2 (S2) and sample 3 (S3), the concentrations of CTAB are used as 0.0036 and 0.0018 mol, respectively. After reaction, the autoclave was cooled to room temperature naturally and the products were collected by centrifugation, washing three times with deionized water and ethanol. After dried in air at 60 °C for 12 h, the final products (S1, S2 and S3) were obtained. The yield of the products was calculated to be 91.72%, 90.43% and 92.56% for S1, S2 and S3, respectively.

2.3. Characterization

Crystal phases of the obtained samples were characterized by powder X-ray diffraction (XRD, Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered Cu K_α radiation). The crystal structure picture was drawn by the Diamond program and the refinements of XRD were operated by General Structure Analysis System (GSAS). The morphology of the powders was examined by the scanning electron microscope (SEM; JEOL JSM-5600) and transmission electron microscopy (TEM; Hitachi H-800, 100 kV accelerating voltage). The absorption spectra of the samples were collected on finely ground samples by a UV–visible (UV–vis) spectrophotometer (PE lambda 950) using $BaSO_4$ as a reference in the range 200–700 nm. The emission, excitation spectra, and decay curves were measured on a FLS920T fluorescence spectrophotometer. All characterizations were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

The crystal structure of $CaWO_4$ is shown in Fig. 1a. $CaWO_4$ is of scheelite structure with $I4_1/a$ space group and tetragonal system. It has two molecular units in the primitive cell. The lattice parameters of bulk the $CaWO_4$ were calculated by R. M. Hazen et al. as $a = b = 0.52429$ nm and $c = 1.13737$ nm [33]. In the structure, the Ca^{2+} and W^{6+} occupy the sites of S_4 point group symmetry. There are eight O^{2-} ions surrounding Ca^{2+} and four O^{2-} ions surrounding W^{6+}, inducing $[CaO_8]$ dodecahedron and $[WO_4]$ tetrahedron. The $[WO_4]$ group is regular tetrahedron approximately, in which the electron could be transferred between O^{2-} to W^{6+} ions arousing the characteristic absorption and emission of $CaWO_4$ [34].

The crystallinity and phase purity of the as-prepared samples were examined by X-ray diffraction (XRD). Fig. 1b plots the experimental and calculated results of the XRD refinement of S1 sample. The observed peaks satisfy the reflection condition, $R_p = 5.32\%$ and $R_{wp} = 5.17\%$, which suggests that the refinements are reliable. On analyzing the result, it is found that S1 sample is of scheelite structure with $I4_1/a$ space group and tetragonal system. Moreover, all diffraction peaks could be indexed, which are the same as that of $CaWO_4$ (JCPDs Card No. 77-2234). Therefore, the obtained S1 sample is determined to be $CaWO_4$ single phase. The XRD patterns of the other samples are similar and also characterized to be single phase (as shown in the inset of Fig. 1). In addition, it is observed in the inset that the diffraction peaks of the hydrothermal samples are all broadening to a certain extent, which suggests that the particle size is very small [35]. From the Debyer-Scherrer equation, the average crystallite sizes of the hydrothermal-samples are calculated as 28 nm (S1), 44 nm (S2) and 69 nm (S3), respectively. The different particle sizes of the phosphors could be induced by the concentration of surfactant CTAB since the other conditions of the synthesis were same. With an increase in the concentration of CTAB, the interaction between CTA^+ cations and metal anion group ($WO_4{}^{2-}$) would be enhanced, and thus more CTA^+ cations could be absorbed on the surface of $CaWO_4$ seeds. As

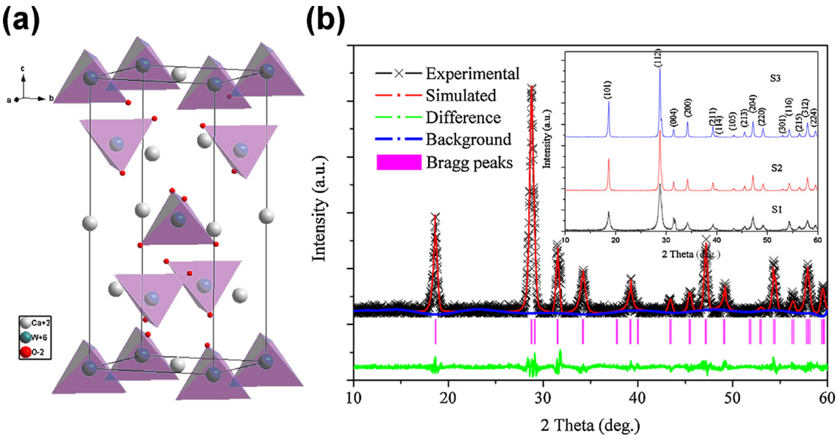

Fig. 1. (a) Crystal structure image of $CaWO_4$ crystalline; (b) Experimental and calculated results of the XRD refinement of S1 sample; the inset in (b) is the XRD patterns of S1, S2 and S3 samples.