

Surface and Photoluminescence Characteristics of CdNb₂O₆ Nanocrystals

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Abstract: Photoluminescence characterization on CdNb₂O₆ oxides by the solid state reaction were investigated in this work. The products were characterized by X-ray diffraction, scanning electron microscopy, photoluminescence spectroscopy and absorption spectra. The excitation wavelengths at 272 and 330 nm, were associated with charge transfer bands of [NbO₆]⁷⁻ and oxygen deficient niobate groups [NbO₄]³⁻. The measured photoluminescence of the sample after 1000 °C annealing revealed the blue emission peaks was located at 460 nm. Furthermore, the visible light absorption edge of the CdNb₂O₆ annealed at 1000 °C was 355 nm, which corresponded to band-gap energy of 3.50 eV.

Keywords: CdNb₂O₆, photoluminescence, solid state reaction, absorption.

1. INTRODUCTION

The electro-optical properties of metal niobates have attracted a great amount of interest for applications [1-2]. Metal niobates are known as interesting photoactive host materials, and the luminescent properties of LiNbO₃ [3], KNbO₃ [4] and LaNbO₄ [5] have been studied extensively. However, there are few investigations on metal niobate (e.g., CdNb₂O₆). CdNb₂O₆ is an important intermediate phase for the preparation of Cd₂Nb₂O₇ ferroelectric ceramics [6], which is formed due to distortions on octahedral NbO units, and in consequence the formation of short Nb-O bonds takes place. CdNb₂O₆ is also suitable reference material for dielectric ceramic [7].

The solid state reaction method has some drawbacks such as high temperature, large particle size and a limited degree of chemical homogeneity, but it is simple to operate and one can utilize the cheap oxides as starting materials. Therefore, the main purpose of this work was to explore a mixed oxide synthetic route for the production of CdNb₂O₆ powders *via* a rapid vibro-milling technique. The rapid vibro-milling technique was potentially employed in obtaining nano-sized powders, which would in turn lead to lower required firing temperature.

In this work, the phase formation, morphology and photoluminescence (PL) characteristics of CdNb₂O₆ oxides calcined at various temperature conditions will be studied and discussed.

2. EXPERIMENTS

Vibrating milled solid-state reaction method was used to synthesize CdNb₂O₆ polycrystalline. The raw materials were 99.9% pure cadmium carbonate (CdCO₃) and niobium oxide

(Nb₂O₅) powders. These powders combined with the correct proportional amounts of the different materials were vibrated milled for 1 hour and then the CdNb₂O₆ powders were obtained after calcinations at 700-1100 °C for 3 h.

The phase identification was performed by X-ray powder diffraction (Rigaku Dmax-33). The surface morphology and microstructure were examined by scanning electron microscopy (SEM, S4200, Hitachi). The excitation and emission spectra were recorded on a Hitachi-4500 fluorescence spectrophotometer equipped with xenon lamp. The absorption spectra were measured using a Hitachi U-3010 UV-Vis spectrophotometer. All of the above measurements were taken at room temperature.

3. RESULTS AND DISCUSSION

Fig. (1) shows the XRD patterns of CdNb₂O₆ powders annealed at different temperatures of 700~1100 °C for 3 h. It can be found CdNb₂O₆ phase (JCPDS file No., 38-1428) and an interphase Cd₂Nb₂O₇ (JCPDS file No., 18-0258) at 700 °C calcined temperature. The samples exhibited a single phase and all of the peaks were found to be orthorhombic CdNb₂O₆ phase at high temperature of over 900 °C. The CdNb₂O₆ phase appeared due to interphase (Cd₂Nb₂O₇) was decomposed. The variation of the relative amount of each phase as a function of calcining temperature could be explained by the homogenization of the composition with the enhancement of the diffusion process.

The SEM pictures of the materials sintered at 800, 900, 1000 and 1100 °C are shown in Fig. (2a-d). We can see that the CdNb₂O₆ powders sintered at more than 1000 °C have obvious differences morphology by Fig. (2). The circular particles seemed to be distributed homogeneously as shown in Fig. (2c, d). The particle diameters of CdNb₂O₆ powders annealed at 1000 and 1100 °C were about 1.0 and 1.9 μm, respectively. It is well-known that the higher temperature leads to the larger crystallite and grain size. Therefore, the particle size increased as the sintering temperature was increased.

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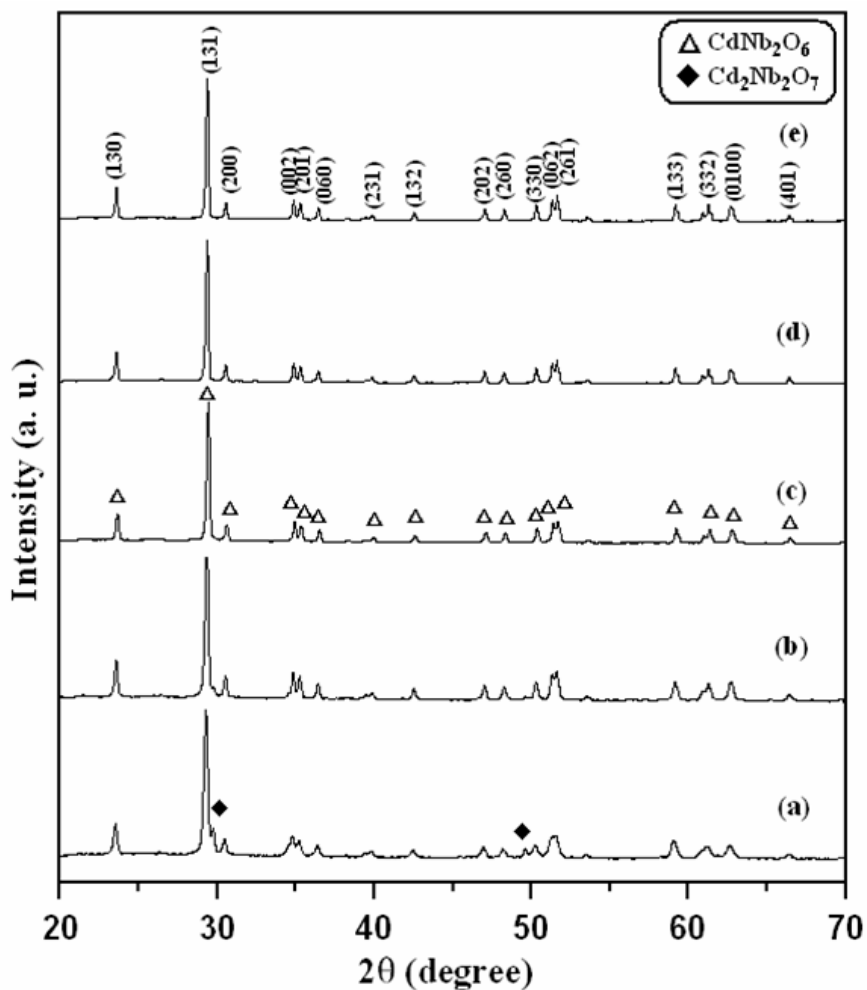


Fig. (1). X-ray diffraction patterns of CdNb₂O₆ powders annealed at (a) 700, (b) 800, (c) 900, (d) 1000, and (e) 1100 °C for 3 h.

Fig. (3a) shows the excitation spectra of the CdNb₂O₆ samples at temperatures of 800-1100 °C. The photoluminescence results reveal that the sample prepared at 1000 °C has greater absorption intensity at 272 nm than other samples. The improvement in photoluminescence performance may result from improved crystallinity leading to higher oscillating strengths [8] or reduced internal reflections of the emitted light due to rougher surfaces [9]. Where both of the peaks were observed at wavelengths of 272 and 330 nm, respectively. Blasse [10] reported that the niobate complexes had two kinds of absorbing groups [NbO₆]⁷⁻ and [NbO₄]³⁻, respectively. These peaks are associated with the direct excitation of the CdNb₂O₆ host itself, *via* the charge transfer (CT) transition between Nb and O. Therefore, both peaks of excitation, at about 272 and 330 nm, were associated with charge transfer bands of [NbO₆]⁷⁻ and [NbO₄]³⁻ in the CdNb₂O₆ system. The CdNb₂O₆ has an ordered columbite structure where the pentavalent cations form pairs by face sharing of their coordination octahedral. Furthermore, in our experiment, rapid calcinations, incomplete crystallization, and the departure of the Cd/Nb stoichiometric ratio may generate various structural defects, such as oxygen vacancies and Cd vacancies or interstitials. So, the concentration of extrinsic niobate groups (i.e., groups with an oxygen deficiency or excess positive charge) [11,

12] cannot be avoided. Therefore, the excitation bands at 330 nm, may be attributed to the defects and impurities with different densities generating from extrinsic niobate groups (i.e., oxygen deficient niobate groups [NbO₄]³⁻). The Stokes shift associated with the octahedral niobate group [NbO₆]⁷⁻ indicated that the excitation wavelength increased with the calcination temperature in Fig. (3a). The luminescence properties of the perovskite-like compounds are determined mainly by the extent of delocalization of the excited state [13]. This effect depends on the structure, and in particular on the M-O-M angle (M=Nb⁵⁺, Ta⁵⁺, Ti⁴⁺...) between the corner-sharing octahedra [14]. In this study, the delocalization is large, and the [NbO₆]⁷⁻ is observed at high sintering temperature. Therefore, the maximum of the excitation band of the luminescence of CdNb₂O₆ will shift to lower energy when the samples sintered at lower temperatures.

The PL emission spectral wavelength distribution curves of CdNb₂O₆ powder under 272 nm excitation at room temperature are shown in Fig. (3b). The PL spectra show a broad and strong blue emission peaks at about 460 nm. Here, the edge-shared NbO₆ groups are efficient luminescent centers for the blue emission, which may be ascribed to self-trapped exciton recombination [15]. This luminescence effect depends on the Nb-O-Nb bonding that the conduction

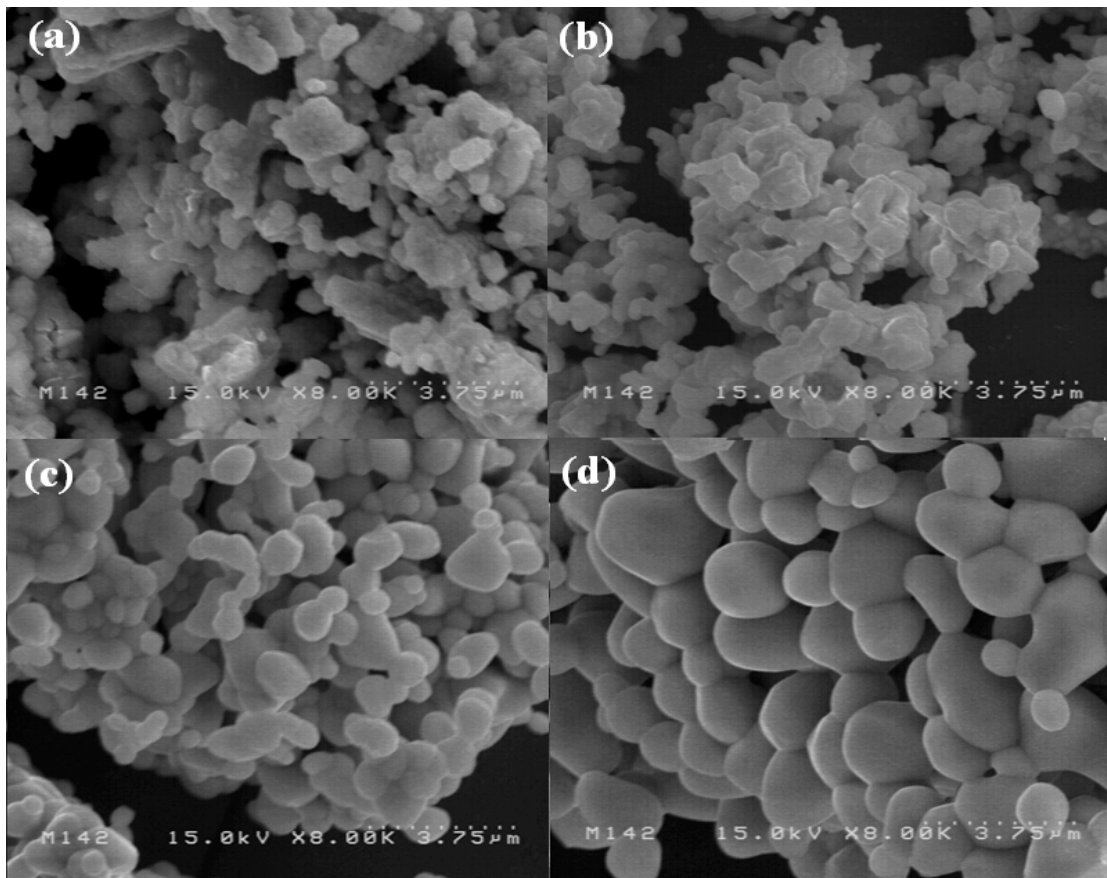


Fig. (2). Scanning electron micrographs of CdNb_2O_6 powders annealed at (a) 800, (b) 900, (c) 1000, and (d) 1100 °C and for 3 h.

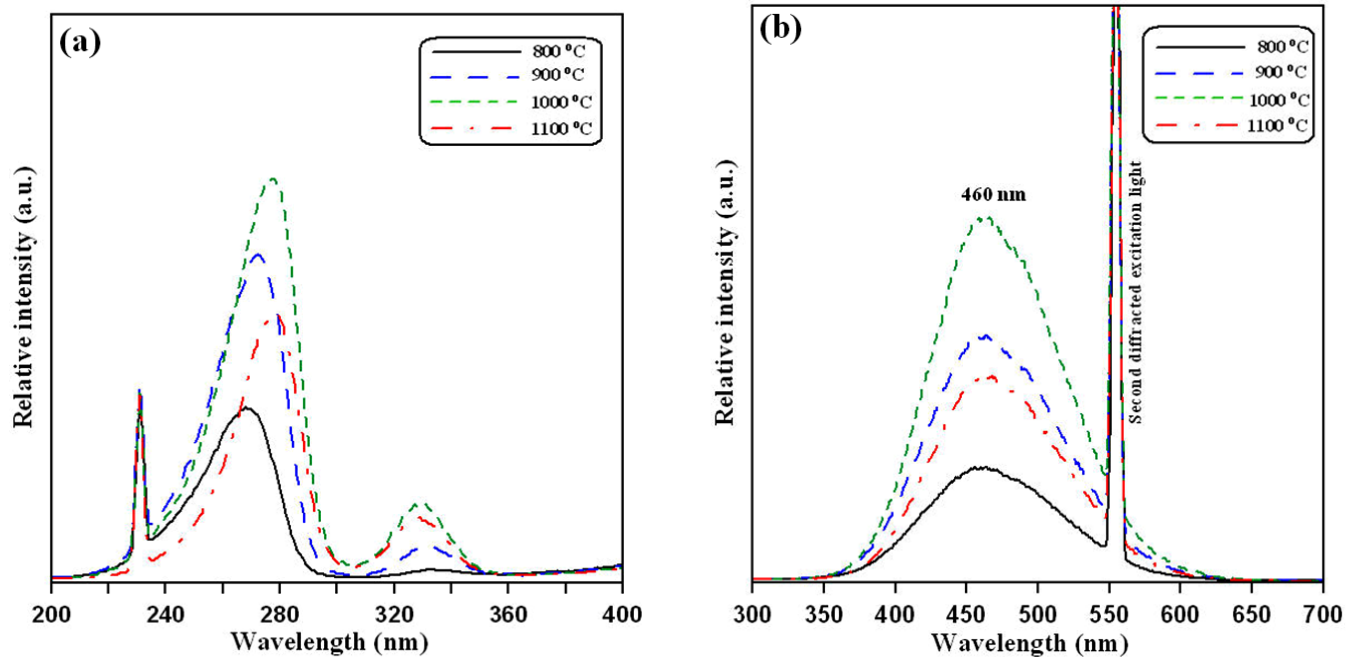


Fig. (3). The room-temperature (a) excitation ($\lambda_{\text{em}} = 460$ nm) spectra, and (b) emission ($\lambda_{\text{ex}} = 272$ nm) spectra of CdNb_2O_6 phosphors heat-treated at various temperatures.

band is composed of Nb^{5+} 4d orbitals, and the valence band of O^{2-} 2p orbitals between the corner-sharing octahedra [16]. In other word, this luminescence was originated from the crystals of absorbing groups of the niobate octahedra group

$[\text{NbO}_6]^{7-}$. The sample that was heat-treated at 1000 °C yields the most intense emission spectra ($\lambda_{\text{ex}} = 272$ nm), associated with the higher absorbing intensity of the $[\text{NbO}_6]^{7-}$ group.

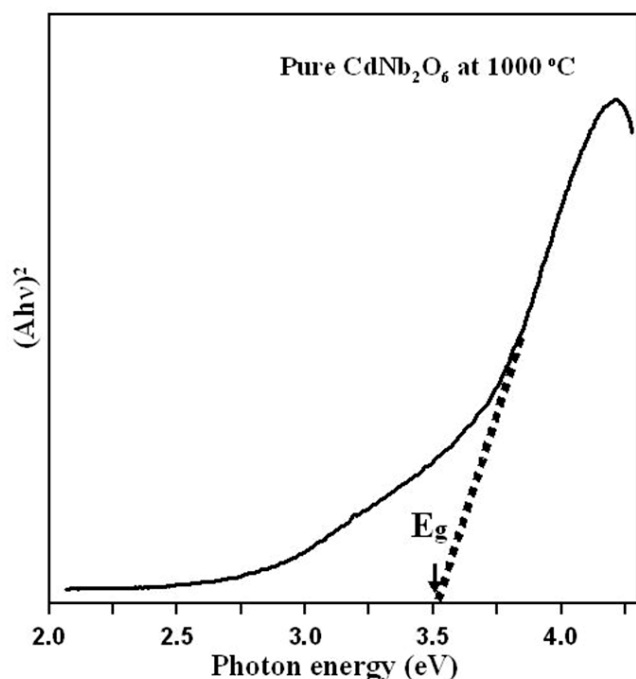


Fig. (4). Absorption spectra of CdNb₂O₆ powders annealed at 1000 °C for 3 h measured at room temperature.

The UV-Vis absorption spectra of the as-synthesized CdNb₂O₆ crystals are shown in Fig. (4). The absorption edges were calculated according to the method reported by Khan *et al.* [17]. The visible light absorption edge of 1000 °C sample was at 355 nm, which corresponded to bandgap energy of 3.50 eV. According to previous literatures [11], the bandgap energy of ZnNb₂O₆ nanoparticle is 3.31 eV. Therefore, the sample CdNb₂O₆ powders had more insulating than ZnNb₂O₆ nanoparticle.

4. CONCLUSION

CdNb₂O₆ crystal was successfully prepared by a solid-state reaction method. The pure orthorhombic CdNb₂O₆ can be obtained by heat-treatment at more than 900 °C. The particle diameters of CdNb₂O₆ powders annealed at 1000 and 1100 °C are estimated to be 1.0 and 1.9 μm, respectively. The 272 and 330 nm excitation wavelengths were associated with charge transfer bands of [NbO₆]⁷⁻ and oxygen deficient niobate groups [NbO₄]³⁻. The photoluminescence results show that the sample prepared at 1000 °C has a broad and strong blue emission peaks at about 460 nm compared to the other samples. The visible light absorption edge of 1000 °C sample was located at 355 nm, which corresponded to bandgap energy of 3.50 eV.

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