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Synthesis and the luminescent properties of CdNb₂O₆ oxides by sol-gel process

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ABSTRACT

Synthesis and luminescence properties of $CdNb_2O_6$ oxides by the sol-gel process were investigated. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), highresolution transmission electron microscopy (HRTEM), photoluminescence spectroscopy and absorption spectra. The PL spectra excited at 272 nm have a broad and strong blue emission band maximum at 460 nm, corresponding to the self-activated luminescence center of $CdNb_2O_6$. The optical absorption spectra of the 700 °C sample exhibited the band-gap energies of 3.35 eV. Furthermore, the microstructure and luminescence spectra of the products were investigated.

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1. Introduction

The synthesis and electro-optical properties of metal niobates have been intensively investigated during the past half century [1–3]. Additionally, niobates are known as interesting photoactive host materials, and the luminescent properties of LiNbO₃ [4], KNbO₃ [5], LnNbO₄ (Ln = La, Gd, and Y) [6,7] and KNb₃O₈ [8] have been studied extensively. However, to the best of our knowledge, there are few investigations into the metal niobates (e.g., CdNb₂O₆).

 $CdNb_2O_6$ is an important intermediate phase for the preparation of $Cd_2Nb_2O_7$ ferroelectric ceramics [9], which is formed due to distortions on octahedral NbO units, and, as a consequence, the formation of short Nb–O bonds takes place [10]. $CdNb_2O_6$ is also a suitable reference material for dielectric ceramics [11].

Therefore, the main purpose of this work is to explore a sol-gel synthetic route for the preparation of single phase $CdNb_2O_6$ oxides with a columbite structure. The major advantage of sol-gel process is that it is a low-temperature process. Chemically synthesized ceramic powders often posses better chemical homogeneity and a finer particle together with better control of particle morphology than those produced by the mixed oxide route, and these features often result in improved sinterability [12]. However, there are few studies of works of the niobate-based complexes formed by the sol-gel method, and the luminescence properties of $CdNb_2O_6$ oxides have been investigated by a sol-gel for the first time in this paper.

2. Experiments

The CdNb₂O₆ powders were prepared by the sol-gel method using cadmium nitrate [Cd(NO₃)₂·6H₂O], niobium chloride (NbCl₅), ethylene glycol (EG) and citric acid anhydrous (CA), with purities of over 99.9%. First, the stoichiometric amount of cadmium nitrate, and niobium ethoxide were dissolved in distilled water. Niobium ethoxide, Nb(OC₂H₅)₅, was synthesized from niobium chloride and ethanol, C₂H₅OH, according to the general reaction [1]:

$$NbCl_5 + 5C_2H_5OH \rightarrow Nb(OC_2H_5)_5 + 5HCl.$$
(1)

A sufficient amount of citric acid was added as a chelating agent to form a solution. Citric acid to the total metal ions in the molar ratio of 3:2 was used for this purpose and EG is also added as a stabilizing agent. The precursor containing Cd and Nb was dried in an oven at 120 °C for 10h, and then the CdNb₂O₆ powders were obtained after calcinations at 400–700 °C for 3 h in air.

The burnout behaviors of powders were analyzed by differential thermal analysis and thermogravimetry analysis (DTA–TGA, PE–DMA 7). 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) and transmission electron microscopy (HR-TEM, HF-2000, Hitachi), respectively. The excitation and emission spectra were recorded on a Hitachi-4500 fluorescence spectrophotometer equipped with a 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

The amorphous metal–organic gel was heat-treated to pyrolyze the organic components for crystallization. XRD patterns of the precursor powders at heat-treatment temperatures of 400–700 °C for 3 h are shown in Fig. 1. When calcined at temperatures of 400 °C the powders showed some interphases such as Cd(OH)₂ (JCPDS file No., 18-0258) and H₄Nb₆O₁₇·nH₂O [13]. The content of the CdNb₂O₆ phase had a rapid product at 500 °C due to decompose interphases.



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Fig. 1. X-ray diffraction patterns of $CdNb_2O_6$ precursor powders annealed at (a) 400, (b) 500, (c) 600 and (d) 700 °C for 3 h.

When the precursor sintered at temperatures above $600 \,^{\circ}$ C, the samples exhibited a single phase and all of the peaks were found to be the orthorhombic CdNb₂O₆ phase (JCPDS file No., 38-1428). 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 TG and DTA curves of the dry $CdNb_2O_6$ precursor are shown in Fig. 2. The endothermic peak at about 105 °C and small peak at about 155 °C in DTA accounted for 11% of the initial weight loss in TG, and this was assigned to the loss of ethanol and free water. A fast weight loss stage of about 48% in the range of 160–440 °C was accompanied by two exothermic peaks at 320 and 440 °C. The exothermic peak at 320 °C was due to the burnout of the low boiling organic species, and the other exothermic peak originated from the burnout of the organic groups in citric acid. The exothermic peak around 440 °C was associated with the decomposition into the oxide from the amorphous gel to second phase



Fig. 2. DTA and TG curves for CdNb₂O₆ percursor.

(e.g., Cd(OH)₂ and H₄Nb₆O₁₇·*n*H₂O), and that around 480 °C corresponded to the formation of the CdNb₂O₆ phase from XRD (Fig. 1). In addition, an exothermic peak appeared around 575 °C, which was associated with the decomposition of the second phase into main phase CdNb₂O₆. In this experiment, the possible chemical reactions for the synthesis of CdNb₂O₆ powders can be expressed as follows:

$$Cd(NO_3)_2 + 2Nb(OC_2H_5)_5$$

$$\xrightarrow{CA} (1-x)CdNb_2O_6 + xCd(OH)_2 + \frac{x}{3}H_4Nb_6O_{17} \cdot nH_2O$$

$$+2HNO_3 + 10C_2H_5OH \uparrow \rightarrow CdNb_2O_6 + NO_2 \uparrow +H_2O \uparrow +CO_2 \uparrow$$
(2)







Fig. 3. Scanning electron micrographs of $CdNb_2O_6$ precursor powders annealed at (a) 500 °C, (b) 600 °C and (c) 700 °C for 3 h.



Fig. 4. TEM images of as-synthesized $CdNb_2O_6$ powders at $600^{\circ}C$. The inset is the electron diffraction pattern of the selected area corresponding along the $CdNb_2O_6$ [200] zone axis.

Therefore, the weight loss between 155 and $650 \,^{\circ}$ C in the TG curve was caused by the generation of organic groups and many kinds of gas from the precursor.

The SEM pictures of the material sintered at 500, 600 and 700 °C are shown in Fig. 3a–c. The rod-like particles seem to be distributed homogeneously in Fig. 3c. It is believed that a higher temperature

enhanced higher atomic mobility and caused faster grain growth. Therefore, the particle size increased along with the sintering temperature.

TEM analysis of the crystal provided further insight into the structural properties of as-synthesized CdNb₂O₆ at 600 °C. Fig. 4 shows the low-magnification TEM image, and the morphology is clearly observed. The diameters of the crystals are in the range of 80-200 nm. However, the big particles were condensed by assembled nanograins, as found in the previous SEM results. It is conjectured that the assembly effect arising from the nanocrystals is responsible for the decrease in surface energy. The associated selected area electron diffraction (SAED) pattern in Fig. 4, recorded perpendicular to the axis, can be indexed for the [200] zone axis of crystalline CdNb₂O₆. The well-defined SAED pattern clearly shows the diffraction spots representing $\{020\}$ and $\{130\}$ lattice planes of CdNb₂O₆, and the interplanar spacing of the diffraction spots in patterns and the experimental d values are well-fitted with the JCPDS card. The results confirm that the crystalline phase was CdNb₂O₆.

Fig. 5a presents the excitation spectra of the CdNb₂O₆ samples at temperatures of 500–700 °C. The photoluminescence results reveal that the sample prepared at 700 °C exhibits greater absorption intensity at 272 nm than other samples by monitoring fluorescence at a wavelength of 460 nm. Both peaks were observed at wavelengths of 272 and 330 nm, respectively, with the calcining temperature at 600 °C. Blasse [14] indicated that the niobate complexes had two kinds of absorbing groups, $[NbO_6]^{7-}$ and $[NbO_4]^{3-}$, respectively. This result corresponds to the excitation wavelengths in Fig. 4 at calcining temperature 600 °C. Therefore, both peaks of excitation, at about 272 and 330 nm, were associated with charge



Fig. 5. The room-temperature (a) excitation (λ_{em} = 460 nm) spectra, (b) emission (λ_{ex} = 272 nm) and (c) emission (λ_{ex} = 330 nm) spectra of CdNb₂O₆ phosphors heat-treated at various temperatures.



Fig. 6. Absorption spectra of CdNb₂O₆ precursor powders annealed at 600 and 700 $^\circ\text{C}$ for 3 h measured at room temperature.

transfer bands of $[NbO_6]^{7-}$ and $[NbO_4]^{3-}$ 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. Therefore, the concentration of extrinsic niobate groups (i.e., groups with an oxygen deficiency or excess positive charge) [15,16] cannot be avoided. Thus, the excitation bands at 330 nm, may be attributed to the defects and impurities with different densities generated from the extrinsic niobate groups (i.e., oxygen deficient niobate groups [NbO₄]³⁻).

The PL emission spectral wavelength distribution curves of CdNb₂O₆ phosphors under 272 nm excitation at room temperature are shown in Fig. 5b. The PL spectra show a broad and strong blue emission peak 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 [17]. This luminescence effect depends on the Nb-O-Nb bonding when the conduction band is composed of Nb⁵⁺ 4d orbitals, and the valence band of O^{2-} 2p orbitals between the corner-sharing octahedra [18]. In other words, this luminescence originated from the crystals of the niobate octahedra group [NbO₆]^{7–}. Fig. 5c presents the emission spectra of CdNb₂O₆ under 330 nm excitation at a calcining temperature of 600 °C. The emission peak (λ_{ex} = 330 nm) with absorbing groups NbO₄ yield around 467 nm is caused by weak intensity from the CdNb₂O₆ system. The emission spectra is shifted slightly as the excitation wavelength is changed, affected by the different absorbing groups NbO₆ and NbO₄.

The UV–vis absorption spectra of the as-synthesized $CdNb_2O_6$ crystals are shown in Fig. 6. The absorption peak was shown at about 300 nm. Some observed differences in the excitation and absorption spectra peaks are ascribed to the absorption of defect levels in the host [19]. In particular, the oxygen vacancies played an impor-

tant role in the formation of these defect levels. In our experiment, organic networks fiercely burnt out in a very short time, and this process consumed a great amount of oxygen, which induced the absence of oxygen sites and a great deal of oxygen vacancies [20]. In this way, the shifted absorption peak at 300nm may be caused by the absorption of defect levels in nanosized $CdNb_2O_6$. The absorption edges were calculated according to the method reported by Khan et al. [21]. Band-gap energy both was similar between 600 and 700 °C. The visible light absorption edge of 700 °C sample was at 370 nm, which corresponded to the band-gap energy of 3.35 eV.

4. Conclusions

CdNb₂O₆ crystal was prepared by a sol-gel synthesis using [Cd(NO₃)₂·6H₂O] and NbCl₅. The well-crystallized orthorhombic CdNb₂O₆ can be obtained by heat-treatment at 600 °C from XRD. The excitation wavelengths at a calcining temperature of 600 °C, at about 272 and 330 nm, were associated with charge transfer bands of [NbO₆]^{7–} and oxygen deficient niobate groups [NbO₄]^{3–}. The PL spectra under 272 nm excitation show a broad and strong blue emission peak at about 460 nm, originating from the niobate octahedra group [NbO₆]^{7–}. The visible light absorption edge of the 700 °C sample was at 370 nm, which corresponded to the band-gap energy of 3.35 eV.

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