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Sol-gel synthesis and the luminescent properties of CaNb₂O₆ phosphor powders

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ABSTRACT

Synthesis and luminescence properties of CaNb₂O₆ 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 257 nm have a broad and strong blue emission band maximum at 457 nm, corresponding to the self-activated luminescence of the niobate octahedra group $[NbO_6]^{7-}$. The optical absorption spectra of the 700 °C sample exhibited the band-gap energies of 3.53 eV.

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1. Introduction

The electro-optical and the luminescent properties of metal niobates of LiNbO₃ [1], KNbO₃ [2], LnNbO₄ (Ln = La, Gd, and Y) [3,4] and ANb₂O₆ (A=Ba, Sr and Ca) [5-7] compounds have been studied extensively. The initial investigations of calcium niobate CaNb₂O₆ was of interest because this particular crystal has shown to be a strong source of coherent light that could be useful in holography applications [8]. CaNb₂O₆ exhibits very strong blue luminescence with excitation by ultraviolet radiation of 253 nm, even at room temperature [9]. Ballman et al. [10], as well as Yariv and Gordon [11], reported that it was used both as a laser and a laser host material. It was also proposed as a low cost lamp phosphor when doped with Eu³⁺ and co-doped with Ti⁴⁺ [12].

The main purpose of this work is to explore a sol-gel synthetic route for the preparation of single phase CaNb₂O₆ oxides with a columbite structure (orthorhombic, space group *Pbcn*). The major advantage of sol-gel processing is that there is a lowtemperature processing. 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 [13]. Recently, works of the niobate-based complex formed by the citric gel method are few. Therefore, the luminescence and optical absorption properties of CaNb₂O₆ nanocrystals have been investigated by a sol-gel for the first time.

2. Experiments

The CaNb₂O₆ powders were prepared by the sol-gel method using calcium nitrate Ca(NO₃)₂, niobium chloride (NbCl₅), ethylene glycol (EG) and citric acid anhydrous (CA). Their purities are 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 as follows:

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

Sufficient amount of citric acid were added to the former solution 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. EG is also added to the above solution as a stabilizing agent. The precursor containing Ca and Nb were dried in an oven at 120 °C for 10 h and then the CaNb₂O₆ powders were obtained after calcinations at 600-700 °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 Xray powder diffraction (Rigaku Dmax-33). The morphology and microstructure were examined by transmission electron microscopy (HR-TEM, HF-2000, 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.



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Fig. 1. DTA and TG curves for CaNb₂O₆ precursor.

3. Results and discussion

The TG and DTA curves of the dry CaNb₂O₆ precursor are shown in Fig. 1. The endothermic peak at about 110 °C in DTA accounted for 10% of the initial weight loss in TG, was assigned to the loss of ethanol and free water. A fast weight loss stage of about 46% in the range of 110–400 °C that was accompanied by one exothermic peak at 370 °C. The exothermic peak at 370 °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. In addition, a manifest exothermic peak around 610 °C, that was associated with the decomposition the amorphous gel into main phase CaNb₂O₆. In this experiment, the possible chemical reactions for the synthesis of CaNb₂O₆ powders can be expressed as following:

$$Ca(NO_3)_2 + 2Nb(OC_2H_5)_5 \xrightarrow{CA} CaNb_2O_6 + NO_2 \uparrow +H_2O \uparrow +CO_2 \uparrow +C_2H_5OH \uparrow$$
(2)

Therefore, the weight loss between 110 and 610 °C in the TG curve was caused by the generation of organic groups and many kinds of gas from the precursor.

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 500-700 °C for 3 h are shown in Fig. 2. Calcined temperatures at 500 °C had shown almost amorphous phases. The content of CaNb₂O₆ phase had a rapid product at 600 °C that is due to decompose amorphous gel. When the precursor sintered at temperatures 700 °C, the samples exhibited a single phase and all of the peaks were identified to be the orthorhombic CaNb₂O₆ phase (JCPDS file No. 71-2406). Note that the intensity of the diffraction peaks becomes sharper at higher temperatures, indicating that the crystallinity of CaNb₂O₆ increases with the increase of the calcination temperature. The average grain sizes were determined from XRD powder pattern according to the Scherrer's equation [14],

$$D = \frac{k\lambda}{\beta \,\cos\theta} \tag{3}$$

where *D* is the average grain size, *k* is a constant equal to 0.89, λ is the X-ray wavelength equal to 0.1542 nm, θ is the (311)



Fig. 2. X-ray diffraction patterns of $CaNb_2O_6$ precursor powders annealed at (a) 500, (b) 600 and (c) 700 °C for 3 h.

peak angle, and β is half the peak width. The average grain sizes of powders calcined at 600 and 700 °C were about 22.3 and 28.6 nm, respectively. The particle size increased as the sintering temperature was increased. It is believed that a higher temperature enhanced higher atomic mobility and caused faster grain growth.

TEM analysis of the crystal provided further insight into the structural properties of as-synthesized $CaNb_2O_6$ at 700 °C. Fig. 3a showed the low-magnification TEM image, and the morphology was clearly observed. The big particles were condensed by assembled nanograins. It was conjectured that the assemble effect arising from nanocrystals, are responsible for the decreasing of surface energy. There was only one orthorhombic crystalline phase existing in the ceramic matrix. The well-defined selected area electron diffraction (SAED) pattern clearly shows the diffraction spots in Fig. 3b, that was calculated the inter-planar spacing of the diffraction spots in patterns and the experimental *d* values well-fitted the JCPDS card. The EDS results confirmed the composition with Ca and Nb ion content and the molar ratio of Ca to Nb almost about 0.5 in Fig. 3c.

Fig. 4 presents the excitation spectra of the $CaNb_2O_6$ samples at temperatures of 600 and 700 °C. The photoluminescence results reveal that the sample prepared at 700 °C exhibits greater absorption intensity at 257 nm than other samples by monitoring fluorescence at a wavelength of 457 nm. Blasse [15] indicated that the niobate complexes had two kinds of absorbing groups [NbO₆]^{7–} and [NbO₄]^{3–}, respectively. Only one peak was observed at wavelengths of 257 nm, as the calcining temperature at 600 and 700 °C. Therefore, the peaks of excitation, at about 257 nm, were associated with charge transfer bands of [NbO₆]^{7–} in the CaNb₂O₆ system. The crystal structure of CaNb₂O₆ was described as a layer structure built up by edge-sharing of NbO₆ trigonal prisms [16].

The PL emission spectral wavelength distribution curves of $CaNb_2O_6$ phosphors under 257 nm excitation at room temperature are shown in Fig. 4. The PL spectra show a broad and strong blue emission peaks at about 457 nm. Here, the edge-shared NbO₆



Fig. 3. (a) TEM images of as-synthesized nanocrystals at 700 °C, (b) high-resolution TEM image of the nanocrystal and electron diffraction pattern and (c) EDX analysis of CaNb₂O₆ nanocrystal.



Fig. 4. The room-temperature excitation (λ_{em} = 457 nm) spectra and emission (λ_{ex} = 257 nm) spectra of CaNb₂O₆ phosphors heat-treated at 600 and 700 °C.

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 that 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 word, this luminescence was originated from the crystals of absorbing groups of the niobate octahedra group [NbO₆]^{7–}.

We have measured the UV-vis absorption spectra of the asprepared $CaNb_2O_6$ nanocrystals and estimated the band gap from the absorption inset in Fig. 5. For a direct band gap semiconductor, the absorbance in the vicinity of the onset due to the electronic transition is given by the following equation [19]:

$$\alpha = \frac{C(h\nu - E_g)^{1/2}}{h\nu} \tag{4}$$

where α is the absorption coefficient, *C* is the constant, $h\nu$ is the photon energy and E_g is the band gap. The inset of Fig. 5 shows the relationship of $(\alpha h\nu)^2$ and $h\nu$. Extrapolation of the linear region gives a band gap of 3.53 eV. In particular, the oxygen vacancies played an important 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 small absorption peak about at 360 nm may be caused by the absorption of defect levels in nanosized CaNb₂O₆.



Fig. 5. Absorption spectra of CaNb_2O_6 precursor powders annealed at 700 $^\circ\text{C}$ for 3 h measured at room temperature.

4. Conclusions

CaNb₂O₆ crystal was prepared by a sol-gel synthesis using Ca(NO₃)₂ and NbCl₅. The well-crystallized orthorhombic CaNb₂O₆ can be obtained by heat-treatment at 700 °C from XRD. The excitation wavelengths at about 257 nm, were associated with charge transfer bands of [NbO₆]^{7–}. The PL spectra under 257 nm excitation showed a broad and strong blue emission peaks at about

457 nm, were originated from the niobate octahedra group. The visible light absorption edge of 700 °C sample was at 352 nm, which corresponded to band-gap energies of 3.53 eV.

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