



Synthesis and characterization of Ca²⁺ substituted barium niobate nanoparticles for photocatalytic and luminescence applications



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ABSTRACT

Ca²⁺ substituted barium niobate i.e. Ca_xBa_{1-x}Nb₂O₆ (x=0.3) compound in nanoparticles form was synthesized by a simple co-precipitation method for the first time and its structural characterization has been done by using powder X-ray diffraction data. Other characterizations were done by using transmission electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and ultraviolet-visible spectroscopy. It was found that the Ca_xBa_{1-x}Nb₂O₆ (x=0.3) compound stabilizes in the orthorhombic phase (*Pbcn* space group) with the lattice parameters **a** = 14.984 Å, **b** = 5.761 Å and **c** = 5.216 Å. A representative TEM image shows the irregular sphere like morphology of the synthesized particles with the size ranging from 70 to 120 nm. The optical band gap energy was found to be 3.74 eV. It was observed that the synthesized nanoparticles exhibit excellent H₂ evolution tendency and self-activated photoluminescence under the excitation of UV light. These activities were assigned to the nanocrystalline nature of the synthesized material.

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1. Introduction

Various structural modifications of the alkaline earth compounds including niobates, and their applications such as electrooptics, photorefractive, microwave dielectric, ferroelectric, photocatalysis, etc. are relevantly discussed in the literature [1,2]. The literature survey also shows that the stable and frequently reported crystal symmetries of CaNb₂O₆, BaNb₂O₆, SrNb₂O₆ and Sr_xBa_{1-x}Nb₂O₆ compounds are *Pbcn*, *C222₁*, *P2₁/c* and *P4bm*, respectively. It was realized that the *Pbcn* and *P4bm* space group compounds i.e. CaNb₂O₆ and Sr_xBa_{1-x}Nb₂O₆ respectively, have a certain well-liked edge over the rest. This is because- CaNb₂O₆ and Sr_xBa_{1-x}Nb₂O₆ are extremely important compounds for the laser and holographic applications [3–6]. Therefore, getting structural modifications of the alkaline earth niobates in either *Pbcn* or *P4bm* space group is highly appreciable.

The metaniobate BaNb₂O₆ compound has five polymorphic phases. Three are α-BaNb₂O₆ (*P2₁/c*), β-BaNb₂O₆ (*C222₁*), γ-BaNb₂O₆ (*Pmma*), and other two are isomorphous to NdFeO₆ (*Pbcn*) type and BaTa₂O₆ (*P6₃/mmm*) type [1]. BaTa₂O₆ type has a hexagonal modification; α-BaNb₂O₆ has a hexagonal/pseudo-

orthorhombic modification, whereas the rest have orthorhombic modifications [1,7]. According to Roth and Waring [7], the orthorhombic modifications are stable and the hexagonal modifications are unstable. Kim and Chon [8], however, observed the hexagonal metastable modification in BaNb₂O₆ polycrystalline samples prepared by a polymerized complex method (a wet chemical synthesis method) at 800 °C and above. This indicates that the other existing polymorphic phases of BaNb₂O₆ might also be obtained by using appropriate wet-chemical synthesis techniques at lower temperatures.

Low-temperature reaction methods such as sol-gel, co-precipitation, polymerized complex, hydrothermal, combustion, etc are extensively used, now-a-days, for the synthesis of nanoparticles [9–16]. Indeed, the nanocrystalline level is itself a very exciting particles size region as novelties in the physical properties of the compounds are reported for the nanoparticles in comparison with their respective bulk or single crystals [9,16,17]. Enhancement in properties like photocatalytic water splitting by TiO₂, ZnO, CdS, etc compounds [18–22] and photoluminescence by niobates [23] as consequences of nanodimensional particles are also reported in the literature.

Since, factors like synthesis technique, reaction temperature, reaction time, starting materials used for the synthesis, etc are greatly affecting the properties of nanomaterials [13,16,17,24,25],

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the enhancement of a particular phase modification out of possible polymorphic phases also depends on these factors.

Recently, wet-chemical synthesis techniques like citrate-gel and co-precipitation were used for the synthesis of orthorhombic metaniobate BaNb_2O_6 nanoparticles [26,27]. The XRD patterns depicted in these studies, however, clearly show that the phase modifications by these methods are other than 'Pbcn' type. To the best of our knowledge, the NdFeO_6 type (Pbcn) modifications of BaNb_2O_6 were reported only in single crystals and not in nanocrystalline materials. Therefore, in the present work, an attempt has been made to stabilize the BaNb_2O_6 in Pbcn phase symmetry by substituting Ca^{2+} in it. The logic behind this substitution is:—as CaNb_2O_6 generally prefers the 'Pbcn' space group to stabilize and as BaNb_2O_6 also bears the Pbcn symmetry at some intermediate level, the presence of Ca enforces the BaNb_2O_6 to prefer a Pbcn space group to stabilize. Although the Ca^{2+} (30 mol %) substitution makes the compound as $\text{Ca}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$, but the interest was not affected by this, as our goal was to synthesize a Pbcn or P4bm space group alkaline earth niobate. Ca^{2+} with 30 mol % substitution was deliberately preferred because, the tetragonal tungsten bronze (TTB) type phase modifications in single crystals of $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ ($x=0.2-0.4$) grown by high-temperature reactions were already reported recently [28–31].

By the present synthesis technique a 'Pbcn' space grouped orthorhombic structured $\text{Ca}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ (CBN30) compound was obtained for the first time; therefore, its structural and optical study are reported. In addition to this, self-activated luminescence (luminescence without doping PL activator impurity) and photocatalytic applications are also presented.

2. Material and methods

The synthesis of Ca^{2+} substituted barium niobate (CBN30) compound in nanocrystalline form was carried out by a simple co-precipitation method using AR grades starting chemicals. The procedure is similar to the earlier one which was used for the synthesis of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ nanoparticles [32]. The starting materials were Nb_2O_5 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. They were taken according to the stoichiometric ratio 1:0.3:0.7. The precursor obtained by the process was calcined at 650°C for 4 h. It was then ground thoroughly to improve homogeneity and reheated at the elevated temperature 800°C for 6 h to increase crystallinity of the particles.

X-ray diffraction (XRD) data of the CBN30 was collected by using an X-ray diffractometer (D8 ADVANCE, BRUKER, GERMANY) employing $\text{Cu-K}\alpha$ radiation (1.54 \AA) with the step size of 0.02° . Rietveld program 'FULLPROF' was used to refine the XRD data. The powder cell program (PCW) was used to visualize the cell structure of the compound. Formation of the single phase was spectrographically confirmed by FT-IR spectrum obtained by using a FT-IR spectrometer (THERMO NICOLET, AVATAR 370). The morphology of the particles was studied by using transmission electron microscopy (TEM) (TECNAI G2 20 ULTRA-TWIN, FEL, NETHERLANDS) and scanning electron microscopy (SEM) (ZEISS, EVO 18). Constituents of the compounds were confirmed by the energy dispersive X-ray spectroscopy (EDX).

UV–vis diffused reflectance a spectrum of CBN30 with reference to the mirror was obtained by using an UV–vis spectrometer (UV–vis 1700, SHIMATZU, JAPAN). For this measurement, pellets of the synthesized compound were prepared by mixing the powder with a few drops of 1 wt% solution of polyvinyl alcohol and then pressing isostatically under the pressure of 6t for 5 min. The pellets were heat-treated at 800°C for 5 h to remove the binder.

The photoluminescence excitation and emission spectra of the synthesized material were recorded by using a spectrofluorometer (F-7000, HITACHI, JAPAN).

Photocatalytic activity of the synthesized CBN30 nanocrystalline particles was studied by H_2 generation from pure water. In the process, 50 mg photocatalyst (CBN30) was added to 200 ml pure water taken in a glass beaker. It was stirred about 20 min to form a suspension. The suspension was then transferred to the photocatalytic reactor and exposed under the ultraviolet radiations. The suspension was kept under the constant stirring. A 200W high-pressure ultraviolet lamp was used as a source of radiations which was maintained at a distance of 10 cm from the reactor. H_2 gas evolved out from the suspension was collected in a measuring cylinder which was filled with water and placed inversely in a water-filled jar. H_2 gas generation was confirmed by the gas chromatography (SHIMATZU 2014, Japan) with TCD detector. It was also analyzed volumetrically.

3. Results and discussion

3.1. Structural and morphological analysis

Fig. 1 shows the refined XRD pattern of the synthesized CBN30 compound along with the observed pattern, difference in observed and refined pattern, and Bragg's positions. The goodness-of-fit (square root of χ^2) value for the refined XRD pattern was found to be 2.13. This value indicates a well refinement of the pattern in orthorhombic phase with the 'Pbcn' space group. The lattice parameters were found to be $a=14.984 \text{ \AA}$, $b=5.761 \text{ \AA}$ and $c=5.216 \text{ \AA}$. Atomic positions and occupancies of various constituent atoms of the compound are shown in Table 1. The lattice parameters and atomic coordinates (Table 1) were used for the determination of cell structure. The cell structure of CBN30 as visualized by the Powder Cell (PCW) program is shown in Fig. 2.

These results indicate that the Ca^{2+} ions actively participated in the structure formation. Out of five different polymorphic phases of BaNb_2O_6 , the NdFeO_6 type modification was enhanced due to the presence of Ca^{2+} ions. No TTB like phase was observed even when the sample was heat-treated at 800°C . At nanocrystalline level, by varying the composition of Ca and Ba, reaction temperature and method of synthesis, the TTB phase might be observed. In such cases, the phase transition between two polymorphic phases of CBN30 will be an interesting aspect.

It was found from Table 1 and Fig. 2 that the Ca^{2+} ions do not share the same Wyckoff sites with the Ba^{2+} ions. Most probably it is due to the ionic radii mismatch. The ionic radii of Ca^{+2} and Ba^{+2} ions are 1.00 \AA and 1.35 \AA respectively. The product of occupancy and multiplicity factor of the atoms as given in Table 1 also confirms the formation of $\text{Ca}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$. This result gives an excellent

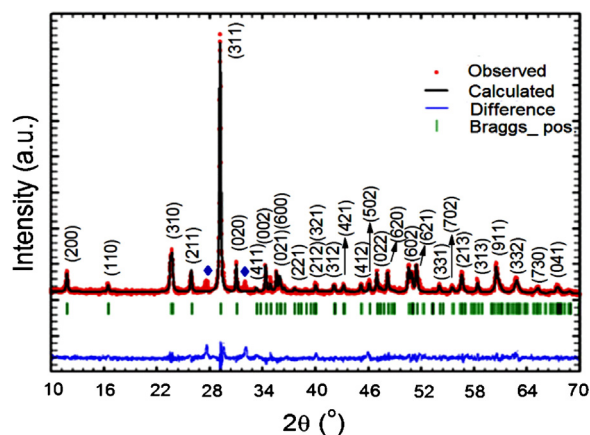


Fig. 1. Refined and well indexed X-ray diffraction pattern of orthorhombic CBN30 nanoparticles (251658240) (unidentified minor impurity peaks).

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