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ScienceDirect

Ceramics International 41 (2015) 2869–2875

CERAMICS INTERNATIONAL

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Photocatalytic degradation of methylene blue on nitrogen doped layered perovskites, $CsM_2Nb_3O_{10}$ (M = Ba and Sr)

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Received 10 September 2014; received in revised form 13 October 2014; accepted 17 October 2014
Available online 28 October 2014

Abstract

Layered transition metal perovskite oxides of general formula $AB_2M_3O_{10}$ (A = K, Rb, Cs; B = Ca, Sr, Ba; M = Nb, Ta) have been studied as photocatalysts for the decomposition of organic dyes and production of hydrogen via water splitting. In the present investigation, we have prepared nitrogen doped layered perovskite, $CsM_2Nb_3O_{10}$ (M = Ba, Sr). The N-doped analogues were obtained by heating $CsM_2Nb_3O_{10}$ and urea at 400 °C. All compounds were characterized by powder X-ray diffraction, FT-IR, SEM–EDS and UV–visible diffuse reflectance spectra. Compared to parent oxides the bandgap energy of nitrogen doped layered oxides were reduced considerably. The photocatalytic activity of all samples was studied by the degradation of methylene blue (MB). The nitrogen doped compounds show higher photocatalytic activity than the corresponding parent oxides.

Keywords: Layered perovskite; Doping; Bandgap; Photocatalytic activity

1. Introduction

The rapid industrialization all over the world causes severe environmental pollution. Most of the paper, chemical, medicinal and cosmetic industries release a large quantity of organic pollutants including dyes into the aquatic habitats. These organic pollutants are dangerous and do not decompose quickly. Photocatalytic degradation of these pollutants using sunlight is an attractive solution [1–3]. Extensive studies have been performed to degrade toxic organic pollutants under irradiation. Semiconductors such as TiO_2, ZnO, In_2O_3, Fe_2O_3, $NaTaO_3$ and $KNbO_3$ have been used as highly active photocatalysts [4–7]. However, the utility of these semiconducting oxides is limited due to their large bandgaps. These semiconductors can be used under UV light only which is about ~4–5% of the solar spectrum. The major part of solar light is visible light which accounts to about 40–50% of the total radiation. Moreover, the number of photocatalytic materials known up to now is yet limited and their activity is still low. Therefore, it is an indispensable need to develop a new type of visible light harvesting photocatalysts with higher activity.

Over the last several years extensive studies have been performed on layered perovskites, because of their wide range of physical and chemical properties [8–10]. The layer perovskite oxides are often classified as either Ruddlesden–Popper (R–P) $A'_2[A_{n-1}B_nO_{3n+1}]$ or Dion–Jacobson (D–J) $A'[A_{n-1}B_nO_{3n+1}]$ (where A′ is an exchangeable alkali metal cation, A is an alkali, alkaline earth, main group and/or rare earth, B is a transition metal, and n is the number of corner-connected BO_6 octahedra in the perovskite layer) structure types, which are derived from the ABO_3 perovskite structure [11]. Both the R–P and D–J phases have in common the $[A_{n-1}B_nO_{3n+1}]$ blocks of perovskite structure, but the main difference between the two phases is the stacking of the perovskite layers and cation density between the perovskite blocks. Interestingly, the chemistry of D–J phases that contain ion-exchangeable cations exhibited several superior properties than R–P phases and were studied broadly in the field of photocatalysis. Compounds in this series

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http://dx.doi.org/10.1016/j.ceramint.2014.10.109
0272-8842/

(D–J) containing transition metals Ti(IV) and/or Nb(V) and/or Ta(V) have been reported as photocatalysts for the degradation of organic pollutants and splitting of water. Typical examples are $La_2Ti_2O_7$, $KLa_2Ti_2NbO_{10}$, $SrBi_2Nb_2O_9$, $H_2La_{2/3}Ta_2O_7$, $RbNdTa_2O_7$ etc. [12–16].

Recently, alkaline and alkaline earth Nb-based photocatalyts have been reported as better photocatalysts for the utilization of sunlight and indoor illumination [17–19]. In 1981, Dion reported the family of layered perovskite type niobates, formulated as $AM_2Nb_3O_{10}$ (A=K, Rb, Cs; M=La, Ca, etc.), which show noticeable photocatalytic activity [20,21]. However, most of the niobium oxides have the bandgap energies that are too large to use solar radiation efficiently. Modifications of semiconductor materials by doping with metal ions have been receiving great attention due to their potential applications in solar driven photocatalysis [22]. Therefore, in continuation of our search for better photocatalytic materials we have chosen layered perovskites ($CsM_2Nb_3O_{10}$, M = Ba, Sr) and aimed to increase its photoactivity strength by doping a foreign ion. Doping of non-metal ion is one of the methods to enhance the photoabsorption of the semiconductor material. For instance, nitrogen is the most popular dopants because of its appropriate ionic radius with oxygen and the partial replacement of O^{2-} by N^{3-} narrows the band-gap of the parent oxides by shifting their valence band upward [23]. In addition, nitrogen doping has been proven to be very promising because the implantation of nitrogen creates oxygen vacancies that act as traps for excited electrons leading to a reduction in recombination of photo-induced electron–hole pairs [24]. Therefore, doping of nitrogen is an appropriate method to improve the photocatalytic activity of the material. To our knowledge, the nitrogen doped $CsM_2Nb_3O_{10}$ (M = Ba, Sr) has not been reported so far. In this paper, we present the preparation, characterization and photocatalytic studies of N-doped layered perovskite, $CsM_2Nb_3O_{10}$ (M = Ba, Sr).

2. Experimental

2.1. Preparation of N-doped layered perovskites

$CsM_2Nb_3O_{10}$ (M = Ba and Sr) was synthesized by conventional solid-state method according to the previous report, and with the modification of the heating temperature for $CsSr_2Nb_3O_{10}$ composition [25]. Reagent grade $CsNO_3$, $Ba(NO_3)_2$, $Sr(NO_3)_2$ and Nb_2O_5 are used as starting materials. All the Chemicals were analytically pure, commercially available, and used without further purification. $CsBa_2Nb_3O_{10}$ ($CsSr_2Nb_3O_{10}$) is prepared by heating a thoroughly ground stoichiometric mixture of $CsNO_3$ (30% excess), $Ba(NO_3)_2$ ($Sr(NO_3)_2$) and Nb_2O_5 at 600 °C/6 h and 850 °C/3 h with intermittent grinding. The resultant materials were washed with distilled water to remove the excess alkali nitrate. The chemical reaction for the formation of $CsM_2Nb_3O_{10}$ (M = Ba and Sr) is given below

$$1.3CsNO_3 + 2M(NO_3)_2 + 1.5Nb_2O_5 \overset{600\ ^\circ C,6h}{\Longrightarrow} \overset{850\ ^\circ C,3h}{\Longrightarrow} CsM_2Nb_3O_{10} + 5.3NO_2 + 0.15Cs_2O + 1.325O_2$$

The nitrogen doped oxides were prepared by heating the finely crushed mixture of parent material and urea at 400 °C for 2 h in a muffle furnace. The weight ratio of $CsM_2Nb_3O_{10}$ (M = Ba and Sr) to urea was 1:2. After the reaction, the product was washed with distilled water and dried in air at 100 °C. Henceforth, the parent $CsBa_2Nb_3O_{10}$ ($CsSr_2Nb_3O_{10}$) and N-doped $CsBa_2Nb_3O_{10}$ ($CsSr_2Nb_3O_{10}$) are designated as CBNO (CSNO) and CBNON (CSNON) respectively.

2.2. Characterization

The room temperature X-ray diffractograms of all samples were recorded using Rigaku MiniFlex 600 X-ray diffractometer (Cu $K\alpha$, $\lambda = 1.5406$ Å, $2\theta = 10–80^\circ$, step size $(2\theta) = 0.02^\circ$ and scan step time = 0.15 s) for phase confirmation. FT-IR spectra were recorded using Shimadzu spectrometer in the form of KBr pellets. The SEM–EDS images were recorded on the HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM). JASCO V-650 UV–vis spectrophotometer was used for UV–vis diffuse reflectance spectra measurements in the range 200–800 nm. $BaSO_4$ was used as the reflectance standard.

2.3. Photocatalytic experiments

The photocatalytic activity of all the samples was evaluated by photodegradation of Methylene blue (MB) using HEBER Visible Annular Type Photo-reactor, model HVAR1234 (Haber Scientific, India), under visible light irradiation using 300 W Tungsten lamp as a light source. In a typical process, 60 ml of aqueous MB solution (initial concentration, $C_o = 2.5 \times 10^{-5}$ mol/l) was stirred with 0.06 g of catalyst individually in a cylindrical-shaped glass reactor at room temperature in air. The suspension was stirred in the dark for an hour to establish adsorption–desorption equilibrium. Then the solution was exposed to light with continuous stirring. At regular 30 min intervals, about 3 ml of solution was collected and centrifuged to remove the catalyst particles. The change in the concentration of MB was obtained by recording the absorbance at 664 using a UV–vis spectrophotometer.

3. Results and discussion

The reported preparation of $CsSr_2Nb_3O_{10}$ involves sequential heating of the mixture of $CsNO_3$ (30% excess), $SrCO_3/Sr(NO_3)_2$ and Nb_2O_5 at 900 °C/6 h, 1250 °C/24 h and 1300 °C/12 h [25]. In the present investigation, we have obtained phase pure $CsSr_2Nb_3O_{10}$ at 600 °C/6 h and 850 °C/3 h with intermittent grinding, which is lower than the reported temperature. The phase formation of the as prepared samples was analyzed by recording their powder diffraction patterns. Fig. 1 shows the powder X-ray diffraction (XRD) patterns of CBNO, CSNO, CBNON and CSNON. The powder XRD profiles of CBNO and CSNO indicate the formation of a typical D–J layered structure and all the diffraction peaks are consistent with reported XRD profiles of $CsBa_2Nb_3O_{10}$ (JCPDS 53-1046) and $CsSr_2Nb_3O_{10}$ (JCPDS 53-1047), respectively. The similarity of the powder