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# Photooxidation of $NO_x$ using scheelite-type $ABO_4$ (A = Ca, Pb; B = W, Mo) phases as catalyts

E. Luévano-Hipólito [a,b,*], A. Martínez-de la Cruz [a]

[a] CIIDIT, Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Ciudad Universitaria, C.P. 66451 San Nicolás de los Garza, NL, Mexico
[b] CONACYT, Facultad de Ingeniería Civil-Departamento de Ecomateriales y Energía, Cd. Universitaria Universidad Autónoma de Nuevo León, C.P. 66455 San Nicolás de los Garza, NL, Mexico

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ABSTRACT

The scheelite-type compounds have been investigated due to their interesting properties of photoluminescence and recently, they have been applied as photocatalysts in air and water purification trough the removal of different organic and inorganic pollutants. In this work, four scheelite-type $ABO_4$ (A = Ca, Pb; B = W, Mo) compounds were prepared by co-precipitation method and its capacity to act as photocatalyst was evaluated in the removal of $NO_x$ gases using the oxidation of nitric oxide (NO) as model reaction. The photocatalytic activity of the samples decreased in the following order: $CaMoO_4 > PbWO_4 > PbMoO_4 > CaWO_4$, which was related with the electronic properties associated with each sample. When the photocatalyst with the highest photocatalytic activity ($CaMoO_4$) was activated under UV radiation, the selectivity for the formation of $NO_3^-$ ions was 35%, revealing the ability of the photocatalyst to carry out a deep oxidation of NO until innocuous products. Based in the modification of the experimental conditions, the mechanism proposed for the photooxidation of NO to $NO_3^-$ ions was mainly by the action of the ion superoxide ($O_2^-$) formed from the $O_2$ adsorbed on $CaMoO_4$ surface.



## 1. Introduction

Scheelite is the name of the mineral $CaWO_4$, and also is often used to describe the crystalline structure of one type of isostructural compounds such as powellite ($CaMoO_4$), stolzite ($PbWO_4$), and wulfenite ($PbMoO_4$). The primitive cell of the scheelite structure is characterized by two $ABO_4$ units, which is highly ionic by the presence of $A^{2+}$ cations and $BO_4^{2-}$ tetrahedral anions. The crystalline structure in the four compounds has the tetragonal space group I41/a listed as No. 88 in the International Tables of Crystallography [1].

The scheelite compounds $ABO_4$ (A = Ca, Pb; B = W, Mo) have been extensively investigated due to their interesting properties of photoluminescence in the search of the dark matter [2–4]. In addition, recently the scheelite-type compounds $CaWO_4$, $CaMoO_4$, $PbWO_4$, and $PbMoO_4$ were applied as photocatalysts for water purification trough the mineralization of different organic pollutants [5–7]. In heterogeneous photocatalysis, an ideal photocatalyst should have a high specific surface area, low crystallite size, adequate conduction and valence bands, and an efficient charge separation to carry out the oxidation/reduction of pollutants adsorbed in its surface. In addition, there are several studies about the relationship between the charge separation and the crystal structure of the photocatalysts [8–11]. In this sense, when compounds with scheelite crystal structure have been applied as photocatalyst, the dipole moment generated by the distortion of its structure promotes an efficient charge separation, as well as the mobility of electrons and holes by the action of an electric field applied [10].

The scheelite-type compounds have been used as photocatalyst for dyes removal from water, and as photoanode for oxygen evolution [5–12]. To the best of our knowledge no study has been reported about the photocatalytic oxidation of nitrogen oxides ($NO_x$) using the scheelite-type compounds: $CaWO_4$, $CaMoO_4$, and $PbMoO_4$ as photocatalyst. Only $PbWO_4$ was previously tested as photocatalyst in the nitric oxide (NO) photooxidation reaction reaching a removal rate of 100 ppb $min^{-1}$ when was used as hollow spheres [12]. In addition, the isostructural scheelite compound $BiVO_4$ was also reported as photocatalyst for this reaction [13]. They report that 100 mg of scheelite compound ($BiVO_4$) reached

* Corresponding author at: CIIDIT, Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Ciudad Universitaria, C.P. 66451 San Nicolás de los Garza, NL, Mexico.
*E-mail addresses:* eluevano@conacyt.mx, edithlue@gmail.com (E. Luévano-Hipólito).

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a 50% of NO removal when it was irradiated with a tungsten halogen lamp of 300 W and under 70% of relative humidity (RH). Nevertheless, in these reports was not reported the selectivity of the photooxidation reaction of NO for the formation of innocuous nitrate ions, and by this reason is difficult to make a real evaluation of the photocatalyst.

The photocatalytic removal of nitrogen oxides ($NO_x$) gases has gained interest in the scientific community as a new alternative to mitigate air pollution. The pollutant emissions of $NO_x$ are formed by the oxidation at high temperatures of the molecular nitrogen present in fuels. The main source of these type of pollutants is the combustion of engine vehicles followed by the industrial activity. Particularly $NO_x$ gases have a negative impact in the environment and in human and animal health. Depending of the $NO_x$ concentration, these can cause nausea, difficulty in breathing, skin irritation, and cancer [14]. For vegetation, $NO_x$ gases can be phytotoxic promoting a decreased in its shoot length [15]. On the other hand, $NO_x$ gases can react with molecules of $H_2O$ producing acid rain, which can damage in a several ways vegetation and building constructions. In the present work is proposed the use of four different scheelite-type compounds as photocatalysts to purifying air by using light irradiation. The selectivity of the photooxidation reaction will be also investigated.

## 2. Experimental

### 2.1. Synthesis of scheelite compounds

The scheelite-type compounds were prepared by co-precipitation method in basic medium without chemical additives such as complexing agents or surfactants. The chemical reagents $Ca(NO_3)_2{\cdot}4H_2O$ (Aldrich, 99%), $Pb(NO_3)_2$ (Aldrich, 99%), $H_2WO_4$ (Fermont, 99%), and $H_2MoO_4$ (Fermont, 99%) were analytical grade and were used without a further purification. The method consisted in the preparation of aqueous solutions of the chemical reactants. For this purpose, stoichiometric amounts of each compound were dissolved in 100 mL of deionized water with continuous stirring. After 30 min, the solution of calcium or lead, as the case may be, was added into the solution that contained $H_2WO_4$ or $H_2MoO_4$. The pH of the solutions in all cases was adjusted to 9 using a 7 M $NH_4OH$ (DEQ, 26%) solution. The resulting solutions were stirred for 1 h and aged for one day at room temperature. Later, the precipitate obtained in each case was washed several times with deionized water and dried at 70 °C for 12 h. In the case of $PbWO_4$, it was necessary an additional thermal treatment at 300 °C for 24 h in order to obtain the compound free of impurities. The general chemical reaction of the formation of the $ABO_4$ scheelite compounds is described by the Eq. (1).

$$A(NO_3)_2 + H_2BO_4 \rightarrow ABO_4 + 2HNO_3 \quad (1)$$

### 2.2. Characterization

The structural characterization was carried out by X-ray powder diffraction using a Bruker D8 Advance diffractometer with Cu Kα radiation (40 kV, 30 mA). A typical run was made between the $2\Theta$ angles from 10° to 70° with a step size of 0.05° and a dwell time of 0.5 s. The morphology and particle size of the samples were analyzed by scanning electron microscopy (FEI Nova NanoSEM 200 with an accelerating voltage of 30 kV). The UV–Vis diffuse reflectance absorption spectra of the samples were obtained using an Agilent Technologies UV–Vis-NIR spectrophotometer model Cary 5000 series equipped with an integrating sphere. The energy band gap values ($E_g$) were calculated using the Kubelka-Munk function $[F(R_\infty)]$ using Eq. (2), where $R_\infty$ is the absolute reflectance, $h\nu$ corresponds with the photon energy, and n denotes the nature of the transition being 1/2 and 2 for indirect and direct transitions.

$$[F(R_\infty)h\nu]^{1/n} = \frac{(1-R_\infty)^2}{2R_\infty} \quad (2)$$

The BET surface area measurements were carried out by $N_2$ adsorption-desorption isotherms by means of a Bel-Japan Minisorp II surface area and pore size analyzer. The isotherms were evaluated at −196 °C after a pretreatment of the samples at 150 °C for 24 h.

### 2.3. Photocatalytic activity

The photocatalytic activity of the scheelite-type compounds was evaluated in the photooxidation reaction of NO in gaseous phase. The experiments were carried out in a continuous flow reactor designed according with the ISO 22197-1 [16]. The photocatalytic reactor was made of stainless steel with a volume of 0.8 L, and it was equipped with a window in its superior part. The mass of the photocatalyst (0.1 g) was coated over an area of 0.08 $m^2$ of a glass substrate by brush a dispersion of the photocatalyst in ethanol. In previous reports, we found that 0.1 g was the optimal mass of photocatalyst to reach a higher NO photooxidation considering a substrate of 28 × 29 cm [17]. As inlet gas was used a 3 ppm of NO mixture stabilized in $N_2$. The concentration of inlet gas was adjusted to 1 ppm in NO with synthetic air (20.5 vol% $O_2$ and 79.5 vol% $N_2$) and the flow rate of gas was adjusted to 1 L $min^{-1}$. The source of light irradiation consisted in two fluorescent black lamps (TecnoLite) of 20 W, which emission spectrum is showed in Fig. 1. The lamp has its maximum emission in 365 nm, and have another two emissions in 400 and 430 nm. The energy provided by the lamp is enough to carry out the activation of the semiconductors proposed in this work as can be seen in the spectra also shown in the Fig. 1. The UVA intensity in the center of the photocatalytic reactor in a typical experiment was 8.2 W $m^{-2}$ (radiometer MANNIX 340). For additional experiments, the UVA intensity was increased to 10.1 W $m^{-2}$ by adding nine lamps of the same power.

A typical experiment was performed only with the presence of residual water steam, which is present in the air used as the balance of the reaction mixture. Although this value is less than 0.4 ppm, it is a significant $H_2O$ vapor concentration because it is

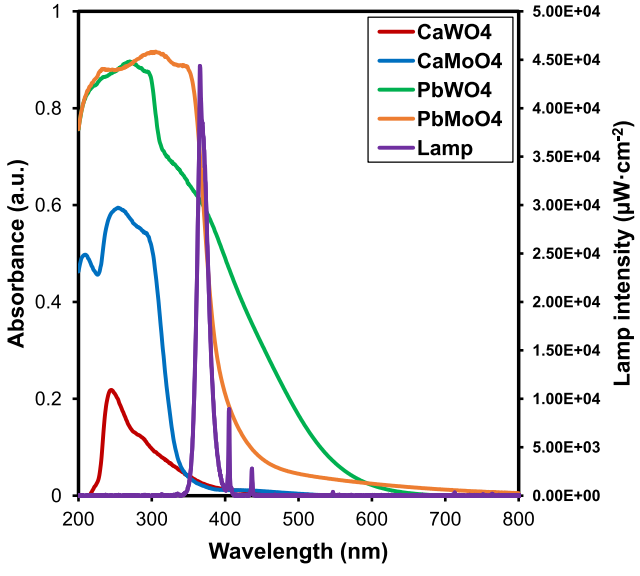


**Fig. 1.** Lamp spectrum and absorbance of the scheelite samples prepared by different methods.

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