

Single step hydrothermal based synthesis of M(II)Sb₂O₆ (M = Cd and Zn) type antimonates and their photocatalytic properties

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Abstract. Experiments involving single step hydrothermal reactions of the divalent metal (Zn²⁺, Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺ and Mn²⁺) salts with ilmenite NaSbO₃ yielded pure divalent antimonates in the case of CdSb₂O₆ crystallizing in the PbSb₂O₆ type structure and ZnSb₂O₆ crystallizing in the trirutile structure type. In the case of Pb²⁺, Cu²⁺, Ni²⁺ and Mn²⁺ divalent cations, phase pure product could not be obtained. The obtained powders were characterized by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and UV-visible diffuse reflectance spectroscopy. The oxide powders obtained possessed lower crystallite size as compared to their solid-state synthesized counterparts. This was evident from the broadening of the powder X-ray diffraction peaks. The antimonates were photocatalytically active for the decomposition of methylene blue (MB) dye under UV light irradiation.

Keywords. Hydrothermal; antimonates; photocatalytic; methylene blue.

1. Introduction

Transition metal oxides are appropriate candidates for many applications including heterogeneous catalysis, gas sensors, photoelectrolysis, semiconductor or superconductor devices (Rao 1989) and photocatalysis (Linsebigler *et al* 1995; Fox and Dulay 1993) etc to mention a few. Transition metal antimonates, with the general formula MSb₂O₆ (M = Zn, Cd, Pb, Ni, etc) have been investigated primarily because of their interesting structure, electronic and optical properties. These oxides (M = Zn, Ni) crystallize in the trirutile crystal structure in the space group *P4₂/mmm*. The exceptions are CuSb₂O₆ (Nakua *et al* 1991; Jiao *et al* 2007) and MnSb₂O₆ (Reimers and Greedan 1989). The former adopts a monoclinically distorted trirutile structure with the space group, *P2₁/n* and the latter with the columbite structure having the space group, *P321*. The trirutile structure (figure 1) has AB₂O₆ stoichiometry and is an ordered variant of the rutile structure. PbSb₂O₆ structure type (figure 1) results from the rutile structure when the radius of the *M*-site cation is increased. It contains two-dimensional layers of edge-sharing Sb₂O₆ octahedra. The Pb²⁺ ions fill the octahedral holes above and below the vacant octahedral site in the Sb₂O₆ layers.

It has been widely recognized that the *nd*¹⁰ or *ns*² orbital of metal cations can hybridize with the *O2p*⁶ orbital of the valence band, giving rise to the modified energy band structure with a narrowed bandgap which helps in photocatalytic applications of the resultant oxide materials. Semiconductor oxide photocatalysts based on the metal

cations with *d*⁰ and *d*¹⁰ configurations usually respond only to the UV light irradiation (Kudo 2007). Antimonates constitute a large family of wide bandgap *p*-block semiconductors, which have been identified as good photocatalysts for UV light irradiation. Many *p*-block metal oxides with antimony such as M₂Sb₂O₇ (M = Ca, Sr) (Sato *et al* 2002), CaSb₂O₆ (Sato *et al* 2002) and NaSbO₃ (Sato *et al* 2002) have been reported to photochemically split water under UV light irradiation. We reported the silver antimony-based oxides with ilmenite structure, AgSbO₃, (Singh and Uma 2009) and Sn²⁺-based antimonates with pyrochlore structure (Uma *et al* 2009) capable of photocatalytic decomposition of various organic compounds such as methylene blue, rhodamine B, methyl orange and 4-chlorophenol under UV and visible light irradiation. PbSb₂O₆ has been known to decompose methylene blue, an organic dye under UV light irradiation (Zhang *et al* 2006). Photocatalytic activity depends upon the electronic structure which again is decided by the structural features of the mixed metal oxides. Tunnel structure combined with the charge separation caused by the distortion of the metal-oxygen octahedra has been shown to enhance the photocatalytic decomposition of organic compounds (Matsuoka *et al* 2007).

The synthesis of antimonates such as (MSb₂O₆ where M = Cd, Zn, Pb, Cu, Ni and Mn) has been reported in the past through conventional solid-state method from the mixture of corresponding oxides and requires high temperature and multiple steps of grinding and heating. CdSb₂O₆ and ZnSb₂O₆ have been prepared by heating at 1170 and 1270 K for many hours (Mizoguchi and Woodward 2004). Similarly, the solid-state preparation of PbSb₂O₆ requires heating

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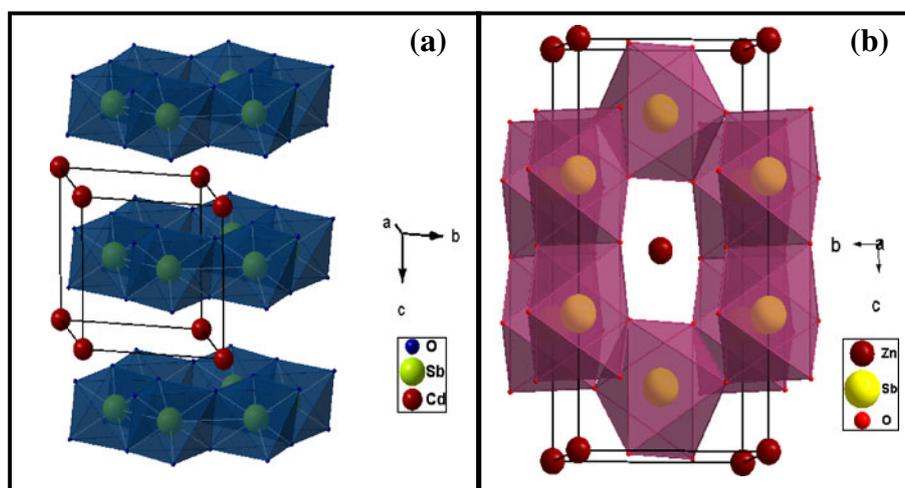


Figure 1. Crystal structure of (a) CdSb_2O_6 having PbSb_2O_6 structure type and (b) ZnSb_2O_6 having trirutile structure.

of the reactant oxides at 873 and 1023 K for several hours (Zhang *et al* 2006). CuSb_2O_6 (Nakua *et al*), MnSb_2O_6 (Scott 1987) and CoSb_2O_6 (Reimers and Greedan 1989) could be prepared at temperatures 1273, 1173 and 1323 K, respectively. Herein, we detail the results of our investigation based on hydrothermal reaction of the ilmenite NaSbO_3 with the divalent metal salt solutions for the successful synthesis of CdSb_2O_6 and ZnSb_2O_6 . This method has also led to the smaller crystallite size of the oxides as evident from the broadening of the peaks in the powder X-ray diffraction. The crystallite size was calculated from the Scherrer's formula and was found to be 15 and 19 nm for CdSb_2O_6 and ZnSb_2O_6 , respectively. The products are characterized for their optical absorption behaviour followed by photocatalytic measurements for the decomposition of methylene blue (MB) under UV light irradiation.

2. Experimental

2.1 Synthesis

Antimonates of the type $\text{M(II)Sb}_2\text{O}_6$ where $\text{M} = \text{Zn, Cd, Pb, Cu, Ni}$ and Mn were investigated by the reaction of ilmenite, NaSbO_3 , with divalent metal chloride solutions under hydrothermal conditions. Stoichiometric amounts of ilmenite, NaSbO_3 , prepared by the solid-state method (Nalbandyan *et al* 2006) along with respective metal salts such as CdCl_2 (Qualigens, 95%), ZnCl_2 (Speckpure, AR, 98%), PbCl_2 (Thomas Baker), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (CDH, AR, 98%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Spectrochem, 99%) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (CDH, AR, 99.5%) were taken with appropriate volume of water in a teflon-lined hydrothermal vessel. Various temperatures ranging from 150–240 °C for different time durations were investigated. The obtained powders were filtered, washed with water and dried in air.

2.2 Characterization

The powder X-ray diffraction patterns were recorded using PANalytical X'pert Pro diffractometer employing $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). SEM micrographs of the samples were recorded in JEOL 200 KeV instrument. The elemental compositions were determined using QUANTA 200 FEG (FEI, The Netherlands) scanning electron microscope with EDX attachment. SEM images were also recorded from Carl-Zeiss scanning electron microscope with EDS attachment. UV-visible diffuse reflectance data were collected over the spectral range, 200–1000 nm, using Perkin Elmer Lambda 35 scanning double beam spectrometer equipped with a 50 mm integrating sphere. BaSO_4 was used as a reference. The data were transformed into absorbance with the Kubelka–Munk function.

2.3 Photocatalytic decomposition of dye, methylene blue (MB)

Photocatalytic experiments were carried out using a 500 W Xenon arc lamp (Oriel, Newport, USA) along with a water filter to cut down IR radiation and glass cut-off filters to provide UV light as desired. The visible cut-off filter used was Melles Griot-03SWP602 to permit only UV light ($\lambda < 400 \text{ nm}$) radiation as desired. The experimental details of the photochemical reactor have been reported earlier (Singh and Uma 2009). A typical experiment of degradation was carried out as follows: 0.25 g of catalyst was added to 150 ml of aqueous solution of methylene blue (MB) with an initial concentration of $10 \times 10^{-6} \text{ mol/L}$ for UV irradiation experiments. Prior to irradiation, suspension of the catalyst and dye solution was stirred in dark for 30–60 min, so as to reach the equilibrium adsorption. 5 ml aliquots were pipetted out periodically from the reaction mixture. The solutions were centrifuged and the concentration of the solutions were

determined by measuring the maximum absorbance ($\lambda_{max} = 665$ nm) for MB.

3. Results and discussion

3.1 Synthesis and structure

The reaction of $NaSbO_3$ with $CdCl_2$ and $ZnCl_2$ solutions under hydrothermal conditions has been found to be effi-

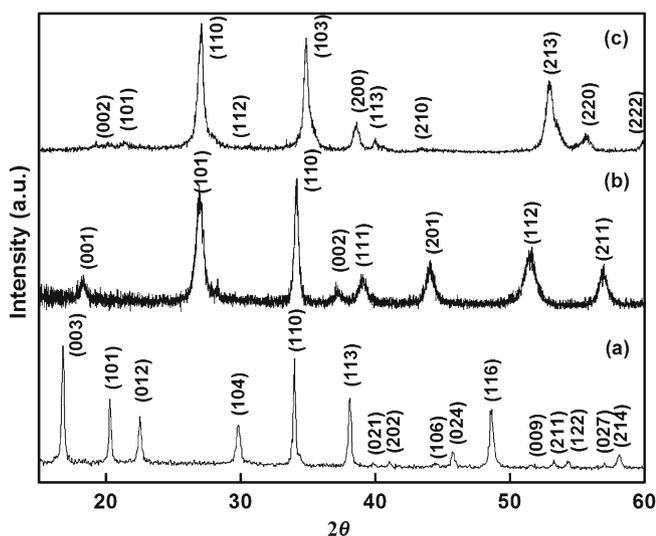


Figure 2. Powder X-ray diffraction patterns of (a) $NaSbO_3$, (b) $CdSb_2O_6$ and (c) $ZnSb_2O_6$.

cient for the preparation of $CdSb_2O_6$ and $ZnSb_2O_6$. These products were readily obtained, respectively at the reaction temperatures of 210 °C (3 days of reaction duration) and 230 °C (4 days of reaction duration). Powder X-ray diffraction patterns of the products confirmed the formation of phase pure $CdSb_2O_6$ and $ZnSb_2O_6$ (figure 2). Lattice parameters were obtained by the Le Bail fitting of the as-prepared samples using TOPAS refinement software (Coelho 2003). Ilmenite, $NaSbO_3$, crystallizes in $R\bar{3}$ space group with the lattice parameters, $a = 5.292(9)$ and $c = 15.930(1)$ Å. The lattice parameters of $CdSb_2O_6$ with $PbSb_2O_6$ structure type (space group $P\bar{3}1m$) were $a = 5.325(7)$ and $c = 4.694(1)$ Å. The refined lattice parameters for $ZnSb_2O_6$ with trirutile structure (space group $P4_2mm$) were $a = 4.6827(8)$ and $c = 9.277(1)$ Å. The lattice parameters were found to agree with those reported in the literature (Mizoguchi and Woodward 2004). In the case of $NiSb_2O_6$ and $CuSb_2O_6$, pyrochlore phase formation was also seen in addition to the desired products, while the reaction was incomplete in the case of $PbSb_2O_6$. The reaction of $NaSbO_3$ with divalent metal salt solutions producing the oxides $CdSb_2O_6$ and $ZnSb_2O_6$ may be considered as ion exchange because of the rigidity and stability associated with the presence of the layers formed by the edge-shared antimony oxygen octahedral structure observed in $NaSbO_3$, $CdSb_2O_6$ and $ZnSb_2O_6$ oxides. The other possibility of the reaction occurring after the decomposition of the reactants could not be ruled out under the present experimental conditions. However, it is to be noted that a single step of reacting $NaSbO_3$ with the divalent metal ions under hydrothermal conditions provides an efficient method for the

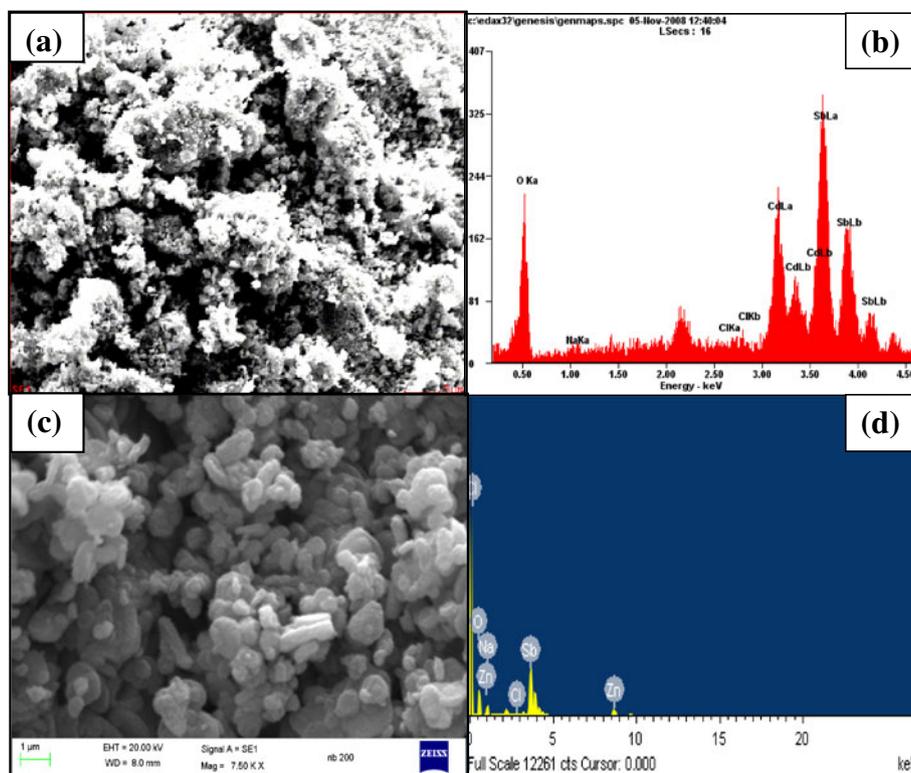


Figure 3. SEM images and EDAX analysis of (a) and (b) $CdSb_2O_6$ and (c) and (d) $ZnSb_2O_6$.

synthesis of these oxides. The SEM images of CdSb_2O_6 and ZnSb_2O_6 are shown in figure 3. The crystallites are agglomerated in both the cases and are in the micrometer range. The EDAX results confirm the 1:2 ratio of Cd:Sb and Zn:Sb in the final products as shown in figure 3.

3.2 Optical properties

Figure 4 shows the absorption spectra of CdSb_2O_6 and ZnSb_2O_6 , respectively. The insets in the figures show the plot of absorbance vs photon energy to estimate the bandgaps. The bandgaps of CdSb_2O_6 and ZnSb_2O_6 were found to be 3.74 and 3.00 eV, respectively. The bandgap of 3.8 eV reported for CdSb_2O_6 matched very well with that of the present work. The reported bandgap for ZnSb_2O_6 was slightly higher (3.5 eV) than the observed value of 3.00 eV found for the sample prepared under hydrothermal conditions. The absorption edge of CdSb_2O_6 with the creamy white colour was observed in the UV region with an extended tail into the visible region. In the absorption spectrum of ZnSb_2O_6 , the absorption edge is closer to the 380–400 nm range and again with a tail reaching up to 450 nm in the visible region. In the Kubelka–Munk spectrum of ZnSb_2O_6 , a large KM absorbance was found in the near IR range because of the excitations originating from the plasma frequency due to free electrons in the conduction band. The free carriers arise from the presence of a small oxygen deficiency. This NIR absorption is responsible for the greenish colour observed in ZnSb_2O_6 (Mizoguchi and Woodward 2004).

3.3 Photocatalytic properties

The parent compound, ilmenite (NaSbO_3) could degrade MB under UV light irradiation, despite with a slow decomposi-

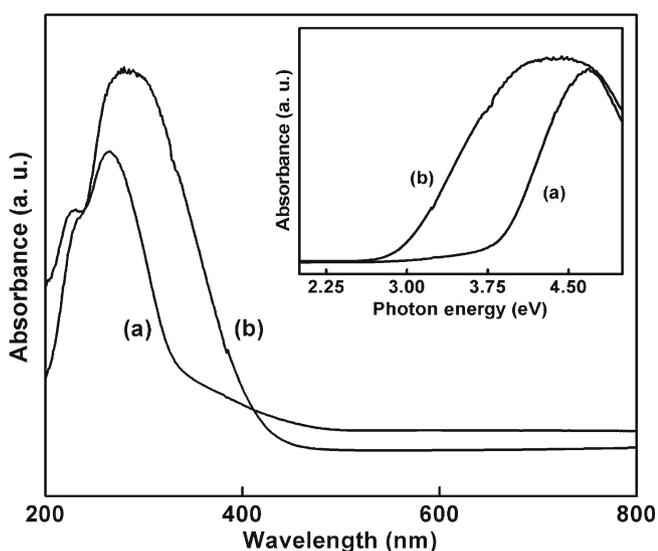


Figure 4. UV-visible diffuse reflectance spectrum of (a) CdSb_2O_6 and (b) ZnSb_2O_6 . Inset shows plot of absorbance vs photon energy of (a) CdSb_2O_6 and (b) ZnSb_2O_6 .

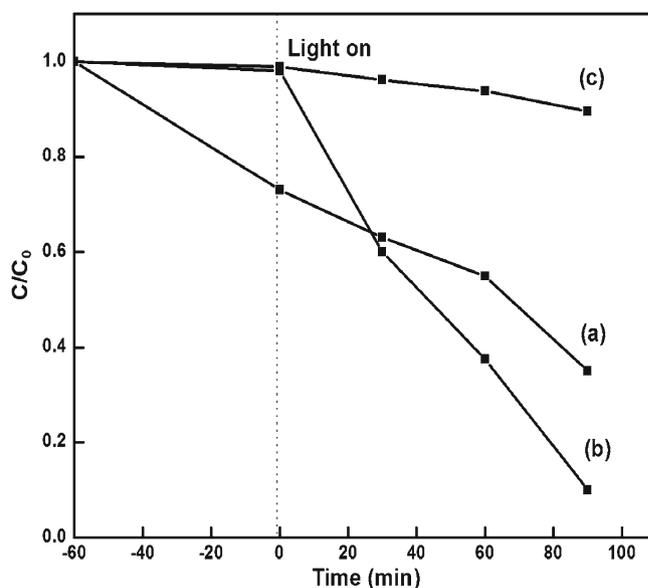


Figure 5. Photodegradation of methylene blue as indicated by concentration (C_0 is initial concentration and C is concentration at any time, t) of MB with time under UV radiation, (a) on CdSb_2O_6 , (b) on ZnSb_2O_6 and (c) on CdSb_2O_6 synthesized by solid state method.

tion rate (Singh and Uma 2009). We were interested to study the effect of the divalent cations in improving the photocatalytic property for the decomposition of various organic compounds under UV light irradiation. The degradation of MB over the prepared divalent antimonates was investigated under UV ($\lambda < 400$ nm) light radiation (figure 5). The aqueous MB solution has the maximum absorbance around 660 nm. The decomposition of the dye was complete at around 90 min in the UV light irradiation for both CdSb_2O_6 and ZnSb_2O_6 . This was confirmed by the decrease in the intensity at 665 nm of MB-dye molecule. In each of the cases, the concentrations of MB solutions were plotted with time. For comparison, we have given the photocatalytic activity for CdSb_2O_6 synthesized by the solid-state method. It is clear that the CdSb_2O_6 synthesized in the present study showed higher photocatalytic activity for the decomposition of MB solution under identical experimental conditions. Further experiments involving the decomposition of other dye solutions may be useful to validate the role played by the method of synthesis.

4. Conclusions

Reactions of the ilmenite, NaSbO_3 , with divalent metal salts under hydrothermal conditions resulted in the formation of divalent antimonates CdSb_2O_6 and ZnSb_2O_6 in a single step. Because of the hydrothermal method of preparation, the resulting oxide powders exhibited lower crystallite sizes as indicated by the broadening of the peaks in the powder X-ray diffraction patterns. Binary oxides in trirutile and PbSb_2O_6 type phases, viz. CdSb_2O_6 and ZnSb_2O_6 , were found to

be photocatalytically active for the decomposition of the methylene blue dye under UV light irradiation.

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