

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

A novel composite material based on antimony(III) oxide and amorphous silica

Ludmila A. Zemnukhova, Alexander E. Panasenko*

Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences, 690022 Vladivostok, Russia

ARTICLE INFO

Article history:

Received 11 September 2012

Received in revised form

1 February 2013

Accepted 3 February 2013

Available online 11 February 2013

Keywords:

Silica

Antimony oxide

Composite materials

Hydrolysis

Optic properties

ABSTRACT

The composite material $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ was prepared by hydrolysis of SbCl_3 and Na_2SiO_3 in an aqueous medium. It has been shown that the composition of the material is influenced by the ratio of the initial components and the acidity of the reaction medium. The morphology of the material particles and its specific surface area have been determined. The thermal and optic properties were also investigated.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Double oxides of silicon and various metals excite a heightened interest due to their valuable optic, electric, mechanical and chemical properties. Homogeneous systems of silicon oxide and various metals (calcium, magnesium, aluminum, titanium, iron, nickel, etc.) oxides are used in manufacturing most of glasses, as sorbents, catalysts (as both substrate and active phase), ionic conductors, gas sensors, and semiconductors [1–4]. Usage of silicon dioxide in particular promotes fabrication of finely dispersed materials with highly developed surface that usually has a positive effect on the product properties. Mixed oxides including those of antimony have high catalytic activity and selectivity in the reactions of organic synthesis. Their sorption properties that allow producing ion-exchange materials, molecular sieves, and ion-selective sorbents are also of interest [5–9]. Presently, the information on the oxide system $\text{Sb}_2\text{O}_3\text{--SiO}_2$ is insignificant. It is generally known that such substances can be obtained from aqueous solutions, but their properties are not yet investigated in detail [10].

The objective of this work consisted in development and optimization of the method of synthesis of mixed antimony(III) and silicon oxides $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$, investigation of the mechanism of their formation, determination of their structure,

morphology, and specific surface area as well as studies of thermal behavior and optic parameters depending on the composition and synthesis conditions.

2. Experimental section

In order to establish regularities of formation of the mixed antimony(III) and silicon oxides and optimize the conditions of their fabrication, a series of synthesis was carried out from aqueous solutions by hydrolysis under variable conditions.

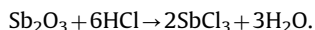
The initial substances for the experiments were: antimony oxide Sb_2O_3 “Merck”, chem. pure grade; amorphous silicon dioxide SiO_2 , GOST 9428-73, pure grade; hydrated silicic acid $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, GOST 4214-78, pure grade; NaOH, chem. pure grade; concentrated HCl, analytical grade. Synthesis was carried out at molar ratios $\text{Sb}_2\text{O}_3\text{:SiO}_2$ from 1:0.5 to 1:10 through interaction of SbCl_3 aqueous solutions (prepared by dissolving Sb_2O_3 in concentrated HCl) and Na_2SiO_3 (prepared by dissolving SiO_2 in 5 M NaOH solution at heating). Mixing of these solutions resulted in simultaneous hydrolysis and formation of a bulky white precipitate. It was separated using a filter, washed out with water and acetone and dried in air at room temperature.

Identification of the products and determination of their composition were carried out by the chemical and X-ray analysis and IR spectroscopy method. The antimony(III) content in the samples was determined by the bromatometric titration. To determine the water amount, a sample was treated with

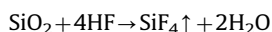
* Corresponding author. Fax: +7 423 231 18 89.

E-mail address: panasenko@ich.dvo.ru (A.E. Panasenko).

concentrated hydrochloric acid and annealed at 600 °C. As a result, antimony(III) oxide turned into antimony(III) chloride having the boiling temperature of 223 °C:



Total water and antimony oxide contents were calculated from the change of the sample weight. The weight of evaporated water was found from the Sb_2O_3 content measured by titration. The amount of SiO_2 was found from the change of the sample weight (Sb_2O_3 was removed by the above-mentioned way) after treatment with the mixture of sulfuric and hydrofluoric acids followed by annealing:



The phase composition of the reaction product was determined according to the X-ray diffraction patterns recorded at a “Bruker D8 Advance” diffractometer. The IR absorption spectra were registered in the range 400–4000 cm^{-1} using a “Shimadzu FTIR Prestige-21” Fourier-spectrometer. The thermogravimetric curves were recorded at a synchronous Netzsch STA 449C Jupiter analyzer at the heating rate of 5° per minute. The morphology of the substance was studied on the basis of the microimages obtained at a JSM 7700F scanning electron microscope.

The diffuse reflection spectra of the samples pressed into tablets before the photometric measurements were recorded at a Hitachi U-3010 spectrophotometer. The whiteness (W) value was calculated using the standard formula [11]:

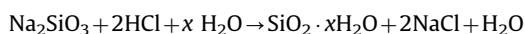
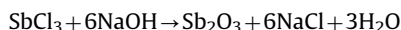
$$W = 2R_{430} - R_{670},$$

where R —the reflection coefficient at respective wavelength.

The specific surface area value was defined according to the BET-theory by the nitrogen sorption method at the liquid nitrogen temperature at a “Sorbtomer-M” analyzer. Particle size distribution was studied using the laser diffraction method at a “Mastersizer 2000” analyzer.

3.discussion",5,1,1> Results and discussion

Mixing of Sb^{3+} acid solution and SiO_3^{2-} alkali solution results in simultaneous hydrolysis of these ions with producing respective oxides. The process of hydrolysis can be represented through the following reactions:



Thus, the hydrolysis product has the composition $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (Table 1). The X-ray diffraction analysis shows that, depending on SiO_2 contents, this substance can be either amorphous (due to the amorphous character of silica and small contents of antimony oxide) or partially crystalline (the X-ray diffraction pattern consists of a halo of the amorphous phase and reflections of the crystal $\beta\text{-Sb}_2\text{O}_3$ one at the same time) (Fig. 1). In its IR spectrum, one can see the absorption bands related to SiO_2 and $\beta\text{-Sb}_2\text{O}_3$ (Fig. 2) [12,13].

Hydrolysis of Sb^{3+} and SiO_3^{2-} ions proceeds simultaneously, however, at different rates. Antimony oxide is formed much faster producing relatively large crystal concretions, which surface is further coated with the deposited silicon dioxide. At the microphotographs (Fig. 3(c)), one can clearly see Sb_2O_3 needle crystals of a thickness of 50–150 nm and of a length of 0.3–1 μm . Such a shape is typical for orthorhombic $\beta\text{-Sb}_2\text{O}_3$, valentinite. Multiple Sb_2O_3 crystals form dense concretions of an irregular shape of a size 2–10 μm . In case of amorphous samples, as seen from Fig. 3(b), almost the whole antimony oxide surface is coated with

Table 1
Compositions of composite material ($n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$) depending on the synthesis conditions (the initial molar ratio Sb:Si equals 1:1).

No.	Acidity of reaction medium (pH)	Crystal state according to X-ray data	Contents (%)	
			Sb(III) compound	SiO_2
1	0.09	Cryst.	$\text{Sb}_4\text{O}_5\text{Cl}_2$, 70.3	23.5
2	0.30	Cryst.	$\text{Sb}_4\text{O}_5\text{Cl}_2$, 73.6	24.0
3	0.40	Amorph.	Sb_2O_3 , 64.0	13.7
4	0.52	Amorph.	Sb_2O_3 , 65.4	22.8
5	0.75	Amorph.	Sb_2O_3 , 64.0	23.4
6	0.90	Amorph.	Sb_2O_3 , 61.7	25.5
7	7.00	Amorph.	Sb_2O_3 , 64.8	18.1
8	13.34	Amorph. + cryst.	Sb_2O_3 , 68.6	14.5
9	13.56	Cryst.	Sb_2O_3 , 86.3	6.7
10	13.73	Cryst.	Sb_2O_3 , 79.7	10.9
11	14.00	Cryst.	Sb_2O_3 , 92.5	1.67

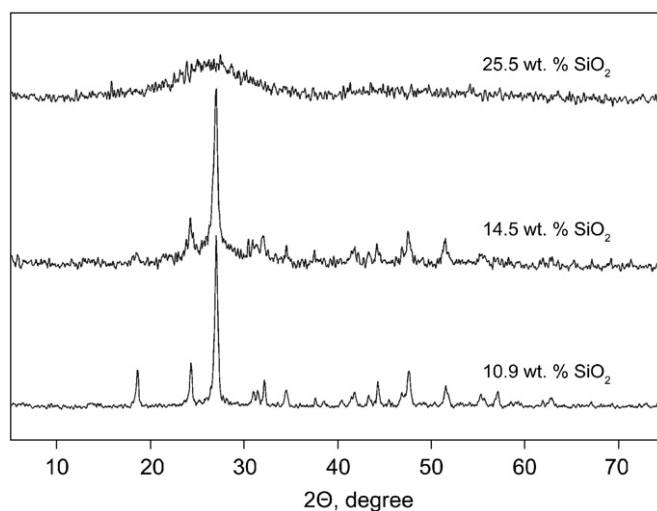


Fig. 1. X-ray diffraction patterns of composite materials with various SiO_2 contents (samples 6, 8 and 10 in Table 1).

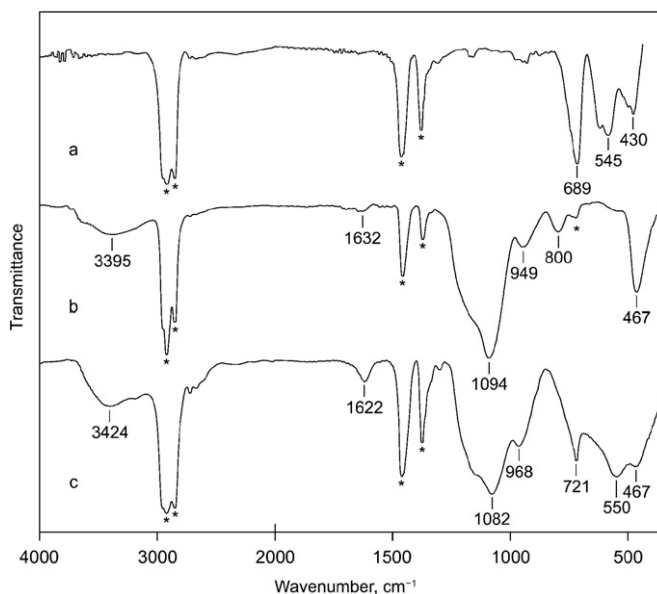


Fig. 2. IR-spectra: (a) $\beta\text{-Sb}_2\text{O}_3$, (b) $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, (c) prepared material $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (samples 3 in Table 1).

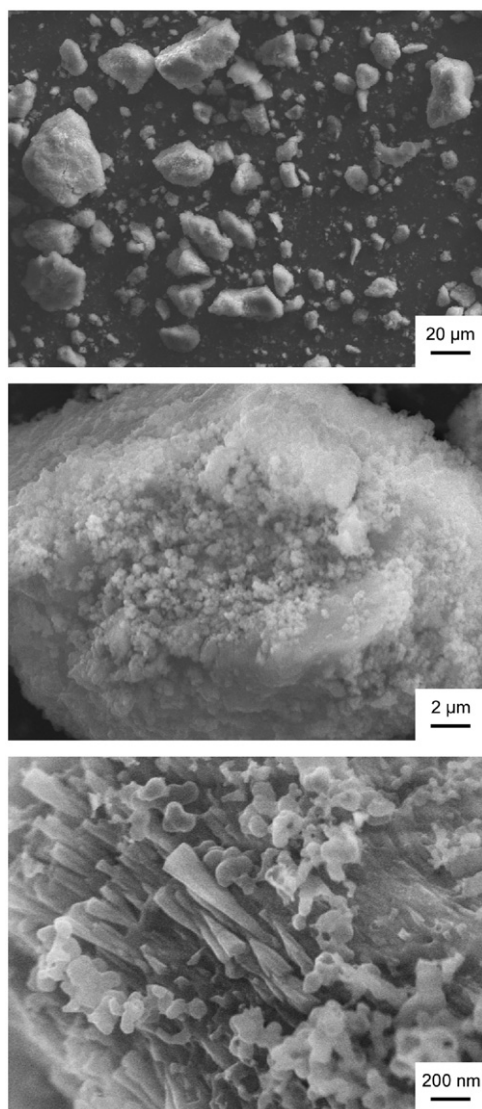


Fig. 3. Microphotographs of $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

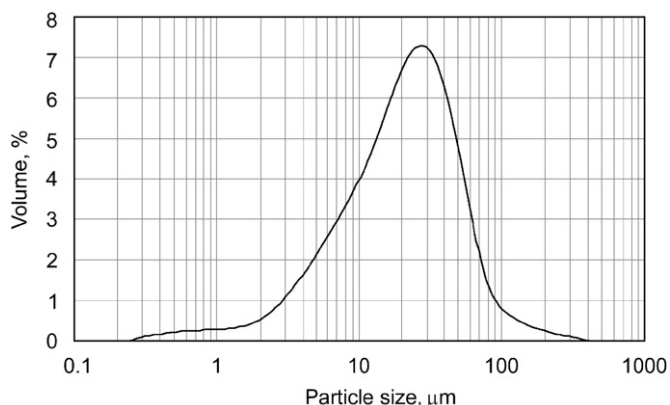


Fig. 4. Distribution of particles by sizes (sample 5 in Table 1).

the layer of high-dispersed silicon dioxide forming a gauze-like structure with predominance of particles of a size of 30–100 nm. In general, the size of such composite particles varies from several up to several dozen μm . The particle size distribution determined by the laser diffraction method shows that 75% of particles have a

size from 10 up to 60 μm (Fig. 4). The specific surface area of the materials calculated by the BET method (nitrogen adsorption) equals to 25–32 m^2/g for various samples. Moreover, the substance does not virtually have micropores and its porosity is represented by meso- and macropores.

One can vary the composition of the reaction product in a wide range through varying the Sb:Si ratio or the amounts of acid and alkali in initial solutions (Table 1, Fig. 5). For the equivalent amounts of acid and alkali (the initial molar ratio Sb:Si equals 1:1), the hydrolysis product contains 64.8% Sb_2O_3 and 18.1% SiO_2 . In strong alkali medium (pH 14), SiO_2 contents in the reaction product is less than 2%. In the strong acid one (pH < 0.4), SbCl_3 is not hydrolyzed completely, and the reaction product is oxochloride $\text{Sb}_4\text{O}_5\text{Cl}_2$ (by the X-ray diffraction data).

Silicon oxide obtained by its precipitation from silicate solutions always contains a certain water amount. In the IR spectra, the absorption bands near 3400 and 1630 cm^{-1} relate to valence and deformation vibrations of water molecule bonds, whereas those at 950–960 cm^{-1} characterize silanol groups (Fig. 2(b and c)). The water content in the samples investigated attained 9.7%. Like usual silica gels, water adsorbed on the surface (about 8%) is removed at heating up to 200 $^\circ\text{C}$ (Fig. 6). The following heating up to 340 $^\circ\text{C}$ results in detachment of water from silanol groups proceeding with formation of Si–O bonds (weight loss about 1.5%). Above 450 $^\circ\text{C}$, the sample weight increases, which is caused by oxidation of Sb(III) to Sb(V) with atmospheric oxygen and corroborated by the X-ray diffraction data.

Up to present, antimony oxide and silica are have been widely used as white pigments. The material obtained is also promising

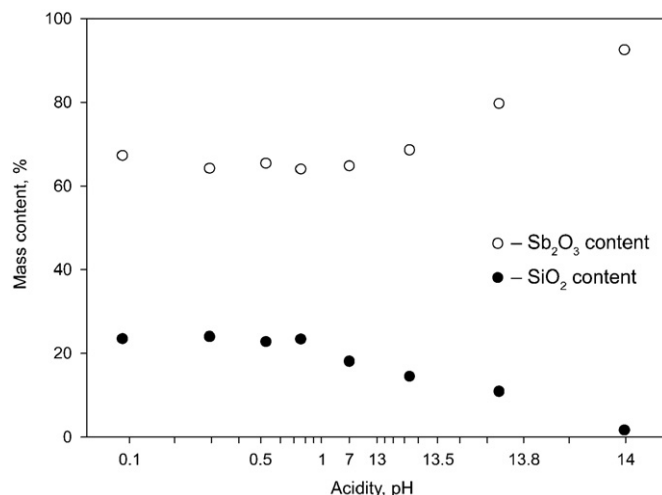


Fig. 5. Dependence of composition of samples on the acidity of reaction medium.

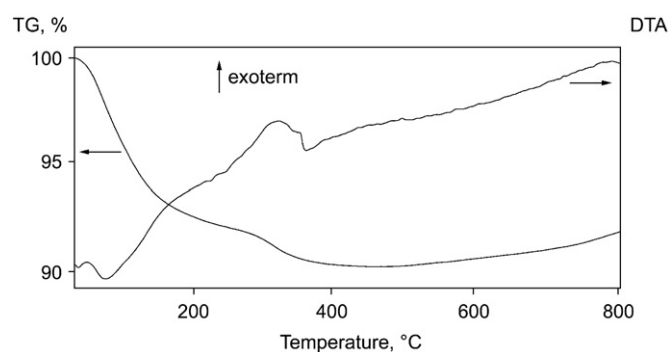


Fig. 6. Thermogravimetric curves of $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ with Sb_2O_3 content 33.7%.

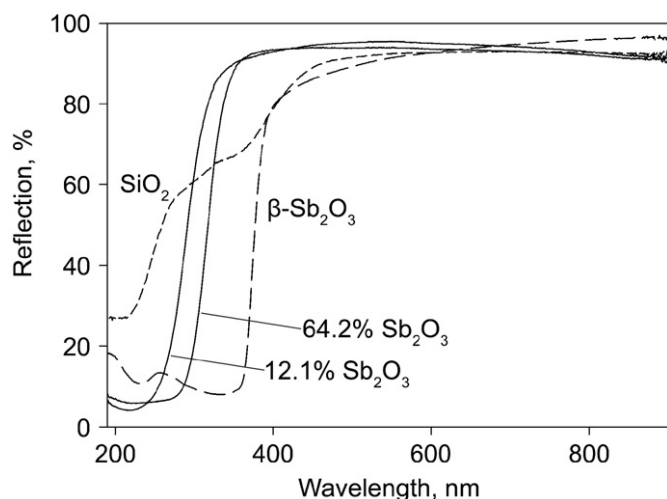


Fig. 7. Total reflection spectra of commercial SiO_2 (GOST 9428-73), antimony oxide ($\beta\text{-Sb}_2\text{O}_3$) and composite materials $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ of various compositions.

as a filling pigment for enamels, glazes, plastics, and rubbers. As can be seen from the reflection spectra (Fig. 7), pure Sb_2O_3 and SiO_2 have a high-reflection area (80–95%) in the visible and IR ranges and a low-reflection one (4–8%) in the UV range that is typical for powders of various oxides. In general, the reflection spectra of the samples of the composite material $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ are between those of pure Sb_2O_3 and SiO_2 . However, in the range 300–350 nm their reflection coefficient is much higher than that of pure substances and attains 95.5% in the maximum. The whiteness values vary from 82.1 up to 94.2%. Thus, as was described above, through varying the synthesis conditions one can obtain a material, which not only combines a desirable ratio of optic properties and technological quality typical to silica and antimony oxide, but also surpasses them by in the reflection coefficient due to the synergic effect.

4. Conclusion

The method of fabricating the composite material $n\text{Sb}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$, whose composition can be controlled by variation of

the ratio of the initial components and the acidity of the reaction medium, is suggested. It was shown that its particles were aggregates of $\beta\text{-Sb}_2\text{O}_3$ crystals coated with the layer of high-dispersed amorphous SiO_2 . The sizes of individual Sb_2O_3 crystals and SiO_2 particles are about 100 nm while total size of the composite particle is 10–60 μm . It has been established that in the blue range of the spectrum the reflection coefficient of this material is higher than those of pure antimony and silicon oxides.

Acknowledgments

The work was supported by the FEBRAS grant “Synthesis and properties of mixed antimony(III) and silicon oxides”. The authors are grateful to G.A. Fedorishcheva, V.G. Kuryavyi, and K.N. Galkin for their assistance in the experiments as well as L.G. Kharlamova and D.V. Marinin for providing language help.

References

- [1] K. Laatikainen, J. Pakarinen, M. Laatikainen, R. Koivula, R. Harjula, E. Paatero, *Sep. Purif. Technol.* 75 (2010) 377–384.
- [2] A. Hilonga, J.-K. Kim, P.B. Sarawade, H.T. Kim, *Powder Technol.* 199 (3) (2010) 284–288.
- [3] S.A. El-Safty, Y. Kiyozumi, T. Hanaoka, F. Mizukami, *Appl. Catal., A* 337 (2) (2008) 121–129.
- [4] T.V.S. Sarma, S. Tao, *Sens. Actuators, B* 127 (2) (2007) 471–479.
- [5] D. Mao, J. Xia, B. Zhang, G. Lu, *Energy Convers. Manage.* 51 (6) (2010) 1134–1139.
- [6] B. Li, S. Li, Y. Wang, N. Li, X. Liu, B. Lin, *J. Solid State Chem.* 178 (2005) 1030–1037.
- [7] M. Mee, B.C. Davies, R.G. Orman, M.F. Thomas, D. Holland, *J. Solid State Chem.* 183 (2010) 1925–1934.
- [8] E.S. Ribeiro, S.L.P. Dias, Y. Gushikem, L.T. Kubota, *Electrochim. Acta* 49 (5) (2004) 829–834.
- [9] V.A. Ignatova, O.I. Lebedev, U. Watjen, L.V. Vaeck, J.V. Landuyt, R. Gijbels, F. Adams, *Mikrochim. Acta* 139 (2002) 77–81.
- [10] A.G. Gritsenko, B. Jovanovic, US Patent 20090214658.
- [11] E.F. Belen'kii, I.V. Riskin, *Khimiya i Tekhnologiya Pigmentov, Khimiya, Leningrad*, 1974.
- [12] C.A. Cody, L. DiCarlo, R.K. Darlington, *Inorg. Chem.* 18 (6) (1979) 1572–1576.
- [13] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fifth ed., John Wiley and Sons, New York, 1997.