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Novel organo-colloidal synthesis, optical properties, and structural analysis of antimony sesquioxide nanoparticles

Ivana Lj. Validžić · Nadica D. Abazović · Miodrag Mitrić · Milan V. Lalić · Zoran S. Popović · Filip R. Vukajlović

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Abstract We report the novel colloidal syntheses in organic media of antimony sesquioxide (Sb₂O₃) spherical nanoparticles (30-250 nm) and octahedron microand nanocrystals $(100 \text{ nm} - 4 \mu \text{ m})$ depending on the synthetic method conditions. It is observed that small differences in the synthetic procedure cause large differences in the very changeable morphology. The structure of Sb₂O₃ powders was refined down to the Rfactors of 9.57, 7.44, 9.19, 9.78, and 8.30 %. The refinement showed that Sb₂O₃ powder belongs to the cubic crystal type with space group $Fd\bar{3}m$ (No. 227). The values of estimated standard deviations, as well as reliability factors, confirmed that the structure of Sb₂O₃ was well refined. Ultraviolet and visible (UV-Vis) absorption spectroscopy and diffuse reflectance measurements (DRS) reveal that the optical band gap energies found for the Sb₂O₃ octahedrons and nanoparticles, micro- and nanocrystals, respectively, are quite independent of the synthetic method conditions

M. V. Lalić

Departamento de Física, Universidade Federal de Sergipe, P.O. Box 353, São Cristóvão, SE 49100-000, Brasil

F. R. Vukajlović

"Vinča" Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia

and synthesized morphology and is found to be between 4.1–4.4 eV. No peaks in both photoluminescence (PL) emission and excitation spectra have been observed for a broad spectral range, typical for this material. In order to discriminate between conflicting experimental results concerning the band gap energy of this compound, we investigated theoretically the electronic structure and optical properties of one of the cubic sesquioxide Sb₂O₃ samples synthesized here. This has been done on the basis of density functional theory (DFT) with the generalized gradient approximation (GGA) and improved version of exchange potential suggested recently by Tran and Blaha (TBmBJ). The main characteristic of the calculated TBmBJ electronic structure is the significant improvement of the band gap value, which is in perfect agreement with our experimental measurements. The real and imaginary parts of the dielectric tensor are also calculated and interpreted in terms of the obtained electronic structure.

Keywords Optical materials and properties · Luminescence · Electron microscopy · X-ray technique · Electronic structure calculations

Introduction

Antimony sesquioxide (Sb_2O_3) , an important member of V-VI main group compounds, has been widely used for functional filters, covering agents, catalyst agents,

I. Lj. Validžić $(\boxtimes) \cdot N.$ D. Abazović \cdot M. Mitrić \cdot Z. S. Popović

[&]quot;Vinča" Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia e-mail: validzic@vinca.rs

flame retardants, glasses, sensors, and serves as the anode material for Li-ion batteries (Geng et al. 2011; Deng et al. 2006; Naidu et al. 2009). Because of their unique optical and optoelectronic properties, as well as their potential applications in the micro/nanoscale electronic and optoelectronic devices, special attention has been paid to Sb₂O₃ micro- or nanostructures. Also, Sb₂O₃ has a very high electrical resistance that recommends it for applications in the fields of solar cells, light-emitting devices, flat panel displays, etc. (Tigau et al. 2003, 2008). Up to now, various strategies have been reported on synthesis of Sb₂O₃ materials such as microemulsion method (Zhang et al. 2002; Guo et al. 2000), hydrothermal method (Ma et al. 2004; Liu et al. 2010; Chen et al. 2008), solution phase reduction method (Ye et al. 2006), γ -ray radiation-oxidization method (Liu et al. 1997), thermal vacuum evaporation method (Tigau et al. 2004), vapor condensation method (Zeng et al. 2004), hybrid induction and laser heating (HILH) method (Zeng et al. 2004), vapor transport and condensation method (Xu et al. 2007), vacuum evaporation method (Qiu et al. 2006), electrochemical preparation (Mohan et al. 2007), biosynthesis (Jha et al. 2009), etc. To the best of our knowledge, the synthesis of micro- or nanoparticles of Sb₂O₃ via an organo-colloidal method has not been reported, although it is known that the properties are strongly dependent on the synthesis methods (Shun et al. 2010). On the other hand, antimony sesquioxide Sb₂O₃ is an interesting semiconductor that may exhibit unique optoelectronic properties. Generally, band gap energy values of Sb₂O₃ reported almost fourty years ago are: 3.3 and 4.0 eV for orthorhombic and cubic crystal form, respectively (Wood et al. 1972; Wolffing et al. 1973). Since then very little attention has been paid to this subject. The complete understanding of the material properties is only possible when its structure and composition are precisely known.

In the present paper, the structural, morphological, and optical properties of the novel synthesized Sb_2O_3 spherical nanoparticles and octahedron micro- and nanocrystals are investigated. Special attention has been paid to the refinement of the crystal structures and the band gap values of the synthesized materials. To complete the analysis we also present theoretical calculations of electronic and optical properties of this compound.

Experimental method

All chemicals (antimony (III) acetate $(Sb(CH_3COO)_3)$ (99.0 % min Alfa Aesar), oleic acid (OA) $(C_{18}H_{34}O_2)$ (65 % GC Fluka), trioctylphosphine (TOP) (tech., 90 %, Aldrich), 1-octadecene (\geq 95 %, Aldrich), hexan (J. T. Baker), isopropyl alcohol (J. T. Baker), and methanol (J. T. Baker) were of the highest purity available and they were used without further purification.

In a typical synthesis of Sb₂O₃ nanoparticles and octahedron micro- and nanocrystals, depending on the synthetic method conditions, both Sb(III)-oleic acidcomplex precursor solutions and OA/TOP/octadecene solutions were prepared simultaneously. Sb(III)-oleic acid complex solutions were prepared by adding 0.6 g of Sb(CH₃COO)₃ to 2 ml oleic acid (OA). Mixtures were kept at 150 °C and stirred for 30 minutes until Sb(III)-acid complex was formed. The other flasks were loaded with 2 ml oleic acid (OA), 4 ml trioctylphosphine (TOP) (syntheses marked with A, B, C, and D), 8 ml trioctylphosphine (TOP) (synthesis marked with E), and different amounts of octadecene; 10 ml (A), 5 ml (B), and no octadecene present (C, D, and E). Procedures of synthesis for every separately synthesized sample (A, B, C, D, and E) are presented in Table 1. Mixtures were kept at 150 °C for about 30 minutes. Then, Sb(III)-oleic acid complex solutions were swiftly injected into the OA/TOP/octadecene solutions, respectively. The mixtures were maintained at 270 °C under continuous stirring. The as-synthesized Sb₂O₃ precipitates (A, B, C, D, and E) at 270 °C were heated for 5 minutes from the moment when Sb_2O_3 species appear. After this time, reaction was stopped by injection of hexane/isopropyl mixture (1/1,v/v). The resulting solid precipitates were retrieved by centrifugation and washed/precipitated a few times with methanol/isopropyl alcohol. The final products were dispersible in isopropyl alcohol.

The scanning electron microscopy (SEM) observations and measurements were performed using JEOL JSM-6460LV instrument (Tokyo, Japan). The Sb_2O_3 samples were coated with a thin layer of gold deposited by sputtering process.

Absorption spectra of the Sb_2O_3 samples in isopropyl alcohol were recorded using Thermo Scientific Evolution 600 UV–Vis spectrophotometer.

The X-ray Powder Diffraction (XRPD) patterns of investigated samples were obtained on a Philips PW-

$2 \text{ mlO.A.} + 0.6 \text{g Sb}(\text{CH}_3\text{COO})_3$								
A	В	С	D	Е				
2 ml O.A. +	2 ml O.A. +	2 ml O.A. +	2 ml O.A. +	2 ml O.A. +				
4 ml TOP +	4 ml TOP +	4 ml TOP	6 ml TOP	8 ml TOP				
10 ml octadecene	5 ml octadecene							

Table 1 Synthetic procedure used to obtain samples (A, B, C, D, and E)

1050 automated diffractometer using Cu K_{α} radiation (operated at 40 kV and 30 mA). A fixed 1° divergence and 0.1 mm receiving slits were used. Diffraction data for structural analysis were collected in the 2θ range of $10^{\circ}-120^{\circ}$, with scanning steps of 0.02° and expositions time of 12 s. Structure analysis was done by the use of the KOALARIE computing program (Cheary et al.1992) based on the Rietveld full profile refinement method (Rietveld 1969). Samples for XRPD measurements were prepared using standard protocol (Pecharsky et al. 2005).

Theoretical method

The calculations were carried out using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code (Blaha et al. 2001). The unit cell is partitioned into non-overlapping muffin-tin spheres around the atomic sites and interstitial region. For these two regions different basis sets were used and the Kohn-Sham equations were solved selfconsistently on an $8 \times 8 \times 8$ k-mesh in the first Brillouin zone (BZ) resulting in 29 irreducible kpoints. The exchange correlation potential was treated using: (a) the generalized gradient approximation (GGA) as parametrized by Perdew et al. (Perdew et al. 1996) (we will refer to this calculation as PBE) and (b) the Tran-Blaha recipe applied on a modified version of Becke and Johnson exchange potential (Becke et al. 2006) for the calculation of band gaps and other electronic properties, as explained in the recent works (Tran et al. 2009; Koller et al. 2011) (we will refer to this calculation as TB-mBJ). The parameter $RKMAX = R_{MT} \cdot K_{MAX}$ determines convergence, where $R_{\rm MT}$ is the smallest muffin-tin sphere radius and K_{MAX} is the plane wave cut-off. We take this parameter to be RKMAX = 7 while the reciprocal space truncation was controlled by parameter GMAX for which we used 12 Bohr⁻¹.

The interband contribution to the imaginary part of the dielectric function $\varepsilon_2(\omega)$ can be computed from the electronic structure by adding up all possible transitions from the occupied valence states (*n*) to the unoccupied conduction states (*n'*), taking into account the appropriate vertical transition for the dipole matrix elements (Ambrosch-Draxl et al. 2006):

$$\operatorname{Im}\left[\varepsilon_{\alpha\beta}(\omega)\right] = \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{n,n'} \int_{\mathrm{BZ}} d\mathbf{k} p_{\alpha;\mathbf{n}',\mathbf{n},\mathbf{k}} p_{\beta;\mathbf{n}',\mathbf{n},\mathbf{k}} \delta(E_{n'}(\mathbf{k}) - E_n(\mathbf{k}) - \hbar\omega)$$
(1)

where ω is the frequency of the incident radiation, *m* is the electron mass, *p* is the electron momentum operator, and α and β stand for the projections *x*,*y*,*z* of the incident light polarization.

On the basis of the calculated electronic structure (i.e., knowing the Kohn-Sham orbitals) of Sb₂O₃ we computed $Im[\varepsilon_{\alpha\beta}(\omega)]$ up to incident radiation energy of $\hbar\omega = 40eV$. Then the real part of the dielectric tensor is determined using the Kramers-Kronig relation. Both real and imaginary parts of $\varepsilon_{\alpha\beta}$ were calculated with a mesh of 29 **k**-points in the irreducible wedge of the first Brillouin zone. All other optical constants of the material (such as reflectivity, refraction index, and electron energy loss) could then be calculated by combining the real and imaginary part of the dielectric tensor. All graphs were produced with Lorentzian broadening of 0.06 eV. The scissors operator, which shifts the conduction band bottom, was not applied.

Results and discussion

Diffraction data showed that Sb_2O_3 diversely synthesized powders belong to the face-centered cubic type of structure, where all diffraction peaks could be indexed to a pure phase of Sb_2O_3 (JCPDS 01-071-



Fig. 1 Final Rietveld plots of Sb_2O_3 powders obtained for different synthetic procedure (A–E), and the standard pattern of Sb_2O_3 with corresponding planes (JCPDS 01-071-0365 (f))

Table 2 The structure R factors and the structural lattice parameters (*a*) values obtained for different synthesized samples (A, B, C, D, and E)

	А	В	С	D	Е
R (%)	9.57	7.44	9.19	9.78	8.30
a (Å)	11.1659	11.1641	11.1665	11.1659	11.1645

0365). The appearance of a cubic phase follows from the fact that cubic Sb₂O₃ will be formed when heating is conducted below 570 °C (Shun et al. 2010). The structure refinements were performed in the space group $Fd\bar{3}m$ (No. 227) in As₄O₆ structure type with the following crystallographic positions: Sb³⁺ ions are in special crystallographic position 32e[x, x, x] with local symmetry 3m. while the O^{2-} ions are in 48f[x, 0, 0] crystallographic position with local symmetry mm. Results of the final Rietveld refinements for all five samples with various synthetic procedures are depicted in Fig. 1A–E. The corresponding diffraction maxima for the standard pattern of Sb₂O₃ are given in Fig. 1F. Different procedures of synthesis for every separate sample (A, B, C, D, and E) are given in Table 1. The structure of antimony sesquioxide was refined down to the *R*-factor of 9.57 % (A), 7.44 % (B), 9.19 % (C), 9.78 % (D), and 8.30 % (E) presented in Table 2. The structural lattice parameters (a) (a =11.1659 Å (A), a = 11.1641 Å (B), a = 11.1665 Å (C), a = 11.1659 Å (D), and a = 11.1645 Å (E)) are

Sample	ATOM	$X(\sigma(X))$	$Y(\sigma(Y))$	$Z(\sigma(Z))$	B(σ (B))
A	Sb	0.8853(2)	0.8853(2)	0.8853(2)	0.863(7)
	0	0.1886(5)	0	0	1.421(9)
В	Sb	0.8861(8)	0.8861(8)	0.8861(8)	1.189(1)
	0	0.1917(2)	0	0	0.997(6)
С	Sb	0.8854(8)	0.8854(8)	0.8854(8)	1.219(5)
	0	0.1881(9)	0	0	1.719(1)
D	Sb	0.8855(2)	0.8855(2)	0.8855(2)	1.344(3)
	0	0.1853(3)	0	0	1.549(1)
Е	Sb	0.8853(1)	0.8853(1)	0.8853(1)	0.652(3)
	0	0.1909(8)	0	0	2.057(2)

Table 3 The structure of Sb₂O₃

Space group: $Fd\bar{3}m$ (No. 227). Unit cell dimensions $a = 11.1659\text{\AA}$ (A), $a = 11.1641\text{\AA}$ (B), $a = 11.1665\text{\AA}$ (C), $a = 11.1659\text{\AA}$ (D), and $a = 11.1645\text{\AA}$ (E). Cell content: 16 Sb₂O₃ molecules per unit cell

also given in Table 2. In Table 3 the unit cell dimensions as a result of the final refinements are presented. Values of estimated standard deviations as well as reliability factors confirmed that these data are reliable and that the structure was well refined.

The morphology of the Sb₂O₃ diversely synthesized powders was observed by scanning electron microscopy (SEM). SEM photographs of five samples prepared with different procedures of synthesis are shown in Fig. 2A-E. The morphology of the synthesized powder was found to be very dependent on the procedure of synthesis (cf. Table 1; Fig. 2), from Sb₂O₃ spherical nanoparticles to octahedral microand nanocrystals. To be exact, spherical nanoparticles are synthesized only by the procedure B (in the presence of octadecene). All other samples are characterized mostly by octahedral micro- and nanocrystals with quite broad size distribution. It is also important to mention that the largest morphological differences were observed for samples A (the largest mostly micrometer sizes octahedrons) and B (spherical nanoparticles) where the different amounts of octadecene were used. In the samples with no octadecene present the morphological differences are not significant. Fig. 3 presents the distribution of particles size deduced from SEM micrographs for the Sb₂O₃ diversely synthesized powders (A, B, C, D, and E).

Since Sb₂O₃ is a useful optical material, besides the explanation of new types of synthesis procedures and the structural and morphological characterizations of

our samples (cf. Tables 1, 2; Figs. 1, 2, and 3), we shall further put our thrust on the detailed experimental and theoretical investigations of the optical properties of this material. These investigations are essential, bearing in mind previously obtained different results even for such a basic electronic property as the band gap energy. Generally, the band gap energy values of Sb₂O₃ reported almost forty years ago are: 3.3 and 4.0 eV for orthorhombic and cubic crystal form, respectively (Wood et al. 1972; Wolffing et al. 1973). Tigau et al. (2005) measured optical response in the energy region up to 4.5 eV. They obtained the band gap energies of 3.6-3.4 eV for their polycrystalline Sb₂O₃ thin films with a thickness of 800 nm, deposited on glass substrates at different temperature ranges 300-573 K, while Zhang et al. (2012) reported the optical absorption edge energy to be 4.0 eV in their reflectance measurements.

Optical absorption measurements have been carried out using the UV–Vis spectroscopy, which provide a simple and effective method of explaining some features concerning the band structure. Since all experimental results, including XRPD and SEM observations, suggest that Sb_2O_3 spherical nanoparticles and octahedral (nano and micro) crystals are in pure high-quality crystalline phases, we can assume that the absorption spectrum represents the true absorption behavior of Sb_2O_3 bulk material.

Figure 4A shows the typical UV–Vis absorption spectra taken from slightly turbid Sb_2O_3 dispersions obtained from different procedures of synthesis (A, B,



Fig. 2 SEM images of Sb_2O_3 spherical nanoparticles and octahedron micro- and nanocrystals obtained from different procedures of synthesis (A–E)

C, D, and E, see Table 1). One of the common ways of extracting band gap from absorption spectra is to get the first derivative of absorbance with respect to photon energy and find the maxima in the derivative spectra at the lower energy sides (Becerril et al. 2004;

Morales et al. 2007). The E_g is associated to the maximum in the spectrum, i.e., to the photon energy where the absorbance reaches maximum. In Fig. 4B such derivative spectra of the samples are presented. The observed band gap energies for all samples,



Fig. 3 Particle size distribution deduced from SEM micrographs for all of the as-synthesized Sb_2O_3 spherical nanoparticles and octahedron micro- and nanocrystals (A–E)

obtained by different procedures of synthesis (A, B, C, D, and E), are almost identical and are $\sim 4.4 \text{ eV}$. By calculating the first derivative of absorbance we limited energy region for the determination of E_g .

Another and complementary way to estimate the direct and indirect band gap energies of our samples is to use the well-known relation: $\alpha = k(hv)^{-1}$ $(hv - E_{\sigma})^{n/2}$. In this equation, α is the experimental absorption coefficient, k is a constant (in our case equal to 1), hv is the photon energy, and n is the exponent dependent on the type of optical transitions characteristic for our five samples. Plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ versus E for our Sb₂O₃ samples are shown in Fig. 4B as insets. As can be seen from this figure, all five plots made in order to find direct and indirect band gap energies are quite linear. The values obtained by extrapolating the straight portions to energy axis corresponding to zero absorption coefficient gave the direct and indirect band gap energies between 4.1 and 4.3 eV for all five samples. Thus, it appeared possible to fit all plots for direct $(\alpha hv)^2$ and indirect $(\alpha hv)^{1/2}$ allowed transitions. Based on these experimental results we cannot distingunish whether the band gaps

of our samples are direct or indirect. The closer inspection of the absorption curves show that most of them are quite broad, thus allowing easy fitting to Gaussians.

In Fig. 4C the absorption spectra of the Sb_2O_3 nanoparticles obtained for the different procedures of synthesis B, D, and E are fitted to two Gaussian peaks. It should be emphasized here that all curves exhibit the same position of the Gaussian peaks. Further plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ versus E for the Gaussian maxima obtained in this manner, gave direct and indirect band gap energies of almost identical values of 4.3 and 4.1 eV (insets in Fig. 4C). Before we analyze the optical results in more detail, we emphasize here that, in order to avoid the difficulties in obtaining E_{g} from the absorption spectroscopy of dispersed samples, diffuse reflectance measurements (DRS) of dry powders were also performed (spectra not shown). The values obtained from reflection spectra using the Kubelka-Munk function for all five samples were found to be in the range 4.2-4.4 eV. This result is in a very good agreement with information extracted from the absorption spectra.



Fig. 4 UV–Vis absorption spectra of the Sb₂O₃ products dispersed in isopropyl alcohol, **B** first derivative absorption spectra of the Sb₂O₃ products and corresponding plots for determination of the direct and indirect band gap energies E_g , for every separate procedure of synthesis (*A*, *B*, *C*, *D*, and *E*) (*A* (*solid line*), *B* (*dashed line*) and *C* (*dotted line*), *D* (*dashed dotted*)

line), and *E* (*dashed dotted dotted line*)). Further, **C** UV–Vis absorption spectra of the Sb₂O₃ nanoparticles obtained from procedures of synthesis *B*, *D*, and *E* with their deconvoluted Gaussian peaks and plots (*as inset*) for determination of the direct and indirect band gap energies (E_g)

Since we observed spherical nanoparticles with average sizes around 100 nm (see Fig. 3, sample B) and octahedral micro- and nanocrystals (most of the particles observed are in micrometer size range with quite broad size distribution), we do not expect that the corresponding E_g is very different from that of the bulk material.

In order to prove this conjecture we performed detailed theoretical electronic structure calculations of

cubic Sb_2O_3 with lattice parameters of sample A (Tables 2, 3) in the framework of the FP LAPW method with the TB-mBJ exchange-correlation potential (Tran et al. 2009).

Figure 5 shows the calculated band structure around the band gap for the pure Sb_2O_3 . The calculated indirect band gap of 4.34 eV is found to be in excellent agreement with the experimentally measured value in this work (in the range 4.1–4.4 eV).



Fig. 5 Sb₂O₃ band structure calculated along several symmetry lines using the TB-mBJ potential (Koller et al. 2011). The Fermi level is at zero energy. The band gap is an indirect one since the valence band maximum is at L point, while the conduction band minimum is at Γ point



Fig. 6 Sb₂O₃ density of states calculated by the FP-LAPW method with the TB-mBJ potential. The Fermi level is positioned at zero energy. The lower two panels show atomic and orbital DOS decomposition. *Red, green*, and *blue curves* denote atomic *s*, *p* and *d* states, respectively. In the top panel, the total DOS and the interstitial contribution to the DOS are presented(*blue* and *gray* curves, respectively). Here several characteristic energy regions that are important for optical analysis are denoted with numbers. Region 1 is a mixture of Sb-*s* and O-*p* states, region 2 is mainly of O-*p* character, region 3 is a mixture of Sb-*s* b-*p* and interstitial states, while region 5 is formed mainly of interstitial states. (Color figure online)

The weak \mathbf{k} -dispersion of the upper valence band indicates the large effective mass of the holes and their low mobility. The absence of significant dispersion is



Fig. 7 The real (*bottom panel*) and imaginary part (*top panel*) of dielectric function for cubic Sb₂O₃ calculated using the FP-LAPW with the TB-mBJ modification. The imaginary part is directly proportional to the optical absorption spectrum of the material. It is decomposed according to the electronic transfer between different bands annotated in Fig. 6. *Colored* regions denote transitions from occupied band 3 to unoccupied states, while hatched regions correspond to transitions from the band 2 to the unoccupied states. Owing to the cubic symmetry of the Sb₂O₃, its dielectric tensor consists of the three equal diagonal elements and only one diagonal component is depicted ($\varepsilon_{xx}(\omega) = \varepsilon_{yy}(\omega) = \varepsilon_{cz}(\omega) \equiv \varepsilon(\omega)$). (Color figure online)

observed in all symmetric directions of the first BZ. The orbital character of the calculated bands can be determined analyzing the partial density of states (DOS) diagrams shown in Fig. 6. The lower part of the conduction band (denoted by number 4 in Fig. 6), which is about 5.5 eV wide, is composed mainly of anti-bonding Sb-5*p* and O-2*p* states. The valence band (the block 3 in Fig. 6) has predominantly the O-2*p* character, except at the top, where the O-2*p* states are mixed with the Sb-5*s* and the Sb-5*p* states. The very bottom of the valence band (the block 1 in Fig. 6), around -8 eV, is formed by the bonding combination of the Sb-5*s* and O-2*p* states.

The calculated optical absorption (OA) spectrum for the Sb_2O_3 , shown in Fig. 7, is interpreted in terms of the electronic structure presented in Fig. 6. The correspondence between the absorption peaks and the electron transitions which are causing them is simple to establish, due to relatively clear and simple electronic structure. Colored regions in Fig. 7 represent electronic transitions caused by absorption from the occupied band 3 to the unoccupied bands 4 and 5. Hatched regions represent electronic transitions caused by absorption from the occupied band 2 to the empty bands 4 and 5. The contributions $3 \rightarrow 4$ and $2 \rightarrow 4$ determine the most intensive, principal part of the OA spectrum, up to 12.5 eV. They originate from electronic transitions from the occupied O-p and the Sb mixed s and p states to the empty O-p and the Sb-p states. The higher energy part of the OA spectrum (from 12.5 to 25 eV) is dominated by the electron transfer from the same occupied states to the high energy part of the conduction band, characterized mainly by the mixture of delocalized, interstitial electronic states (contributions $3 \rightarrow 5$ and especially $2 \rightarrow 5$). The weight of permitted optical transitions from the occupied band 1 to the unoccupied bands 4 and 5 is practically equal to zero. Therefore, these transitions are not presented in Fig. 7.

In summary, it could be said that the whole Sb_2O_3 OA spectrum is dominated by the charge transfer from neighboring O's to the Sb atoms and by the $s \rightarrow p$ transitions between the nearest Sb atoms. Unfortunately, we cannot make more detailed comparison between our calculated absorption spectra and the experimental data because, to the best of our knowledge, there does not exist any published experimental work devoted to the energy region considered for the Sb₂O₃. We hope that TB-mBJ calculations presented here describe the optical absorption spectrum of the Sb_2O_3 as successfully as the band gap value that is obtained. The optical experiments in near and far ultraviolet region are very welcome in order to better reveal the electronic structure details and finally valorize the accuracy of various types of exchangecorrelation terms in the Kohn-Sham Hamiltonian.

Concluding this section, it is important to emphasize that we performed PL spectroscopy measurements as an equally important and nondestructive tool for evaluating the optical nature of the as-synthesized materials. No peaks in both PL emission and excitation spectra have been observed for a broad spectral range, typical for this Sb₂O₃ material.

Conclusion

In summary, a novel low-cost organo-colloidal strategy for the preparation of antimony sesquioxide (Sb_2O_3) spherical nanoparticles and octahedral micro- and nanocrystals has been demonstrated. The refinement of the diffraction data was employed to confirm the structures and the high purity of the synthesized powders. UV–Vis absorption and diffuse reflectance spectra of the synthesized samples give the optical absorption edge energies. No peaks in the PL emission and excitation spectra have been observed. Thorough analysis of optical properties gives the experimental estimate of the band gap energy for the sesquioxide Sb_2O_3 in the range of 4.1–4.4 eV. It should be emphasized here that our band gap energies are 10-15 % greater than previously published ones (Wood et al. 1972; Wolffing et al. 1973; Tigau et al. 2005; Zhang et al. 2012). From the experimental results we were not able to distinguish whether the band gaps of our samples are direct or indirect. On the basis of the state-of-the-art first-principles calculations with Tran-Blaha modified Becke–Johnson exchange potential we obtained the indirect gap for the cubic sesquioxide Sb₂O₃ equal to 4.34 eV (between L and Γ symmetry points in BZ). This value is in excellent agreement with the above-mentioned experimental range for band gap energies of five samples synthesized in the present work.

Our band structure results depicted in Fig. 5 can explain the experimental problems encountered in order to distinguish the type of the band gap. Namely, the extremely weak dispersion of the upper valence band (less than 0.15 eV in the whole **k**-region) imposes severe restrictions to the experimental accuracy which can hardly be fulfilled. We also calculated absorptive and dispersive parts of the dielectric function (Fig. 7). The correspondence between the absorption peaks in the $Im[\varepsilon(\omega)]$ and the electron transitions which are caused by them was established on the basis of the calculated band structure. We expect that future experiments in broader energy range will prove the correctness of the main theoretical features calculated in this work.

We hope that the presented results support organocolloidal synthesis as a good candidate for a large scale synthesis of Sb_2O_3 nanoparticles and microcrystals (and probably other oxides) at least competitive with the currently accepted synthetic methods.

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