Study of structure and vibrational spectra of silicon and titanium dioxide nanoclusters for technology of composite materials

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Abstract. The formation of structure and IR spectra of the \((\text{SiO}_2)_n\) (\(n = 1-4\)) and \((\text{TiO}_2)_n\) (\(n = 1-3\)) clusters with the increasing of their size \(n\) are simulated using the B3LYP/6-31G* method of density functional theory. It is shown that the structural fragments of the low-lying isomers of even small \((\text{SiO}_2)_n\) and \((\text{TiO}_2)_n\) clusters are exhibited in IR spectra of the SiO\(_2\) and TiO\(_2\) films. The IR absorption bands calculated by us for structures of the \((\text{SiO}_2)_n\) and \((\text{TiO}_2)_n\) clusters are in good agreement with the bands observed in IR spectra of the SiO\(_2\) and TiO\(_2\) films.

1. Introduction

Nanoclusters of silicon and titanium oxides are building blocks in preparation technology of a number of nanomaterials. The interest to silicon oxide clusters has increased highly after synthesis of silicon nanowires [1,2], in which the nucleation and growth of nanowires have been achieved by either laser ablation or thermal evaporation of Si powder mixed with SiO\(_2\). A high yield of nanowires has been obtained when the elemental composition of Si:O \(\approx 1\). The important role of oxide participation in the synthesis of nanosilicon has thus been demonstrated.

Over the past two decades, the essential efforts have been made to prepare, characterize, and employ nanocrystalline forms of TiO\(_2\), as a result of which the films consisting of TiO\(_2\) nanoparticles in the 1-100 nm size range are now known (see, for example, [3]). Compared with the bulk, the nanocrystalline forms of TiO\(_2\) are characterized by a dramatically increased surface-to-bulk ratio, which makes them attractive for photocatalytic and photoelectrochemical applications (see, for example, reviews [4-6]).

Up to now the pure and composite SiO\(_2\) - TiO\(_2\) films were also prepared by the sol - gel technology, and their optical and structural properties were investigated by IR spectroscopy method [7], and in paper [8] by atomic force microscopy, ellipsometry, thermal gravimetric analysis, UV - visible spectroscopy, Fourier transform IR spectroscopy, x-ray photoelectron spectroscopy and Raman spectroscopy.

The database on IR absorption spectra of the SiO\(_2\) and TiO\(_2\) nanoclusters is necessary for the monitoring of the technological processes of production of nanostructured films of composite materials. In this paper on the basis of density functional theory [9] by the GAUSSIAN98 computer

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code [10], the structure and vibrational spectra of the (SiO$_2$)$_n$ (n = 1-4) and (TiO$_2$)$_n$ (n = 1-3) clusters are calculated with the aim of the database formation. The Becke’s hybrid three-parameter exchange functional [11] along with the Lee-Yang-Parr’s correlation functional [12], i.e., B3LYP functional, was used. The Pople’s 6-31G* basis set [10] was chosen as the optimal one in all our calculations. It consists of the contracted [5s4p2d1f]$_{\text{Ti}}$ + [4s3p1d]$_{\text{Si}}$ + [3s2p1d]$_{\text{O}}$ basis functions. The basis set 6-31G* is more complete and flexible than the LANL2DZ basis set used in paper [13] under study of electronic structure and stability of (TiO$_2$)$_n$ clusters since the external polarization functions of $f$- type at Ti atoms and $d$- type at O atoms are absent in the LANL2DZ basis set.

2. Results and discussions
The information on IR spectra of the (SiO$_2$)$_n$ clusters is practically absent in the literature. Only zero-point energies of the (SiO$_2$)$_n$ clusters with n = 1-5 are given in paper [14]. The paper [15] contains more information. It is shown in it that the molecular rings (see figure 1) have the characteristic IR bands distinguishing them from molecular chains. The calculated 12-membered chain harmonic frequencies have the following modes 866, 915, 838 cm$^{-1}$, and the 12-membered ring has modes 902, 886, 933 cm$^{-1}$. The corresponding experimental data 908, 888, 932 cm$^{-1}$ obtained for the silica surfaces are in remarkable agreement with the above-indicated calculated values of IR frequencies for molecular rings. This surface-like signature of rings contrasts in properties with chain structures, which also display modes from terminal oxygen atoms at frequency 1321 cm$^{-1}$.

![Figure 1. Structures of the (SiO$_2$)$_{12}$ molecular ring and chain. Bond lengths are in Å, angles in degrees.](image)

Because of the information deficit on IR spectra for the (SiO$_2$)$_n$ clusters, there is a necessity to carry out our studies of the formation of their IR spectra absorption with the increasing of the size n of clusters. One of the examples of the structures and IR spectra, calculated by us for the (SiO$_2$)$_n$ clusters, is shown in figure 2.

The analysis of IR spectra [16] in the 750-1650 cm$^{-1}$ range for the SiO$_2$ films (see figure 3) has revealed a number of absorption bands. The absorption band at ~ 800 cm$^{-1}$ agrees with the band at 799 cm$^{-1}$ observed and assigned in [7] to transverse optical component of the Si - O - Si mode of in-plane symmetric stretching vibrations. Our calculations of IR spectra of the (SiO$_2$)$_n$ clusters by B3LYP/6-31G* method also have shown that the sufficiently strong band at 765-778 cm$^{-1}$ is characteristics for in-plane vibrations of the SiO$_2$Si cycle. In our calculations, the out-of-plane vibrations of the SiO$_2$Si rhombus fragment at 915 - 923 cm$^{-1}$ correspond to the absorption band between 850 and 950 cm$^{-1}$ and agree with the mode 915 cm$^{-1}$ from theoretical paper [15]. According to our calculations, the six-atomic ring structure is distinctly displayed at 1036 - 1044 cm$^{-1}$ that correlates with the band near 1050 cm$^{-1}$ (figure 3) and also with the band at 1076 cm$^{-1}$ detected in paper [7] for transverse optical component of Si - O - Si asymmetric stretching vibrations. In the same region at frequency of 1048 cm$^{-1}$, the fundamental band due to Si - O stretching vibrations of silica network is identified in Fourier transform IR spectra [8].
In IR spectra of figure 3 between 1150 and 1250 cm$^{-1}$, it is presented the shoulder that is assigned in [7,8] to longitudinal optical component of the Si - O - Si asymmetric stretching vibrations at ~ 1200 cm$^{-1}$. In our cluster calculations, such mode is not found, but there is the very strong band at 1321-1334 cm$^{-1}$ caused by stretching vibrations of terminal Si - O bonds (see figure 2), and revealed besides in paper [15] under calculations of 12-membered chain structure of the (SiO$_2$)$_n$ clusters. However, the corresponding absorption band is absent in IR spectra of the SiO$_2$ films that means a small concentration of terminal Si - O bonds in the film samples. The absorption band between 1550 and 1650 cm$^{-1}$ of figure 3 is attributed to bending vibrations of H$_2$O molecule adsorbed on the surface of SiO$_2$ films at 1632 cm$^{-1}$ [7] and 1627 cm$^{-1}$ [8]. In IR spectra of films [16] there is a wide absorption band between 3000 and 3700 cm$^{-1}$ that is assigned (at 3390 cm$^{-1}$ [7] and 3400 cm$^{-1}$ [8]) to fundamental stretching vibrations $v$(OH) of hydroxyl groups as products of water hydrolysis on the SiO$_2$ surface.
If to compare our calculated IR spectra for \((\text{TiO}_2)_n\) \((n = 2, 3)\) with IR spectra [7] measured for the TiO\(_2\) films, the following features become clear. The IR absorption bands calculated by us for compact bulk structures, \(C_3\), for \((\text{TiO}_2)_2\) at 275 cm\(^{-1}\) and \(C_5\), for \((\text{TiO}_2)_3\) at 286, 298 cm\(^{-1}\), are consistent with the band at 260 cm\(^{-1}\) observed in [7] for TiO\(_2\) films. In ours theoretical IR spectra, the bands at 430 cm\(^{-1}\), 421 cm\(^{-1}\) correlate with the band at 435 cm\(^{-1}\) [7], and the bands at 892 cm\(^{-1}\), 854 and 902 cm\(^{-1}\) are in accordance with the band at 839 cm\(^{-1}\) [7]. Whereas the predicted in theoretical paper [13] characteristic bands in the 530-760 cm\(^{-1}\) range were not observed in IR absorption spectra [7] of the TiO\(_2\) films, that puts under doubt the validity to use the B3LYP/LANL2DZ method under study of the \((\text{TiO}_2)_n\) clusters \((n = 1-9)\) [13] and \((n = 10-16)\) [17] because of the LANL2DZ basis set limitations (see above). It is worth to note that the strong IR absorption bands near 1100 cm\(^{-1}\) due to the terminal Ti-O bonds are not found in IR spectra of TiO\(_2\) films that means a small concentration of the appropriate structural fragments in samples of films.

3. Conclusions
The B3LYP/6-31G* method of density functional theory may be recommended for study of the size and elemental composition nanoclusters influence on the IR absorption spectra of nanostructured films of composite materials. Using this method, we have established for the first time the tendencies in IR spectra formation of the \((\text{SiO}_2)_n\) clusters with the increasing of their size \(n\). The IR absorption bands calculated by us for structures of the \((\text{SiO}_2)_n\) and \((\text{TiO}_2)_n\) clusters are in good agreement with the bands observed in IR spectra of the SiO\(_2\) and TiO\(_2\) films. Therefore, the obtained in this work database on IR absorption spectra of the SiO\(_2\) and TiO\(_2\) nanoclusters may be applied to control the technological processes of fabricating nanostructured films of the ceramic and composite materials.
Acknowledgments

Work was supported by Russian ministry of education and science within framework of program “Development of scientific potential of high school” (Grant No. 2.1.1/2637).

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