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Formation and Luminescent Properties of $\text{Al}_2\text{O}_3:\text{SiOC}$ Nanocomposites on the Base of Alumina Nanoparticles Modified by Phenyltrimethoxysilane

D. V. Kysil^{1*}, A. V. Vasin^{1,5}, S. V. Sevostianov², V. Ya Degoda³, V. V. Strelchuk¹, V. M. Naseka¹, Yu. P. Piryatinski⁴, V. A. Tertykh², A. N. Nazarov^{1,5} and V. S. Lysenko¹

Abstract

$\text{Al}_2\text{O}_3:\text{SiOC}$ nanocomposites were synthesized by thermal treatment of fumed alumina nanoparticles modified by phenyltrimethoxysilane. The effect of annealing temperature in inert ambient on structure and photoluminescence of modified alumina powder was studied by IR spectroscopy as well as photoluminescence spectroscopy with ultraviolet and X-ray excitation. It is demonstrated that increase of annealing temperature results in formation of silica precipitates on the surface of alumina particles that is accompanied by development and spectral evolution of visible photoluminescence. These observations are discussed in terms of structural transformation of the surface of Al_2O_3 particles.

Keywords: Fumed alumina, $\text{Al}_2\text{O}_3:\text{SiOC}$ nanocomposite, Phenyltrimethoxysilane, Photoluminescence

Background

Recently, it was reported that silica nanoparticles with surface carbonized by pyrolysis of phenylmethoxy groups exhibit strong visible photoluminescence (PL) under ultraviolet excitation [1]. Materials that demonstrate effective broad band visible PL at room temperature without heavy metal activators are of great interest as a potential alternative to expansive rare earth-doped ceramic phosphors for artificial white light sources on the base of compact gas-discharge lamps and light-emitting diodes. Though similar $\text{SiO}_2:\text{C}$ materials have been reported previously to demonstrate broadband visible PL [2–5], origin of light emission centers is unclear until now. One of the basic hypothesis associates emission centers in $\text{SiO}_2:\text{C}$ with carbon nanoclusters [1, 2, 5]. In frame of this model, SiO_2 nanopowder can be considered as morphological template with high specific surface area that provides high concentration of carbon-related emission centers located on the silica surface. Verification of

this hypothesis obviously needs further study of luminescent properties of carbonized surface in related nanostructured materials. Fumed alumina is a well candidate as morphological template with relatively high specific surface area. Excellent mechanical properties, good chemical inertness, and electronic structures make alumina-based ceramics widely used as high-temperature functional materials in electrical and optical devices [6–11]. Optically and X-ray excited PL in superfine Al_2O_3 powder with intentionally carbonized surface of nanoparticles is analyzed in the present report. Procedure of surface carbonization was similar to that used for carbonization of fumed silica in [1], i.e., successive procedure of chemical grafting of phenylmethoxy groups to the surface of nanoparticles followed by thermal calcinations in chemically inert ambient.

Methods

Pyrogenic Al_2O_3 powder (89 m^2/g , particle size 30–50 nm) was treated with a phenyltrimethoxysilane (PhTMS) toluene solution (1.73 ml of PhTMS per 10 ml of toluene) at 70 °C for 4 h in the presence of triethylamine as a catalyst. The aim of this procedure is grafting of phenylmethoxy groups to the alumina surface. The reaction product

* Correspondence: kdmtr93@gmail.com

¹Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine, Kyiv 03680, Ukraine

Full list of author information is available at the end of the article

(hereafter “phenyl-alumina”) was dried and subjected to thermal annealing at temperatures of 400, 500, 600 °C, for 30 min in flow of pure nitrogen at atmospheric pressure.

Interatomic bonding was studied by IR spectroscopy. The Fourier transform infrared (FTIR) analysis was performed in transmission mode using vacuum Bruker Vertex 70 V. The FTIR spectra were recorded at room temperature in spectral range of 400–5000 cm^{-1} using the KBr sample tablets. Photoluminescence was studied under ultra-violet (290 nm) and X-ray (13–14 keV) excitation. Photoluminescence under ultra-violet excitation was studied using excitation by a 290-nm semiconductor laser (5 mW). The spectra were recorded using spectrometer LIFESPEC II (Edinburgh Instruments). The X-ray luminescence was excited by X-ray radiation with energy of 13–14 keV. Radiation of the samples was recorded using a monochromator MDR-2 and a photomultiplier FEP-106.

Results and Discussion

IR Spectroscopy

FTIR transmission survey spectra of pristine alumina and phenyl-alumina are shown in Fig. 1. Amorphous aluminum oxide structural matrix in pristine alumina is represented by broad absorption bands at 540 and 800 cm^{-1} (Fig. 1, spectrum 1). It is well known that crystalline aluminum oxide exists in a variety of metastable structures (transition aluminas— χ , γ , δ , η , θ) as well as in its stable α - Al_2O_3 phase. Structure of metastable polymorphs can be classified in terms of the structure of oxygen anion sublattice (face-centered cubic or a hexagonal close-packed) and the distribution of aluminum cations into this sublattice in tetrahedral (AlO_4) and/or octahedral (AlO_6) interstitial sites [12]. In amorphous solid, there is no sense of crystalline polymorphism but vibration properties of local bonds are also determined by Al atom coordination. Two broad bands at 540 and

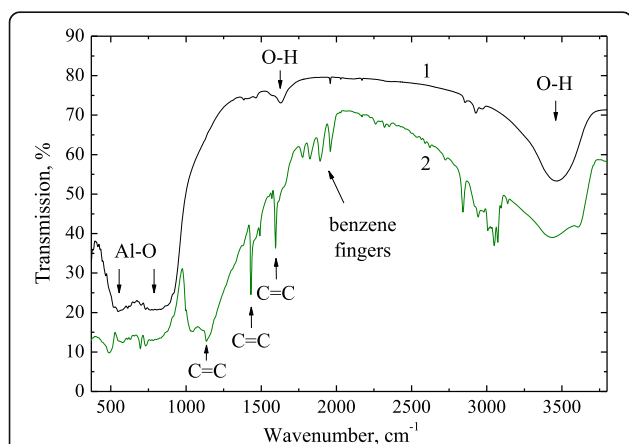


Fig. 1 FTIR transmission spectra of pristine fumed alumina before (spectrum 1) and after chemical treatment (spectrum 2). Spectra are offset along the ordinate axis for clarity

800 cm^{-1} in FTIR spectrum of pristine fumed alumina (Fig. 1, spectrum 1) can be assigned to mixture of absorption by Al–O stretching vibrations in tetrahedral and octahedral coordination respectively [13, 14].

The broad absorption band in the range of 3000–3800 cm^{-1} and the narrow band at 1630 cm^{-1} (Fig. 2) are attributed to stretching and bending vibration modes of O–H bonds respectively due to both surface hydroxyl groups in Al_2O_3 and water absorbed by KBr sampling

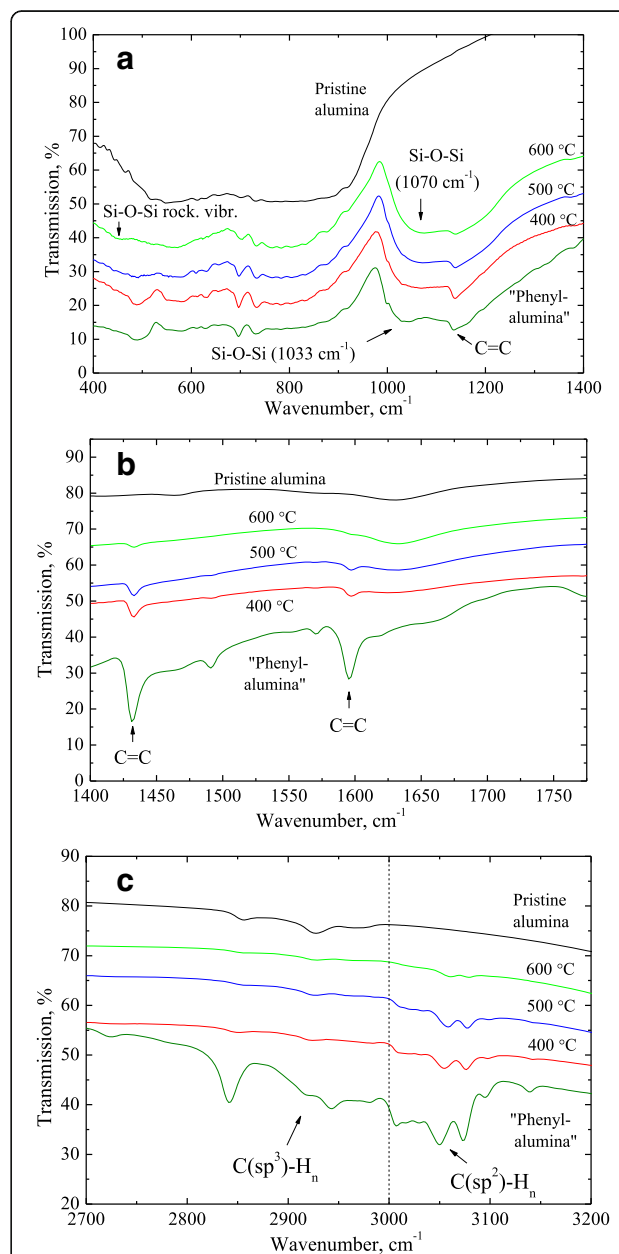


Fig. 2 Selected spectral ranges of FTIR spectra of pristine alumina (spectrum 1), and phenyl-alumina before and after annealing at 400, 500, and 600 °C in the spectral ranges 400–1400 cm^{-1} (a), 1400–1775 cm^{-1} (b), and 2700–3200 cm^{-1} (c). Spectra are offset along the ordinate axis for clarity

pellet [15]. A weak absorption in $2800\text{--}3000\text{ cm}^{-1}$ ($\text{C}(\text{sp}^3)\text{--H}_n$) is due to organic contaminations absorbed from atmospheric ambient. It is worth noting that after annealing of pristine alumina at temperature up to $600\text{ }^\circ\text{C}$, the only change in FTIR spectrum was disappearance of C–H-related band at $2800\text{--}3000\text{ cm}^{-1}$.

Some additional absorption bands appeared after chemical treatment (Fig. 1, spectrum 2). Absorption band in spectral range $2800\text{--}3000\text{ cm}^{-1}$ ($\text{C}(\text{sp}^3)\text{--H}_n$) became much stronger and now is accompanied by absorption at $3000\text{--}3100\text{ cm}^{-1}$ ($\text{C}(\text{sp}^2)\text{--H}_n$) due to hydrogen bonded to benzene rings. Benzene rings of phenyl groups give rise to the narrow bands at 1136 , 1430 , and 1590 cm^{-1} ($\text{C}=\text{C}$ vibration in benzene rings) as well as to the “benzene fingers” at $1700\text{--}2000\text{ cm}^{-1}$ due to overtone/combination vibrations in benzene rings. A strong and broad absorption band in range of $980\text{--}1200\text{ cm}^{-1}$ and centered at 1033 cm^{-1} is obviously due to siloxane bonds. A similar band was observed in phenyl-siloxane based polymers and associated with crosslinking of siloxane bonds into network [16, 17]. This band indicates formation of polymer-like siloxane precipitates on the surface of Al_2O_3 particles during chemical treatment procedure.

Most informative spectral ranges of the FTIR spectra of phenyl-alumina before and after annealing are shown in Fig. 2. IR bands related to benzene rings (1136 , 1430 , and 1590 cm^{-1}) strongly reduced after annealing at $400\text{ }^\circ\text{C}$ and at higher temperature (Fig. 2ab). Increase of the annealing temperature up to $600\text{ }^\circ\text{C}$ results in high-frequency shift of Si–O related band from 1033 to 1070 cm^{-1} indicating transition from polymer-like to ceramic structure. Spectral position and shape of this band became typical for silicon oxide indicating formation of silica structural network presumably on the surface of aluminum oxide. It is approved by appearance of the shoulder at $450\text{--}460\text{ cm}^{-1}$ that can be assigned to Si–O–Si rocking vibrations.

Figure 2b shows that increasing of an annealing temperature causes decrease the intensity of the narrow absorption bands at 1430 and 1594 cm^{-1} and which is assigned to $\text{C}=\text{C}$ stretching vibrations in phenyl rings. It is worth noting that traces of absorption by phenyl groups are detected up to highest annealing temperature. Destruction of benzene rings does not cause formation of amorphous pyrolytic carbon typically characterized by broad absorption band about 1600 cm^{-1} . The absence of carbon precipitation can be explained by thermally activated carbon diffusion from surface inside Al_2O_3 particles during annealing in inert ambient. Carbon-doped aluminum oxide ($\text{Al}_2\text{O}_3\text{:C}$) is well known material widely used in dosimetry [11] and significant diffusion rate of carbon in Al_2O_3 is observed even at temperature as low as $400\text{ }^\circ\text{C}$ [18].

Figure 2c illustrates evolution of C–H-related bands at $2800\text{--}3100\text{ cm}^{-1}$. It is seen that absorption bands at

$2800\text{--}3000\text{ cm}^{-1}$, which corresponds to stretching vibrations of $\text{C}(\text{sp}^3)\text{--H}_n$ bonds in methyl groups as well as group of absorption bands at $3000\text{--}3100\text{ cm}^{-1}$, which corresponds to $\text{C}(\text{sp}^2)\text{--H}_n$ bonds in phenyl rings reduced strongly after annealing that is well consistent with thermally activated degradation of phenyl groups.

Photoluminescence

Pristine fumed alumina powder shows relatively weak broad band photoluminescence in spectral range $300\text{--}600\text{ nm}$ under 290 nm excitation (Fig. 3a, spectrum 1). Broad band is composed by at least three constituents with maxima at about 335 , $390\text{--}400$, and 470 nm . The band with a peak at 335 nm is likely due to oxygen vacancy with trapped electron (F^+ -centers) [9]. According to [19], the band with a maximum $390\text{--}400\text{ nm}$ can be associated with anion-cation vacancy pairs (P^- -centers) or surface F^+ -centers (F_5^+ -centers). The band with a maximum at 470 nm is possibly associated with F_2 -centers [20], but its correct identification needs further analysis.

Intense PL band with maximum at 340 nm appears in Al_2O_3 after chemical treatment (Fig. 3a, spectrum 2). This band is presumably associated with excimer states in closely located phenyl groups grafted to alumina surface [21–23]. Decomposition of phenyl groups during annealing leads to disappearance of this band (Fig. 3b).

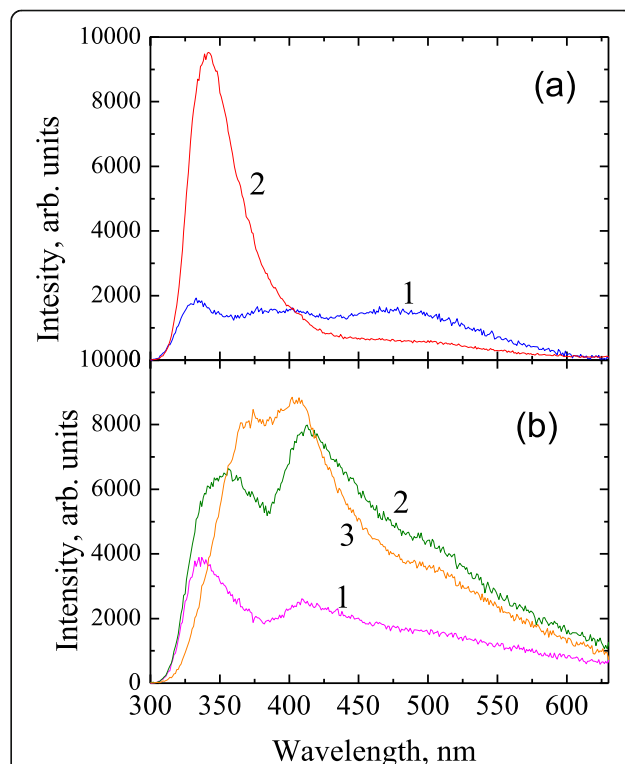


Fig. 3 PL spectra under 290 nm excitation. **a** Pristine fumed alumina (1) and phenyl-alumina before annealing (2). **b** Phenyl-alumina after annealing at $400\text{ }^\circ\text{C}$ (1), $500\text{ }^\circ\text{C}$ (2), and $600\text{ }^\circ\text{C}$ (3)

Emission band remains obviously multicomponent after annealing but increase of annealing temperature results in complicated evolution of intensity and spectral distribution. Increase of annealing temperature up to 500 °C leads to increasing of integrated PL intensity. It should also be noted that in the PL spectrum of sample annealed at a temperature of 500 °C it is observed low energy shift and broadening of UV peak (Fig. 3b, spectrum 2). Increasing of the annealing temperature up to 600 °C leads to a further shift of this band to 370 nm. Spectral position of emission peak at 410 nm and shoulder at 500 nm remained almost unchanged after annealing at 400–600 °C. As it was demonstrated by IR study, the structure of these samples can be represented as silica precipitates (presumably with carbon groups) on the surface of alumina nanoparticles. Such materials can be indicated as $\text{Al}_2\text{O}_3/\text{SiOC}$. Mechanism of formation of SiOC surface precipitates is believed to be similar to polymerization and structural crosslinking in polymer-derived SiOC ceramics obtained from phenyl-containing organosilicon precursor [17]. It is important also to note that pristine alumina annealed at the same conditions does not show any noticeable photoluminescence. Hence, it is reasonable to expect contribution of silica *and/or carbon*-related emission centers in visible PL band. Unfortunately, at present time we are not able to identify correctly the evolution of PL band of these samples.

Using of UV emission allows exciting electron states with excitation energy far below the band gap of alumina and silica (commonly, it is electron states associated with bulk and surface defects). Alumina and silica have a very large band gap (9–10 eV), and examination of the effect of band-to-band excitation needs high-energy photons, for example X-ray excitation. Normalized PL spectra of the pristine alumina (spectrum 1), phenyl-alumina (spectrum 2), and phenyl-alumina (spectrum 3) annealed at 400 °C excited by X-ray at 90 K are illustrated in Fig. 4. PL spectra of pristine alumina and phenyl-alumina are quite similar representing broad band with maximum intensity about 470 nm. No detectable PL was observed at room temperature. Spectral similarity of the bands in pristine and chemically modified samples allows assigning this band to emission from alumina-related centers. Excimer PL in phenyl groups seems to be not excited by high-energy radiation. A narrow and almost symmetrical PL band centered at about 550 nm appears in the spectrum of the sample of the phenyl-alumina after annealed at 400 °C (spectrum 3). A weak but well pronounced broad PL background band is also observed. The origin of this broad background presumably associated with alumina structural network.

Taking into account that (1) narrow green PL band is observed only under X-ray excitation (i.e., high energy of excitation photon) and (2) formation of silica structural network after annealing at 400 °C it is reasonable to

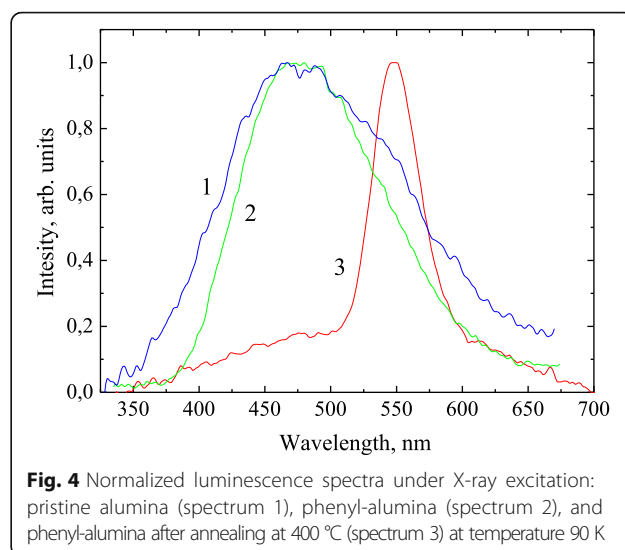


Fig. 4 Normalized luminescence spectra under X-ray excitation: pristine alumina (spectrum 1), phenyl-alumina (spectrum 2), and phenyl-alumina after annealing at 400 °C (spectrum 3) at temperature 90 K

assign this emission band to self-trapped exciton in silica structure. Spectral position of PL band is well consistent with that reported in [24].

Conclusions

$\text{Al}_2\text{O}_3:\text{SiOC}$ nanocomposites were synthesized using thermal treatment of fumed alumina nanopowder modified by phenyltrimethoxysilane. Hydroxyl groups on the surface of alumina nanoparticles were replaced with phenylsiloxane groups followed by annealing in temperature range 400–600 °C. It is demonstrated that increase of annealing temperature results in pyrolysis of phenyl groups and formation of silica precipitates. No carbon precipitation was detected after pyrolysis of organosilicon groups. It is suggested that development of photoluminescence after thermal treatment is due to formation of carbonized silica on the surface of alumina particles.

Abbreviations

$\text{Al}_2\text{O}_3:\text{C}$: Carbon-doped aluminum oxide; $\text{Al}_2\text{O}_3:\text{SiOC}$: Alumina/organosilicon nanocomposite; F^+ -center: Oxygen vacancy with trapped electron; F_2^- -center: Two adjacent F-centers; F-center: Oxygen vacancy with two trapped electrons; F_3^- -center: Surface analog of F^+ -center; FTIR: Fourier transform infrared; IR: Infrared; P^- -center: Anion-cation vacancy pairs; PhTMS: Phenyltrimethoxysilane; $\text{SiO}_2:\text{C}$: Carbonized nanocomposite materials based on silica

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Authors' Contributions

SSV and TVA synthesized fumed alumina samples. PYUP and DVYA conducted study of photoluminescence properties using 290 nm and X-ray excitation respectively, SW and NVM recorded transmission infrared spectra. KDV carried out thermal annealing, summarized and interpreted all experimental data in cooperation with VAV. NAN and LVS participated in discussion and coordination of the study. All authors revised and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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Author details

¹Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine, Kyiv 03680, Ukraine. ²Institute of Surface Chemistry of the NAS of Ukraine, Kyiv, Ukraine. ³Taras Shevchenko National University, Kyiv, Ukraine. ⁴Institute of Physics, NAS of Ukraine, Kyiv, Ukraine. ⁵National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine.

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