Silicon Dioxide and the Luminescence of Related Materials

Silicon Dioxide and the Luminescence of Related Materials:

Crystal Polymorphism and the Glass State

By

Anatoly Trukhin

Cambridge Scholars Publishing

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This book first published 2021

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

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ISBN (10): 1-5275-7131-9
ISBN (13): 978-1-5275-7131-0

To
My brother Vasily Nikolaevich Trukhin
Who taught me and inspired me to experiment

Isaac Newton, who said in *Fragments from a Treatise on Revelation*:
“Truth is ever to be found in simplicity, and not in the multiplicity
and confusion of things.”

Sir Nevill F. Mott:
“Structure and structural features are the basis for explaining experimental
data in solid-state physics.”

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FOREWORD

This book is devoted to the study of the properties of materials that can be in a crystalline and glassy state. Its central focus is the physics of solids, whose structure is disordered, since the existing theories of solids are based on crystal structures. The approach adopted here is based on the comparison of data for crystals and glasses formed by the same atoms, paying particular attention to the under-explored glass-forming crystals. The book will be of interest to graduate students, solid states researchers, glass technologists, and young scientists beginning research in the field of experimental physics.

PREFACE

When we started the study of quartz glass in 1967-1968, the monograph *The Effect of Radiation on Inorganic Glasses* was very positive [1]. It presented compressed literature data existing at that moment. Currently, such a concise idea of the state of the physics of quartz glass is impossible because the number of different directions of research mentioned in the title of the monograph is too large. Even in the direction of this study, the number of articles is large, and only a review of a specific topic is possible. Even with a limited number of topics, the bibliography reaches infinity.

Already in our previous monograph [2] we (Silin and Trukhin) presented the circle of our interest, connected with point defects and elementary electronic excitations. More than 25 years after the appearance of our monograph, new experimental data appeared and they need to be collected together.

The chosen topic of the monograph is based on my early interests. I proceeded from the assumption that a quartz crystal can serve as a basis for understanding the properties of quartz glass. It should be recognized that there is another example of a material in a crystalline and glassy state; BeF_2. Its crystal has an α-quartz structure. As stated in a private conversation with Adrian Wright, BeF_2 is "more" α-quartz than silicon dioxide; however, he added that this is a very toxic material.

At that time, quartz glass was at the very beginning of its technological development. Corning Glass samples 7940 and 7943 already existed but we did not have access to them and were studying KI and KV glasses made from natural quartz raw materials. Impurities of aluminum and alkaline ions play a decisive role, both in the properties of quartz glass and in natural crystals. Therefore, the idea was to study properties that were not very dependent on these impurities. Thus, we studied the intrinsic absorption edge of both crystal and glass, and the properties associated with intrinsic absorption, such as the energy absorbed by the atoms of the host materials, silicon and oxygen, which transferred to the impurity center of luminescence. In reality, these transfer spectra are apparently independent of impurities and reflect the properties of the host material. At this time, intrinsic reflection spectra from Loh and Phillip appeared, and these spectra showed a very large similarity between glass and crystal.

This was also emphasized by the similarity of the energy transfer spectra for crystal and glass. Moderate differences in our data [2], and that of Loh [3] and Phillips [4], on glass and crystal allow us to formulate the basic properties of glass based on the established physics of the crystal. The reflection spectra in the glass are broader, and the level of energy transfer efficiency in the glass is noticeably lower than in the crystal under more or less similar samples and experimental conditions. Later, when we start researching pure quartz glass, as KY-1 is “wet” and essentially KS-4V is “dry”, a method of comparison with the properties of quartz crystals remains and samples of pure quartz crystals become available.

In the late 1960s, we had a good example of natural quartz from Siberia, presented by geologists. It was the purest natural quartz (without blackening after 50 hours of x-ray irradiation), and we observed a strong visible luminescence excited by x-ray radiation. It possessed a strange thermal dependence of intensity. These are two steps. It was later demonstrated that this is the luminescence of self-trapped excitons and that two-stage thermal quenching is a “cart for visiting” a self-trapped exciton in an α-quartz structure, independent of the purity. These two stages of thermal quenching were also found in α-structured quartz $AlPO_4$, $GaPO_4$, and GeO_2, but not in cristobalite or coesite which have a different structure to α-quartz. Only one type of STE was found in cristobalite and coesite. On the other hand, in stishovite, a silica crystal with a rutile structure, there was no self-trapped exciton. Thus, only silicon dioxides with a tetrahedral structure and related materials have the effect of a self-trapped exciton.

At the same time, in the late 1960s, our laboratory received a visitor from the USA; Prof. Schulman from the Naval Research Laboratory in Washington, DC. He was well known for his monograph with Compton on alkali-halide physics. It was an extraordinary event for anyone to have a visitor from one of the largest laboratories in the United States. Most significant for us was his presentation of the last result obtained by the NRL at that time by young scientists (he does not say who, but we now know it was D. L. Griscom [5]) that the above-mentioned luminescence of silicon dioxide under the influence of a fast electron beam with 300 kV correlates with transient absorption at 5.6 eV. From the literature, we already know that the only radiation-induced defect of the quartz host material is the center E'', which has an absorption band at 5.6 eV, discovered by R. Weeks [6] in the mid-1950s. And the E’ center is an oxygen vacancy. In addition, the photoexcitation of most samples of natural quartz in the range of 200 nm or 6 eV provides strong visible luminescence [7]. Therefore, we came to the linear conclusion that the

glow is due to an oxygen vacancy, and this point of view dates back to the early 1970s when a strange effect was discovered. A higher intensity of PL excited in the region of optical transparency of α-quartz corresponds to a lower intensity of x-ray luminescence excitation of crystalline quartz. We begin to think about the reason for such a contradiction. Direct measurement of the impurity content by Boganov at the Institute of Silicate Chemistry showed a huge concentration of aluminum in samples of natural quartz with high PL efficiency. And the purest samples of synthetic quartz crystals, in which PL excited defects at 200 nm have the highest x-ray luminescence yield. Thus, it turns out that the luminescence of a pure quartz crystal upon x-ray excitation is not at all associated with a defect. As shown below, this is due to the self-trapped exciton, which we wrote about in 1978. At this time, the publication of D. L. Griscom [5] appears with the data on transient absorption, which we know about from the lecture of Prof. Shulman and, in [5], the possible participation of a self-trapped exciton in luminescence is also proposed.

We began to study silicon dioxide when we were asked about the problem of the radiation coloring of the quartz glass windows of a spaceship. This problem was brought to us by people in the industry responsible for window production. A whole world of scientists was busy with this problem at that time. While our success in tackling this problem has been moderate, our proposal to use cleaner silica for windows has been heard by people in the industry. Thus, we gradually began to get acquainted with the cleaner silica used for windows, and also spread our efforts to find a pure quartz crystal. Studies on cleaner silica make it possible to determine the actual position of the intrinsic absorption edge of silica at 8.1 eV for silica glass and 8.5 eV for α -quartz and their compliance with the Urbach rule for the dependence of the intrinsic absorption edge as a function of temperature [8]. It should be noted that in this thermal behavior we did not find a significant difference between the crystal and the glass. Urbach's rule was exactly the same as for alkali-halide crystals, where it was attributed to the "instantly created self-trapped exciton", interpreted by Toyodzawa and his school of scientists. We wondered why there were so few different properties for silicon dioxide crystal and glass. This applies to the mentioned center E', as it was known at that time. Professor Karapetyan, one of the main players in the study of glass at that time, enthusiastically told us that if we want to see the specific properties of glass, we must begin the study of multicomponent silicate glasses. This is what we did later with professors M. Tolstoy and L. Glebov, but gradually we found differences between quartz glass and α-quartz crystal. They were found in the properties of a

self-trapped exciton. Of course, studies by other scientists have also revealed other differences, but we will mainly look at our experiments. Simultaneously, with the study of the optical absorption of irradiated quartz glass in the specialty Laboratory of Semiconductor Physics at the University of Latvia, research photoluminescent tests were started. It was found that even a low-intensity hydrogen discharge light source can excite two band PL in the blue and UV spectral ranges in KI and KV silica glasses excited at 240 nm. We found that this case has already been described in the literature thanks to the mentioned book [1], where studies of Garino-Canino have been reported since the early 1950s. Garino-Canino investigated samples of quartz glass doped with germanium. It was a long time before Garino-Canino's original articles could only be read as we did not have the appropriate magazines in Riga. We asked our colleagues from the Institute of Physics, I. Plavina and A. Tale, to try to measure the kinetics of the decay of luminescence. They were able to detect luminescence, even if their source of excitation did not give light of 240 nm. Their source of excitation only provided light at 300 nm. Much later, L. Skuja [9] explained this curious effect as caused by the low-intensity absorption band in silica samples at 300 nm. Now I can point out another strange effect. The decay kinetics was purely exponential; this does not mean there is any difference with the known emission centers of alkali metal halides, as detailed in the studies by I. Plavina. I wondered why, in the observed phenomena, there were no differences with alkali-halide crystals. In this context, we found that it is not only Ge-doped silica glass that has excited luminescence at 240 nm, but also pure KS-4V glasses made under conditions of oxygen deficiency which have two similar luminescence bands. In addition, the luminescence decay is exponential for electronic intra-center transitions. On the other hand, there is the effect of destroying the luminescence centers by certain technological impurities, such as hydrogen, fluorine, or chlorine. It is significant that, with these impurities, PL is observed under continuous excitation. However, when measuring the kinetics of decay with short pulses of exciting light, PL is not visible. This means the absence of a luminescent center, while continuous excitation shows that this center is recreated in a multi-step process. We would consider the details of this in the text, but the existence of impurities and intrinsic point defects in quartz glass, which have properties similar to those of the well studied alkali-halide crystals, is still strange when we do not observe some specific properties of the glass. Moreover, there was a later observation of the migration of excitons in quartz glass of a special type III and, in 1981, an extraordinary diffusion length of about 5000 μm was obtained for an

exciton for type III quartz glass doped with copper [10]. The qualitatively extraordinary efficiency of energy transfer was not clear in the early 1970s. Even in a crystal, such a huge value of diffusion length was rarely observed.

On the other hand, the literature contains many theoretical studies on localized states in a network of disordered structures. For quartz glass, the properties of localized states were not revealed. While for multicomponent glasses, models were put forward using the localized state approach. M. Tolstoy and L. Glebov proposed to study photoinduced darkening of glasses made of pure sodium silicate, which was the matrix for a neodymium laser. For this material, radiation coloring, luminescence excited by x-ray radiation, and electron spin resonance has already been studied in detail [11]. Also, in soda-silicate glasses, Glebov discovered that the intrinsic absorption of glass obeys the Urbach rule in a form different from crystals. Thus, for alkali-halide crystals, α-quartz, and quartz glass, the absorption spectra measured at different temperatures on a semilogarithmic scale converge at one point; a variant of the Urbach rule explained by Toyozawa. Sodium silicate glass has a parallel shift with temperature on a semilogarithmic scale. Later it turned out that this is a common property of optical glasses (except for quartz glass). At first, such an Urbach rule was found for semiconductor glasses.

At the time when we began to study glassy and crystalline silicon dioxide, interest in solid-state physics was expanded from a pure crystalline state to a disordered and amorphous state. The representation of localized states due to disorder was introduced in the early 1950s by Gubanov [12] and Lifshitz [13]. At the same time, Kolomiyets began a physical study of semiconductor chalcogenide glasses [14]. The apotheosis of the study of amorphous semiconductor materials was associated with the awarding of the Nobel Prize to Sir Nevill Mott in 1977 (see, for example, [15]) for the states located in amorphous materials, and P. W. Anderson for the article published in 1958; “Absence of Diffusion in Certain Random Lattices” [16]. The latter was based on the limitation of the properties of electrical conductivity in donor or acceptor semiconductors for electronic devices. Mott defined localized states as “traps,” meaning electrical properties. The conductivity on these traps was “zero”, despite the overlapping wave functions [17]. In solid-state physics, it was understood that disorder should lead to localization of excitations. This understanding was apparently based on experimental data regarding the electrical properties of disordered semiconductors. The properties of localized states in wide-gap oxide glass with practically zero electrical

conductivity should be determined. Therefore, we are in the moment of the development of the physics of localized states.

Studies of many different disordered systems make it possible to introduce the classification of electronic states into localized and delocalized states separated by a mobility threshold [15]. The main spectrum of intrinsic absorption of a material belongs to delocalized states. The motion of delocalized electron excitation is determined by an intermediate order structure. The absence of long-range order explains the low efficiency of the transfer of absorbed energy. Below the mobility edge, localized states can play an important role in many properties of disordered material. Typically, such states arise at the edge of intrinsic absorption. When we started the study of sodium silicate glasses, which are good insulators, and the experimental approach with measuring conductivity was not applicable, the main experimental approach taken was to use optical methods with the study of PL in the region of intrinsic absorption. Thus, localized states of sodium silicate were detected, and structurally they were directly associated with sodium oxide with the accompanying rich phenomena; luminescence, trapped charge, and recombination of the trapped charge providing recombination luminescence. Fortunately, the center of luminescence of sodium silicate glass is anisotropic. It provides a polarized luminescence when excited by polarized light. The polarized luminescence excited in the region of intrinsic absorption is remarkable. It is a direct sign of localized states in a disordered solid state. Spectral and temperature studies show that the edge of mobility depends on the temperature. Kangro, Vitols, and Tolstoy [18] had also discovered the tunneling processes between localized states, some of which are temperature independent and some of which are temperature dependent.

A study of the localized state in sodium silicate glass shows that the localized state is associated with the structure with the lowest energy state—the intrinsic absorption edge. And this absorption associated with sodium oxide and sodium oxide is a glass modifier, while SiO_4 is a glass former. In the case of quartz glass, there is no modifier. A key study was conducted at the beginning of the study of germanium dioxide. At the first stage, the intrinsic absorption of the Li_2GeO_3 crystal was measured with the idea of determining the absorption of the "modifier" in this crystal, namely Li_2O [19]. The crystal structure of Li_2GeO_3 consists of infinite tetrahedral GeO_4 chains with lithium ions between them. The shocking result was that this lithium germanate crystal has its own position of the adsorption edge, which exactly coincides with the position for the GeO_2 crystal with the α-quartz structure and in both cases occurs at 6 eV. In

addition, the parameters of the Urbach rule (Toyozawa style) exactly match for these two crystals. Thus, the lowest states of these crystals are determined by electronic transitions associated with the GeO_4 tetrahedral. Then we studied the optical absorption of ultrapure sodium germanate glasses. The intrinsic absorption edge of these glasses is independent of the modifier and amounts to 4.6 eV. This almost exactly coincides with the intrinsic position of the absorption of the GeO_2 crystal with the structure of rutile [20]. It is known that alkali ions are catalysts that stimulate the development of GeO_2 with a rutile structure. A. Weispals, using an admixture of sodium bicarbonate, created for us such a GeO_2 crystal with a rutile structure. Germanate glasses also have strong absorption at 4.6 eV, and A. Weispals created for us a thin film of amorphous GeO_2 on an aluminum oxide plate. The measured optical absorption of this sample shows two edges [19]. One at 4.6 eV and the other, more intense, at 6 eV. It was concluded that amorphous GeO_2 contains both octahedral rutile-like and tetrahedral quartz structures. The luminescent properties of two-component germanate glasses and amorphous germanium dioxide are similar, with excitation at 4.6 eV. It was concluded that the localized states of the germanate glasses are associated with the rutile-like structure of the glass former. The electronic states of the modifier are at high energies and affect the properties of localized states more weakly than in alkali-silicate glasses. It follows that to understand the properties of quartz glass, comparison with α-quartz was insufficient and it was necessary to study other polymorphs, such as cristobalite, coesite, and stishovite.

After a long time, we got access to cristobalite, coesite, and stishovite samples (see, for example, [21].) These samples were difficult to study. The cristobalite sample, although very clean, was a polycrystalline type of ceramic and was not suitable for detailed optical studies, such as absorption and reflection spectra. The luminescence excited by x-rays was investigated and the luminescence of the STE type was revealed. The coesite and stishovite samples were single crystals and were of very small sizes, ~ 0.1 mm^3. Due to their small size, considerable efforts have been made to collect experimental data. For a stishovite single crystal of silicon dioxide with a rutile structure, the position of the intrinsic absorption edge is 8.75 eV, regardless of temperature. Therefore, this edge is higher in energy than that of α-quartz, which is located at 290 K at 8.5 eV and is very sensitive to temperature. The position at 8.75 eV for α-quartz occurs only at 4.5 K. For stishovite, we did not find evidence of the existence of STE, while the luminescence of stishovite strongly resembles the luminescence of pure oxygen-deficient silica glass. It must be emphasized that in an unirradiated α-quartz crystal, luminescence similar to oxygen-

deficient quartz glass has never been observed. Only strong irradiation with neutrons, gamma, and a dense electron beam provides the appearance of a similar luminescence.

The position of the absorption edge of coesite is the same as that of α-quartz with a similar temperature dependence. STE luminescence of coesite was discovered, and this was explained as a property of the crystalline tetrahedral. However, the luminescence of some defects was also detected in coesite. Some similarities with the case of oxygen-deficient quartz glass were found.

If we imagine the structure of quartz glass as fluctuating in density, the influence of the structure of coesite, and even stishovite, are possible. Taking into account primarily the results of studies of germanates glasses, the role of the rutile structure is revealed. However, it is clear that with optical absorption similar to the case of germanate glasses, it was not possible to detect the absorption of the octahedron in quartz glass due to the position of the stishovite edge being higher in energy among all known modifications of silicon dioxide.

Localized states were also studied in phosphate glasses, in lead silicate glasses, and some similarities were found (see, for example, [22]). In the case of intrinsic absorption, luminescence polarization was also the main argument for the nature of the localized states. The case of sodium silicate glasses in which second glass-forming agents, such as germanium dioxide or lead oxide, were added, makes it possible to estimate the concentration of localized states in sodium silicate glasses. This was determined at 1%. This concentration of the corresponding structural elements sets the boundary between localized states and extended states.

Thus, the mutual compensation of localized states occurs with the addition of a second glass former to the glass. Only if the concentration of the second glass former exceeds a certain level can we say, regarding the creation of a new material, that the property of other localized states can be revealed. This is an example of the Kolomiyets principle that glass cannot be alloyed.

A clear contrast begins to appear in quartz glass when a difference in properties is detected due to point defects and extended defects associated with oxygen deficiency [23]. Indeed, the first studies of pure KS-4V quartz glass with controlled oxygen deficiency have already been studied. It was found that there is an absorption band at 7.6 eV, which is higher for a high deficit, but there is no constant connection with another absorption band at 5 eV, which is also proportional to the oxygen deficiency. This last strip corresponds to twofold-coordinated silicon, which is a point defect. The 7.6 eV band cannot be attributed to a point defect in the excited

luminescent properties as it is very similar to the properties of a localized state in other glasses. Therefore, this band is associated with a localized state. However, the possibility of observing this band only occurs if the quartz glass has oxygen deficiency; this is what we call the localized state for "normal" glasses, such as germanate, sodium silicate, etc. We can only imagine that, like germanate glass, the localized states of quartz glass are associated with the absorption of a dense modification manifesting itself on experiments in the presence of oxygen deficiency. The absorption edge of stishovite (8.75 eV) is much higher than that of even ultrapure quartz glass (8.1 eV).

The success of performed experiments is based on many areas of investigation possessing extreme properties. The materials were created in many laboratories and needed the cooperation of many scientists in developing them. Pure and doped silica glasses were created by A. G. Boganov and V. S. Rudenko (Institute of Silicate Chemistry, St. Petersburg, Russia) and K. M. Golant (Kotelnikov Institute of Radio-engineering and Electronics at the Russian Academy of Sciences, Troitsk, Russia). Pure sodium silicate and germanate glasses were provided by M. N. Tolstoy and L. B. Glebov (Vavilov State Optical Institute, St. Petersburg, Russia). Small single crystals of stishovite and coesite were created by T. I. Dyuzheva, L. M. Lityagina, and N. A. Bendeliani (Vereshchagin Institute of High Pressure Physics at the Russian Academy of Sciences, Troitsk, Russia).

The author is deeply indebted to L. Skuja who created many friendly computer programs for the automation of measurements and the treatment of measured experimental data.

The author is thankful to R. A. Weeks and D. L. Griscom, who selflessly introduced the publications of my research in English beginning in 1991.

ACKNOWLEDGMENTS

Latvian Science Council Grant No LZP-2018/1-0289 and the University of Latvia as the Centre of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART² are greatly acknowledged for financial support in the process of completing.

LIST OF ABBREVIATIONS

ArF	argon fluor excimer laser with 193 nm photon
CL	CL or electron beam excited luminescence
F2	fluorine excimer laser with 157 nm photon
KrF	krypton fluoride excimer laser with 248 nm photon
MO	molecular orbits
N2	nitrogen laser with 337 nm photon
ODC	oxygen-deficient center
PL	photoluminescence
PLE	photoluminescence excitation
SPCVD	the surface-plasma chemical vapor deposition
STE	self-trapped exciton
TSL	thermostimulated luminescence
XL	x-ray excited luminescence
ZFS	zero-field splitting

CHAPTER 1

STRUCTURE AND NATURE OF CHEMICAL BONDS

1.1 SiO_2 α-Quartz, GeO_2 α-Quartz, $AlPO_4$ α-Quartz, $GaPO_4$ α-Quartz, SiO_2 Cristobalite, SiO_2 Coezite, SiO_2 Stishovite

An experimental study of the optical properties of the investigated materials was conducted. A theoretical review of the optical properties and their correspondence to experimental data was performed.

With the exception of stishovite, the tetrahedron is the main element of the structure. The tetrahedral structure is associated with sp^3 hybridization of the silicon valence shell and sp hybridization of oxygen. For the stishovite octahedral structure, it is based on sp^3d^2 hybridization of silicon valence electrons and sp^2 hybridization in the case of oxygen. Theoretical calculations [24] show 0.19s, 0.26p, and 0.11d electrons in each Si atomic sphere; therefore, they emphasize the importance of sp^3d^2 hybridization. Oxygen in stishovite has triple coordination. Stishovite has a remarkable property; insensitivity to hydrofluoric acid. This is used to extract stishovite from the soil of the Arizona Barringer meteorite crater [25].

The structure of α-quartz is built by two helices of tetrahedra, Fig.1-1.

Table 1-1

Material/ bond	d(1) (Å)	d(2) (Å)	a (Å)	c (Å)
α-SiO_2 quartz	1.608	1.611	4.913	5.405
α-GeO_2 quartz	1.74	?	4.972	5.648

d(1)–short and d(2) long Si-O (Ge-O) bonds, a, c–cell parameters

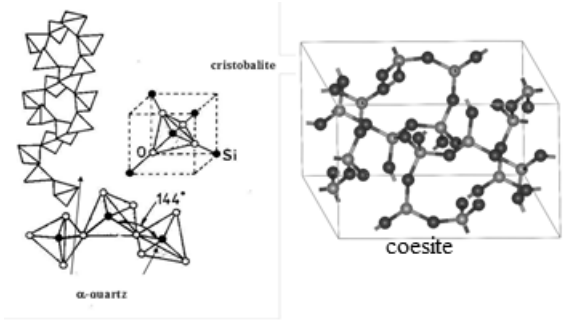

Fig.1-1. Structural models of α-quartz, cristobalite (upper picture), and coesite (two types of rings Si_4O_8 and Si_8O_{16} are seen), [26].

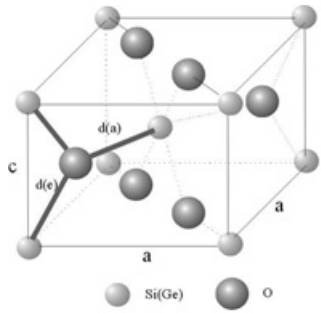

Fig.1-2. Models of the structure of SiO_2 and GeO_2 crystals with the structure of rutile. d(a): apical bond (two per cation). d(e): equatorial bond (four per cation) [24].

It also presents the structure of cristobalite and coesite. The structure of α-quartz contains channels along the c-axis and the x, y axes. Coesite contains Si_4O_8 and Si_8O_{16} rings. The structure associated with stishovite is shown in Fig.1-2.

In the case of the $AlPO_4$ α-quartz, the $GaPO_4$ α-quartz structure is the same as in Fig.1-1, and the tetrahedra with Al (Ga) are surrounded by PO_4 tetrahedra. The density of states calculated for α-quartz is shown in Fig. 1-3 (see, for example, [26]). As can be seen, the main contribution to the valence band is oxygen; however, there are also states of silicon. Silicon states make the main contribution to the conduction band; however, there is a contribution from oxygen states with a smaller fraction. The data for $AlPO_4$ are presented in the Fig. 1-4 below.

Table 1-2

Material/ bond	d(a) (Å)	d(e) (Å)	a (Å)	c (Å)
t-SiO_2 stishovite	1.81	1.757	4.179	2.665
t-GeO_2	?	?	4.395	2.859

Fig.1-4, [27] shows that the situation there is similar. The valence band is due to oxygen states with a very small contribution of P and Al, while in the conduction band the role of P is basic.

Fig.1-5 presents the charge distribution for the case of α-quartz, keatite, coesite, and stishovite [28]. It can be seen that the case of stishovite is very different from other modifications of silicon dioxide. The valence band does not have a gap, which is present in the case of α-quartz and other investigated crystals with the main element of the structure tetrahedron. Therefore, there is no energy separation of binding and non-binding states in stishovite. However, the upper valence band in all the listed materials is constructed mainly from 2p oxygen states.

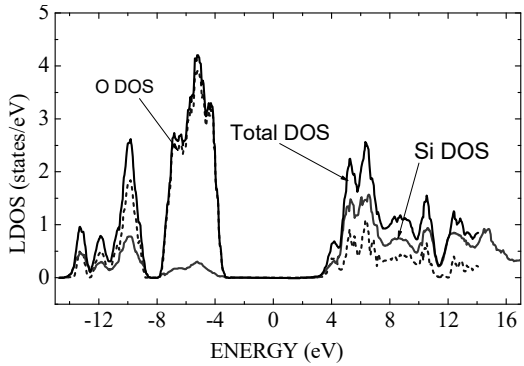

Fig.1-3. Bonding in alpha-quartz (SiO_2): A view of the unoccupied states, [26].

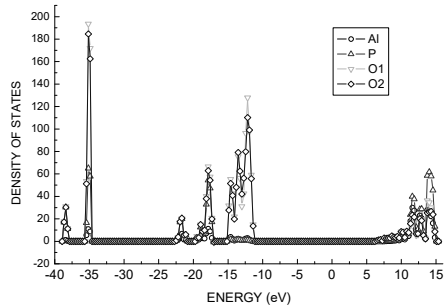

Fig.1-4. Density of states calculated for $AlPO_4$. Vlad Puchin, private communication (1996).

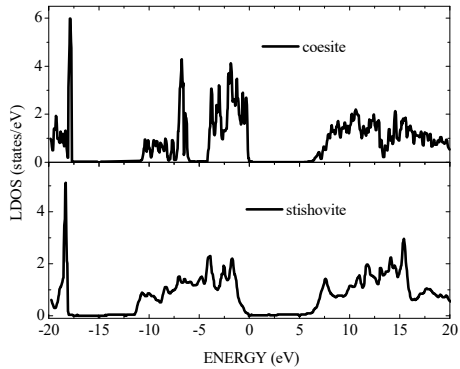

Fig.1-5. Density of state calculated for coesite and stishovite. Remarkable lack of gap in stishovite valence band [28].

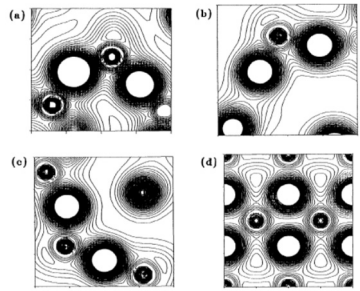

Fig.1-6. Charge density contour in (a) α-quartz, (b) keatite, (c) coesite, (d) stishovite [28].

Description of the Structure of Glassy SiO_2

There is a good review by Adrian S. Wright [29] on the structure of quartz glass. It talks about history, research methods, and interpretation problems. Historically, the first was the crystallite theory of glass structure developed by Lebedev. X-ray diffraction of oxide glasses shows diffuse halos that coincide with the known Bragg peaks of the crystalline powder. Later, Warren rejects the theory of crystallites, because the x-ray at low angles does not show a signal from the voids between the crystallites. Zachariasen introduces the theory of random networks in which structural units, which are both in glass and in crystal, are randomly connected in glass. The two main methods of studying the structure of glass are x-ray and neutron diffraction and they are complementary. The actual spatial correlation function is obtained after the Fourier transform of the diffraction data. An example of this function is shown in Fig.1-7.

Range I shows the short-range order associated with the tetrahedron. Range II shows the distances between atoms in connected tetrahedra. Range III is an intermediate order. The Si–O–Si angle for quartz glass has a distribution of angles from 120 to 180 degrees with a maximum at 144 degrees.

Progress in the model of random networks appears when Bell and Dean [30] create a "ball and stick" with their own hands, which provides a fairly good spatial correlation function in accordance with x-ray and neutron diffraction.

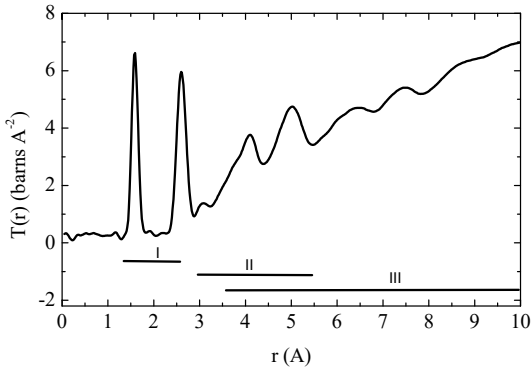

Fig.1-7. The correlation function T(r), obtained by the neutron scattering method for glassy SiO_2, showing the degree of contribution in the range of I, II, and III orders. [29].

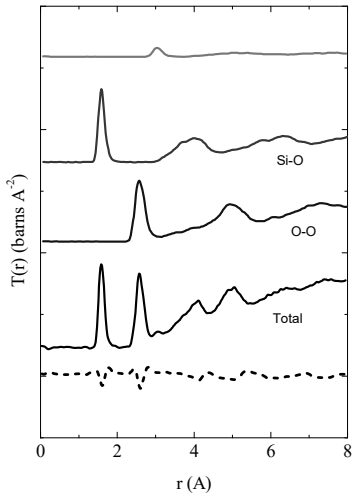

Fig.1-8. The neutron correlation function for the molecular dynamics simulation of vitreous SiO_2 by Vessal [31], compared to the neutron data of Ref.[32]. Line-experiment; dash-difference curve (simulation -experiment)

The “ball and stick” computer model almost exactly provides an experimental curve. One of the results is shown in Fig.1-8, where the nature of all spatial correlation function peaks is seen. Thus, the existence of the SiO_4 tetrahedron was established. That is also supported by the random network model. Specific details should be studied by other methods.