Original Paper

Synthesis, structure and electron spectra of fused quartz doped with titanium, cerium and neodymium

Maria Lączka and L. Stoch
Mining and Metallurgical Academy, Department of Glass, Kraków (Poland)

Vitreous silica doped with titanium, cerium or neodymium having specific optical properties was produced by fusing rock crystal or quartz minerals in an electrical vacuum furnace. The dissolution of titanium, cerium and neodymium compounds in vitreous silica is facilitated by aluminum, either present in the raw material or introduced for this purpose in the form of added chemical compounds. The role of the doping ions in the structure was interpreted on the basis of their electron spectra.

Synthese, Struktur und Elektronenspektren von titan-, cer- und neodymdotierten Kieselgläsern

In einem elektrischen Vakuumofen wurden mit Titan, Cer und Neodym dotierte Gläser aus Bergkristall und Gangquarz erschmolzen, die besondere optische Eigenschaften aufweisen. Die Auflösung der Titan-, Cer- und Neodymverbindungen wird erleichtert, wenn im Quarz primär Aluminium enthalten ist oder Aluminiumverbindungen zugegeben werden. Der Einfluß der zur Dotierung verwendeten Ionen auf die Struktur wurde an Hand ihrer Elektronenspektren interpretiert.

1. Introduction

The increasing demand for high-temperature-resistant materials of specific optical properties recently stimulated the interest in vitreous silica doped with transition and rare earth elements. From such glasses among other products selective optical filters, emitters of radiation of various energy, as well as radiation-hardened materials are produced [1 and 2].

Earlier publications address predominately doped vitreous silica obtained by chemical co-precipitation or by sol-gel methods based on alcoholate solutions. Not enough attention, however, has so far been given to the process of doping natural quartz and to fitting the process to the conditions in an electrical vacuum furnace.

Previous research has demonstrated that the solubility of transition and rare earth elements in vitreous silica is limited by phase-separation phenomena. The region of solubility can be widened by the addition of aluminum and alkali compounds. So far, however, no work has been published considering the potential utilization of impurities present in natural quartz by their incorporation in the structure of the glass.

Aiming at this industrial goal it has been attempted to produce various silica glasses doped with titanium, cerium or neodymium by electrical fusion in vacuum. At the same time the position of the dopant ions in the structure of the glass was tried to infer from the evaluation of their optical spectra.

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2. Experimental procedure

The doped silica glasses were obtained from two varieties of natural quartz distinguished by their impurities: from rock crystal, and from quartz minerals from Lower Silesia. The chemical compositions of these two raw materials as well as those of the resulting glasses (Atomic Absorption Spectrometry (AAS) analysis) are given in table 1.

Titanium, cerium and neodymium were introduced as the chemically pure oxides TiO_2, CeO_2 and Nd_2O_3. It was also attempted to dope the glasses simultaneously with $AlCl_3 \cdot 6\,H_2O$. The quantities (in mol%) introduced were: 0.1 to 1.0 TiO_2, 0.01 to 0.1 Ce_2O_3, 0.01 to 0.5 Nd_2O_3, 0.1 to 1.5 Al_2O_3.

The steps for introducing titanium and rare earth were: ground quartz (grain sizes 0.2 to 0.5 mm) was introduced in an aqueous suspension of the respective oxides and evaporated on the water bath. The residue was dried and homogenized mechanically. In the case of simultaneous doping with aluminum suspensions of the oxides in aqueous solutions of $AlCl_3$ of the desired concentration were used.

The glasses were melted in graphite crucibles in a vacuum furnace (according to Balzers, Liechtenstein) in 100 g batches. The heating schedule was: 0 to 1000 °C at 50 to 70 K/min, 1000 to 1500 °C at 2 to 3 K/min, 1500 to 1860 °C at 5 to 6 K/min. Macroscopic descriptions of some of those glasses containing characteristic concentrations of dopants are given in table 2.

From glasses of good quality test samples with polished parallel planes were made. Spectra of these samples were obtained in the visible and the UV region (SPECORD UV-VIS). The characteristic

Table 1. Impurity contents of quartz raw materials and glasses prepared from them

impurities in ppm	iron	titanium	calcium	magnesium	potassium	sodium	lithium	aluminum
rock crystal	1.0	1.0	2.1	1.0	4.2	14.1	1.7	16.2
glass from rock crystal	1.0	1.0	1.1	1.0	3.8	9.6	1.1	18.2
quartz mineral	5.0	5.0	18.0	10.0	96.1	150.2	20.0	1528.0
glass from quartz mineral	4.8	3.8	9.6	5.5	9.8	15.5	1.8	1421.0

Table 2. Dopant content and macroscopic description

raw material	content in dopants in mol%			Al_2O_3 introduced as $AlCl_3 \cdot 6\,H_2O$	Al_2O_3 originally contained in raw material	Al_2O_3/X	macroscopic description of glasses
	TiO_2	Ce_2O_3	Nd_2O_3			$X = TiO_2$, Ce_2O_3, Nd_2O_3	
rock crystal	0.05	–	–	–	–	–	glass
	0.10	–	–	–	–	–	glass
	0.20	–	–	–	–	–	darkly colored inclusion
	0.20	–	–	0.10	–	0.5	darkly colored inclusion
	0.20	–	–	0.20	–	1	bluish glass
	0.20	–	–	0.50	–	2.5	bluish glass
quartz mineral	0.20	–	–	0.10	0.15	1.25	bluish glass
	0.20	–	–	0.20	0.15	1.75	bluish glass
rock crystal	–	0.05	–	–	–	–	colorless glass
	–	0.08	–	–	–	–	colorless (bubbles)
	–	0.10	–	–	–	–	phase separation
	–	0.10	–	0.10	–	1	phase separation
	–	0.10	–	0.20	–	2	colorless glass (bubbles)
	–	0.10	–	0.30	–	3	colorless glass
quartz mineral	–	0.10	–	–	0.15	1.5	phase separation
	–	0.10	–	0.10	0.15	2.5	colorless glass
	–	0.10	–	0.20	0.15	3.5	color glass
rock crystal	–	–	0.05	–	–	–	violet-pink glass
	–	–	0.08	–	–	–	violet-pink glass
	–	–	0.10	–	–	–	phase separation
	–	–	0.20	–	–	–	phase separation
	–	–	0.10	0.10	–	1	phase separation
	–	–	0.10	0.20	–	2	violet-pink glass
	–	–	0.10	0.30	–	3	violet-pink glass
quartz mineral	–	–	0.10	–	0.15	1.5	phase separation
	–	–	0.10	0.10	0.15	2.5	violet-pink glass
	–	–	0.10	0.20	0.15	3.5	violet-pink glass

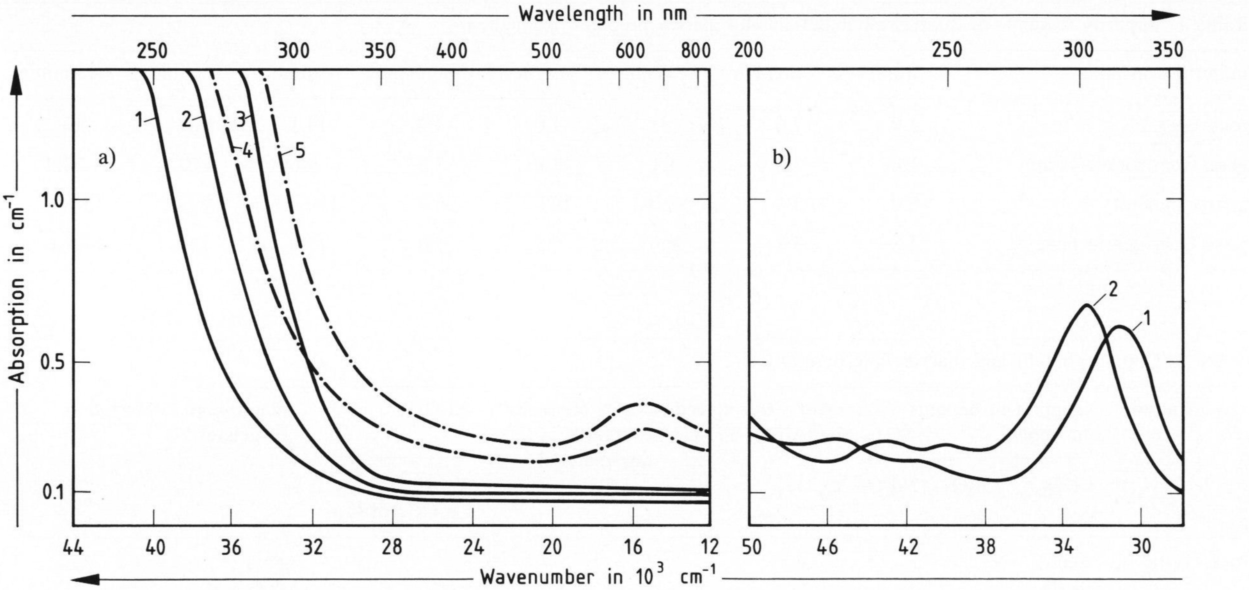
spectra are presented in figures 1a and b and 2. Table 3 lists the parameters of spectra used as the basis of more detailed evaluation.

3. Results and discussion

The macroscopic observation of glasses containing various dopants in various concentrations (table 2) indicated that titanium, cerium and neodymium can be introduced into pure vitreous silica only in limited quantities ($TiO_2 < 0.1$, Ce_2O_3 or $Nd_2O_3 < 0.08$ mol%). At concentrations of > 0.1 mol% TiO_2 the glasses contained darkly colored inclusions of incompletely dissolved titanium oxide. In glasses containing > 0.08 mol% cerium or neodymium oxide phase separation became clearly evident.

Aluminum either contained in the raw material or introduced in the form of $AlCl_3$ favored the dissolution of titanium, cerium, neodymium. Already for a molar ratio of $Al_2O_3/TiO_2 = 1$, TiO_2 was completely dissolved. In the case of rare earths, phase separation was suppressed already at Al_2O_3/Ce_2O_3 (Nd_2O_3) = 2. Glasses from rock crystal doped with titanium were colorless, those that also contained aluminum were faintly blue. The respective spectra are presented in figure 1a.

From the absorption spectra it is concluded that in the pure glass titanium appears as Ti^{4+} ion [1 and 3],



Figures 1a and b. Absorption spectra of a) titanium in silica glasses (sample thickness 5 mm); curve 1 = 0.01 TiO_2, curve 2 = 0.05 TiO_2, curve 3 = 0.1 TiO_2, curve 4 = 0.1 TiO_2 + 1.0 Al_2O_3, curve 5 = 0.3 TiO_2 + 1.0 Al_2O_3, b) cerium (sample thickness 1 mm); curve 1 = 0.01 Ce_2O_3, curve 2 = 0.01 Ce_2O_3 + 0.05 Al_2O_3. All introduced quantities are given in mol%.

Table 3. Characteristic parameter of absorption spectra of Ce^{3+} and Nd^{3+} ions in silica glasses

dopant content (mol%)			Al_2O_3/X	position of long wave absorption band for Ce^{3+} in mm	halfwidth in cm^{-1} of band
Al_2O_3	Ce_2O_3	Nd_2O_3	$X = Ce_2O_3$, Nd_2O_3		$^4I_{9/2} \rightarrow {}^2G_{9/2}$, $^4G_{5/2}$ for Nd^{3+}
–	0.01	–	–	320	–
0.01	0.01	–	1	320	–
0.02	0.01	–	2	320	–
0.03	0.01	–	3	315	–
0.04	0.01	–	4	305	–
0.05	0.01	–	5	305	–
0.05	0.05	–	1	320	–
0.10	0.05	–	2	320	–
0.20	0.05	–	4	305	–
0.50	0.05	–	10	305	–
–	–	0.05	–	–	680
–	–	0.08	–	–	682
0.05	–	0.05	1	–	680
0.10	–	0.05	2	–	652
0.15	–	0.05	3	–	582
0.20	–	0.05	4	–	565
0.25	–	0.05	5	–	565
0.50	–	0.05	10	–	570
0.40	–	0.10	4	–	565
0.50	–	0.10	5	–	565
1.00	–	0.10	10	–	568

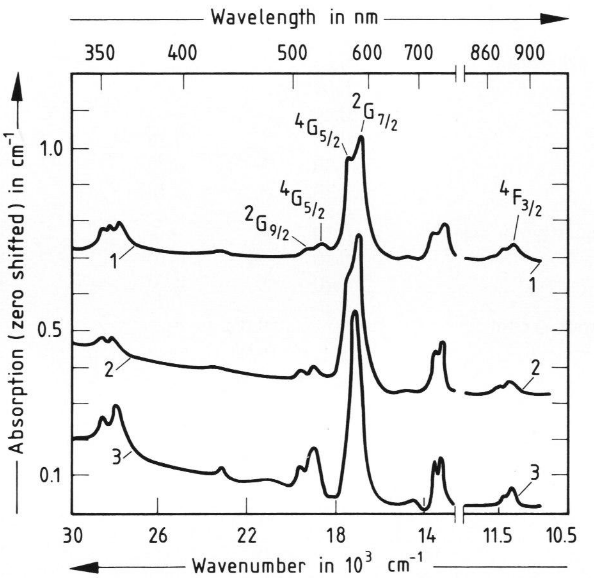


Figure 2. Absorption spectra of neodymium in silica glasses (sample thickness 10 mm): curve 1 = 0.05 Nd_2O_3, curve 2 = 0.05 Nd_2O_3 + 0.1 Al_2O_3, curve 3 = 0.05 Nd_2O_3 + 0.2 Al_2O_3. All introduced quantities are given in mol%.

since Ti^{4+} ion is characterized by an intensive charge-transfer absorption in the UV, with an absorption edge depending on concentration.

Glasses doped with both aluminum and titanium show besides the intensive absorption in the UV a weaker band at larger wavelengths (with a maximum at 660 nm). Optical and Electron Paramagnetic Resonance (EPR) investigations seem to indicate that this band is associated with Ti^{3+} ion in tetrahedral coordination [3]. Ti^{3+} ion has the electron ground configuration $4d^1$, and light absorption is caused by d–d transitions.

Since all silica glasses were melted under identical conditions it may be concluded that the reduction to Ti^{3+} ions and the incorporation of these ions into the silicon–oxygen network was made possible only by the presence of Al^{3+} ions.

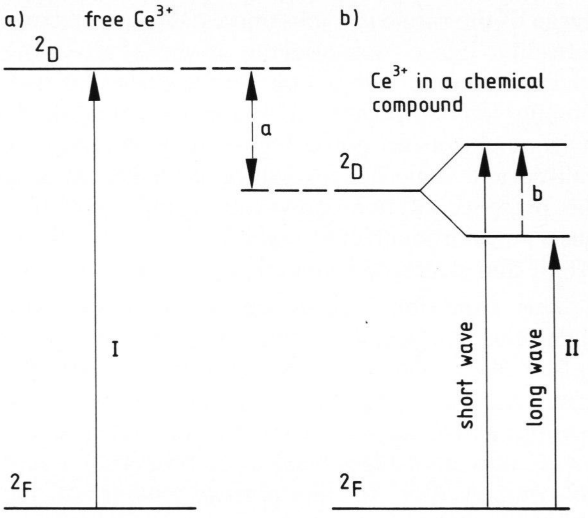
All cerium-doped glasses were colorless and showed the absorption band in the visible region. But an intensive absorption band was observed in the UV spectrum (figure 1b). The maximum of this band lay at 320 to 305 nm. Weaker, less pronounced bands were observed, too, in the region of shorter wavelengths. Intensity as well as localization of these bands suggested attribution to Ce^{3+} ion [1 and 5]. With the ground configuration of the cerium ion of $4f^1$ a doublet ground state of ^2F corresponds. For the absorption observed, the transition of 4f electrons from the ground state to the levels $5d/^2D$ split in the ligand field is responsible.

In the case of a glass doped only with cerium the maximum of the long wave Ce^{3+} band was at 320 nm. Addition of aluminum shifted this band towards shorter wavelengths. The largest shift (15 nm) was observed at a molar ratio $Al_2O_3/Ce_2O_3 = 4$. A further increase caused no further shift (table 3).

From a theoretical viewpoint the shift of the Ce^{3+} absorption bands may be caused either by a change in bond covalency – influencing the site of the center of gravity of 5d orbitals and thus energy – or by changes in the ligand field which are responsible for the splitting of the ^2D term. The proposed scheme interpreting the optical spectra of Ce^{3+} is presented in figures 3a and b. A decrease in covalency of the cerium–oxygen bond as well as a weakening of the ligand field are considered leading to the shift of the long wave Ce^{3+} band towards shorter wavelengths. Thus the optical spectra of the silica glasses investigated suggest that the addition of aluminum to the cerium-doped glasses weakens the interaction between the cerium ions and the surrounding oxygen ions.

In spite of the identical localization of these bands distinct differences in the sharpness of the optical spectra were observed for the different investigated glasses: the halfwidths of the absorption bands were clearly different. This was most pronounced in the case of the most intensive band which corresponds with the electron transition from the ground state $^4I_{9/2}$ to the neighboring terms $^2G_{7/2}$, $^4G_{5/2}$ (figure 2, table 3). The most diffuse and at the same time asymmetric spectrum corresponding with $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ with a noticeable fine structure was observed in the case of pure silica glass. Aluminum additions increased sharpness substantiated by a significant decrease in the halfwidth of the bands. At the same time the fine structure vanishes in comparison to the pure silica glass. The sharpest spectrum was observed at the molar ratio $Al_2O_3/Nd_2O_3 = 4$. Any further increase of this ratio did no longer affect the character of the spectrum.

From a theoretical viewpoint these changes in the fine structure as well as those in halfwidth associated with f–f transitions can be related to a disturbance of the cubic symmetry of the neighbor ions or to changes in the ligand field [4, 6 and 7]. Investigations carried



Figures 3a and b. Schematic of electronic transitions 4f–5d in free (I) and bound (II) Ce^{3+} a) covalency phenomenon, b) ligand phenomenon.

out so far unequivocally demonstrate that in solutions as well as in crystals the symmetry of the environment of the Nd^{3+} ions is less than cubic. It can thus be assumed that these conditions prevail in glasses. A non-cubic symmetry of the ions surrounding the neodymium ion moreover was indicated by the noticeable asymmetry of the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ band observed both in the pure and the aluminum-doped glasses. This asymmetry results from the splitting of the $^4F_{3/2}$ term present in fields of lower symmetry, while absent in fields of cubic symmetry. Since the terms $^2G_{7/2}$ and $^4G_{5/2}$ show maximum splitting in cubic-symmetrical fields, the $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ band – which showed the largest differences in halfwidth – must be considered less sensitive to the symmetry of neighbor ions. Therefore, this observed decrease in halfwidth seems to be caused mostly from a weakening of the ligand field which diminishes the splitting of the $^2G_{7/2}$ and $^4G_{5/2}$ terms. These changes are caused by the introduction of aluminum at a ratio of $Al_2O_3/Nd_2O_3 = 4$.

Stable absorption centers have been formed which are no longer influenced by a further increase in aluminum. Thus the interpretations for both lanthanides appear quite similar.

Investigations so far have shown that the symmetry condition of nearest neighbors is increased by co-doping with aluminum [8]. This appears to agree quite well with the interpretation of the electron spectra of Ce^{3+} and Nd^{3+} ions on the basis of bonding character. The rare earth ions with their larger radius most likely assume free space in the glass network and a high coordination. In the pure silica glass in which, besides the rare earth ions, other ions are present only in trace concentrations, the lanthanides act as typical modifiers. In their presence oxygen bridges are disrupted and non-bridging oxygens are formed. This permits compensation of the positive charge of the rare earth ions and establishes electron neutrality. Since non-bridging oxygens are more polarizable, their interaction with cerium and neodymium ions is greater. However, in practice an environment of just non-bridging oxygens cannot be realized and some ligands will be bridging oxygens. The presence of non-equivalent ligands may thus cause an additional deformation of the coordinate system and decrease symmetry.

This condition is changed by co-doping with aluminum. The smaller aluminum ions most likely replace silicon ions in the Si–O tetrahedra and the cerium and neodymium ions will compensate for the resulting excess negative charge in the network. Of course, now no bridges need to be broken to assure the compensation of the positive charge of the lanthanide ions.

The conclusion is justified that co-doping with aluminum eliminates the presence of non-bridging oxygen near the rare earth elements, thus weakening chemical bonding and increasing symmetry.

3. Summary

The results of this investigation show that the preparation of special optical glasses by electrofusion of quartz is strongly influenced by the concentration of transition and rare earth elements. These elements can be introduced only in limited amounts. Aluminum, either present in the raw material or added deliberately, plays an important role in processing these glasses. Aluminum enhances the solubility of transition and rare earth elements in silica glass and affects its optical properties. In the case of doping with titanium, reduction to Ti^{3+} introduces an absorption band with a maximum at 660 nm in the visible spectrum. In the case of doping with cerium, the spectrum characteristic for Ce^{3+} ions is shifted towards shorter wavelengths by co-doping with aluminum; in the case of doping with neodymium sharpness of the spectrum is increased. These effects of aluminum are advantageous for the preparation of special optical and laser glasses.

4. References

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