Optical absorption and structure of impurity Ni\textsuperscript{2+} center in tungstate-tellurite glass

V.G.Plotnichenko\textsuperscript{*} and V.O.Sokolov\textsuperscript{†}
Fiber Optics Research Center of the Russian Academy of Sciences
38 Vavilov Street, Moscow 119333, Russia

G.E.Snopatin and M.F.Churbanov
Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences
49 Tropinin Street, Nizhny Novgorod 603600, Russia

Absorption spectra of Ni\textsuperscript{2+} ions in 22WO\textsubscript{3}–78TeO\textsubscript{2} tungstate-tellurite glass were studied and Ni\textsuperscript{2+} extinction coefficient spectral dependence was derived in the 450 – 2700 nm wavelength range. Computer modeling of the glass structure proved Ni\textsuperscript{2+} ions to be in trigonal-distorted octahedral environment in the tungstate-tellurite glass. Tanabe-Sugano diagram for such an environment was calculated and good description of the observed spectrum of Ni\textsuperscript{2+} ion was obtained. Basing on both absorption spectral range width and the extinction coefficient, nickel should be considered among the most strongly absorbing impurities in the tellurite glasses.

PACS numbers: 71.55.-i, 71.70.Ch, 78.20.Bh, 78.20.Ci, 78.40.Pg
Keywords: tellurite glasses; defect centers; glasses containing transition metal ions; optical spectroscopy; computer simulation

I. INTRODUCTION

Tellurite glasses are known to have wide transmission range (0.35 – 6.0 \(\mu\)m), high linear and nonlinear refractive indices and potentially low optical losses in the near- and mid-IR ranges. Because of this tellurite glasses are of considerable interest as fiber optics materials. Glasses intended for optical fibers manufacturing should contain low amount of impurities responsible for optical loss. 3d transition metals ions (V, Cr, Mn, Fe, Co, Ni and Cu) giving rise to intense absorption in the visible and near infrared region represent one of the main groups of the limiting impurities.

In the literature there are no quantitative data on the influence of 3d transition metals impurities on optical absorption in the transmission spectral range of tellurite glasses. On the other hand, absorption spectra of 3d transition metals ions in zirconium fluoride- and silica-based glasses are studied to a considerable extent \cite{1,5}. In zirconium fluoride-based glasses the optical absorption in the 1 – 2 \(\mu\)m range is limited by Co\textsuperscript{2+}, Fe\textsuperscript{2+} and Ni\textsuperscript{2+} impurities with extinction coefficient 100 – 500 dB km\textsuperscript{−1} ppm\textsuperscript{−1} \cite{4}. Cr, Co, Fe and Cu impurities with extinction coefficient 300 – 700 dB km\textsuperscript{−1} ppm\textsuperscript{−1} in the silica transparency range, 1.3 – 1.6 \(\mu\)m, are known to be the most limiting impurities in silica fibers \cite{5}.

Extinction coefficient relates optical absorption intensity to impurities content. Hence knowledge of the extinction coefficient spectral dependence is needed, on the one hand, to control undesirable impurities content in optical materials using the materials transmission spectra, to develop justified requirements for the acceptable content of impurities and to adjust technology to improve the optical parameters of materials; on the other hand, to control the content of dopants explicitly added to the material to optimize the characteristics of the developed lasers, optical amplifiers and converters.

The purpose of the present work is to study the transmission spectra of nickel-doped tungstate-tellurite glasses, WO\textsubscript{3}–TeO\textsubscript{2}–Ni\textsuperscript{2+}, to determine the spectral dependence of Ni\textsuperscript{2+} extinction coefficient in the 450 – 2700 nm wavelength range and to relate absorption spectra of Ni\textsuperscript{2+} ions in the tungstate-tellurite glass with structure of their environment. Tungstate-tellurite glasses is known to be one of the most crystallization-resistant binary tellurite glasses. Nickel as a dopant is chosen for the investigation on account of its abundance in oxides used as raw materials and of the only valence state, +2, of nickel in oxides. The latter is of importance in view of oxidizing nature of TeO\textsubscript{2} as macro component of the glass under consideration.

II. EXPERIMENTAL

A. Preparation of Ni\textsuperscript{2+}-doped tungstate-tellurite glasses

Tungstate-tellurite glasses were prepared by cooling molten 22WO\textsubscript{3}–78TeO\textsubscript{2} high-purity oxides mixture \cite{6}. TeO\textsubscript{2} and WO\textsubscript{3} oxides with nickel impurity content as low as 1.0 · 10\textsuperscript{−4} wt.% Ni were used as raw components. Mixture of powdered raw components were pre-dried to remove water and then melted in platinum crucible heated by high-frequency inductor placed in oxygen atmosphere with 0.8 ppm humidity. The melt was homogenized for 1 hour at a temperature of 800\textdegree C (monitored by an optical pyrometer).

After homogenizing melting, part of the melt was solidified into 22WO\textsubscript{3}–78TeO\textsubscript{2} glass for later use to di-
lutine nickel-doped glass melts. Nickel oxide was added to the rest of the melt to obtain doped glass containing 1 wt.% NiO. Once the nickel-doped melt was homogenized, part of it was vitrified and the previously prepared 22WO$_3$–78TeO$_2$ diluent glass was added to the rest of the melt in the crucible. Repeating the process several times, 22WO$_3$–78TeO$_2$:Ni$^{2+}$ glasses containing from 0.786 up to 9.4·10$^{-3}$ wt.% Ni were obtained. Nickel oxide concentration in the solidified glass was calculated from material balance equation.

22WO$_3$–78TeO$_2$:Ni$^{2+}$ glasses samples with thickness from 0.5 to 50 mm with optically polished faces were prepared. Transmission spectra of these samples in visible and infrared spectral ranges were measured using Perkin Elmer Lambda 900 spectrophotometer (in the 400 – 3000 nm range) and Bruker IFS 113v Fourier spectrometer (in the 1000 – 10000 nm range) with spectral resolution better than 4 nm.

**B. Measurements**

Fig. 1 shows transmission spectra of 0.5 mm-thick samples containing from 0.009 to 0.786 wt.% Ni. As viewed in Fig. 1 in the absorption spectrum of 22WO$_3$–78TeO$_2$:Ni$^{2+}$ glass there are two broad bands with maxima near 810 and 1320 nm and a band with maximum at wavelength < 450 nm falling within the short-wavelength edge of 22WO$_3$–78TeO$_2$:Ni$^{2+}$ glass transparency range. The absorption intensity in all the bands increases with nickel content growth.

Transmission spectra were measured for the optical path length from 0.5 to 22 mm for samples with different nickel content. This allowed us to determine the extinction coefficient relating absorption of Ni$^{2+}$ ion with concentration of such ions in 22WO$_3$–78TeO$_2$:Ni$^{2+}$ tellurite glass in the 450 – 2700 nm spectral range. By the way of example, Fig. 2 shows the light attenuation in the peak of the 1320 nm band in glasses containing 0.053 wt.% Ni on the sample length and its linear approximation.

**Figure 1. Transmission spectra of 22WO$_3$–78TeO$_2$:Ni$^{2+}$ tellurite glasses 0.5 mm-thick samples with different nickel oxide content (1 0.012, 2 0.029, 3 0.068, 4 0.16, 5 0.27, 6 0.51, 7 1.01 wt.% NiO)**

**Figure 2. Dependence of the radiation attenuation in the maximum of the 1320 nm absorption band in 22WO$_3$–78TeO$_2$:Ni$^{2+}$ tellurite glasses containing 0.053 wt.% Ni on the sample length and its linear approximation**

**Figure 3. Dependence of the bulk absorption coefficient at 1320 nm wavelength on the nickel content in 22WO$_3$–78TeO$_2$:Ni$^{2+}$ tellurite glasses**
vs. the sample thickness together with linear approximation of the experimental points. The $A$ coefficient of the approximation is mostly due to Fresnel reflection losses and the line slope ($B$ coefficient) represents the bulk absorption coefficient of the bulk glass with given nickel content.

In Fig. 4 are shown the experimental data and the approximation of the bulk absorption coefficient for the 1320 nm band for all the samples studied with Ni content up to approximately 0.12 wt.% Ni. As evident from Fig. 3 in this range of nickel content absorption in the maximum of the 1320 nm band is well fitted by a linear function of the absorbing Ni$^{2+}$ ions concentration. The straight line slope representing the extinction coefficient is equal to $20.2 \pm 0.8$ cm$^{-1}$ (wt.% Ni)$^{-1}$ or $870 \pm 35$ dB km$^{-1}$ (wt. ppm Ni)$^{-1}$.

Since both the number of absorption bands and their shapes do not depend on nickel content in the glass, it is possible to derive the spectral dependence of the extinction coefficient shown in Fig. 4. For reference, Table I represents Ni$^{2+}$ impurity ions absorption at different wavelengths in several glasses with 1 ppm Ni content. The above-obtained Ni$^{2+}$ extinction coefficient spectral dependence allows us to estimate the content of impurity nickel ions in WO$_3$–TeO$_2$:Ni$^{2+}$ tellurite glasses able to get certain optical losses in glass at different wavelengths. Thus, optical losses as low as 100 dB km$^{-1}$ in the 600 – 2000 nm spectral range are possible for nickel content not more than 1·10$^{-5}$ wt. % Ni or 0.1 wt. ppm Ni.

Table I. Absorption (dB km$^{-1}$) caused by 1 wt. ppm impurity Ni$^{2+}$ ions in various glasses

| glass                     | absorption band wavelength, µm | Ref. |
|---------------------------|--------------------------------|------|
| ZrF$_4$-based (Zr–Ba–La–Al–Na–Pb–F) | 650  200  90   30  [2]           |      |
| ZrF$_4$-based (Zr–Ba–La–Al–Na–F)  | 360  100  < 30  < 3  [3]           |      |
| SiO$_2$                   | 2500 200       —       —  [5]           |      |
| 22WO$_3$–78TeO$_2$        | > 5000 750  200  30  this paper    |      |

III. MODELING OF THE WO$_3$–TEO$_2$:NI$^{2+}$ SYSTEM

Modeling of the structure of impurity nickel centers in tungstate-tellurite glass network was performed using periodic model constructed on the basis of the supercell containing 32 TeO$_2$ groups (96 atoms in total), with the initial atoms arrangement corresponding to paratellurite lattice. Two TeO$_2$ groups in the supercell were substituted by NiO and WO$_3$ ones. So the supercell composition was (NiO) (WO$_3$) (TeO$_2$)$_{30}$. The described model was used to find the equilibrium configurations of impurity nickel atoms and tungsten atoms in the WO$_3$–TeO$_2$ tellurite glass network by means of ab initio (Car-Parrinello) molecular dynamics [2] with final complete geometry optimization by gradient method. All calculations were performed in the generalized gradient approximation of density functional theory in the plane waves basis using the Quantum-Espresso package [2]. Calculations were performed in two approaches, using either norm-conserving Troullier-Martins pseudopotentials [2] or ultrasoft pseudopotentials [10–12]. The norm-conserving Troullier-Martins pseudopotentials and ultrasoft pseudopotentials were developed for the tellurium atoms, oxygen, nickel and tungsten with the help of Bio98PP [13] and USPP v. 7.3.6 [14] programs, respectively. 3d, 4s and 4p shells were taken to be the valence ones in the case of nickel atom.

Calculations showed that Ni$^{2+}$ ion is sixfold coordinated in the WO$_3$–TeO$_2$ glass network ion, its environment being trigonally (D$_3$) distorted octahedron with oxygen atoms in its vertices forming Ni–O–Te linkages (Fig. 5). It should be remarked that Ni$^{2+}$ turns out to be surrounded by pure TeO$_2$ network: no tungsten atom occurs in three nearest coordination shells.

Using the geometric parameters obtained in this modeling we calculated electronic states of Ni$^{2+}$ ion in WO$_3$–TeO$_2$ glass network corresponding to d$^7$ electronic configuration of the Ni$^{2+}$ ion. The calculation was performed using AOMX program [15] in angular overlap model of the ligand field theory [16–18]. The model parameters were optimized demanding the best reproduction of experimental values of the absorption bands wave-
Racah parameters

lengths: the crystal field parameter $\Delta \approx 10988 \text{ cm}^{-1}$, Racah parameters $B \approx 958 \text{ cm}^{-1}$ ($\Delta/B \approx 11.5$) and $C \approx 3330 \text{ cm}^{-1}$, the angular overlap parameters $e_\sigma \approx 3663 \text{ cm}^{-1}$ and $e_\pi \approx 183 \text{ cm}^{-1}$. With these parameters the Tanabe-Sugano diagram [19] was designed for Ni$^{2+}$ in the d$^8$ electronic configuration in WO$_3$-TeO$_2$ glass network. The diagram is shown in Fig. 6 where the $\Delta/B$ parameter value corresponding to the Ni$^{2+}$ absorption bands experimentally observed in WO$_3$-TeO$_2$:Ni$^{2+}$ glasses and the transitions wavelengths are marked. Fig. 7 presents the scheme of calculated levels and main E1 transitions in octahedrally coordinated Ni$^{2+}$ ion in the d$^8$ electronic configuration in WO$_3$-TeO$_2$ glass network both in O$_h$ cubic and D$_3$ trigonal environments in comparison with free Ni$^{2+}$ ion [20].

Results of the modeling allow us to interpret the observed absorption spectrum of Ni$^{2+}$ ions in WO$_3$-TeO$_2$:Ni$^{2+}$ glass as follows.

In the case of cubic O$_h$ symmetry of the Ni$^{2+}$ ion octahedral environment three main absorption bands are known to occur (see e.g. [21] [23]). The bands correspond to spin-allowed E1 transitions from the ground state, $^3$A$_{2g}$ ($^3$F), to the excited states, $^3$F$_{2g}$ ($^3$F) (($a$) transition in Fig. 6 typically in the 1100 – 1200 nm range); $^3$F$_{1g}$ ($^3$F) (($b$) transition in Fig. 6 typically in 630 – 770 nm range); and $^3$F$_{1g}$ ($^3$P) (($c$) transition in Fig. 6 typically in 380 – 500 nm range).

Besides, weak absorption band caused by spin-forbidden transition from the $^3$A$_{2g}$ ($^3$F) ground state to the $^1$E$_g$ ($^1$D) excited state is sometimes observed near the (b) band ($b_1$) transition in Fig. 6. Notice to avoid confusion that all these transitions are parity-forbidden but become slightly allowed owing to vibronic contributions. Calculation using the above-listed parameters yields the these transitions wavelengths for Ni$^{2+}$ ion in O$_h$ environment to be (a) 1000 nm, (b) 600 nm, (c) 350 nm, (b$_1$) 723 nm, in satisfactory agreement with the typical values for O$_h$ environment given above.

In D$_{3d}$ or D$_3$ trigonally distorted octahedral environment of the Ni$^{2+}$ ion, the ground state turns out to be $^3$A$_{2g}$ ($^3$F) and each of the $^3$F$_{1g}$ ($^3$F), $^3$F$_{2g}$ ($^3$F), and $^3$F$_{1g}$ ($^3$P) excited states is split into two states, $^3$A$_{1g}$ ($^3$F), $^3$E$_{1g}$ ($^3$F); $^3$A$_{2g}$ ($^3$F), $^3$E$_{2g}$ ($^3$F); $^3$A$_{2g}$ ($^3$P), $^3$E$_{2g}$ ($^3$P), respectively. The $^1$E$_g$ ($^1$D) is not split. In the case of D$_3$ distortion E1 transitions from the $^3$A$_{2g}$ ($^3$F) ground state to the excited $^3$A$_{1g}$ ($^3$F), $^3$E$_{1g}$ ($^3$F) and $^3$E$_{2g}$ ($^3$P) turn out to be both spin- and symmetry-allowed ($a'$, $a''$, $b'$, and $c''$) transitions in Fig. 6 while transitions to the $^3$A$_{2g}$ ($^3$F) and $^3$A$_{2g}$ ($^3$P) excited states are symmetry-forbidden. In the case of D$_{3d}$ distortion all the E1 transitions from the $^3$A$_{2g}$ ($^3$F) ground state to the $^3$A$_{1g}$ ($^3$F), $^3$E$_{1g}$ ($^3$F), $^3$E$_{2g}$ ($^3$P), $^3$A$_{2g}$ ($^3$F), and $^3$A$_{2g}$ ($^3$P) excited states, are symmetry-allowed. The transition from the $^3$A$_{2g}$ ($^3$F) ground state to the $^1$E$_g$ ($^1$D) excited one is still spin-forbidden ($b_1$) transition in Fig. 6. The remark concerning the vibronic contributions remains valid.

In our case, ($a'$) and ($a''$) transitions from $^3$A$_{2g}$ ($^3$F) to $^3$A$_{1g}$ ($^3$F) and $^3$E$_{1g}$ ($^3$F) correspond to the absorption band near 1300 nm; ($b'$) transition from $^3$A$_{2g}$ ($^3$F) to $^3$E$_{2g}$ ($^3$F) corresponds to the absorption band near...
Figure 7. Energy levels and main E1-transitions in octahedrally coordinated Ni$^{2+}$ ion in the WO$_3$–TeO$_2$ glass network in $d^8$ electronic configuration in the cubic $O_h$ and trigonal $D_3$ environment in comparison with free Ni$^{2+}$ ion.
800 nm; (b1) transition from $^3A_{2(g)}$ ($^3F$) to $^1E_{g}$ ($^1D$) corresponds to the weakly pronounced band near 740 nm; and (c″) transition from $^3A_{2(g)}$ ($^3F$) to $^3E_g$ ($^3P$) corresponds to the absorption band in the < 500 nm range.

Thus, in binary tungstate-tellurite glasses, due to strong trigonal distortion of the octahedral environment of Ni$^{2+}$ ions, absorption bands of these ions turn out to be shifted substantially towards longer wavelengths in comparison with the absorption pattern typical for nickel-doped crystals. In this case, obviously, the IR absorption band (near 1320 nm) should be strongly heterogeneously broadened while the (heterogeneous) broadening of the other absorption bands should be relatively weak.

IV. SUMMARY

In this study we measured transmission spectra of 22WO$_3$–78TeO$_2$:Ni$^{2+}$ tungstate tellurite glass samples containing from 1 to 1.2 · 10$^{-2}$ wt.% NiO and obtained spectral dependence of Ni$^{2+}$ ions extinction coefficient in this glass in the 450 – 2700 nm wavelength range. These measurements together with our computer modeling of WO$_3$–TeO$_2$:Ni$^{2+}$ glass structure suggest Ni$^{2+}$ ions in such glasses to occur in strongly trigonally distorted octahedral sites. This results in corresponding absorption bands shifted significantly towards longer wavelengths compared to typical nickel-doped crystals and the absorption intensity being much higher than in silica- and zirconium fluoride-based glasses. So regarding both width of the absorption spectral range and the extinction coefficient value, nickel should be considered among strongly absorbing impurities in the tellurite glasses.

[1] G.R.Newns, P.Pantelis, D.L.Wilson, R.W.J.Uffen, R.Worthington, Optical Quant. Electronics 5 (1973) 289.
[2] Y.Ohishi, S.Mitachi, T.Kanamori, T.Manabe Phys. Chem. Glasses 24 (1983) 135.
[3] P.W.France, S.F.Carter, J.R.Williams, Materials Science Forum 5 (1985) 353.
[4] C.R.Day, P.W.France, S.F.Carter, M.W.Moore, J.R.Williams Optical Quant. Electronics 22 (1990) 259.
[5] P.C.Schultz, J. Am. Ceram. Soc. 57 (1974) 309
[6] M.F.Churbanov, A.N.Moiseev, G.E.Snopatin, V.V.Dorofeev, V.G.Pimenov, A.V.Chilyasov, A.S.Lobanov, T.V.Kotereva, V.G.Plotnichenko, V.V.Koltashev, Yu.N.Pyrov, Phys. Chem. Glasses 49 (2008) 297.
[7] R.Car, M.Parrinello, Phys. Rev. Lett. 55 (1985) 247.
[8] P.Gianozzi, S.Baroni, N.Bonini, M.Calandra, R.Car, C.Cavazzoni, D.Ceresoli, G.L.Ciarotti, M.Cococcioni, L.Dabo, A.Dal Corso, S.Fabris, G.Fratesi, S.de Gironcoli, R.Gebauer, U.Gerstmann, C.Gougoussis, A.Kokalj, M.Lazzeri, L.Martin-Samos, N.Marzari, F.Mauri, R.Mazzarello, S.Paolini, A.Pasquarello, L.Paulatto, C.Sbraccia, S.Scandolo, G.Sclauzero, A.P.Seitsonen, A.Sinopoli, P.Ulardi, M.Wentzcovitch, J. Phys.: Condens. Matter 21 (2009) 395502 (http://www.quantum-espresso.org).
[9] N.Troullier, J.L.Martins, Phys. Rev. B 43 (1991) 1993.
[10] D.Vanderbilt, Phys. Rev. B 41 (1990) 7892.
[11] K.Laasonen, R.Car, C.Lee, D.Vanderbilt, Phys. Rev. B 43 (1991) 6796.
[12] K.Laasonen, A.Pasquarello, C.Lee, R.Car, D.Vanderbilt, Phys. Rev. B 47 (1993) 10142.
[13] M.Fuchs, M.Scheffler, Computer Phys. Commun. 119 (1999) 67.
[14] D.Vanderbilt, 2006. (http://www.physics.rutgers.edu/~dhv/uspp)
[15] H.Adamsky, AOMX, an Angular Overlap Model Computer Program. Theoretical Chemistry, Heinrich Heine Universitaet Duesseldorf, 1995. (http://www.aomx.de)
[16] C.K.Jorgensen, J. Chem. Phys. 39 (1963) 1422.
[17] C.E.Schaaffter, Pure and Applied Chemistry 24 (1970) 361.
[18] P.E.Hoggard, Optical Spectra and Chemical Bonding in Inorganic Compounds (Structure & Bonding vol. 106). Springer, 2003. P. 37.
[19] Y.Tanabe, S.Sugano, J. Phys. Soc. Japan 9 (1954) 753; 9 (1954) 766.
[20] A.G.Shenstone, J. Opt. Soc. Am. 44 (1954) 749.
[21] L.Galoisy, G.Calas, Am. Mineralogist 76 (1991) 1777.
[22] V.P.Soltsev, E.G.Tsvetkov, A.I.Alimpiiev, R.I.Mashkovtsev, Phys. Chem. Minerals 33 (2006) 300.
[23] T.Suzuki, Y.Arai, Y.Ohishi, J. Luminescence 128 (2008) 603.