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Photoluminescence of copper ion exchange BK7 glass planar waveguides

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Abstract Copper–alkali ion exchange technology was used to prepare BK7 glass planar waveguides. The photoluminescence spectra of the waveguides were studied with fluorescence spectrophotometer. It was observed that there were strong emission peaks at around 520 nm, which were strongly influenced by the ion-exchange times. Besides the time, the ion-exchange temperature was important factor as well, the higher ion-exchange temperature was found to bring a blue shift of emission spectra. The blue–green emission band originates from different transition mechanism of energy level. The spectroscopy features of copper within the glass host were also affected by the excitation wavelength, which resulted in a shift of the emission band peaks.

Introduction

The ion-exchange process has been extensively studied for many years in the case of alkali ions substitutions, and it represents a useful procedure to fabricate optical waveguide in glass [1, 2], and meanwhile copper ion-exchange technique has been researched for potential application in glass waveguides as well [3–7]. The copper ion-doped waveguide is of great advantage for the nonlinear optical and blue–green luminescence properties [8], with the application in all-optical switch and laser technology.

There are different oxidation states in the copper ion-exchange waveguides, coming into being a number of unique optical features. It is well established that the main spectral features of the luminescence from ionic impurities in glassy matrices strongly depend on the type of matrix. For copper impurities, the local environment plays an important role as well [9]. The spectroscopic features of copper within the glass host can be related to its structural and electronic configuration [10–12]. There have been many researches focusing on the research of optical absorption and luminescence properties of copper ions for silicate glasses hosts; however, there were few reports considering ion-exchange time and ion-exchange temperature as controllable parameters simultaneously, as the copper state is very sensitive to the doping route, making it essential to put up the work.

Thus, photoluminescence techniques turn into extraordinary powerful tools to study copper-doped materials. In this article, the photoluminescence spectra of copper ion exchange BK7 glass planar waveguides are studied through the analyses on the characteristics of excitation and emission spectra. The aim of this study is for the sake of obtaining additional information on the behavior of the copper ions inside of the matrix.

Experiments

The BK7 glass was used for the experiment, and its main components (quality percentage) are as below: 69.13% SiO_2, 10.14% Na_2O, 0.36% As_2O_3, 10.75% B_2O_3, 6.29% K_2O, 3.02% BaO, and 0.05% others. A compound of different composition, namely, copper sulfate and sodium

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Table 1 The fabrication conditions and waveguide properties of the copper ion exchanged samples

Sample name	Treatment time (min)	Processing temperature (°C)	Modes TE/TM	Depth (μm)
T12	5	570	2/2	–
T36	15	570	3/3	6.4
T40	15	596	3/3	5.7
T47	20	570	3/3	5.8
T58	20	582	3/3	6.6
T61	20	596	4/4	9.1

sulfate (molar ratio of 50:50), was melted into a eutectic salt bath. Then each pre-cleaned BK7 glass sample was immersed in it thoroughly, where the ion exchange took place. The process was put up at different ion-exchange times and temperatures, ranging from 5 to 20 min and 570 to 596 °C, respectively. The preparing conditions are revealed concretely in Table 1.

Prism coupling setup was used to measure the waveguide properties of the fabricated samples, the modes of which were got by means of the setup. The angles were measured at which the guided modes are selectively excited by a He–Ne polarized laser beam at $\lambda = 632.8$ nm, in order to get the number of modes. The inverse Wentzel–Kramers–Brillouin (IWKB) method [13] was applied to construct the refractive index depth profiles for both TE- and TM-guided modes.

Excitation and emission spectra were taken using a Hitachi F-4500 spectrophotometer equipped with a continuous emission xenon lamp. Optical absorption spectroscopy was performed with a Shimadzu UV-1700 spectrophotometer in the ultraviolet-visible range.

Results and discussion

The sampled all appeared transparent and slightly yellow color after the ion exchange, which were associated with the ion-exchange time and temperature. The ion-exchange time can be controlled accurately, as BK7 glass is of excellent quality and the speed of ion exchange taking place in it can be slower compared with the treatment in soda-lime glass. There is strong competition occurring between copper–sodium and copper–potassium ion exchanges and copper ions and alkali species interdiffuse independent of their different mobilities [14]. This effect makes it even more difficult to treat the interdiffusion process and related optical properties phenomenologically [15]. The optical properties are very sensitive to the substrate composition as well as to the doping route. So in the soda–lime glass case, since the limited concentration of K_2O in the glass, the ion-exchange process is much simpler in which copper–sodium ion exchange exclusively performed in the exchange process [12]. In this study, we just focus on the copper–alkali ion exchange in BK7 glass. The fabrication conditions and waveguide properties of the copper ion-exchanged samples are given in Table 1. The depth values in Table 1 are the depth values of waveguides, which are determined by program calculation on the best fitted profiles of the refractive index by IWKB method. It has been found that Cu^{2+} ions are always present near the surface of the exchanged region; however, Cu^{+} ions can diffuse into a much larger depth under the surface [7, 16]. Copper was observed to diffuse into the glass matrix for a few microns, largely overcoming the solubility limit of copper in glass. After the exchange, copper is present in different oxidation states, following different equilibrium ratios. X-ray absorption measurements showed that Cu–O bond length is significantly shorter than that of Na–O bond in the glass, indicating a local rearrangement of the glass structure near Cu^{+} ions [12]. As TE and TM modes are equal to each other, birefringence turned out to be negligible, indicating that significant stress fields are not built up during the exchange process.

The successful formation of optical waveguides was confirmed by the prism-coupling analysis. Figure 1 shows the mode refractive indices measured by prism-coupling method and the refractive index depth profiles. The method used to reconstruct the refractive index profiles is IWKB method [13]. As Fig. 1 reveals, the refractive index is changed from the surface of the waveguide gradually by having a graded index layer. It was possible to construct refractive index depth profiles and determine the depth of waveguide layers for them, because the construction needs at least three propagating modes for IWKB method [13]. In the case of copper–sodium exchange, the refractive index change in the glass due to copper ion exchange can be considered to mainly result from the changes in ionic

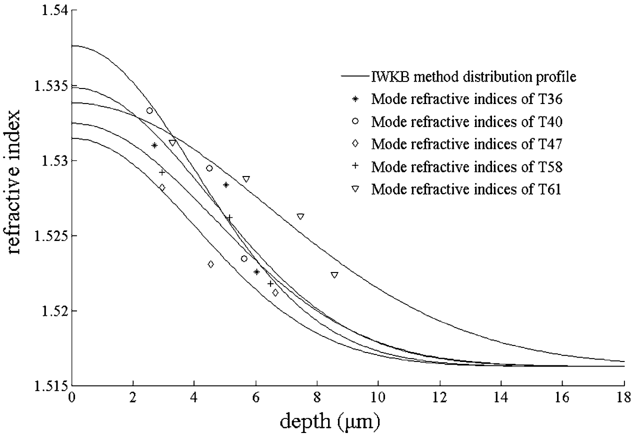

Fig. 1 Refractive index depth profiles of the fabricated waveguides, T36, T40, T47, T59, T61 as from IWKB reconstruction

polarizability [17]. Cu^+ exhibits significantly higher polarizability than that of Na^+, however, the electronic polarizability of Cu^{2+} is comparable to that of Na^+, and much lower than that of Cu^+, so we suppose that the role of Cu^{2+} may be excluded and the refractive index increase is the result of different polarizabilities of the Cu^+ and Na^+ ions [18]. In the case of copper–potassium exchange, although there is a molar volume change as different ionic radii, the stress fields are not built up, causing no further index change [19].

Concerning the spectroscopic features of Fig. 2, which show the experimental photoluminescence excitation spectra at the emission wavelength $\lambda = 515$ nm for the samples prepared at different ion-exchange times, the excitation band is centered between 260 and 310 nm of wavelength. The photoluminescence intensity is observed to increase as the ion-exchange time is increased. And the maximum position of the spectrum shifts toward shorter wavelengths as the exchange time is increased. The band can be related to the presence of Cu^+ ions undergoing a tetragonal distortion with the oxygen ions of the glass matrix, in analogy to the results by Debnath and Das [20]. This excitation band is originated by the transitions from the ground state to states originating from the $3d^9 4s^1$ configuration. Although this transition is forbidden following Laporte rules for the free ion, it may actually take place in the glass because that the low symmetry of the local electric field around the Cu^+ ions in the matrix may partially mix the orbits, allowing some transitions [21]. Wavelength blue shift of the excitation spectra as the ion-exchange times were increased indicates a change in the position of excited electronic levels.

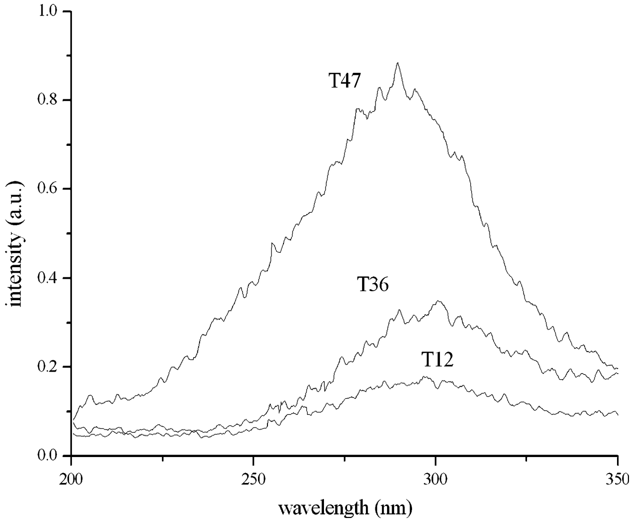

Fig. 2 Fabrication time-dependent shift of the photoluminescence excitation spectra at the emission wavelength $\lambda = 515$ nm for the samples of T12, T36, T47

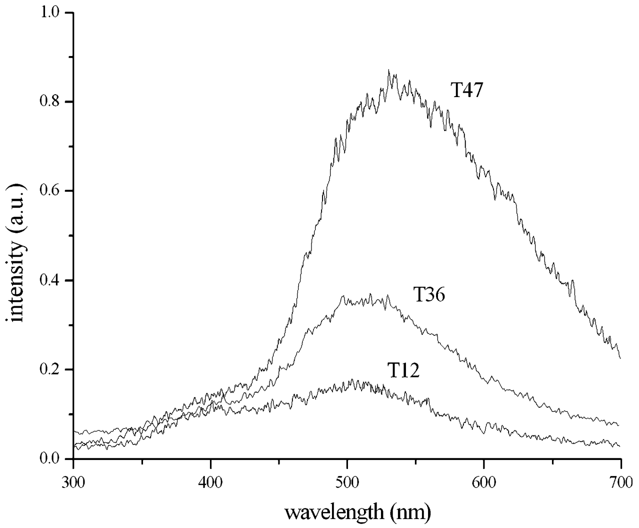

Fig. 3 Experimental photoluminescence emission spectra at the excitation wavelength $\lambda = 280$ nm for the samples of T12, T36, T47

Figure 3 shows the experimental photoluminescence emission spectra at the excitation wavelength $\lambda = 280$ nm for the samples of T12, T36, T47, which were treated at 570 °C for the ion-exchange time 5, 15, 20 min, respectively. It is found that there is a strong emission band around 510 nm for the excitation wavelength of 280 nm. Figure 4 shows the photoluminescence emission spectra at the excitation wavelength $\lambda = 280$ nm for the glass samples of T47, T58, T61, which were ion exchanged for 20 min, at the temperature of 570, 582, 596 °C, respectively. It is also found that there is a strong emission band around 510 nm for the excitation wavelength of 280 nm. From both figures, it is also observed that the full width at

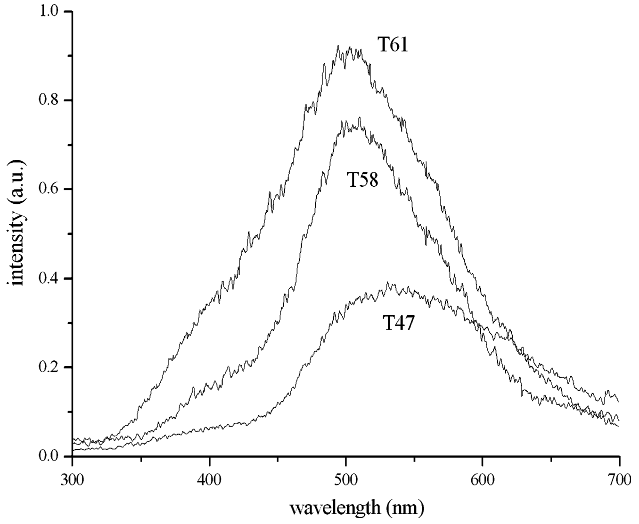

Fig. 4 The ion-exchange temperature's effect on photoluminescence emission spectra at the excitation wavelength $\lambda = 280$ nm for the samples of T47, T58, T61

half-maximum of the emission peak changed gradually with the increase in ion-exchange time or temperature, respectively; however, the photoluminescence intensity is observed to increase as the ion exchanged time or temperature is increased.

The emission bands centered at about 520 nm are typical for the emission of Cu^+ ions that undergo the transition $3d^9 4s^1 \rightarrow 3d^{10}$ electronic configurations [22, 23]. For Cu^+ with octahedral symmetry environment, the interaction with the ligand field gives rise to a splitting of the excited $3d^9 4s$ state in the levels $^1T_{2g}$, $^3T_{2g}$, ^1E_g, and ^3E_g, and the triplet could be then split in other sublevels because of the spin–orbit interaction [22]. In particular, the lowest energy level ^3E_g is split into two spin–orbit components: ^3E_g (T_{1g}) and ^3E_g (T_{2g}). The photoluminescence emission at wavelength of 480–550 nm is related to the transitions from the triplet levels ^3E_g (T_{1g}) and ^3E_g (T_{2g}) to the ground state [24].

The significant variations in the photoluminescence intensity of the emission bands for the different glass samples may be attributed to two reasons. The photoluminescence intensity in BK7 glass samples increases with the concentration of Cu^+ ions, and the Cu^{2+} ions are the reason for the intensity quenching, which is attributed to an electronic excitation energy transfer from Cu^+ to Cu^{2+} [25]. Optical absorption spectra for Cu^{2+} ions in glass were reported with an absorption band centered at about 800 nm of wavelength [14, 26], ascribed to the $^2E_g \rightarrow {}^2T_{2g}$ transition from a tetragonally distorted octahedral site [27]. So it is suggested that there are remunerative conditions for the energy transfer from Cu^+ to Cu^{2+}, since the energy for the $3d^9 4s \rightarrow 3d^{10}$ transition of the Cu^+ ion is higher than the energy for the $^2E_g \rightarrow {}^2T_{2g}$ transition of the Cu^{2+} ion. As our experiment reveals, photoluminescence changes might be attributed to such mechanism. There is also another possible reason. An absorption attributed to charge transfer between Cu^{2+} ions and O^{2-} ions in the glass was found in the ultraviolet region [25], which could violate the excitation of the monovalent copper state because the absorption is in the same spectral region of the $3d^{10} \rightarrow 3d^9 4s^1$ transition of the Cu^+ ion, therewith the absorption deriving from a charge transfer can result in photoluminescence changing as well [28].

It is found in Fig. 3 that the emission bands peaks shift slightly toward longer wavelengths as the ion-exchange time is increased. The observed small shift of the emission bands maximum is probably caused by the variations in the symmetry of the site. It was found that the Cu^+ ions uniformly distributed in a near-pure silica glass structure occupying tetragonally distorted octahedral sites [29]. When the ion-exchange time is increased, the distribution of impurities around the Cu^+ can change greatly, and it can bring on a strong electrostatic infinitesimal disturbance, which can influence the d orbits of Cu^+. In fact, the distortion may significantly lower the triplet emitter level by the splitting of the ^3E_g (T_{1g}) in the two spin–orbit components, as shown in Fig. 5, which shows the level scheme for the Cu^+ ion.

There is also a red shift with the excited wavelength increases for emission band as shown in Fig. 6, in which three different excitation wavelengths have been selected in order to study the site effect on Cu^+ photoluminescence in glass system, in order to study the dependence of emission spectra on the excitation wavelengths [30]. The photoluminescence emission spectra of BK7 glass samples under different excitation wavelength show that Cu^+ ions display a strong emission band at about 520 nm with all three excitation wavelengths employed. It is clear that intensity and peak of the emission band are significantly changing depending upon the excitation wavelengths,

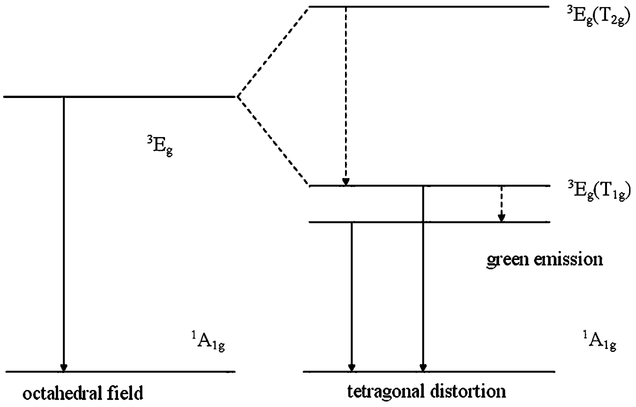

Fig. 5 Energy level diagram for Cu^+ ion under a tetragonal distortion of the octahedral field

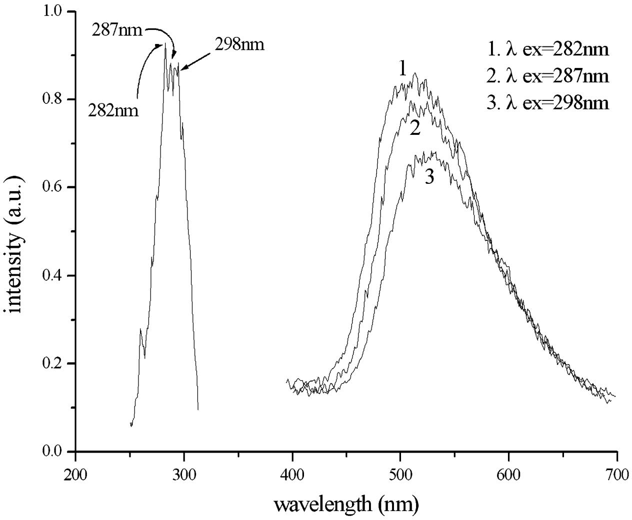

Fig. 6 Experimental photoluminescence excitation spectra at the emission wavelength $\lambda = 515$ nm and emission spectra at different excitation wavelength for sample T40

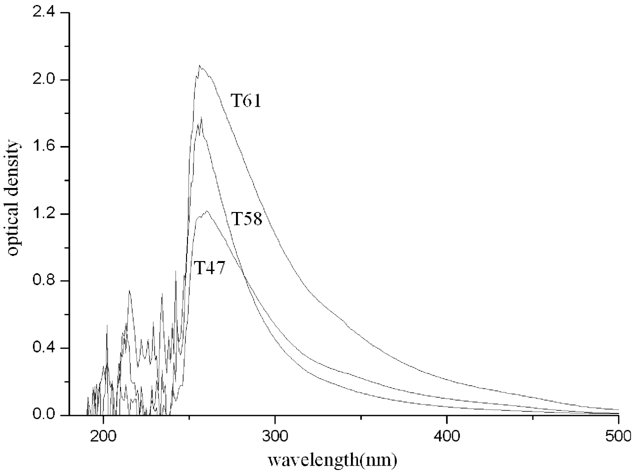

Fig. 7 Experimental optical absorption spectra for the samples of T47, T58, and T61

which could create a variation of excitated electronic levels position of Cu$^+$ ion, strongly affecting the transitions from the excited levels to the ground state and bringing about an emission bands shift [11].

However, it is discovered that the emission band peaks of T58, T61 in Fig. 4 are centered at the wavelength around 500 nm, and there is a blue shift for them compared with T47, which has an emission band peak at 530 nm. So the emission band peak of T58 and T61 is at about 500 nm, which is much shorter than 530 nm. The reason for this may be a coagulation of clusters. The experimental investigation was carried out by optical absorption analysis, which was performed by measuring the transmittance through the waveguide and substrate with a Shimadzu UV-1700 spectrophotometer in the UV–Vis range. The optical absorption spectra of T47, T58, and T61 samples are shown in Fig. 7. The absorption structure arises from the $3d^{10} \rightarrow 3d^9 4s^1$ transition of Cu$^+$ ions, which is another evidence to indicate the Cu$^+$ ion concentration enlarging with increase in temperature [31]. So the enhancement of Cu$^+$ ion concentration may result in coagulation of copper clusters because that higher processing temperature annealed the samples and coagulation of clusters took place in such a way that the smaller clusters moved and got fused to form bigger ones. So the symmetry of the local electric field around the Cu$^+$ ions in the matrix can be partially influenced, indicating a blue shift of emission band [32].

Conclusions

The acquired results illustrate the successful preparation of BK7 glass planar waveguides using the copper–alkali ion exchange in the eutectic salt bath of copper sulfate and sodium sulfate. The formation of the optical waveguides was proved by the prism-coupling method. The planar waveguides exhibited the same TE and TM propagating modes for each sample, indicating that the modal birefringence was negligible.

There is a wavelength blue shift for the excitation spectra as the ion-exchange time was increased. The recorded intensive blue–green emission spectrum band centered at around 500 nm, observed for all examined samples and dependent on the preparation parameters, was attributed to the presence of Cu$^+$ ions located in a distorted octahedral site. Photoluminescence intensity was observed to significantly increase as the ion-exchange time or temperature was increased. Wavelength red shift of the emission band with exchange time increases was mainly attributed to a tetragonal distortion of the octahedral site. Furthermore, increase in different excitation wavelength brought on a red shift of the emission band as well. The wavelength of emission band peak of the sample prepared at higher ion-exchange temperature was becoming smaller, by reason of the coagulation of copper clusters.

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