Superbroad near-to-mid-infrared luminescence from Bi$_5^{3+}$ in Bi$_5$(AlCl$_4$)$_3$

Renping Cao, Mingying Peng, Lothar Wondraczek, and Jianrong Qiu

1Institute of Optical Communication Materials and State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China
2Department of Materials Science, University of Erlangen-Nuremberg, Erlangen 91058, Germany
3equal contribution to this work
4lothar.wondraczek@ww.uni-erlangen.de
5qjr@scut.edu

Abstract: Superbroad near-to-mid infrared (NIR-MIR) photoluminescence was observed from Bi$_5$(AlCl$_4$)$_3$ at room temperature, spanning the spectral range of about 1000 to 4000 nm. On the basis of structural considerations and dynamic analyses, Bi$_5^{3+}$ clusters were identified as the optically active species, inherently differing from the species which is typically believed to be active in NIR-emitting Bi-doped glasses. In comparison to most other NIR-luminescent Bi-doped materials, the MIR-part of the luminescence spectrum is still present at room temperature. Emission intensity and excited state lifetime were found to exhibit abnormal temperature dependence, where the former increases with temperature up to a critical value of about 150 K. This behavior is related to a temperature-dependent overlap between ground state and excited states. The observed stabilization of MIR photoemission at room temperature may be a starting point for the development of Bi-based NIR-MIR light sources with superbroad emission spectrum, where Bi$_5^{3+}$ or similar polycationic species act as optical gain medium.

© 2012 Optical Society of America

OCIS codes: (160.2750) Glass and other amorphous materials; (160.2540) Fluorescent and luminescent materials; (140.4480) Optical amplifiers; (060.4510) Optical communications.

References and links

1. Introduction

In last decade, a new family of near infrared (NIR) emitting bismuth doped laser glasses has been discovered and soon become a subject of intensive study [1–6]. This has been primarily due to the material’s intriguing spectral properties, especially superbroadband photoluminescence in the telecom spectral range, which currently cannot be obtained in traditional rare-earth based materials [1,3–5,7,8]. Reports on basic materials properties and corresponding optical devices have convincingly proven the potential for application in superbroad optical amplifiers for future telecommunication networks and laser sources [1–14]. E.g., only recently, Dvoyrin et al. demonstrated Bi-based fiber laser devices with slope efficiency of up
to 52% at 77 K [5]. The efficiency of Bi-based fiber amplifiers or lasers and the quality of the laser output beam could be improved further when NIR-emitting Bi-species could be precipitated in the material as a single type of emission centers [1,4,8]. For that, knowledge on how to selectively stabilize during glass melting and/or fiber drawing a specific Bi emission species for activity at a specific spectral range is highly desirable. As a prerequisite, an effective model for the mechanism of Bi-related NIR emission is required. Up to now, however, although significant progress has been made, even the nature of the optically active NIR emission centers remains disputed [1–15].

Different hypotheses have been made in this respect, ascribing NIR emission to, e.g., Bi\(^{5+}\), Bi\(^{3+}\), Bi\(^{2+}\) or bismuth clusters (for a recent review, see Ref. 14). On the other hand, Bi\(^{3+}\) and Bi\(^{2+}\) species can readily be excluded because their spectral properties are well known [16,17]. Strongest evidence presently points towards Bi-species of lower valence rather than Bi\(^{5+}\). For example, addition of specific amounts of reducing agents such as carbon powder or gaseous hydrogen to Bi-containing glass batches was observed to enhance NIR emission of the corresponding glasses [18]. Also in crystalline matrices, it was observed that NIR-active Bi-species require treatment in reducing (here: CO) atmosphere [13]. When such NIR luminescent crystals are annealed in oxidizing atmosphere, the centers can be rendered inactive. As another example, exposure of Bi-doped glasses or crystals to femtosecond laser, \(\gamma\)-irradiation or electron beams can lead to the generation of NIR-active centers [4,9,18–20].

An intriguing aspect was added to the dispute with the consideration of atom clusters and metallic polycations [9,21,22]. Bi particles have long been known for their effect on glass coloration, which may reach from pale pink to deep red, brown or even black [9]. Khonthon et al. observed electron spin resonance (ESR) in pink Bi-doped zinc aluminosilicate glasses and glass ceramics [21]. After comparison to ESR spectra of Se\(_2\) or Te\(_2\) containing glasses, they suggested that Bi\(_2\)/Bi may be responsible for NIR luminescence in Bi-doped glasses [21]. Quantum chemical calculations were conducted by Sokolov et al. in 2008 on the electronic states of Bi\(_2\) and Bi\(_2\)^- dimer ions, confirming that Bi\(_2\) and Bi\(_2\)^- could be responsible for NIR luminescence [22]. During Raman spectroscopic analyses of Bi\(_5\)^+ in 1-n-butyl-3-methylimidazolium(Cl/AlCl\(_3\)) with 1064 nm laser excitation [23], Ruck et al. detected bismuth luminescence over the spectral range of 1075-1852 nm. Extremely broad luminescence was observed by Hughes et al. from a bismuth doped chalcogenide glass [6]. In the latter, the tail of the emission peak (~1300 nm) was found to extend to 2000 nm. Two more emission peaks were resolved from this spectrum at a temperature of 5 K, i.e. at 2000 and 2600 nm [6]. In accordance with Sokolov et al.’s previous analyses, they suggested Bi\(_2\)^- as the emission species [6]. More recently, Sun et al. employed Ruck’s approach to synthesize Bi\(_5\)(AlCl\(_3\)) containing Bi\(_5\)^+ clusters [24,25]. They observed a broad fluorescence band spanning the range of 900-1600 nm with a FWHM of more than 510 nm [25]. Assumedly, their material exhibited a much broader emission spectrum which could, only for experimental limitations, not be resolved with the employed InGaAs detector. Both the observations by Ruck et al. and Sun et al. point towards luminescence from Bi\(_5\)^+ also at wavelengths well above 1600 nm [23,25].

The complex structure of glasses strongly complicates accurate assignment of the nature of the NIR-emitting Bi-species [13,25]. As an alternative, crystalline model materials with well-established structure may be considered. E.g., Bi\(_5\)(AlCl\(_3\)) contains only one type of Bi\(_5\)^+ in its lattice, taking the structure of a trigonal bipyramid with three Bi(1) in the equatorial plane and two Bi(2) as apices (see Fig. 1(A)) [23–26]. For the simplicity of this structure, in the present study, we have chosen this material to examine the mechanism of Bi-related NIR photoemission and corresponding excitation processes.

2. Experimental

Bismuth has long been known as an archetype example of an element which may form “naked” (ligand-free) metallic polycations, e.g. Bi\(_3\)^+, Bi\(_4\)^2+, Bi\(_5\)^5+ [23–26]. Such cluster species can be synthesized in several ways, e.g. (1) utilizing Lewis acid ionic liquids as reaction media at sufficiently low temperature [23–25], (2) using molten salt containing a.
strong Lewis acid like AlCl$_3$ at relatively high temperature [26–28], (3) oxidizing elemental bismuth with SbF$_5$ or AsF$_5$ in liquid SO$_2$ [23], or (4) reducing BiCl$_3$ in GaCl$_3$-benzene organic solvents \[^{[0]}\]. In the present study, the molten salt route (2) was employed, where NaAlCl$_4$ was used as solvent [26–28]. The eutectic of (mol.%) 63 AlCl$_3$–37 NaCl was selected as base composition, and the Al:Na ratio was kept constant throughout the study. Noteworthy, excess AlCl$_3$ facilitates formation of Lewis acidic tetrachloroaluminates AlCl$_4^-$ units which further may stabilize the polycationic species. As raw materials, AlCl$_3$ (99.9%), NaCl (99.9%), BiCl$_3$ (99.9%) and Bi powder (99.99%) were employed. 12 mmole batches with nominal molar composition 52.50 AlCl$_3$, 30.83 NaCl-(16.67-x)Bi-xBiCl$_3$ (x = 0.33, 0.67, 1.33, 1.67, 2.00, 2.33) and 63 AlCl$_3$, 37 NaCl were weighed and thoroughly mixed in a glove box in dry nitrogen atmosphere. The mixtures were then put into borosilicate glass tubes, evacuated and flame-sealed. The sample tubes were heated to between 150 and 360°C for 2 - 13 h and subsequently cooled to room temperature. During heating, glass tubes were rocked to improve homogeneity of the melts. To guarantee completion of the reaction $BiCl_3 + 3 AlCl_3 + 4Bi \rightarrow Bi_4(AlCl_6)_3$, excess bismuth metal powder was added to the original batch. After the rocking process, a thin black layer occurred on the bottom of each tube. X-ray diffraction analysis (XRD) was employed to confirm that this layer was metallic Bi which segregated to the bottom of the tube because of its higher density as compared to the salt melt. For convenience, samples with and without bismuth are designated with the acronym ANBx:B and AN, respectively, where x stands for the bismuth content (e.g., ANB1.33B corresponds to the sample with x = 1.33). The upper part of all samples appeared reddish brown and was used for further measurements. Two parallel sets of experiments were performed on ANB1.33B to identify optimal synthesis conditions and to correctly assign the precipitated crystallite phase: (1) individual samples were tempered at 150, 220, 290 and 360°C for 10 h, and (2) a second series of samples was treated at 290 °C for 2, 6, 10 and 13hours, respectively. When ANB1.33B is heated at 150 °C, not any infrared luminescence could be observed. Only with increasing annealing temperature, i.e. to 220 °C, the characteristic broad infrared emission spectrum appeared and subsequently intensified more than three times for even higher annealing temperatures of up to 290 °C. However, when the temperature rises further to 360 °C, the intensity of the emission decreases to only half of its initial value. This observation is attributed to thermal dissociation of the phase of $Bi_4(AlCl_6)_3$ at this temperature [28]. When the preparation temperature was kept constant at 290 °C, prolonging the dwell time from 2h to 10h was observed to lead to strongly enhanced infrared emission intensity, whereas a limit was reached at about 13 h. From these observations, optimal annealing time and temperature were deducted, i.e. 290 °C and 10h.

For comparison, Bi-doped oxide glasses were prepared from analytical grade Al(OH)$_3$, Bi$_2$O$_3$, SiO$_2$, Li$_2$CO$_3$ and 5N GeO$_2$. A 20 g batch with a molar composition 96 GeO$_2$ - 3.5 Al$_2$O$_3$ - 0.5 Bi$_2$O$_3$ and a 100 g batch of 13 Li$_2$O - 23 Al$_2$O$_3$ - 63 SiO$_2$ - 1.0 Bi$_2$O$_3$ were melted in air at 1550 and 1630°C for 20min and 3h, respectively. Reddish-brown glasses were obtained by quenching the melts on a stainless steel plate. Sample were then cut and polished for optical analyses.

X-ray diffraction patterns of the samples were recorded with a Rigaku D/max-III A X-ray diffractometer (40kV, 1.2°min$^{-1}$, 40 mA, Cu-Kα1, $\lambda = 1.5405\text{Å}$). Raman spectra were measured on a Horiba Jobin Yvon LabRAM Aramis spectrometer equipped with a 633 nm He-Ne laser. Excitation spectra as well as static and dynamic emission spectra were recorded in the temperature range of 10-300 K with a high-resolution spectrofluorometer (Edinburgh FLS 920). Photoluminescence between 1000 and 4500 nm was observed with a PbSe detector on a Horiba Jobin Yvon Triax 320 fluorometer, using a 808 nm laser diode as pump source at room temperature.
Fig. 1. (A): Unit cell representation of Bi$_5$(AlCl$_4$)$_3$ drawn on the basis of Rietveld refining results of curve 1 in (B). Aluminum and chlorine atoms are omitted except bismuth for clarity. Purple and green spheres represent Bi(1) and Bi(2), respectively. (B): (1) powder XRD profile of the sample of ANB1.33B prepared at 290°C for 10 hours, (2) and (3) simulated patterns of NaAlCl$_4$ and Bi$_5$(AlCl$_4$)$_3$ with crystallographic data in Refs. 26,37, respectively.

3. Results and discussion

3.1 Phase identification

The powder XRD pattern of sample ANB1.33B prepared at 290°C / 10 h is shown in Fig. 1(B) (curve 1). Comparison to simulated patterns of NaAlCl$_4$ and Bi$_5$(AlCl$_4$)$_3$ reveals coexistence of these two phases in the sample. Dominant diffraction peaks of Bi$_5$(AlCl$_4$)$_3$ locate at 10.44, 10.60 and 14.92° (2θ) in curve 1. These are indexed to (012), (104) and (110) planes, respectively. The presence of Bi$_5^{3+}$ was further confirmed by the typical Raman bands at 123 and 136 cm$^{-1}$ [24,25]. The latter are assigned to $\nu_2(A_1')$ and $\nu_1(A_1')$ vibrational modes of the polycation, similar to 120 and 136 cm$^{-1}$ for Bi$_3^{3+}$ in Bi-GaCl$_3$-benzene and 122 and 138 cm$^{-1}$ in the ionic liquid [BMIM]Cl/AlCl$_3$ [29]. Rietveld refinement (FullProf Suite Program version 2010) of XRD data indicated that the sample of ANB1.33B comprises 9.2% Bi$_5$(AlCl$_4$)$_3$ and 90.8% NaAlCl$_4$, where Bi$_5$(AlCl$_4$)$_3$ crystallizes in rhombohedral R3 c space group with cell parameters $a = 11.8698$ Å and $c = 30.1133$ Å. This is consistent with data reported by Ruck et al. ($a = 11.8712$ Å, $c = 30.1203$ Å) [23] and Krebs et al. ($a = 11.86$ Å, $c = 30.10$ Å) [26]. The crystal structure is illustrated in Fig. 1(A), based on the results of refinement. One lattice cell of the compound containing six formula units with two types of bismuth sites Bi(1) (Wyckoff notation 18e) and Bi(2) (12c) is shown. The occupation ratio of the two sites is 3:2. These bismuth atoms form into a single type of Bi$_3^{3+}$ polyhedron, as noted before composed of three equatorial Bi(1) and two apices Bi(2). In each unit cell, there are on average six Bi$_3^{3+}$ polyhedra (Fig. 1(A)).
3.2 Near-to-mid infrared PL from Bi$_5$(AlCl$_4$)$_3$

Curve 1 in Fig. 2 shows the PL spectrum of sample of ANB1.33B under excitation at 468 nm (as discussed in the following, changing excitation into either of the absorption wavelengths in the curve 5 of Fig. 2 does not alter the shape of emission spectrum). It is representative for all examined Bi-containing samples. Noteworthy, no IR luminescence could be observed from the blank sample of AN ($x = 0$). PL is hence attributed to the presence of Bi$_5$(AlCl$_4$)$_3$. FWHM of the spectrum is ~570 nm, somewhat broader than the value of 510 nm reported by Sun et al [25]. However, the shape of the spectrum appears different from that of Sun et al. They reported a PL spectrum (457.9 nm excitation) peaking at ~1170 nm with a shoulder at ~1400nm [25]. Here, the spectrum of ANB1.33B peaks at ~1500 nm, Fig. 2, and appears to fall-off sharply from 1590 nm to higher wavelength. Correction of curve 1 over the detector sensitivity results in curve 2, Fig. 2, where, clearly, the tail rises steeply. This implies a further luminescence band located at longer wavelength, which has not been noticed before. Subsequent measurement with a broad-band PbSe detector confirmed the presence this band, peaking at ~1700 nm with a shoulder at ~1860nm and persisting to ~4000 nm (curves 3-4 in Fig. 2). For comparison, the Bi-doped reference glasses were considered with the same detection set-up (curves 1 and 2 in Fig. 3). PL from these samples was found to peak at ~1310 and ~1416 nm, respectively, with the FWHM of 342 and 420 nm. The spectra span the range of 1000 to about 2000 nm. At room temperature, neither of the two glass samples shows any luminescence at a wavelength higher than 2000 nm. This situation is similar to Hughes et al’s [6] findings in Bi-doped chalcogenide glasses, where MIR luminescence at > 2000 nm could be found only at low temperature. Low-temperature analyses of the reference glasses considered here may therefore deserve further attention, but lie outside the scope of this study.

Rare earth can emit in the MIR spectral region, but none of them can span this large area of 1000-4000 nm. For instance, Er$^{3+}$ can only cover 2600-to-2900nm [30,31], and Ho$^{3+}$ 1850-to-2100 nm [32]. It is noteworthy that in Bi$_5$(AlCl$_4$)$_3$, the MIR-part of the luminescence spectrum (>2000 nm) is still present at room temperature. Thermal quenching is hence much less pronounced. This may initiate the discovery of new materials activated by species such as Bi$_5^{2+}$ as gain medium for superbroad, tunable NIR-MIR light sources.
Fig. 3. PL spectra of (1) bismuth doped germinate glass, (2) bismuth doped lithium aluminosilicate glass and (3) ANB1.33B sample prepared at 290°C for 10 hours. The spectra were measured under the excitation of 808nm laser with a PbSe detector at room temperature.

Excitation spectra appear practically independent on the monitored emission wavelength in the range of 1000 to 1600 nm (exemplary shown for 1600 nm emission as curve 5 in Fig. 2). Sun et al. observed an unresolved absorption shoulder (330-620 nm), a weak band at 648 nm, and a stronger band at 807 nm by measuring diffuse reflection spectrum [25]. In the present case, the excitation spectrum of ANB1.33B comprises well-resolved absorption bands at 367, 390, 450, 468, 505, 650, 759, 780, 820, 850 and 883 nm. The former five correspond well to theoretical calculations (362, 390, 445, 463, 525 nm for Bi$^{3+}$ in the symmetry of D$_{3h}$ [28]). They can readily be assigned to the transitions of e’→e’(3)(E’), a$_2''$→a$_1''$(A$_2''$) (e''→e’(3)(A$_2''$)), e’(1)→a$_2''$(E’), e’(1)→a$_1''$(E’) and a$_1''$→e’(2)(E’). The remaining two bands probably result from split transitions e’(1)→e’(2)(E’) and e’→e’(2)(E’) [28]. Considering Ruck et al.’s observations, another absorption band should be present at ~1064 nm [23]. Excitation at either of these absorption bands does not alter the shape of emission spectrum, indicating that they all belong to the same emission center. In the future, a complete energy level diagram of Bi$_5^{3+}$ will be needed to accurately assign all absorption and emission bands.

Fig. 4. Dependence of the intensity of infrared emission of sample ANB2.00B prepared at 290°C for 10 hours on pump power of 808nm laser diode.

For fixed preparation temperature and time (290°C, 10 h), the intensity of IR luminescence depends on the content of BiCl$_3$. It monotonically increases by six times as $x$ changes from 0.33 to 2.00. When further increasing $x$ to 2.33, luminescence intensity decreases. The shape of the emission spectrum remains practically unchanged for all values of $x$. From this, we conclude on an optimal dopant concentration of $x = 2.00$. The dependence of emission intensity on pump power was therefore examined on sample ANB2.00B (Fig. 4). Sun et al. found a linear dependences of NIR emission intensity on pump power for excitation at 457.9 and 785 nm. Their measurements, however, were performed at relatively low pump power of < 1mW for both wavelengths [25]. At such power levels, creation of a population inversion seems unlikely. For this reason, we used 808 nm diode laser with significantly higher power of up to > 1 W. As shown in Fig. 4, the emission intensity increases linearly with pump power in the regime of 200 to 1200 mW. In this regime, no severe excited state
absorption occurs. However, when the laser power rises to 1400mW and beyond, emission intensity starts to fall, what we relate to thermal dissociation of Bi$_{5}^{3+}$ under the laser irradiation. Hence, excitation at power in the W-regime would require efficient cooling.

### 3.3 Temperature dependence of IR PL from Bi$_{5}$(AlCl$_{4}$)$_{3}$

The temperature dependence of photoluminescence provides direct information on the efficiency of the photon emission process and eventual overlap with phononic or other thermally activated relaxation processes. For bismuth doped oxide glasses (e.g., germanates and silicates [33,34]), previous studies have revealed that the temperature has only minor influence on fluorescence lifetime in the temperature range of 10 to 300 K. For example, in bismuth doped germanate glass [33], it was recently found that the infrared luminescence intensity decreases monotonically by about 19% when the temperature changes from 10 to 300K. This picture strongly differs for Bi$_{5}$(AlCl$_{4}$)$_{3}$.

![Decay curves](image1)

**Fig. 5.** Decay curves of sample ANB2.00B the emission at 1420nm excited by 468nm at different temperatures (10-300K). Solid black line: fit of the 300-K-data to a single exponential equation ($y = 0.019 + 0.819e^{-x/5.96}$); correlation coefficient 97.08%.

![Integrated intensity and lifetime](image2)

**Fig. 6.** Dependence of integrated fluorescence intensity and lifetime on temperature in sample ANB2.00B. Error bars were added to both intensity and lifetime. Lines are guides for the eye.

Figures 5-6 show the fluorescence decay curves, lifetime and integrated emission intensity of sample ANB2.00B as recorded over a temperature ranging of 10-300 K. All curves follow a first order exponential decay equation, indicating that only one emission center (Bi$_{5}^{3+}$) is active in each case. For example, fitting the curve at 10 K to the equation yields a lifetime of 22.81 µs with a correlation coefficient 99.72%. The coefficient degrades slightly to 97.08% at T = 300 K, as shown in Fig. 5. The observed lifetime first increases slightly from 22.81µs to 23.12µs as the temperature increases from 10 to 50 K (Figs. 5-6), but then decreases strongly to 5.96 µs at 300 K. The intensity of luminescence shows a similar initial trend, but reaches a maximum at 150K before declining sharply. The shape of the PL spectrum in the range of 800-1700 nm remains almost unchanged at all temperatures.

### 3.4 Mechanistic consideration

To understand the observed abnormal temperature dependence of excited state lifetime and NIR emission intensity, a configuration coordinate diagram is proposed (Fig. 7). When
electrons absorb light of 468 nm, they are lifted from the ground state GS to the excited state ES3 (denoted $a_1'(E')$). When these electrons reach ES3, they seek to return to the equilibrium state A via path 1, and another which branches at the crossing point B between states ES1 and ES3, and subsequently relaxes into the equilibrium state C of ES1 (path 2). The latter then transit to D, emitting IR photons, and finally return to O in GS (path 3). Thermal excitation may lead to dephasing of the state A via path 4 and emission of IR photons. When the temperature rises, depopulation of ES3 becomes more probable due to thermal stimulation, and more electrons will flow to C along path 4. Hence, more IR photons are emitted. Lifetime then slightly increases (Fig. 6, $T < 50$ K). Further increasing temperature will push electrons predominantly towards path 5, where more energy is lost nonradiatively via the crossing point of E to O. Then, lifetime and emission intensity decrease significantly (Fig. 6, $T > 150$ K).

Fig. 7. Schematic configurational coordinate diagram for a possible mechanism of temperature-dependent photoemission from $\text{Bi}_5^{3+}$, energy $E$ vs. coordinate $r$. Parabola “GS” refers to the ground states $e'(1)$ and $e''$ of $\text{Bi}_5^{3+}$; parabola “ES1” to the lowest excited state, and parabolae “ES2” and “ES3” to $e'(2)(E')$ and $a_1'(E')$, respectively [28]. For clarity, only the states GS, ES1, ES2, and ES3 are shown. Labels 1-5 refer to the different possible relaxation paths (see text). Excitation transitions are marked as upward arrows; radiative relaxation as downward arrow.

In the same way, this setting also explains why excitation of the sample at different wavelengths always produces the same emission spectrum: all excited states with energy higher than ES1 have a crossing point with ES1, at which relaxation becomes independent of the excitation energy. Another excited state, ES2 (denoted $e'(2)(E')$) is drawn exemplarily.

3.5 Consequences for NIR-emitting Bi-doped glasses

Usually, NIR-emitting Bi-doped oxide glasses absorb at $<370$, $\sim500$, $\sim700$, $\sim800$, $\sim1000$ nm. Luminescence occurs over a wide spectral range from 1000 to 1700nm [1–21,35]. Absorption and emission schemes show a clear dependence on host composition [1,2,6,7,9–17,35,36]. The emission lifetime at room temperature typically ranges from hundreds of microseconds to several milliseconds. An additional absorption band at 1400 nm was observed by Dvoyrin et al. and Bufetov et al. in bismuth doped silica glass [1,3–5]. In a non-oxide glass, Hughes et al. reported absorption at $\sim1180$nm, fluorescence lifetime of 175 $\mu$s at room temperature for an emission peak at $\sim1500$nm [6].

Comparing the situation in $\text{Bi}_5(\text{AlCl}_3)_3$ to these observations allows for the following conclusions: (1) the observed absorption bands approximately correspond to those which occur in glassy matrices; (2) at room temperature, emission from $\text{Bi}_5(\text{AlCl}_3)_3$ covers a much broader spectral range, i.e. up to at least 4000 nm; (3) the emission lifetime of the compound is 5.96 $\mu$s, two to three orders of magnitude shorter than the value found in Bi-doped glasses; (4) IR-emission from the compound exhibits significantly different temperature dependence; and (5) only one type of emission center exists in the compound where glasses typically exhibit a variety of emission centers [4,8,33].
When trivalent bismuth ions are used as starting materials to produce glasses at high temperature, they are typically reduced during the melting process, forming, e.g., Bi\(^{3+}\), Bi\(^{2+}\), Bi\(^{0}\), cluster ions Bi\(_n^{m+}\) etc. For instance, luminescence from Bi\(^{3+}\), Bi\(^{2+}\) and infrared emission centers can be found in silicate glasses \([5]\). Several of the possible species, especially Bi\(^{3+}\), Bi\(^{2+}\) and metallic nanoparticles, do not emit IR radiation \([12,14,34,36]\). Others such as Bi\(^{2+}\) or Bi\(^{0}\) may prevail in germanate, silicate, borate or phosphate glasses where they are responsible for photoemission in the spectral range of 1000-1700 nm \([1–7,9–12]\). In this case, emission from cluster ions plays only a minor role or is obscured by the comparably much longer lifetime of the former species. On the other hand, identifying glass systems in which entities such as Bi\(_5^{3+}\) can be stabilized could be a very attractive route to fabricate MIR-luminescent optical materials.

4. Conclusions

In summary, Bi\(_5\)(AlCl\(_4\))\(_3\) was synthesized via the molten salt route in NaAlCl\(_4\) solvent. Ultrabroad near-to-mid infrared PL with a peak at \(\sim 1700\) nm was observed at room temperature. In comparison to typical NIR-luminescent Bi-doped glasses, due to significantly less-pronounced thermal quenching, the MIR-part of the luminescence spectrum of Bi\(_5^{3+}\) is still present at room temperature. This may initiate the discovery of new materials activated by species such as Bi\(_5^{3+}\) as gain medium for superbroad, tunable NIR-MIR light sources. The luminescence decay of the compound obeys well a first order exponential decay equation, confirming the presence of only one active emission species, Bi\(_5^{3+}\). Apparently abnormal temperature dependence was found for emission intensity and excited state lifetime: both initially increase with temperature up to about 50 K (lifetime) and 150 K (intensity), respectively, and decrease afterwards. This behavior is interpreted with the help of the configurational coordination diagram, where the ground state and the excited states overlap partially. Comparison of the spectroscopic data reveals that the observed polycationic Bi\(_5^{3+}\) groups are not the same emission centers which are dominating in typical infrared-emitting Bi-doped glasses.

Acknowledgments

Financial support from the National Natural Science Foundation of China (Grants no. 51072060 and 51132004), the Fundamental Research Funds for the Central Universities (Grants no. 2011ZZ0001 and 2011ZP0002), Guangdong Natural Science Foundation (Grant no. S2011030001349) and the Chinese Program for New Century Excellent Talents in University are gratefully acknowledged.