Long Fluorescence Lifetime of Ti^{3+}-Doped Low Silica Calcium Aluminosilicate Glass

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This Letter reports the formation of Ti^{3+} in OH^- free aluminosilicate glass melted under vacuum condition, with a very long lifetime (170 μs) and broad emission band shifted towards the visible region. This lifetime value was attributed to the trapping of the excited electrons by the glass defects and detrapping by thermal energy, and it is 2 orders of magnitude higher than those published for Ti^{3+} doped materials. Our results suggest that this glass is a promising system to overcome the challenge of extending the spectral range of traditional tunable solid state lasers towards the visible region.

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One of the greatest challenges in the search for new tunable solid state laser sources in the visible region certainly is the development of noncrystalline solids with emission in wavelengths lower than those of Ti^{3+}:Al_2O_3 crystals. Since the advent of the first lasers in the 1960s, Ti^{3+}-doped crystals and glasses have been extensively studied with aim of the development of reliable laser sources [1,2]. Nowadays, the well-known titanium sapphire laser Ti^{3+}:Al_2O_3 crystal is an important device found in most spectroscopy laboratories. Other transition metals ions of electronic configuration $3d^1$ such as V^{4+}, Cr^{5+}, and Mn^{6+} also have similar characteristics as those of Ti^{3+} [3–5]. The most important spectroscopic features that make materials doped with metal transition relevant for laser applications are high optical gain from visible to near infrared [6], broad emission band [7], the possibility of ultrashort time switch [8], and high fluorescence quantum efficiency [9]. However, it is well known that metal transition in the $3d^1$ configuration usually does not exhibit long lifetime due to the allowed electronic transition and its high sensitivity to the crystal field, as has been observed in several glasses [10,11] and crystals [6,9]. This means that the choice of host matrices for ion doped laser materials is of crucial importance to developing reliable Ti^{3+}-doped laser glass devices.

In this Letter we report the successful formation of Ti^{3+} ions in OH^- free low silica calcium aluminosilicate glass (LSCAS) with very high fluorescence level (illustrated in Fig. 1), broad emission band from about 500 to 800 nm, and with a very long fluorescence lifetime about 2 orders of magnitude higher than those of known Ti^{3+} doped crystals or glasses. In addition, we propose a model to explain the observed long lifetime and its temperature dependence.

The LSCAS glass used as the host for the doping ions combines the superior properties of an oxide glass with phonon energy of the order of 800 cm^{-1}, an intermediate value as compared to silicates ($\sim$1100 cm^{-1}) and nonoxide glasses ($\sim$500 cm^{-1}) [12]. The LSCAS matrices are produced by melting under vacuum atmosphere which, apart from the above characteristics, assures that the sample is free of the oxidizing components, namely, the OH^- molecules. This important aspect regarding the host matrix production to obtain OH^- free glasses has been discussed in the past by Davy *et al.* [13]. Recently, using LSCAS samples doped with several rare earth ions, prepared under this vacuum melting procedure, we have shown that it is possible to obtain glasses with high emission rates [14]. This melting procedure was our adopted route to successfully obtain the Ti^{3+} oxidation state in the LSCAS glass, which is known to be a challenge in the glass science area [11,15–17].

The composition of the samples used in this Letter were (in wt %) 41.5% of Al_2O_3, 47.4% of CaO, 7% of SiO_2, and 4.1-X% of MgO, with $X = 0$ or 2.0% of TiO_2. The mixture was melted in graphite crucible and under vacuum atmo-

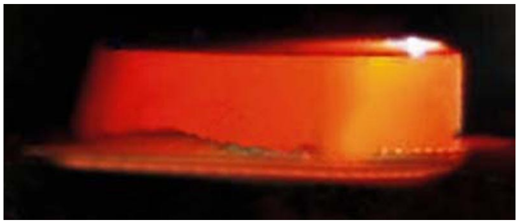

FIG. 1 (color online). Sample photography showing the emission after the excitation at 350 nm.

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sphere at 1600 °C for two hours. After that, the quenching resulted in glasses with excellent optical quality. The sample so obtained was deep brown due to the presence of Ti^{3+} formed in this nonoxidizing host matrix. The emission spectra were recorded after exciting the sample with a Kr^{+} laser at 356.4 nm. Time resolved luminescence was carried out with a third harmonic of a pulsed Nd^{3+}:YAG laser at 355 nm which delivers pulses of 10 Hz with 10 ns of time length and 0.1 cm^{-1} spectral width. The sample emission was analyzed by an Oriel f-125 monochromator with a grating of 400 grooves/mm and detected by an Instaspec *V* detector combined with a gate intensified CCD camera and calibrated with a Hg fluorescent lamp.

Figure 2 shows the optical absorption spectra measured for the undoped and 2.0 wt% TiO_2 doped LSCAS in the spectral range from 200 to 1500 nm. The shoulder around 350 nm is related to Ti^{3+} in the glass [18]. This band is shifted towards the UV region when compared to results in several glasses such as phosphate, aluminophosphate, borate, and silicates [10,15–17]. There is also a broad and weak band near 700 nm that has a tail extending to the near infrared region, which may be related to Ti^{3+}/Ti^{4+} ions pairs interactions [16,18].

To further check for the formation of Ti^{3+} ions we have conducted electron paramagnetic resonance (EPR) measurements in the sample, as prepared, and post annealed for 24 hours in air at 850 °C (just above the glass transition temperature). These additional experiments showed the presence of Ti^{3+} ions in the as-prepared sample, which disappeared when performing the same measurements with the air-annealed sample. These results regarding the bleaching of Ti^{3+} ions in glass samples by post annealing in an oxidizing atmosphere are quite similar to the ones of Hashimoto *et al.* [17]. In order to get Ti^{3+}-free titanophosphate glasses, these authors had either to add oxidizing reagents (e.g., SnO_2) in their glass composition or undergo post annealing in air when working with their original glass composition. It is important to reinforce that our adopted vacuum melting technique (performed during two hours at 1600 °C) leaves the sample with undetectable OH^{-} radicals, which was confirmed by the absence of the 2.8 μm optical absorption band characteristic of these molecules. Therefore, this sample preparation condition favored the Ti^{3+} formation in the glass.

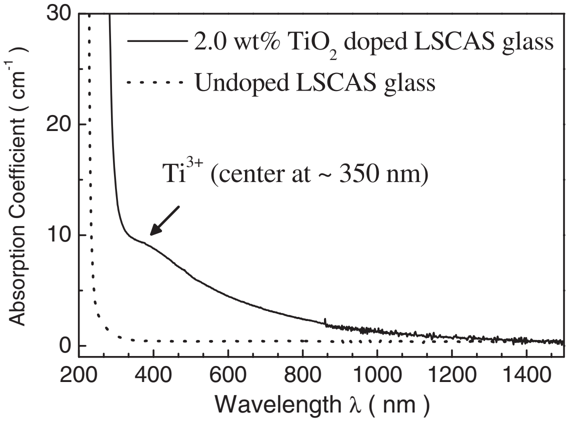

FIG. 2. Optical absorption for undoped and 2.0 wt% TiO_2 doped LSCAS glasses.

Figure 3, curve (a), shows the doped sample emission spectrum at room temperature. For comparison, the $Ti^{3+}:Al_2O_3$ emission spectrum is also shown in curve (b). Both spectra were normalized at their peak position. For the sake of our posterior analysis the base sample emission spectrum is represented in curve (c), showing very low emission intensity in comparison with that of the doped sample. A similar spectrum for the doped sample was obtained at 77 K (not shown), showing an intense red emission band with an apparent Gaussian shape centered at 637 nm (15 698 cm^{-1}) with a FWHM of 190 nm (4236.6 cm^{-1}). This band is broader than that of the traditional $Ti^{3+}:Al_2O_3$ crystal [19] and those for Ti^{3+}:phosphate [10] and Cr^{5+}:silicate [20] glasses. This emission band can be attributed to the transition $^2E \rightarrow {}^2T_2$ from the Ti^{3+} ions in an octahedral site [21]. The peak position of this band is also comparable to that of $Ti^{3+}:YAlO_3$ [22]. The comparison with the $Ti^{3+}:Al_2O_3$ crystal shows that our system presents the emission shifted towards shorter wavelengths, as illustrated in curve (a) of Fig. 3. This emission band is also shifted to the visible region when compared to previous Ti^{3+} doped phosphate and aluminophosphate glasses [10,23]. The occurrence of a second peak with small emission band around 790 nm in Fig. 3 probably has its origin in the interactions of Ti^{3+} ions with structural defects, traces of Ti^{4+}, or other impurities like Fe^{3+} [24].

Figure 4 shows the luminescence time decay at room temperature (a) and 77 K (b). The curves were obtained by measuring the emission decay at a fixed wavelength at

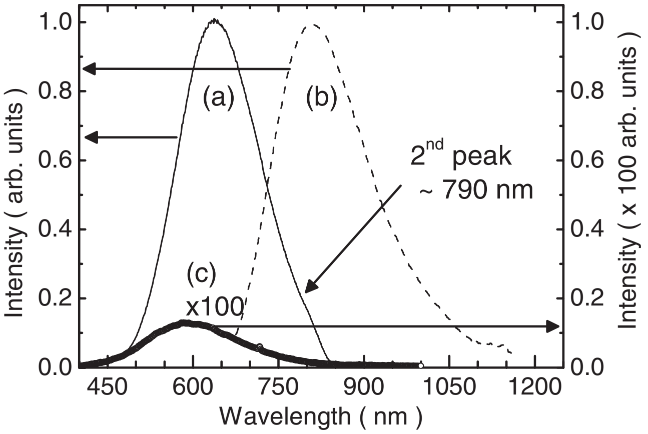

FIG. 3. Luminescence at room temperature for: (a) 2.0 wt% TiO_2 doped LSCAS glass with excitation between 337.5 and 356.4 nm, (b) Ti-sapphire crystal [10,19], and (c) undoped glass with excitation at 356.4 nm.

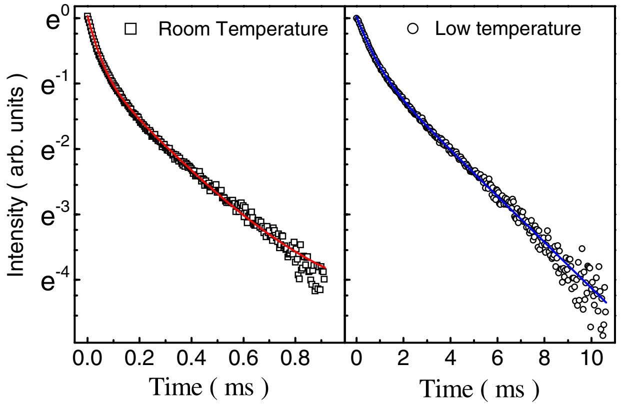

FIG. 4 (color online). Luminescence decay for the 2.0 wt% TiO_2 doped LSCAS glass at room temperature and 77 K. The excitation range was between 337.5 and 356.4 nm.

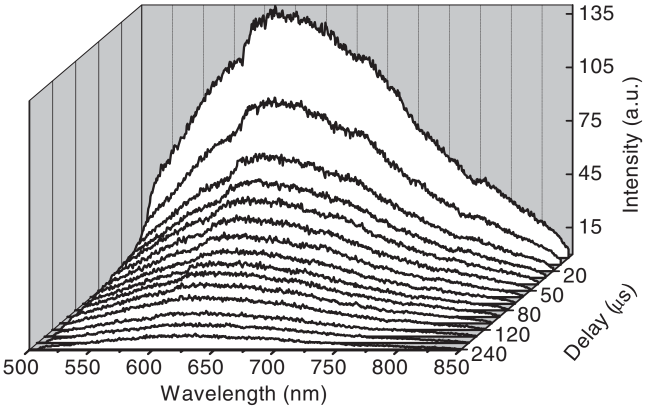

FIG. 5. Time resolved emission spectra illustrating the nonsingle exponential behavior and the occurrence of long fluorescence lifetime in the red-yellow spectral region. The excitation was at 355 nm with 90 ns delay and 10 μs width.

650 nm. A nonexponential decay can be clearly observed with visually evident long lifetime behavior for both fast and long components. Therefore, due to the difficulties to obtain the precise values of each lifetime, we performed the calculation through two different procedures, one of them using the integration method as described in Ref. [25] and the other with two exponential dependences. The integral method provided a value of 170 μs at room temperature, which increased to 2000 μs when the sample temperature was varied from room temperature to 77 K. The two exponentials calculation method provided a value of 41 μs at room temperature for the fast component, and 241 μs for the longest one, while the respective values at 77 K were 609 μs and 2.84 ms. Even at room temperature, the lifetime value for the longest component that is dominant in the decay spectra is about 2 orders of magnitude higher than those for Ti^{3+} doped crystals and glasses, or others $3d^1$ doped materials like V^{4+}, Cr^{5+}, and Mn^{6+}, as shown in Table I. We call attention for the fact that even the fast part of the decay time is very high when compared with those materials. For temperatures around 400 K the values determined by the integration method are still high, around 50 μs. The final confirmation that the emission shape is constant during the time decay was obtained with the time resolved emission spectra, as shown in Fig. 5. The results evidenced again the nonsingle exponential decay and proved the occurrence of a very long lifetime behavior for the mentioned red-yellow fluorescence.

The observed long lifetimes and their strong temperature dependence on Ti^{3+}-doped LSCAS sample can be related to the interaction of Ti^{3+} with structural defects, similar to what has been observed in materials that present mechano and thermoluminescence properties, such as Ti^{4+} [27], Eu^{2+} [28], and Ce^{3+} [29] doped systems. The model we propose to explain these observations is illustrated in Fig. 6. The UV laser (energy = 3.5 eV) excites one electron of the Ti^{3+} ion ground state ($^2T_2$) to an excited band (^2E) from which it is trapped by a vacancy close to the conduction band (CB). After that, there are two possible ways to excite the ^2E metastable band of the Ti^{3+}: first, since the separation of the CB to this excited level is on the order of the magnitude of kT at room temperature, the thermal energy at room temperature promotes the electron to the CB. Then, the electron relaxes back to $(Ti^{3+})^+$ forming Ti^{3+} excited $[Ti^{3+}]^*$, which relaxes emitting a photon at 650 nm (1.9 eV). The second possibility is the

TABLE I. Comparison between optical properties and lifetime values for some $3d^1$- doped laser materials (crystals and glasses) with the Ti^{3+}:LSCAS.

Material	Emission (cm^{-1})	FWHM (cm^{-1})	Lifetime (μs)	Reference
$Ti^{3+}:Al_2O_3$	13 400	3200	3.85	[10,19]
$V^{4+}:CaYAlO_4$	15 500	3400	1.09	[26]
$Mn^{6+}:BaSO_4$	9091	2309	0.56	[6]
$Cr^{5+}:SiO_2$ Glass	14 900	4200	~2.00	[20]
Ti^{3+}:phosphate glasses	11 300	2630	≤10	[10]
Ti^{3+}:aluminophosphate glasses	11 235	···	<17	[11]
Ti^{3+}/color centers:LSCAS	15 698	4237	241[a]	This work

[a] Lifetime obtained from the longest component of the two exponentials fitting method.

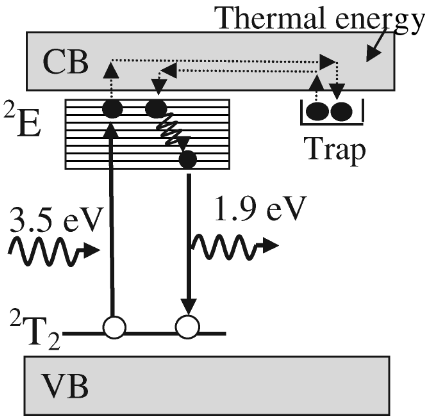

FIG. 6. Model to explain the Ti^{3+} long lifetime. (1st) $Ti^{3+} + h\nu(350\ \text{nm}) \rightarrow (Ti^{3+})^+$ + (electron in a hole center); (2nd) [(electron in a hole center) + kT + $(Ti^{3+})^+ \rightarrow (Ti^{3+})^*$] or [(electron in a hole center) + tunneling + $(Ti^{3+})^+ \rightarrow (Ti^{3+})^*$]; (3rd) $(Ti^{3+})^* \rightarrow Ti^{3+} + h\nu(\sim 650\ \text{nm})$.

electron tunneling directly to the ^2E band, from where the emission would occur.

At higher temperatures, around 400 K, the thermal detrapping is easily achieved, which explains the significant reduction of the lifetime ($<50\ \mu$s). At low temperatures, in contrast, the excited electrons are trapped for a long period of time, which increases the luminescence decay time. In other words, our proposed model predicts that Ti^{3+} ions ^2E level becomes high populated with the excitation and tends to depopulate fast due to the partial allowed electronic transition $^2E \rightarrow {}^2T_2$, resulting in the observed fast component. Then, since this level may be constantly seeded by the detrapping effect from color centers, an increase in the lifetime can take place. This interpretation demands the confirmation of presence of defects in the glass, such as F^+ kind color centers. This was verified by measuring the luminescence of the undoped sample with the excitation performed at 356 nm. The resulting spectrum is shown in Fig. 3, curve (c). Therefore, the long lifetime of the luminescence may be due to the long trapped period of time and not necessarily to the Ti^{3+} excited lifetime. This observation is consistent with the fact that the ^2E band for Ti^{3+}-doped materials has an expected lifetime on the order of 10 μs, similar to the lifetime for the high temperature region where the trapping effect is minimized.

In conclusion, we obtained a Ti^{3+}-doped OH^- free LSCAS glass with a long lifetime ($\sim$2.0 ms at 77 K and 170 μs at room temperature) and a broad emission band of about 4200 cm^{-1} that was shifted 170 nm towards the visible region as compared to the Ti-sapphire crystals. These findings were attributed to the absence of oxidizing OH^- molecules in the sample obtained through the vacuum melting procedure, and to the influence of glass defects in the trapping of the Ti^{3+} excited electrons. The combination of long lifetime and broad emission band has never been reported for a metal transition ion doped glass, suggesting that this Ti^{3+} doped LSCAS may be a promising system for high power tunable solid state lasers.

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