Temperature variation of near-infrared emission from Cr\(^{4+}\) in aluminate glass for broadband telecommunication

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Temperature dependence of fluorescence spectra of Cr\(^{4+}\) in an aluminate glass in the range of 1.2–1.6 µm was investigated from 15 to 300 K. The emission spectra were broadband centered at about 1.3 µm, wider than 200 nm width. The emission intensity drastically increased with decreasing temperature and that of 15 K was 20 times larger than that of 300 K. The bandwidth and mean energy of the emission band changed very slightly with temperature. The emission of Cr\(^{4+}\) in the glass fiber is expected as a tunable laser source and a broadband amplifier for the wavelength-division-multiplexed telecommunication. © 2000 American Institute of Physics.

Owing to rapid increase of information traffic in the telecommunication network, the development of the wavelength-division-multiplexing (WDM) network system becomes important. Among various devices for the WDM optical communication system, broadband amplifiers and tunable lasers should be a key material, because the number of channels depends on the gain bandwidth of the amplifier and laser source. Effort to achieve broadband amplification by Er-doped fiber amplifiers (EDFA) has been carried out by many researchers. A broadband amplifier at L-band was reported in an Er\(^{3+}\)-doped tellurite fiber in 1997, which has 80 nm gain bandwidth.

1 Also a Tm\(^{3+}\)-doped fiber amplifier can work in the range of 1.45–1.50 µm. However, to fully utilize the wide window of telecommunication fiber in the range of 1.2–1.7 µm, multiple number of amplifiers, such as a Tm\(^{3+}\)-doped amplifier and a Raman amplifier should be necessary in addition to EDFA. All of them have a gain bandwidth of less than 100 nm.

It has been well known that the Cr\(^{4+}\) ion shows a broadband emission around 1.4 µm in garnet crystals such as Y\(_3\)Al\(_5\)O\(_{12}\) (YAG) and Gd\(_3\)Ga\(_5\)O\(_{12}\) and thus can be materials for solid-state tunable lasers with high-repetition rate. Until now the laser action has been achieved in various garnets, Mg\(_2\)SiO\(_4\) and Y\(_2\)SiO\(_5\). The broad emission of Cr\(^{4+}\) is mainly due to the coupling of the lattice vibration with the 3\(d\) electronic levels, which is also the reason for large temperature dependence of the fluorescence properties.

In order to construct an optical amplifier with high performance, fiber geometry is preferable because the pumping light can be confined with higher density and longer gain medium is easily achieved. In this viewpoint, the glass medium is easily achieved. In this viewpoint, the glass material can be superior as a host to crystalline materials. The formation of Cr\(^{3+}\) in aluminate glasses and some optical properties have been reported by several groups. It was found that the tetravalent Cr can be formed under weak oxidizing condition in a few compositions of oxides having point defects. However, no systematic studies on the temperature dependence of fluorescence properties of Cr\(^{4+}\) in glasses were reported.

In this study, temperature dependence of fluorescence spectra of Cr\(^{4+}\)-doped aluminate was investigated.

Glass in the composition of 51CaO–42Al\(_2\)O\(_3\)–7SiO\(_2\)–0.05Cr\(_2\)O\(_3\) was prepared by a conventional melting method. The batch was melted with an alumina crucible in air at 1600 °C for 1 h. For comparison of spectra, rare earth doped tellurite glasses were also prepared by melting at 800°C with a gold crucible in the composition of 75TeO\(_2\)–20ZnO–5Na\(_2\)O–0.1Ln\(_2\)O\(_3\), where Ln is Pr, Tm, or Er.

Emission spectra were measured by using a 792 nm laser diode (LD) (Sony 304XT, 1 W) as a pumping source and an InGaAs photodiode (Electro-Optical-System, IGA-010-H, \(f=160\) kHz) as a detector from 800 to 1650 nm with a computer-controlled monochromator (Nikon, G250). The LD was modulated by a function generator and a lock-in-amplifier (NF Co., LI-570A) was used to obtain the output signal of the detector. The sensitivity calibration of this measurement system was done with a broad spectrum of a standard halogen lamp. In the fluorescence measurement the sample temperature was controlled from 15 to 300 K with a helium-cycling cryostat (Iwatani Plantec Co., TCU4). For

![FIG. 1. Comparison of emission spectra of Cr\(^{4+}\)-doped aluminate glass and rare earth doped tellurite glasses at room temperature in the telecommunication wavelength.](image)
thermal conduction and temperature accuracy, a glass of 1 mm thick was attached to a copper holder, which is kept at a low pressure and surrounded by silica windows.

Figure 1 shows the emission spectra of the Cr-doped aluminate glass and the Pr\(^{3+}\), Tm\(^{3+}\), and Er\(^{3+}\)-doped tellurite glasses at room temperature. Since a broad emission around 0.8–1.0 \(\mu m\) was not observed, the emission in the glass is not due to Cr\(^{3+}\) but Cr\(^{4+}\) ions, though both may coexist under the present preparation condition. The emission band of the Cr\(^{4+}\) in the aluminate glass is centered around 1.35 \(\mu m\) and ranges from 1.2 to 1.6 \(\mu m\), which is similar to that of the Cr\(^{4+}\):YAG.\(^{10}\) Although the emission bands of Pr\(^{3+}:1.3 \mu m\), Tm\(^{3+}:1.4 \mu m\), and Er\(^{3+}:1.5 \mu m\) become relatively wide when doped in tellurite glass hosts (nearly 100 nm),\(^{1,9,12}\) the Cr\(^{4+}\) emission almost covers the spectra range of three rare earth ions for telecommunication amplifiers. The difference of the bandwidth is attributed to the nature of electronic transitions and the electron-phonon coupling strength of the 3d levels and that of the 4f levels. In contrast to the 4f transitions of rare earth ions, the mean wavelength of emission bands of 3d transitions can be easily varied with host compositions. In fact, the peak position of Cr\(^{4+}\):Y\(_3\)Sc\(_2\)Al\(_5\)O\(_{12}\) shifts to longer wavelength with increasing Sc content, \(x\) without losing bandwidth and it becomes 1.60 \(\mu m\) at \(x=1.72\).\(^{11}\) It would be possible to realize a whole-range amplifier only with a Cr\(^{4+}\)-doped fiber if the emission band of the glass is located at longer wavelength for the telecommunication window. Usually, continuous modification of glass compositions is often examined in searching the best host material of glass lasers. Thus, aluminate glasses substituted with other cations such as Ga\(^{3+}\) and with other alkaline-earth metals by some compositional ratio can probably be a candidate of amplifier materials with a long-shifted emission band, which completely covers the telecommunication wavelength range from 1.3 \(\mu m\) to 1.65 \(\mu m\) of L\(^{3+}\)-band.

Temperature variation of the Cr\(^{4+}\) emission spectra is shown in Fig. 2. The spectral intensity at 300 K is weak, but it drastically increases with decreasing temperature. The spectra shape did not largely change with temperature. The integrated intensity is plotted as a function of temperature in Fig. 3. The intensity decreases monotonically with increasing temperature and that of 300 K is 1/20 smaller than that of 15 K. This result suggests that the quantum efficiency of the emission is higher at lower temperature and very low at room temperature. This tendency is similar to but more drastic than that of Cr\(^{4+}\):YAG, where the lifetime decreases by 1/6 from 15 to 300 K.\(^{11}\) According to the calorimetric measurement, the quantum efficiency of Cr\(^{4+}\):YAG is estimated to be 14\% at 300 K.\(^{11}\) Since the temperature variation of emission intensity can be correlated with that of the quantum efficiency, \(\eta\), \(\eta\) should be very high at low temperature.

Figure 4 shows the temperature dependence of full width at half maximum (FWHM) and the mean energy of the emission band. The data analyses were done after converting wavelength into wavenumber, because wavelength is not proportional to the energy and the mean wave number is defined as the center of gravity. The bandwidth slightly decreases from 232 to 212 nm by 8\% and the mean wavelength slightly shifted to longer side by 27 nm (2\%) with decreasing temperature from 300 to 15 K. Thus, the wavelength tunable region of this material is not sensitive to temperature in a wide temperature range.

Research effort to find the optimum preparation condition to control the valence of Cr and to improve the quantum efficiency of Cr\(^{4+}\) by composition search should be done.