Broad luminescence band in silica glass for tunable laser operating from 1.8 eV to 4.0 eV region

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Introduction

Solid state tunable laser is becoming more important from the scientific and engineering points of view. Some candidates for a solid state tunable laser in visible region, are proposed; second harmonic generation of Titanium-Sapphire laser, a laser glass which contains photostable organic dyes introduced into composite glass[1,2]. In this paper, new principle to obtain a tunable laser for the range from 1.8 eV to 4.0 eV , is proposed.

Experimental

Many kinds of synthetic pure silica glass made by direct method, plasma method, soot method etc. and BK7 optical glass are used. The pure silica made by the direct method contains lowest concentration of defects. Optical absorption spectra in these samples are measured. The photo luminescence spectra excited by KrF (5 eV) or ArF(6.4 eV) excimer laser light , are measured in every sample.

Results and discussion

Figure 1a) shows luminescence spectra in high purity synthetic silica exited by KrF excimer laser . Broad luminescence band from 1.5 eV to 4.0 eV is observed. The peak appears around 3 eV . No well-known luminescence band caused by some defect centers such as NBOHC, oxygen vacancy, etc. are observed, because the concentration of defects is very low in this sample. Such kind of broad luminescence has never been reported. When we see this luminescence, it looks white, so we will call it white luminescence in this paper . The intensity of this white luminescence is quite low compared with the luminescences caused by some kinds of defects, so nobody who observed this luminescence before, take care of this luminescence. White luminescence is observed in every synthetic pure silica glass, although the intensity shows a sample dependency. The lifetime of the white luminescence is shorter than excitation laser pulse (about 20 nS), so it could not be measured. The white

luminescence and the excitation laser pulse show almost the same time dependency. This means that the lifetime of this luminescence is several nanoseconds or less. When the sample is cooled to 77 K or heated to 600 K, no change in the lifetime is observed.

Figure 2 shows the relation between the excitation laser intensity and the intensity of the white luminescence. The intensity of this luminescence shows a liner relation to the excitation laser intensity . This means that the luminescence is caused by only one photon excitation, five electron volt excitation causes this luminescence.

Two kinds of luminescences have been reported around 3 eV where the white luminescence appears. One is the 2.7 eV luminescence which is caused by oxygen vacancy in silica glass network.[3] It is well-known that this luminescence decays very slowly (lifetime; about 10 mS), and is observed only in oxygen deficient type silica glass. The white luminescence decays very fast (lifetime; nanosecond order or less), and is observed in every kind of pure silica glass (oxygen deficient, oxygen surplus, high OH content and etc.). Thus, the white luminescence is different from the oxygen vacancy luminescence. Another luminescence around 3 eV is self-trapped exciton luminescence who's peak appears 2.2 ~ 2.8 eV. The lifetime of this luminescence is very short at room temperature, however , if the sample is cooled, it becomes longer .[4] To excite this self-trapped exciton luminescence by KrF excimer laser light, two photon absorption process is necessary because the energy gap between conduction band and valence band in silica glass is about 8 eV. The white luminescence decays with a very short lifetime even at 77 K and can be excited by one photon of KrF excimer laser light. The white luminescence is thus different from the self-trapped exciton luminescence.

Figure 2b) shows a luminescence spectrum excited by KrF excimer laser in BK7 glass. The spectrum is similar to that in pure silica sample, and it looks white. The lifetime of this white luminescence is also very short, less than several nanoseconds in the temperature range from 77 K to 600 K. The intensity of this luminescence shows a liner relation to the excitation laser intensity , also. Thus, the white luminescence observed in BK7 is the same one observed in pure silica. The intensity of this luminescence is much higher than that observed in pure silica, because of the much higher optical absorption efficiency for the excitation light in BK7, most of the excitation photons are absorbed at near surface of the BK7 sample however most of the excitation photons transmit the pure silica sample.

Theoretical calculations give information for the band structure of SiO_2 system. Figure 3a) and 3b) show two kinds of examples for theoretical band calculations. The valence band below 0 eV in Fig. 3a) is largely oxygen-like. The oxygens p states split into a nonbonding p π orbital, a weakly bonding p_x

orbital, and a strongly bonding p_y orbital. The nonbonding and weakly bonding states intermix and form the upper valence band, from 0 to -4 eV. The strong bonding states form the broad future from -5 to -13 eV. In case of the result in Fig.3b), we can see almost the same spiriting or band gap in the valence band also.

If a hole transit from lower valence band to upper valence band, a photon will come out. Luminescence caused by such hole transition has never been reported in SiO_2 system, however there are some reports in some other materials. These luminescence is called auger-free luminescence. [7] Auger-free luminescence shows a broad spectrum because the holes in the upper part of the outer most core band (lower valence band in the case of silica glass) can transit to any part of the valence band (upper valence band in the case of pure silica glass). We can assume a spectrum of the auger-free-luminescence in SiO2 system from the theoretical band calculation. The spectrum may spread from1~2 eV to 4~5 eV. This is very similar to the spectrum of the white luminescence. The lifetime of the auger-free luminescence is usually very short or one nanosecond or less. Lifetime of the white luminescence is also very short. Usually, dielectric materials have some amount of holes just above their valence bands. So, it can be assumed that there are some holes just above the upper valence band in pure silica glass and there are many holes in the same state in BK7 which has much larger amount of impurity and dopant than pure silica glass. The holes can be excited to the lower valence band only by 5 eV photon absorption, and when the excited holes transit to upper valence band the white luminescence must be observed. `It can be thus concluded that the white luminescence is caused by the hole transition from the lower valence band to upper valence band.

Optical amplification and laser operation are possible by using a hole transition as shown in Fig. 4. The operatable range is 1~2 eV to 4~5 eV.

References

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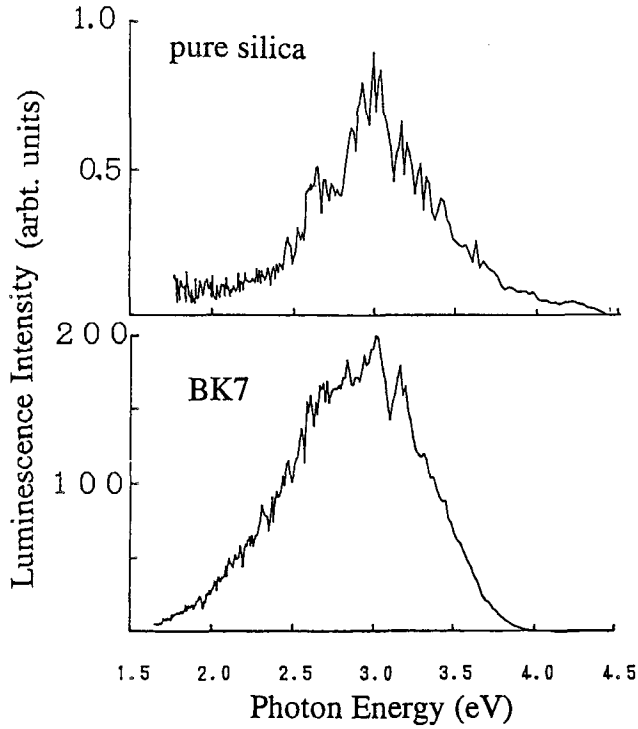

Fig. 1 Photo-luminescence spectra in pure silica and BK7 sample excited by KrF excimer laser. The laser intensity was about 50 mJ/cm^2.

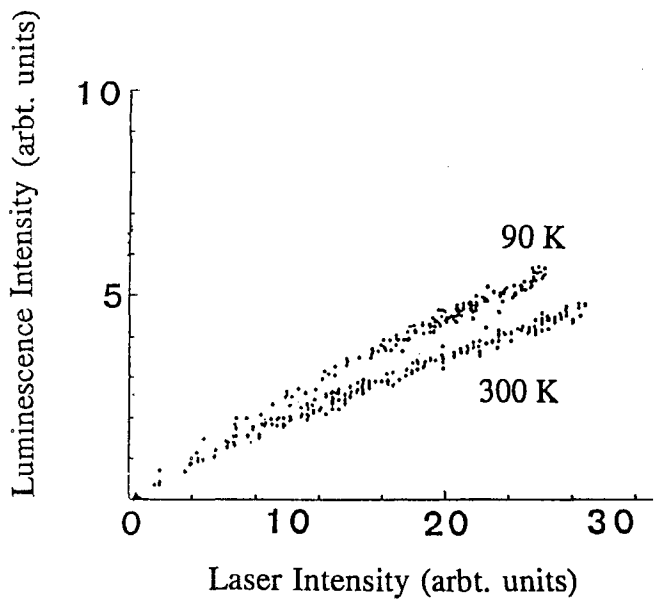

Fig. 2 Relation between the luminescence intensity at 440 nm and the excitation laser (KrF, Max. 70 mJ/cm^2) intensity.

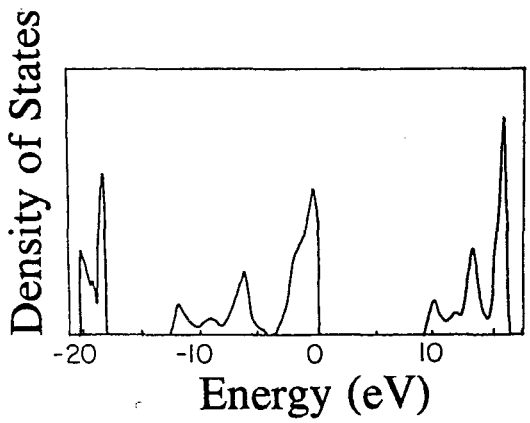

Fig. 3 a) Density of states of SiO_2 (α-quartz).[6]

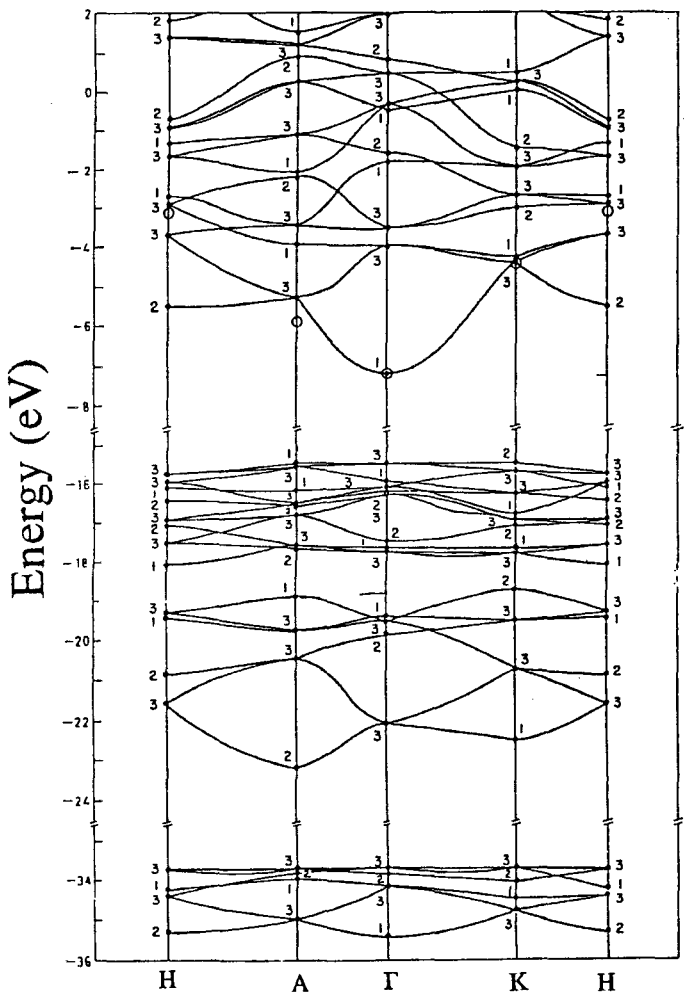

Fig. 3 b) Band structure of α-quartz.[5]

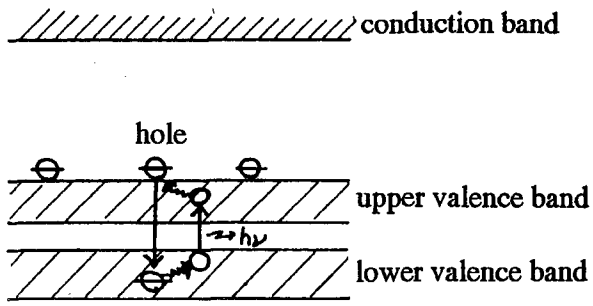

Fig. 4 Hole transition system for laser operation in silica glass.