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Light absorption of silica nanoparticles

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The light absorption of silica nanoparticles generated in a flame has been measured in visible light. It was revealed that the frequency dependence of the light absorption coefficient is nonexponential. Its absolute value in the forbidden band was found to be unusually high. This behavior of light absorption is ascribed to a narrowing of the energy gap due to a high concentration of structural defects that appear during particle generation and growth at high temperatures.

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I. INTRODUCTION

The study of silica nanoparticles has attracted considerable attention in recent years, due in part to their potential applications in mesoscopic research and nanodevices. Bulk silica-based applications, such as protective layers on electronic devices, and optical fibers, are well known and already extensively studied.[1] It is believed that the optical and electronic properties of silica nanoparticles are different from those of bulk materials. Therefore, the use of silica nanoparticles in silica-based nanoscale devices and technology has made their study of great importance. Flame aerosol syntheses are used to produce nanoparticles by gas-phase reactions in flames.[2] The gas-phase method for nanoparticle synthesis has an inherent advantage over wet processes, since the process produces purer nanoparticles. The properties of nanoparticles forming and growing in flames may be different from bulk materials. The large energy evolved during particle growth and formation may occur via electron excited states, and these excitations may exist only during the synthesis.[3] The properties of silica nanoparticles generated in flames are therefore assumed to be different from those of glasses, due to the high concentration of defects that are created during their formation and growth. These structural defects[4] affect the electronic structure, resulting in a narrowing of the band gap, and the forming of localized states at the band tail. The behavior of light absorption reflecting these effects is widely used to determine the optical and electronic characteristics of materials with structural defects.[5]

In recent work, the behavior of absorption in silica glasses has been observed by Saito and Ikushima[6] using vacuum ultraviolet absorption measurements, and by Vainshtein *et al.*[7] using ultraviolet absorption spectra measurements. In contrast to the extensive studies of the optical properties in silica glasses, investigation of silica nanoparticles has rarely been carried out. Recently, the photoluminescence induced by 6.4-eV/ArF laser light in silica nanoparticles has been reported.[8] The effects observed were attributed to the large number of surface structural defects that resulted from the splitting of the Si-O regular bonds due to the obviously large surface/volume ratio of nanoparticles.

An investigation of the defects formed during the generation and growth of nanoparticles might help in understanding the mechanism of particle growth and formation in flames, which could lead to a control strategy for particle generation, growth, and transport. Here it would be fascinating to compare the structural defects that appear during particle growth and formation at high temperatures with those induced by an external source at low temperatures in bulk materials.[9] Furthermore, it is very interesting to study the optical absorption characteristics due to the defects in nanoparticles generated in flames compared to those in bulk glass. The emission spectra of silica nanoparticles produced in flame may then be utilized to detect defects similar to those at low temperature. The light absorption of particles can be extracted from a measured emission spectra through Kirchhoff's law. However, extraction of the absorption of the nanoparticles from the flame luminosity is difficult. One needs to know the actual temperature of the nanoparticles in order to calculate the Planck function, which is a factor in the expression that describes the flame luminosity. Unfortunately, the particle temperature cannot be obtained directly from the measured flame luminosity without prior knowledge of the spectral behavior of the absorption coefficient of the particles.

In this work, we study the luminosity of flame, which generates the silica nanoparticles. Irradiation of a CO_2 laser is applied to the nanoparticles formed in a flame in order to change the temperature of the particles. Comparison of the flame luminosity at different laser powers allows us to reveal the peculiarities of light absorption by silica nanoparticles at different temperatures. So, it is possible to demonstrate the nonexponential frequency dependence in visible light without knowing the exact particle temperature. The particle temperature when there is no CO_2 laser irradiation may not be the same as the ambient gas temperature during the synthesis,[10] so that one cannot use the gas temperature in calculating the absolute value of the absorption coefficient of the particles. However, due to the obvious proximity of these two temperatures in the flame, we may estimate the value of the light absorption coefficient, which is found to be unusually high in the forbidden band.

II. EXPERIMENT

A schematic diagram of the experimental setup for the measurement of the radiant energy emitted by silica nanopar-

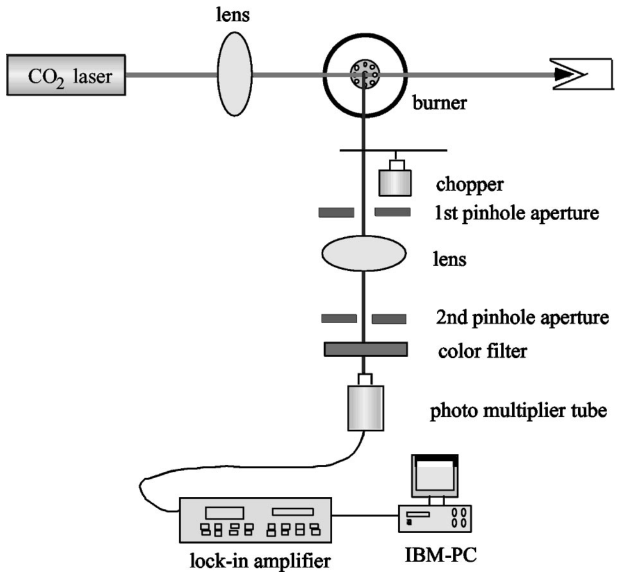

FIG. 1. Schematic diagram of experimental setup for measurement of the radiant energy from silica nanoparticles generated in flame with CO_2 laser irradiation.

ticles generated in a flame when irradiated with a CO_2 laser beam is shown in Fig. 1. The schematic of the burner used in this study is described in detail in Ref. 11. The silica nanoparticles are generated as a result of hydrolysis and oxidation of $SiCl_4$ (Shinetsu Co., 99.9999%) in a co-flow oxyhydrogen diffusion flame. The flow rate of $SiCl_4$ was adjusted to be smaller by two orders of magnitude than those of the oxygen and hydrogen, in order to avoid the change of gas temperature during particle formation.

Here, the flame is irradiated with a CO_2 laser (Bystronic, BTL 2800) beam (wavelength about 10.6 μm) to heat up the silica particles. The laser power can be increased up to 1500 W in steps of approximately 40 W. The flame temperature without $SiCl_4$ injection, T_g, was measured by a *B*-type thermocouple, and corrected for radiative heat loss and was approximately 2000 K in the region where the luminosity is measured. The signal from a photomultiplier (PMT) (Hamamatsu, R928) is fed into a lock-in amplifier (Stanford Research System Inc., SR830) to measure the radiant emittance of the flame at specific wavelengths λ. The wavelength was defined by a color filter whose transparent band is about 10 nm. In order to make an absolute measurement, the PMT was calibrated using a tungsten lamp (Sciencetech Inc., QTH 100W). A scanning transmission electron microscope (Philips CM30), equipped with energy dispersive x-ray spectroscopy (EDX), was used for analysis of the morphology and the impurity level in the particle.

III. RESULTS

The absorption spectra can be represented by two regions according to their photon energy dependence: the high-energy absorption region, the so-called ‘‘Tauc region,’’ and the ‘‘Urbach region.’’ The Tauc region results from transitions between extended electronic states, whereas the Urbach region is characterized by transitions between localized electronic states in one band-tail, and extended states in another band in which the exponential dependence on the energy should occur.[12] Our main interest here was to probe the behavior of light absorption of silica nanoparticles at high temperatures in the Urbach region, and compare it with that in bulk materials.

The light absorption spectrum of silica nanoparticles generated in flames was extracted from the PMT measurement of the flame luminosity. It is simply assumed that SiO vapor emission does not contribute significantly to the flame radiation in visible. This can be easily justified by considering that the lower state of a SiO molecule involved in transitions in visible light is not a ground state of the SiO molecule, but a highly excited one.[13] Therefore, the self-radiation I_λ from the flame-generated silica nanoparticles is the difference between the flame radiant emittances, with and without the presence of silica nanoparticles. The observed self-radiation from the silica nanoparticles is the sum of the radiation emitted by each particle that exists within the flame. It is noted that with no laser irradiation, the flame radiation without $SiCl_4$ has been measured to be smaller by as much as 20 times, compared to that when silica particles are present. It is as much as 200 times smaller than the flame radiation with $SiCl_4$ injection at the highest laser power used (1220 W). Also note that the measured flame luminosity without $SiCl_4$ injection is nearly the same at all laser powers, which means that gas absorption of the CO_2 laser beam may be negligible in our experiment.

The measured radiant emittance of the flame due to the emission of the silica nanoparticles is given by the following equation:

$$I_\lambda = 3q(\lambda) V f_v R_B(\lambda, T_p). \tag{1}$$

Here, R_B is the Planck function given as a function of the wavelength λ, and the particle temperature T_p. V is the measuring volume from which the radiation enters the PMT hole, and f_v is the particle volume fraction. $q(\lambda)$ is the ratio of the particle emissivity to the particle radius and may be expressed by the following equation in the Rayleigh limit:[14]

$$q(\lambda) = \frac{24\pi}{\lambda} \frac{\varepsilon''}{(\varepsilon'+2)^2 + (\varepsilon'')^2}, \tag{2}$$

where $\varepsilon(\lambda) = \varepsilon'(\lambda) + i\varepsilon''(\lambda)$ is the complex dielectric function of a particle. Notice that the absorption coefficient of a particle, q, is similar to that of bulk material $(\alpha = 4\pi k/\lambda)$.[14] Note also that q and α are proportional to each other within a wide spectral range, since the real part of the dielectric function of a particle does not depend significantly on wavelength. The particle volume fraction, f_v, can be estimated from the known flow rate of the injected $SiCl_4$, and the volume V can be calculated using optical parameters. It is then possible to extract the particle absorption coefficient $q(\lambda)$.

Figure 2 shows the spectral dependence of the absorption coefficient of silica nanoparticles without laser irradiation, calculated using the Planck function $R_B(\lambda, T_g)$, at a gas temperature determined from the measured flame luminosity. Note that the error in the estimate of f_v and V does not affect

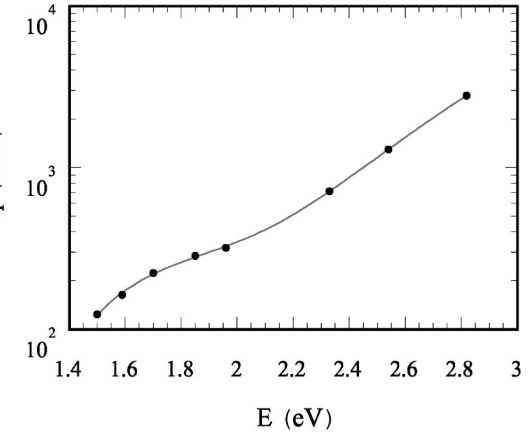

FIG. 2. The spectral dependence of the absorption coefficient of silica nanoparticles without laser irradiation.

the dependence of this spectral character. The measured gas temperature was substituted into the Planck function on the assumption that without laser irradiation the gas and particle temperatures are very proximate. In Fig. 2 one can see that deviation of the absorption coefficient from an exponential frequency dependence occurs at a photon energy of about 1.9 eV. It is easy to show that the existence of this deviation is not connected with the choice of temperature used in the Planck function. Notice that the absolute value of the light absorption is many times larger than that in bulk materials at high temperatures.[15] Furthermore, the value of the Urbach tail parameter E_U defined by $E_U=[\partial \ln q/\partial(h\nu)]^{-1}$ is about 0.4 eV, which also seems to be much larger than that in bulk silica glass.[15] The optical energy gap of the silica nanoparticles could not be determined from the present data since the photon energy corresponding to the Tauc region is beyond our measurement range.

It is important to show that this nonexponential behavior of the absorption coefficient is independent of the accuracy of the measurement and the calibration of PMT, usually this latter being the main source of error. To clearly show the nonexponential behavior and cancel this error, the logarithm of the ratio of the radiation intensities, with and without laser irradiation, was calculated. This ratio is given in the Wien limit of the Planck function by

$$\ln\left(\frac{I_\lambda}{I_{\lambda_0}}\right)=\ln\left(\frac{f_V}{f_{V_0}}\right)+\frac{hc}{k_B\lambda}\left(\frac{1}{T_{P_0}}-\frac{1}{T_P}\right)+\ln\left(\frac{q(\lambda,T_P)}{q(\lambda,T_{P_0})}\right), \tag{3}$$

where the subscript 0 denotes the value when there is no laser irradiation. The PMT signal is proportional to the radiation intensity, so that the calibration of PMT is not needed to evaluate the left-hand side of Eq. (3), which can be determined from the ratio of PMT signals. The accuracy is then connected only with fluctuations in the intensity of light source, which does not exceed 1% in our experiment. The experimentally determined values of $\ln(I_\lambda/I_{\lambda_0})$ at different laser powers are plotted in Fig. 3 as a function of inverse wavelength. Regardless of laser power, a similar pattern, showing an inflection point, is found. The photon energy corresponding to the inflection point is about 1.9 eV, which is similar to that in Fig. 2 where the deviation from the exponential behavior was found. The first two terms in the right-hand side of Eq. (3) depend linearly on the inverse wavelength. The nonlinear behavior of $\ln(I_\lambda/I_{\lambda_0})$ stems from the nonlinear behavior of $\ln[q(\lambda,T_p)/q(\lambda,T_{p_0})]$. This is possible only for the case of a nonexponential frequency dependence of the particle absorption coefficient q, which violates the ‘‘glassy’’ Urbach rule.[7]

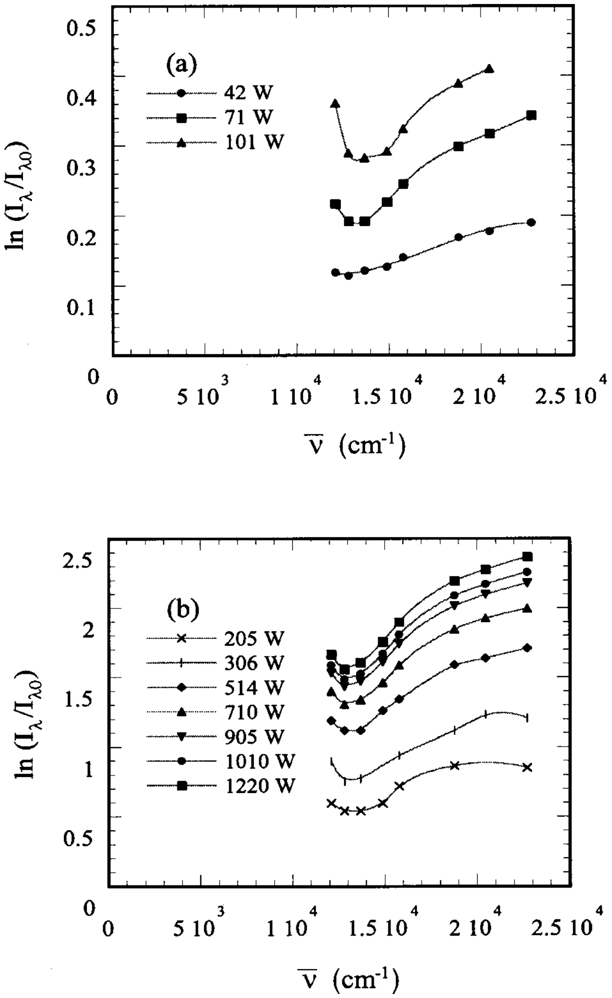

FIG. 3. Ratio of particle radiation with and without laser irradiation for different laser powers.

Even if the use of Eq. (3) allows us to avoid the main source of experimental error as already explained, there still remains the possibility of morphological and/or structural change of nanoparticles during CO_2 laser irradiation, and this may affect the characteristics of the absorption coefficient. To remove this possibility, we compared the spectral behavior of $\ln[I_\lambda(W_1)/I_\lambda(W_2)]$ for all studied laser powers. As expected, the trends and peculiarities of the spectral behavior are exactly the same as in Fig. 3. To confirm that our particles do not contain any foreign ions, which might produce the peculiarities of absorption revealed in the present study, we examined the EDX spectrum of SiO_2 nanoparticles collected on a TEM grid by a localized thermophoretic sampling technique.[16] The particles were found to be composed of only silicon and oxygen. According to the usual detectable limit of EDX measurements,[17] impurities at a level of not less than about 0.5% would be detected. However, because of the high purity of $SiCl_4$ (99.9999%) we tend to believe that the real level of impurities such as metals cannot exceed 0.0001% in our particles.

Therefore, we are confident in claiming that the nonexponential dependence on photon energy, of the absorption coefficient of silica nanoparticles deep in the forbidden band, is connected with intrinsic properties of these particles.

IV. DISCUSSION AND CONCLUSIONS

The nonexponential behavior of light absorption in visible light has been observed in silica nanoparticles generated in flame. Similar behavior in absorption spectra characterized by a ‘‘tail or defect absorption region’’ located just below the Urbach region, has been investigated in other materials such as C_{60} thin films[18] and amorphous silicon.[19] In the tail (or defect) absorption region, the energy range is attributed to transitions involving defect states localized near the Fermi level. According to their results, this behavior was concluded to be due to the oxygen-impurity-induced electronic defect states located in the middle of the gap of C_{60},[18] and to the defect concentration caused by dangling bonds in the amorphous silicon,[19] respectively. However, to our knowledge, the present experiment reveals this nonexponential behavior of light absorption in silica nanoparticles for the first time.

The correlation between nonbridging oxygen hole centers and the 1.9 eV absorption band or the 1.9-eV photoluminescence band excited by visible light has been explored in silica glass.[9] The proximity of the energy where the light absorption peculiarity appears in silica nanoparticles and the energy of the photoluminescence band in silica glass leads us to infer that both these effects have the same nature. Therefore, we believe that the revealed behavior of the light absorption coefficient of silica nanoparticles in flame can be ascribed to nonbridging oxygen hole centers. We suggest that these defects form during particle formation due to the fast rate of its growth, and therefore their concentration may be above the equilibrium. Moreover, the concentration of these defects may be so high that strong Coulomb disorder leads to a significant narrowing of the optical energy gap,[20,21] and as a consequence, this may lead to a large Urbach tail parameter, and large light absorption by silica particles in visible light. It is obvious that the defects due to thermal excitation cannot lead to these high values of light absorption observed in the present experiment. The question about the mechanism of defect formation, however, remains open and requires a further study.

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