Selenium molecules and their possible role in deep emission from glasses doped with selenide nanocrystals

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We report the observation of Raman scattering from a vibration mode with frequency of 320 cm^{-1} and its higher-order harmonics in silicate glasses doped with selenide semiconductor nanocrystals such as CdSe and ZnSe. Comparison with Raman spectra of glasses and alkali halides doped with Se suggests that these modes are caused by the presence of selenium molecules in the glasses. When excited in the blue and green by an Ar^{+} laser, glasses containing Se only are found to emit strong near-infrared luminescence whose peak and line shape are very similar to the so-called ''deep emission'' observed frequently from selenide-doped glasses. Possible effects of Se molecules on the linear and nonlinear optical properties of glasses containing selenide nanocrystals are discussed. © *1996 American Institute of Physics.* [S0021-8979(96)00714-1]

I. INTRODUCTION

In the past decade semiconductor nanocrystals (SNCs) have attracted considerable interest.[1] Among SNCs, CdSe and CdS$_x$Se$_{1-x}$ nanocrystals embedded in a glass matrix is considered a prototypical system that have been extensively studied due to their potential applications in nonlinear optical devices.[2–4] Photoluminescence from these semiconductor-doped glasses (SDGs) is usually utilized to determine the exciton and defect energy levels of the SNC. Often in addition to exciton peaks occurring near the band gap of the nanocrystals, a broad peak centered around 700–800 nm is also observed in glasses containing CdSe or CdSSe nanocrystals. This near-infrared peak has been attributed to recombination of excitons at deep traps in or near surface of nanocrystals[5] and its intensity was found to decrease after intense irradiation; however, the exact nature of these deep traps has never been elucidated. In this article we report the observation of multiphonon Raman scattering from a new vibrational mode in glasses doped with CdSe and ZnSe nanocrystals. By comparing these Raman peaks to those observed in alkali halides and glasses doped with Se alone we identify the presence of Se$_2$ molecules in SDG. Correlating the presence of the Se$_2$ molecules with the so-called ''deep trap emission'' we conclude that their possible contribution to the near-infrared luminescence and other linear and nonlinear optical properties of selenide-doped glasses should be taken into account in interpreting the experimental results.

II. EXPERIMENTAL DETAILS AND RAMAN RESULTS

We have studied SDG grown by ourselves and purchased from commercial sources. The specially developed SDG were made by co-melting the semiconductors (CdSe,

ZnSe, CdS, or Se) with an experimental silicate glass. Details of sample preparation has been described elsewhere.[6] In the case of CdSe-doped glasses two samples after different amount of heat treatment were studied. The commercial sample is a Corning filter glass that contains CdS$_x$Se$_{1-x}$ nanocrystals. Most of the samples have been characterized by absorption and transmission electron microscopy (TEM) measurements to estimate the size of the SNC. Both Raman and photoluminescence spectra were excited with the various lines of an Ar^{+} laser, a He–Cd laser, and the second harmonic of the output from a self-mode-locked Ti:sapphire laser. The scattered light was dispersed by a SPEX triple monochromator and detected either by a cooled GaAs photomultiplier tube using conventional photon-counting electronics or by a liquid-nitrogen-cooled charge-coupled device (CCD) detector. Measurements at liquid-nitrogen temperature were performed with samples attached to the cold finger of an optical cryostat.

Figure 1 summarized the room-temperature Raman spectra of several SDG grown in our laboratory. Samples labeled RE1 and RE7 are both CdSe-doped glasses while RZ2 is a ZnSe-doped glass. For comparison we show also the Raman spectrum of the silicate base glass (labeled BG) without any doping. We notice that the base glass spectrum (a) shows four Raman peaks at 550, 620, 780, and 1085 cm^{-1} (all labeled G). These glass Raman peaks appear to some extent in all the other samples, although their intensities relative to the other Raman peaks vary with samples. In the spectra of the CdSe-doped samples RE1 and RE7, bulklike CdSe LO phonon and its overtones (labeled LO and 2LO, respectively) are observed around 210 and 420 cm^{-1}. In the spectrum of ZnSe-doped sample RZ2, the small peak at 265 cm^{-1} (labeled LO) can also be attributed to bulklike ZnSe LO mode although its frequency is slightly higher than that of bulk ZnSe LO phonon (at 250 cm^{-1}). This difference may be caused by confinement or strain in the nanocrystals since the intensity of this peak increases and its frequency decreases to 250 cm^{-1} with longer heat treatment time.
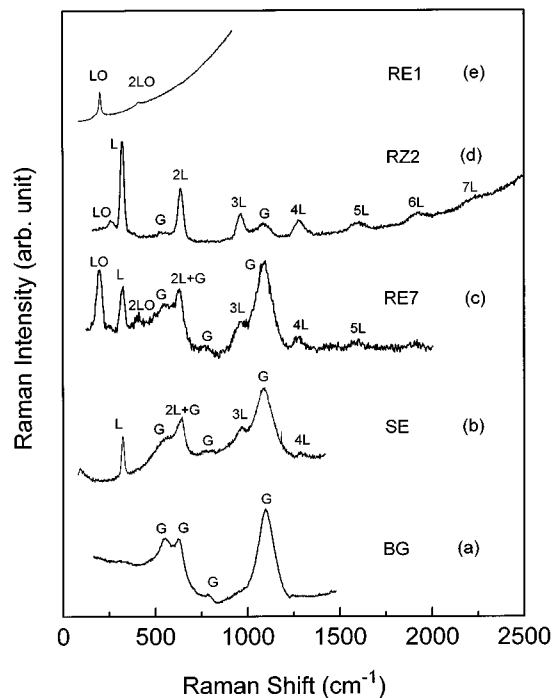
FIG. 1. Raman spectra excited with an Ar$^+$ laser at room temperature. The notations are: (a) BG: base glass; (b) SE: selenium-doped glass; (c) RE7 and (e) RE1: CdSe-doped glass; (d) RZ2: ZnSe-doped glass. The Raman peaks labeled G are due to the base glass. Those labeled LO are bulklike LO phonons of the SNC while L, 2L, ..., etc., denote the highly localized vibrational mode of Se$_2$ molecules and their overtones.

In addition to the above-mentioned Raman peaks, we find, unexpectedly, in the spectra of samples RE7 and RZ2 a series of sharp peaks with frequencies equal to 320 cm^{-1} and its multiples. We have confirmed that these peaks (labeled L, 2L,3L,..., etc.) are Raman modes by the fact that their frequencies relative to that of the excitation laser lines are constant and by the existence of corresponding anti-Stokes peaks. Their peak intensities are sample dependent. Heat treatment can greatly reduce their intensities or even completely eliminate them. This is reflected in the Raman spectrum of the CdSe-doped sample RE1 which is similar to sample RE7, but shows no signs of these peaks.

Since the main thing in common between the CdSe- and ZnSe-doped samples is that both contain a selenide, this prompted us to measure the Raman spectrum of a glass doped with selenium only (labeled Se in Fig. 1). Indeed we find that the 320 cm^{-1} mode and its harmonics (again labeled L, 2L, and 3L in the SE curve) appear now in addition to those of the base glass (peaks labeled G).

III. DISCUSSION OF RAMAN RESULTS

Since the peaks L, 2L, etc., appear only in glasses containing Se or a selenide, they must be caused by the presence of selenium or its compounds. It is highly unlikely that this mode is the result of segregation of selenium into crystals in the glass since the vibrational frequency of trigonal selenium crystal is quite different at 235 cm^{-1}. Also the Raman spectra of bulk Se crystal do not show as many overtones as the seventh harmonic as in RZ2. Similarly we found that the

Raman spectra of amorphous selenium, crystalline SiSe$_2$, and Si$_x$Se$_{1-x}$ glass[7,8] are quire different from the spectrum SE in Fig. 1. The strong multiphonon Raman scattering (MRS) of this unknown mode L, especially in the ZnSe sample RZ2 where overtones up to the seventh order can be observed, suggests that it is a highly localized vibrational mode with strong electron–phonon coupling. MRS is a well-documented phenomenon in materials with strong electron–phonon interactions, such as the polar II–VI semiconductors,[9,10] in impurity centers in crystals,[11] and in molecules. In particular, MRS has been reported in many alkali halide crystals containing negatively charged chalcogen molecules.[12–15] For example, Raman spectra of Se$_2^-$ molecules in alkali halides have been found to contain many overtones[12,13] of the vibrational mode of Se$_2^-$ molecules. The frequency of this mode depends on the host and varies from 322 cm^{-1} in KI to 349 cm^{-1} in KCl but is in the same range of frequency as the mode L we observed in our samples. In addition to forming diatomic molecules, selenium has been found to exist in alkali halides in other molecular forms. Their vibrational frequencies are, however, much lower than that of diatomic selenium. For instance, Se$_3^-$ has vibrational frequencies of 241 and 218 cm^{-1} in KCl and KI, respectively. Based on the similarity between the MRS spectra of the mode L and those of Se$_2^-$ in alkali halides reported in the literature, we propose that selenium is incorporated into samples RZ2, RE7, and SE in the form of diatomic molecules also. To our knowledge the existence of Se diatomic molecules in glasses has not been reported before.

Based on the above proposal we note that selenium molecules in SDGs are more stable than in alkali halides where they are metastable and can be destroyed at room temperature when exposed to light.[15] This difference may be due to a difference in their charge states. It is known that the bond strength or dissociation energy of selenium molecules in alkali halides depends on their charge state, decreasing monotonically from positively charged molecules to negatively charged ones. Our observation of such molecules in glasses at room temperatures and above suggests that they are probably neutral or positively charged in SDGs. There are a few reports in the literature on the vibrational spectra of neutral and positively charged selenium molecules in the gaseous state. Using photoemission spectroscopy Wang et al.[16] measured the vibrational frequencies of Se$_2^+$ and Se$_2$ to be 450 and 385 cm^{-1}, respectively. On the other hand, Yee and Barrow[17] found a frequency of 320 cm^{-1} in gaseous Se$_2$ using absorption and luminescence spectroscopy. Although the vibrational frequency of neutral Se$_2$ molecules seems to depend on experimental technique, the frequency and MRS nature of the 320 cm^{-1} mode we observed in SDGs are both consistent with those of neutral Se$_2$ molecules.

IV. PHOTOLUMINESCENCE RESULTS

Having established the possible existence of Se molecules in SDGs, we have investigated their contribution to the photoluminescence (PL) of these glasses. Fabian and Fischer[15] have performed detailed studies of the emission and excitation spectra of chalcogen molecules in alkali halides. Through PL excitation measurements they found that
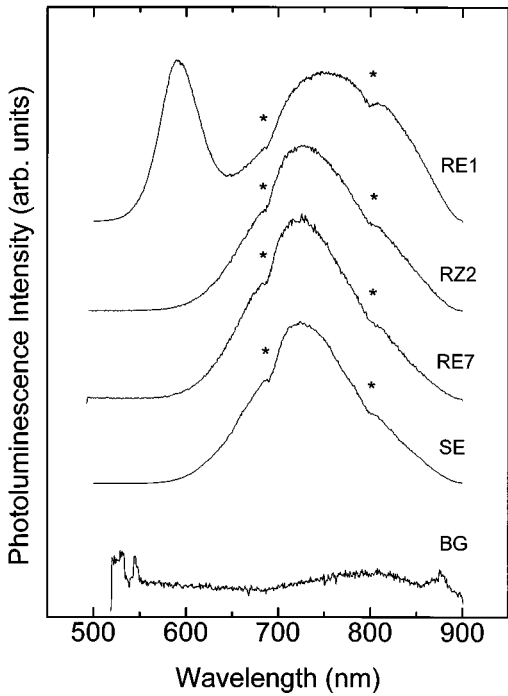
FIG. 2. Photoluminescence spectra excited with 514.5 nm line of an Ar⁺ laser at room temperature. The notations are same as in Fig. 1 BG: base glass; SE: selenium-doped glass; RE1, RE7: CdSe-doped glass; and RZ2: ZnSe-doped glass. Features marked by an asterisk are artifacts resulting from the detection system.

FIG. 3. Room-temperature photoluminescence of (a) CdS-doped glass excited with 441.6 nm He–Cd laser line, and (b) a Corning filter glass containing CdS_xSe_{1-x} nanocrystals excited with 514.5 nm Ar⁺ laser line.

the main absorption peak of Se_2^- molecules lies in the blue-green region and therefore could be excited efficiently with the outputs of an Ar⁺ laser. The PL peak of these molecules is Stokes shifted to the near infrared around 750–800 nm at liquid-nitrogen temperature. They found also that the luminescence peak position depended on the host crystal. It should be noted that these authors observed sharp vibronic features in their Se_2^- luminescence spectra at low temperatures, however, these features depend strongly on the host crystals, being very weak in RbCl.

Figure 2 shows the PL spectra of our selenium- and selenide-doped SDGs excited with an Ar⁺ laser at room temperature. For comparison a similarly obtained spectrum of the base glass is also shown. Minor structures in these spectra around 690 and 800 nm (marked by an asterisk) are artifacts of the detection system and should be ignored. Since ZnSe has a band gap around 2.8 eV, we have also used the 390 nm second harmonic of a femtosecond Ti:sapphire laser as the excitation source for the ZnSe-doped sample RZ2. We found essentially the same PL spectrum as that shown in Fig. 2. The important result to note in Fig. 2 is that the PL intensity from the base glass is negligibly small; however, once it is doped with selenium, a strong broad luminescence peak between 700 and 800 nm appears. The spectra for samples RE7 and RZ2 all show a very similar broad peak in their PL spectra. For sample RE1, in addition to this broad low-energy peak, there is also a sharper peak around 590 nm which can be attributed to band-gap luminescence by comparison with its absorption spectrum. On the other hand, the Raman spectrum of sample RE1 which shows the strongest
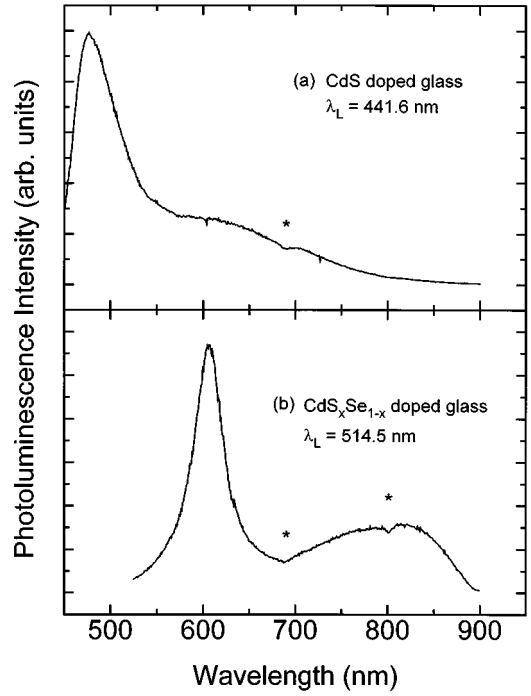
band-gap emission does not contain the Se_2 molecule peaks. This may be explained either by the small amount of SNCs present in the samples RE7 and RZ2 due to their dissociation into Se molecules or by an increase in trapping of photoexcited carriers and subsequent radiative recombination at the selenium molecules. If the latter explanation is correct then one can infer that these Se molecules while located in the glass have to be close enough to the nanocrystals to act as radiative recombination centers. This means that the Se molecules probably exist near the interface between SNCs and their glass host; however, further work is required to test this idea.

We have also measured the PL spectra of our samples at liquid-nitrogen temperature. We found that the line shape of the broad near-infrared peak remained essentially unchanged except for a red shift of about 20 nm in peak position.

To further test the idea that selenium may be responsible for the broad near-infrared luminescence peak, we measured the emission spectra of a CdS-doped glass and a commerical Corning glass filter containing CdS_xSe_{x-1} nanocrystals. In both cases their Raman spectra do not show any sign of the Se molecule vibrational peak at 320 cm⁻¹. It can be clearly seen from the PL spectra in Fig. 3 that the CdS-doped glass shows only bandgap luminescence around 470 nm, but no sign of any peak between 700 and 800 nm. On the other hand, the Corning glass which contains a selenide shows a weak near-infrared peak in addition to band-gap luminescence around 610 nm.

V. IMPLICATIONS OF OUR RESULTS

Our Raman and PL results strongly suggest that presence of selenium molecules in glasses that have been doped with
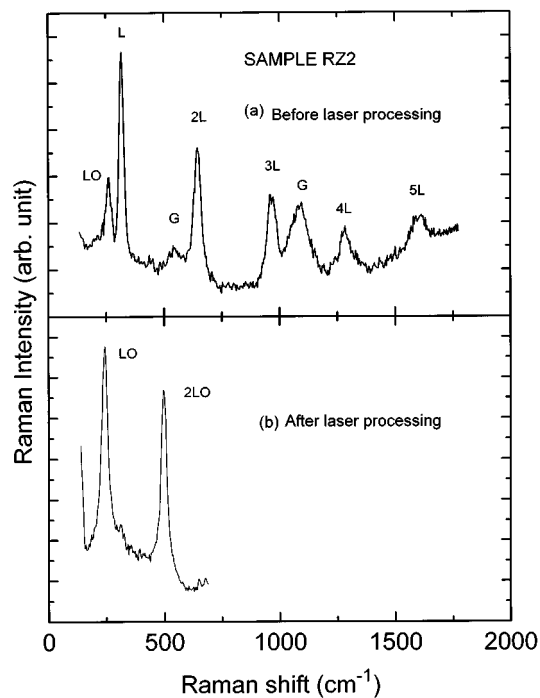
FIG. 4. Raman spectra of RZ2 excited with 457.9 nm line of an Ar⁺ laser at room temperature: (a) before laser processing and (b) after laser processing. Notice that before laser-induced heating the spectrum of the sample in (a) is dominated by scattering from selenium molecules. After laser annealing the sample in (b) shows only strong LO phonon peaks due to ZnSe. Changing the excitation wavelength shows that the Raman spectrum in this case is enhanced by resonance of the excitation photon with the band gap of ZnSe.

selenide-based semiconductors nanocrystals. This implies that during the initial stage of sample preparation when the selenide and the glass are comelted, some selenides dissociate with the formation of diatomic selenium molecules. In the heat treatment stage that follows, semiconductor nanocrystals are supposed to formed and grow in size. Some selenium molecules probably react with metal cations and contribute to the growth of nanocrystals; however, due to the duration and/or temperature of heat treatment, not all Se molecules are eliminated. This explains why in some samples, such as RE7, the amount of Se molecules is large enough to show up both in the Raman and PL spectra while in other samples, such as RE1, their concentration is too small to be observable in Raman scattering but still contributes to the PL spectrum. To test the effect of heat treatment on Se molecules we have focused an Ar⁺ laser beam on sample RZ2 with enough power to heat it up locally so that it melted within the laser focal spot. After this laser annealing process the Raman peak L from selenium molecules almost completely disappeared, while much stronger scattering from ZnSe LO phonon was observed. These annealed RZ2 samples also exhibit very strong resonance effect when excited by blue laser lines (see Fig. 4).

We note that quenching of the near-infrared emission peak by intense laser irradiation has been reported in CdSe-doped glasses by previous workers[5] and has been attributed to nonlinear effects such as saturation of deep traps by photoexcitation. Our results suggest that one should not neglect the effect of intense irradiation on the Se molecules which may be present in samples doped with selenides SNCs. This is especially important if the sample exhibits a strong near-infrared emission peak which may have sizable contribution from Se molecules.

VI. CONCLUSIONS

We have demonstrated the presence of selenium molecules in glasses doped with SNCs of CdSe and ZnSe via Raman scattering and photoluminescence. The amount of Se molecules in such SDGs depends on the way how they are prepared. Since these molecules are stronger emitters of radiation in the near-infrared than Raman scatterers, their presence can be observed via Raman spectra only when their concentration is high. However, it is likely that they are present to some extent in these glasses always since we have found evidence of the near-infrared emission peak around 700–800 nm in nearly all glasses doped with a selenide semiconductor. Due to their strong absorption of blue and green radiation and annealing by the intense radiation, we conclude that the role of selenium molecules on the linear and nonlinear optical properties of selenide-doped glasses cannot be overlooked.

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