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Optical and luminescence properties of Sm^{3+}-doped cadmium–aluminum–silicate glasses

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Sm^{3+}-doped cadmium–aluminum–silicate glasses ($CdO–Al_2O_3–SiO_2$) have been fabricated and characterized optically. Intense visible lights and near-infrared emissions were observed under ultraviolet light and 488 nm laser excitation. The density, refractive index, optical absorption, Judd–Ofelt parameters, and spontaneous transition probabilities have been measured and calculated. Intense fluorescences at 1.2 and 1.29 μm wavelengths were observed, indicating that the glasses are promising materials for laser and optical amplifier applications operating in the 1.2–1.3 μm low-loss window of telecommunication fiber.
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Rare-earth ion-doped glasses have received much attention because of their potential applications in visible and infrared optical lasers and amplifiers.[1–4] Recently, much research has focused on Pr^{3+}-, Tm^{3+}-, and Er^{3+}-doped glasses, because these glasses can be used in the visible spectral region and around 1.31, 1.46, and 1.53 μm low-loss windows of telecommunication fiber.[5–8] Sm^{3+}-doped glasses for optical lasers and amplifiers operating in the 1.2–1.3-μm-wavelength region have not been studied in detail. There are only a few investigations about the electronic structures and spectroscopic parameters of Sm^{3+} in crystals and glasses.[9–12]

Glass host material is a very important factor for developing rare-earth-doped optical devices. Up to now, research efforts have concentrated on fluoride glass systems because of their lower phonon energies compared to silicate glasses. On the other hand, oxide glasses are more suitable for practical applications due to their high chemical durabilities and thermal stabilities. In oxide glasses, silicate glasses are one of the most popular glass hosts for making optical fiber lasers and amplifiers. In particular, heavy-metal silicate glasses possess lower phonon energies than other silicate glasses, and it can be expected that intense visible and near-infrared fluorescence of Sm^{3+} rare-earth ions could be observed in them. Recently, efficient green upconversion and $\sim$1.53 μm emission have been observed in Er^{3+}-doped heavy-metal silicate ($Na_2O \cdot Cd_3Al_2Si_3O_{12}$) glasses.[13]

In this letter, the optical and luminescence properties of Sm^{3+}-doped cadmium–aluminum–silicate ($CdO–Al_2O_3–SiO_2$) glasses are reported. The optical absorption, and the visible and near-infrared fluorescence properties of these glasses were investigated. Judd–Ofelt intensity parameters Ω_t ($t=2,4,6$) were determined, and the spontaneous emission probabilities for various transitions were predicted using the Judd–Ofelt theory.[14,15] Our results indicate that these glasses are suitable materials for developing visible and infrared fiber lasers and amplifiers.

Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses were prepared from cadmium-oxide (CdO), aluminum-oxide (Al_2O_3), silicon-oxide (SiO_2), and samarium-oxide (Sm_2O_3) powders according to the formula $(Cd_{1-x}Sm_x)_3Al_2(Si_{1-x}Al_x)_3O_{12}$. In this work $x=0.01$, and all powders were obtained from Strem Chemical Company (99.5%–99.999% purity). The well-mixed raw materials were first heated for several hours in an Al_2O_3 crucible at 900 °C using an electric furnace, and then a higher melting temperature of $\sim$1280 °C was used. The glasses were subsequently annealed at lower temperatures and then sliced and polished to dimensions of $10\times10\times0.8$ mm^3. The density of the sample was measured to be 4.39 g/cm^3. Hence, the calculated number density of Sm^{3+} ions in the glasses is 1.19×10^{20}/cm^3. Refractive index n of the $CdO–Al_2O_3–SiO_2$ glasses was measured using three wavelengths, and $n=1.7223$, 1.7104, and 1.7059 at $\lambda=486.1$, 589.3, and 656.3 nm, respectively. The refractive indices of the sample at all other wavelengths can be calculated using the Cauchy's equation $n=A+B/\lambda^2$, with $A=1.6858$ and $B=8624$ nm^2.

The Raman spectrum of $CdO–Al_2O_3–SiO_2$ glasses was measured using a Bio-Rid FT Raman spectrophotometer. It was deconvoluted into four bands, and the peaks are at 266, 360, 653, and 745 cm^{-1}, which can be attributed to the different linkages in the glasses. The maximum phonon energy of the glasses is 745 cm^{-1}, and this value is among the lowest in oxide glasses.

The absorption spectrum was obtained using an UV-360 spectrophotometer. The visible fluorescence spectra were measured using a Hitachi MPF-4 spectrophotometer

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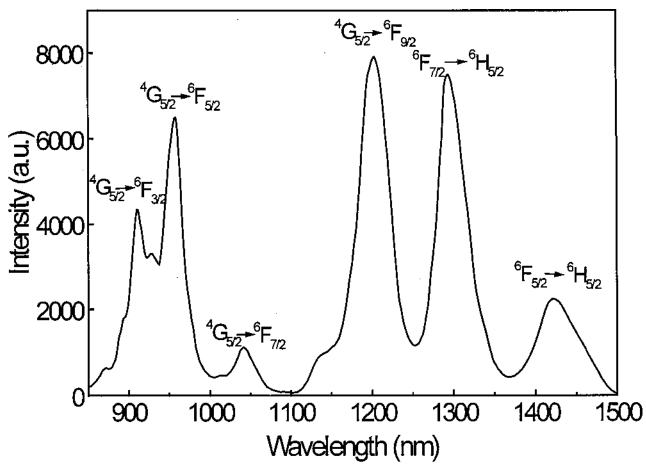

FIG. 1. Absorption spectrum of Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses.

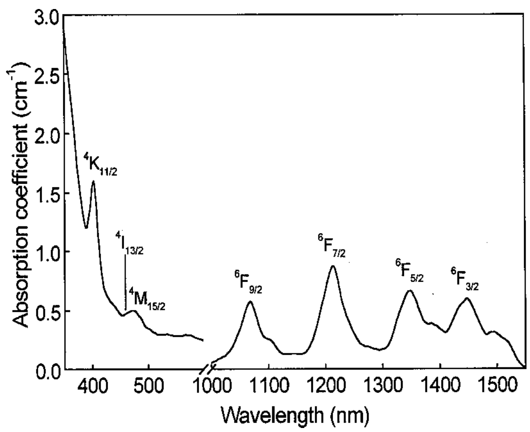

FIG. 2. Visible fluorescence spectrum of Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses under 361 nm excitation.

equipped with a 75 W xenon lamp source. The near-infrared fluorescence spectrum was recorded using a Spex-1269 monochromator with a liquid-nitrogen-cooled germanium detector, and the excitation source was the 488 nm light beam from an argon laser. All the spectra were measured at room temperature.

Figure 1 shows the absorption spectrum of Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses. The band assignments are also indicated in Fig. 1 The radiative transition within the $4f^n$ configuration of a rare-earth ion can be analyzed using the Judd–Ofelt approach.[16–19] Judd–Ofelt intensity parameters Ω_t can be derived from the electric-dipole contributions of the experimental oscillator strengths using a least-square-fitting approach. Since it is not appropriate to consider high-energy levels of Sm^{3+} in this calculation,[10] Ω_t are derived from absorption bands in the low-energy region. The matrix elements given in Ref. 16 are used in the calculation. The measured and calculated oscillator strengths of Sm^{3+} in $CdO–Al_2O_3–SiO_2$ glasses are shown in Table I. The calculated root-mean-square deviation $\delta_{\rm rms}$ (Ref. 13) between the measured and calculated oscillator strengths is 1.68×10^{-7}.

Ω_t are important for investigating the local structure and bonding in the vicinity of rare-earth ions. Parameter Ω_2 is associated with the symmetry of the ligand field in the rare-earth site, and Ω_6 is an indicator of the covalency of the Sm–O bond.[9,10] The values of Ω_2, Ω_4, and Ω_6 are 6.56, 5.14, and 4.08×10^{20} cm^2, respectively. Ω_2 of $CdO–Al_2O_3–SiO_2$ glasses is larger than those of fluorozincate glasses,[17] oxyfluoroborate glasses,[18] lead fluoroborate glasses, and lead borate glasses,[9,10] and is close to those of germanate glasses and borate glasses.[19] These behaviors suggest that the symmetry of the site occupied by Sm^{3+} in $CdO–Al_2O_3–SiO_2$ glasses is lower than those in fluorzincate, oxyfluoroborate, lead fluoroborate, and lead borate

TABLE I. Experimental and calculated oscillator strengths of Sm^{3+} in $CdO–Al_2O_3–SiO_2$ glasses.

Absorption	Energy (cm^{-1})	$P_{\rm exp}$ (10^{-6})	$P_{\rm calc}$ (10^{-6})
${}^6H_{5/2}\rightarrow{}^6F_{3/2}$	6906	1.190	1.197
${}^6H_{5/2}\rightarrow{}^6F_{5/2}$	7418	1.348	1.309
${}^6H_{5/2}\rightarrow{}^6F_{7/2}$	8237	2.065	2.158
${}^6H_{5/2}\rightarrow{}^6F_{9/2}$	9363	1.603	1.469

glasses, indicating higher mixing of the opposite parity electronic configurations, which are responsible for the spectral intensities. In addition, Ω_6 is the largest in $CdO–Al_2O_3–SiO_2$ glasses, showing that the Sm–O bond is more covalent in these glasses than in other glasses.

Some important radiative properties can be calculated using the values of Ω_t, such as spontaneous transition probabilities, branching ratios, and lifetimes of the optical transitions in Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses.[12] The branching ratios for the transitions ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$, ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$, and ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ are 5.6%, 35.8%, and 37.6%, respectively. Thus, intense visible emissions can be expected in $CdO–Al_2O_3–SiO_2$ glasses. In addition, the branching ratio for the transition ${}^4G_{5/2}\rightarrow{}^6F_{9/2}$ is 0.7%, and is much higher than those in borosulphate glasses (0.2%) and lead borate glasses (0.4%),[10,12] therefore, efficient 1203 nm emission can be obtained. Moreover, the spontaneous transition probability of the ${}^6F_{7/2}\rightarrow{}^6H_{5/2}$ transition (1293 nm emission) is 462 s^{-1}, and is even higher than those of ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ and ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ transitions. Thus, efficient near-infrared emissions in the glasses under suitable excitation condition can be expected.

Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses emit intense orange-red light under UV excitation. The fluorescence spectrum in the visible spectral region is shown in Fig. 2. It consists of three emission band peaks at 566, 601, and 649 nm, respectively, attributing to the ${}^4G_{5/2}\rightarrow{}^6H_J$ ($J=5/2$, 7/2, 9/2) transitions. The full widths at half maximum for the three emissions are 12.1, 16.5, and 17.5 nm, respectively. The most intensive emission is the ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition. Potential green, yellow, and red lasers operating at 566, 601, and 649 nm based upon Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses are desirable in high-density optical storage, undersea communications, color displays, and medical diagnostics.

The near-infrared fluorescence spectrum of Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses under 488 nm laser excitation is shown in Fig. 3. Intense emission bands with peak values at 911, 958, 1203, 1293, and 1423 nm were observed, corresponding to the ${}^4G_{5/2}\rightarrow{}^6F_{3/2}$, ${}^4G_{5/2}\rightarrow{}^6F_{5/2}$, ${}^4G_{5/2}\rightarrow{}^6F_{9/2}$, ${}^6F_{7/2}\rightarrow{}^6H_{5/2}$, and ${}^6F_{5/2}\rightarrow{}^6H_{5/2}$ transitions, respectively. The 1203 and 1293 nm emission bands are the strongest and the

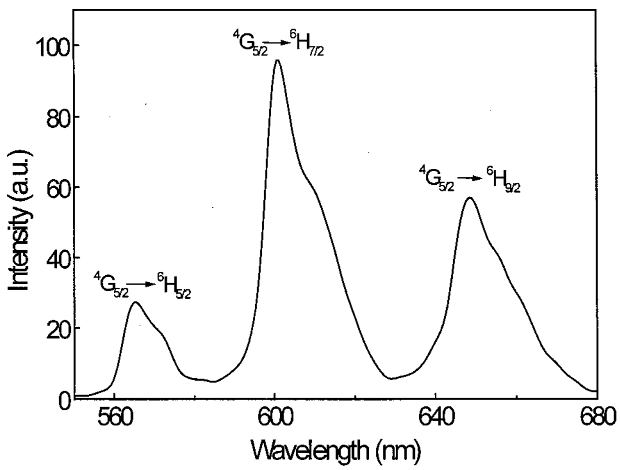

FIG. 3. Near-infrared fluorescence spectrum of Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses under 488 nm laser excitation.

full widths at half maximum are 44.8 and 42.8 nm, respectively.

The $^6F_{7/2} \rightarrow {}^6H_{5/2}$ emission (1293 nm) of Sm^{3+}, which is difficult to observe in fluorozincate glasses,[17] is even stronger than the $^4G_{5/2} \rightarrow {}^6F_{5/2}$ emission in $CdO–Al_2O_3–SiO_2$ glasses. It can be attributed to the energy transfer process between Sm^{3+} ions, as shown in Fig. 4. The pump laser excites electrons from the ground state to the $^4I_{9/2}$ excited state. The excited electrons then relax to the lower level by a nonradiative process, and finally populate the $^4G_{5/2}$ level. When the $^4G_{5/2}$ level is populated, the possible cross-relaxation processes $^4G_{5/2}$, $^6H_{5/2} \rightarrow {}^6F_{9/2}$, $^6F_{7/2}$ may occur, and the population distribution in the $^6F_{7/2}$ level becomes large, resulting in intense $^6F_{7/2} \rightarrow {}^6H_{5/2}$ emission.

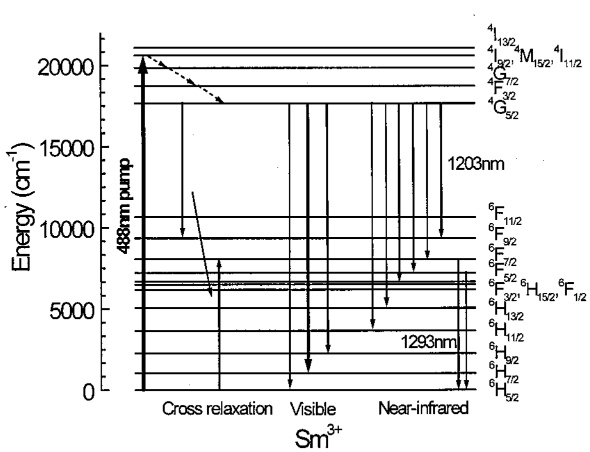

FIG. 4. Schematic diagram showing the mechanisms for fluorescence and cross-relaxation processes of Sm^{3+} ions in $CdO–Al_2O_3–SiO_2$ glasses. The width of the line indicates the intensity of the transition.

The intense 1.203 and 1.293 μm emissions are at the low-loss windows of single-mode fibers.[20] Lasers and amplifiers are being developed adopting the rare-earth ions Pr^{3+}, Tm^{3+}, and Er^{3+}, operating around 1.31, 1.46, and 1.53 μm, respectively. The 1.2–1.3-μm-wavelength region is ignored because of a lack of suitable optical materials. Intense infrared fluorescence in Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glass indicates that the 1.2–1.3 μm spectral regions can also be used in optical communication.

In conclusion, Sm^{3+}-doped $CdO–Al_2O_3–SiO_2$ glasses have been fabricated and characterized optically. The Judd–Ofelt intensity parameters, radiative rates, branching ratios, and fluorescence lifetimes were calculated. Intense visible and infrared fluorescences from Sm^{3+} ions in the glasses were observed at room temperature, indicating that the glasses are promising materials for developing visible and infrared lasers and optical amplifiers, especially for operation in the 1.2–1.3 μm low-loss window region of telecommunication fibers.

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