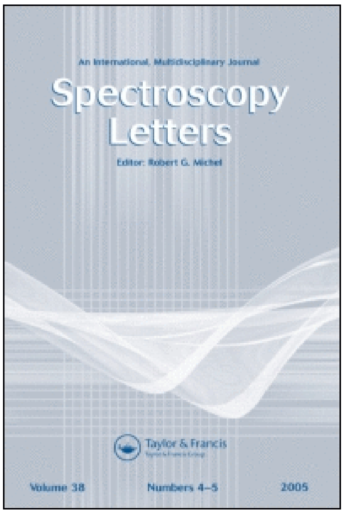

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THE EFFECT OF TEMPERATURE AND EXCITATION ON THE SINGLE- AND TWO-PHOTON EXCITED EMISSION SPECTRUM OF CURIUM IN A GLASS MATRIX*

Key words: Two-Photon Spectroscopy, Curium Emission Spectroscopy, Curium-Doped Glasses

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ABSTRACT

Single and two-photon excited emission has been observed from a curium-doped borosilicate glass matrix at both room and liquid nitrogen temperatures. The

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emission spectrum was measured using several different excitation energies and intensities. In addition to the expected line narrowing, variations in the ratios of emission intensities between states, and between crystal field levels within the each state were observed with cooling. Slight variations in the emission spectrum also arose as a function of the excitation intensity. These variations in the Cm ion's emission spectrum as a function of experimental parameters are presented and discussed.

INTRODUCTION

Variations of the environment of a sample and/or in the conditions of the optical measurements can give rise to interesting changes in the optical spectroscopy of the sample. Such spectral changes can be informative with regard to understanding the chemical nature of the material. A number of variations can be investigated, which can include physical conditions like temperature,[1] pressure,[2] or crystal field of the emitting ion.[3] The variable parameters may be of spectroscopic significance such as the excitation wavelength,[4] the excitation power,[5] or the polarization of the exciting or emitted light.[6] Changes in these parameters can produce spectroscopic differences which may give insight into the particular nature of the sample.

The samples employed in these investigations consisted of a borosilicate glass matrix similar to that used for the disposal of radioactive wastes. Studies of glasses doped with radioactive elements are of both technological and fundamental interest. One aspect is to understand the stability of the doped glass with regard to the chemistry and physical characteristics of the included radioactive species. The chemical form of the radioactive species can have major effects on the physical properties of the glass (e.g. strength and degradation rate) as well as the behavior of the material which have been doped into the glass host (e.g. leachability).

In this study the main goal was to examine the spectroscopic properties of Cm^{3+} ions in a borosilicate matrix with an emphasis placed on emission spectroscopy. We observed both single and two-photon excited emission from the Cm^{3+} ion that had been included in the glass matrix. These investigations were performed at both room temperature and at 77K (immersion of the sample in liquid nitrogen). The excitation wavelength and intensity were also varied to aid in the interpretation of the emission spectrum of glass sample.

EXPERIMENTAL METHODS

The glass sample was based on a lead borosilicate formulation containing 10 wt % La_2O_3. This formulation has been used as a base material for studies of lanthanide and actinide elements since the additional lanthanum maintains a more nearly uniform *f*-element content upon the addition of 1-5 wt % of other *f*-elements.

Curium was added (1-5 wt %) as it's oxide to a fine powder of the borosilicate matrix material and mixed by mechanical grinding. The sample was then heated to a molten state in a platinum boat for 3 hours at 1450°C. When dissolution was complete, the material was cooled to room temperature and a small portion of the sample placed in a sealed quartz capillary which was then enclosed within a glass sample cell for the optical studies.

Both single and two-photon excitation were accomplished using a six-Watt argon ion laser (Coherent Radiation, model number: Innova 300). The laser was focused onto the sample in a Raman macrosample chamber. Cooling of the samples was accomplished by immersion in liquid nitrogen in an optically transparent Dewar centered in the sample chamber. The emitted light was collected at 90° from the incident laser light and focused on the entrance slit of the monochromator. The double-meter monochromator (Jobin Yvon/Instruments SA, model number: Ramanor HG.2S spectrophotometer) has a resolution of 0.5 cm^{-1} at 514.5 nm. The light from sample was dispersed by the monochromator and then detected by a photon counting system. This detection system consisted of a cooled photomultiplier tube (Hamamatsu, model number: R636) and multichannel analyzer (Nicolet, model number: 1170) interfaced with a personal computer using "Spectra Calc" software (Galactic Industries, version 2.12).

RESULTS AND DISCUSSION

The emission spectrum of the Cm^{3+} ion is well known,[7,8] as are the energy levels from which the emission arises. The large gap between the ground state and the excited states of Cm^{3+} makes interpretation of the Cm^{3+} ion's emission spectrum straight forward. The accepted energy levels[7,8] associated with Cm^{3+} are shown in Figure 1 together with the energies of the four laser excitation lines used in this investigation. Transitions originating from the three lowest excited states are frequently observed by single-photon excited emission spectroscopy using argon-ion laser sources. Emission maxima corresponding to transitions between many of the higher energy levels of Cm^{3+} can be observed via two-photon excited emission spectroscopy.

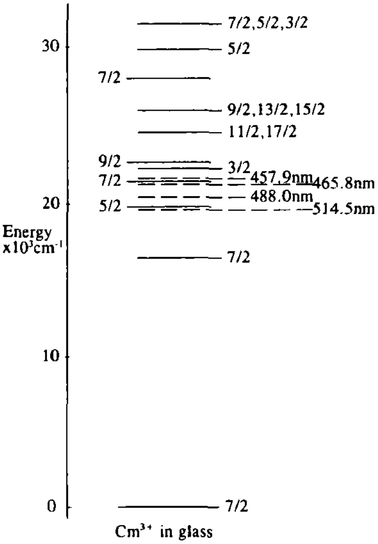

Figure 1. The energy levels of Cm^{3+} in glass and the laser wavelengths used in this investigation.

Temperature Variations

Increasing or decreasing a sample's temperature during collection of it's emission spectrum may affect it's emission spectrum. A decrease in temperature will narrow emission bands by reducing the probability of vibrational levels influencing the spectrum. In atoms with lower-energy excited states, a decrease in temperature can also reduce the thermally-induced population of these states. Such a temperature change can also increase or decrease the rate at which an excited atom can non-radiatively de-excite (i.e. lifetimes) of individual states. Based on a nephelauxetic effect, a shift in the energy of the emission features is expected with variations in temperature.

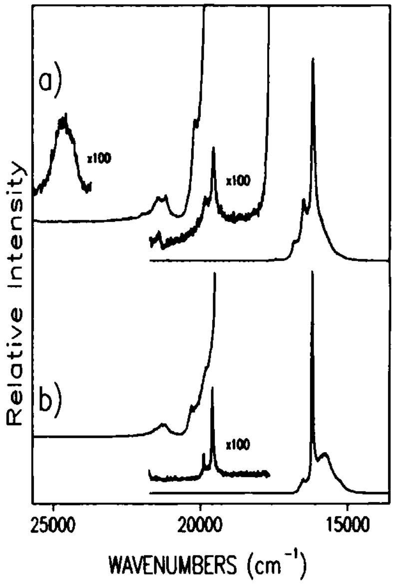

Figure 2. Single- (left, 514nm exc.) and two-photon (right, 457nm exc.) excited emission spectrum of Cm^{3+} in borosilicate glass at room temperature (a) and 77K (b).

In these investigations a sample of Cm-doped borosilicate glass was studied at both room temperature and at 77K. The emission spectra from the sample at these temperatures are shown in Figure 2. One effect of lowering the temperature was the decrease in the emission from higher-energy bands in favor of the emission from lower energy states. In the single-photon excited emission, this is most obvious as an absence of the transition originating in the second $J=7/2$ state, which is found in the spectrum collected at room temperature at 21400 cm^{-1}. Similarly, the two-photon excited emission also shows a analogous disappearance of the emission band found at an energy of 24300 cm^{-1}, which originates from overlapping states, which include $J=11/2$ and $J=17/2$.

A decrease in the overall intensity of the two-photon excited emission, when compared to the single-photon excited emission, was also observed when the sample was studied at 77K. This enhancement of the lower energy transitions probably results from an increase in the luminescence lifetimes of the various levels due to cooling of the material. This increase allows the excited curium atom more time to non-radiatively de-excite to a lower energy level, which increases the probability that emission will be seen from a lower level.

A similar observation can be made regarding the crystal-field levels making up the states from which the transitions arise. At room temperature, four peaks are readily apparent in the feature found at 17000 cm^{-1}, which are comprised of transitions originating in the lowest J=7/2 excited state. The crystal-field splitting of the J=7/2 ground state is assumed to be negligible; therefore, four peaks arise from the four levels associated with the J=7/2 excited state. When the emission spectrum is observed at 77K, only two of these peaks are readily identifiable, while a third is just visible. This is also the case for the feature seen at 19750 cm^{-1}, which originates from the J=5/2 state. At room temperature, the higher-energy peak is about half the intensity of the lower-energy peak. At 77K, the former decreases to one-fourth the height of the stronger transition. This phenomena is believed to arise from similarly enhanced non-radiative de-excitation as discussed above. This results in an increased probability that higher-energy levels within a state will non-radiatively de-excite to lower levels within the state prior to emission.

Also evident in Figure 2, is the expected line narrowing. This is best seen as increased resolution of the single-photon excited transition originating from the J=5/2 state (19750 cm^{-1}). It is also evident by the narrowing of the feature found at about 17000 cm^{-1}, which results from transitions from the first J=7/2 excited state to the 7/2 ground state. In the two-photon excited emission, line narrowing is not as obvious. An apparent loss of resolution is observed in the emission arising from the second J=7/2 state at 21400 cm^{-1}. This decreased resolution is thought to result from the diminished emission intensity from the two-photon excited states. First, a loss of intensity may bury the spectrum in instrumental "noise", lowering the resolution of the feature. Secondly, if the high-energy peak of the pair making up this transition looses intensity, as compared to the more intense peak, it may become lost in the background of the larger transition (similar to transitions in the single-photon spectra).

Temperature-induced shifting of the energies of the emission features is also expected. The position of the main peak in the emission feature corresponding to transitions from the lowest J=7/2 state shifts over 30 cm^{-1} (from 16177 cm^{-1} to 16203 cm^{-1}). The dominant feature in group associated with transitions from the J=5/2 state shifts similarly, from an energy of 19548 to 19581 cm^{-1}. The less-intense emission feature shifts from 19858 to 19871 cm^{-1}, a shift of about 13 cm^{-1}. These shifts result from an increase in the crystal field effect on the emitting ion caused by the thermal contraction of the cooled matrix.

A final effect of cooling is seen in the broad emission observed at slightly lower energy than the lowest energy feature attributable to Cm^{3+}. This band may result from defect sites within the glass matrix. The defect sites giving rise to this emission are likely formed by ionizing radiation given off by the curium atoms within the matrix.[9,10]

Wavelength of Excitation

Our investigations of the variation of excitation wavelength were confined to single-photon excited emission studies. This is due to the absence of two-photon excited emission for all excitation wavelengths except at 514.5 nm. This observation is important in the implications for the system; these include the need for a nearly resonant absorption transition, as well as high excitation intensity for the observance of two-photon excited emission.

The two major excitation energies available from an argon-ion laser, at 514.5 and 488.0 nm, are available at greater than a watt of power in our system. However, if the energy levels of the Cm^{3+} ion are considered (see Figure 1), only the energy of the 514.5 nm line corresponds to an excited level ($J=5/2$). The energy from the 488 nm line falls between levels of the Cm^{3+} ion and must be absorbed through a phonon assisted or another nonresonant route.

Considering the other two laser lines, at 457.9 and 465.8 nm, both fall near/resonant to the second $J=7/2$ excited state of Cm^{3+}. However, two-photon excitation is not observed with these lines, which may be due to insufficient power (only 500mW at 457.9 nm and 100mW at 465.8 nm were available). A second possibility is that the lifetime of the $J=7/2$ state is shorter than that of the $J=5/2$ state, which allows de-excitation preceding the absorption of the second photon. It is of interest to note that two-photon emission from $CmBr_3$ has been observed using these weaker laser lines.[1]

In the single-photon excited emission, very little difference was observed in the Cm^{3+} emission spectrum with variation of the in the excitation wavelength. The emission from the first J=7/2 state, when excited with the four laser lines, is shown in Figure 3. Included in Figure 3 are the graphs of the emission features arising from the J=5/2 state, when excited using the 457.9 nm and 465.8 nm laser lines.

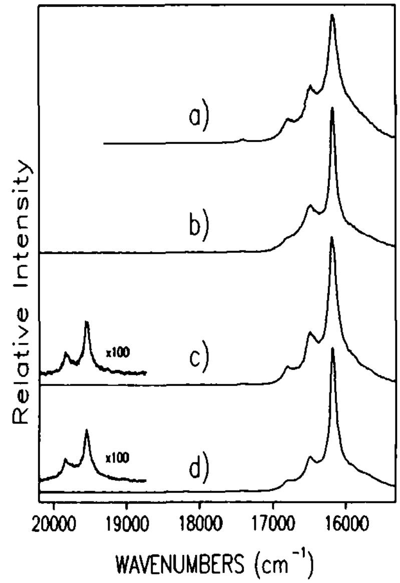

Figure 3. Single-photon excited emission from Cm^{3+} in borosilicate glass when excited by 514.5nm (a), 488.0nm (b), 465.8nm (c), and 457.9nm (d) light.

The only variation noted is the decrease in the apparent resolution of the emission features when the sample is excited using the 488.0 nm laser line. This is opposite to the expected increase due to increased laser power, and to the corresponding decrease in the instrument's slit widths. The decrease in resolution probably results from the vibronic mechanism for the absorption of the 488.0 nm laser line. Since the 488.0 nm line is not nearly resonant with the Cm^{3+} absorption maxima, it is likely absorbed via a phonon assisted route. If this hypothesis is correct, the different excitation lines can be qualitatively listed in order of resonance. Thus the 488.0 nm line is the least resonant, followed by the 457.9 nm line, the 465.8 nm line, and the 514.5 nm line which has the highest resolution and would be assigned the most nearly resonant excitation energy.

Intensity of Excitation

The emission originating in the lowest J = 7/2 excited state, excited by the 514.5 nm laser line was chosen the study the effect of changes in the intensity of the excitation light on the emission of Cm^{3+} in the borosilicate glass. The emission spectra are shown in Figure 4.

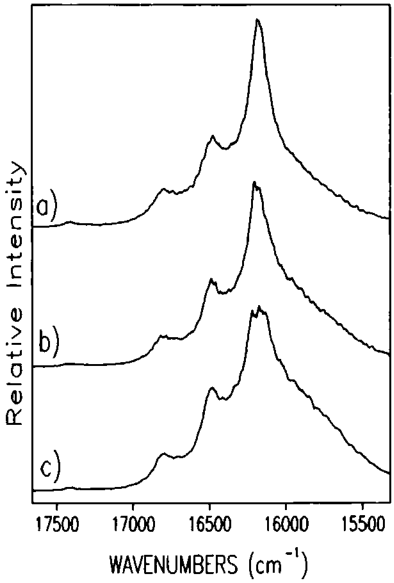

Figure 4. Emission from Cm^{3+} when excited at 514.5nm at 500 mW (a), 10 mW (b) and 2.5 mW (c).

The greatest variations as seen in emission spectrum of the Cm^{3+} ion in this glass matrix are: the breadth of the transitions; and the increased intensity of the shoulder at 16000 cm^{-1}. The increase in the width of the transitions results from increased instrumental slit width at lower excitation powers which was required to observe the less intense emission. The increase in the shoulder's intensity is probably a result of the formation of defect centers within the glass. Such centers may be produced by either nuclear or electromagnetic radiation.[9,10] Thus the radioactive decay of the Cm^{3+} ions or the high intensity of our laser excitation could result in defect sites.

CONCLUSION

Sample temperature, excitation energy, and excitation intensities all affected the emission spectrum recorded from Cm^{3+} ions residing in the lead borosilicate glass matrix. The effects of these parameters vary in nature and strength depending on different factors. A lower temperature narrows and shifts the emission bands, while decreasing intensities of transitions from higher-energy excited levels. This decrease is seen both between and within emission manifolds. Variations of emission due to changing excitation wavelength are small and appear to depend primarily upon the quality of the resonance of the laser line with the absorption bands of the Cm^{3+} ion.

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