

[For publication in J. Nuclear Science and Technology, as the proceedings of "Actinides 2001, held in Hayama, Japan, November 4-9, 2001"]

Spectral Properties of Americium(III) in Silicate Matrices: Concentration-Dependent Up-conversion Emission*

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[*Sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, BES, US Dept. of Energy, under contract DE-AC05-00OR22725 with ORNL, managed & operated by UT-Battelle, LLC]

Spectral Properties of Americium(III) in Silicate Matrices: Concentration-dependent Up-conversion Emission.

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We have been pursuing the spectroscopic properties of actinide ions in silicate matrices. One facet of these studies involves the behavior of Stokes and anti-Stokes emissions exhibited by Am³⁺ in these hosts. Several attributes have been found to influence the spectral profile, which include excitation wavelength, laser power, and dopant-concentration. Excitation with the 514.5 nm (19435 cm⁻¹) line of argon laser provides anti-Stokes emissions at 21100 and -19920 cm⁻¹ in the boro-silicate matrices. This up-conversion was found to proceed through a multi-photon scheme, and its' efficiency increases with increased dopant concentration. Based on our concentration-dependent studies, the up-conversion is suggested to involve a cross-relaxation process [⁵D₁, ⁷F₀] (⁷F₆, ⁷F₂) between neighboring americium ions.

Keywords: *americium, up-conversion, concentration-dependent, spectroscopy, emission*

I. Introduction

Luminescence studies involving f-elements in glassy matrices has attracted interest due to the implication to solid-state laser and related optical applications^{1,2}. In addition, borosilicate glasses are also known to have significant technological application in nuclear waste disposal and storage schemes.³

Studies involving energy up-conversion processes are of fundamental interest. The up-conversion phenomenon is usually displayed in the form of an anti-Stokes emission, and requires the absorption of two or more low-energy photons to produce a higher energy luminescent excitation. One motivation for pursuing these studies involves development of IR-to-visible converting phosphors⁴. The overall process may involve one active center, or proceed cooperatively among multiple ions. Several mechanisms are proposed, but a common factor is the requirement for long-lived intermediate level⁵. Hence, f-element species are suitable for these studies, as f-f transitions frequently involve several closely spaced electronic levels. One or more of these states could act as the intermediate level.

While most of the lanthanide species are known⁶ to display energy up-conversion in different matrices, examples involving actinide systems are limited. Among the transuranium elements, curium has been investigated the most. It showed up-converted emission in the tri-halides^{7,8}, when doped in CsCdBr₃⁹, and in borosilicate glasses¹⁰. Californium has also shown¹¹ similar property when doped in LuCl₃.

The focus of this paper is on Am³⁺ incorporated in selected silicate matrices. Am³⁺ has a well established

system of electronic levels, which could exhibit multi-photon events, although none have been reported to date. We present here our investigation of energy up-conversion process of Am³⁺ doped in a borosilicate glass. To our knowledge, this is one of the first examples of up-conversion emission that has been reported for americium(III).

II. Experimental

The glass sample used in this study has a composition, expressed as mole percentages, of SiO₂ (50 %), B₂O₃ (18%), Na₂O (24%), CaO (3%). After grinding thoroughly, the solid mixture was melted until a complete dissolution was attained (-850 °C). The molten material was then cooled slowly to room temperature to yield a clear glass. Americium was introduced into this material by remelting the glass together with AmO₂ using a hot platinum arc, a technique developed in our laboratory for preparing small quantities radioactive species in matrices.

The spectroscopic investigations were conducted using an argon-ion laser (Coherent Models 306 and 90) as the excitation source. The initial spectroscopic studies were conducted with a double meter spectrophotometer (Model HG.2S, Jobin-Yvon/Instrument SA), which has a resolution of 0.5 cm⁻¹ at 514.5 nm. Emission from the samples was detected by a photon counting system, which employed a photomultiplier tube (Hamamatsu R636) and a multichannel analyzer (Nicolet 1170) interfaced with a personal computer. Data analyses was conducted with a Grams 32 Software (Galactic, version 5.1). Additional optical studies were conducted using Instrument SA's optical system that consists of a monochromator (model 1000M) attached with

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a CCD, PMT and IR detectors and a 400 W Xe lamp. A microscope is also attached to the system via fiber optics setup. For absorption work, the white light from the Xe lamp was delivered into the microscope with fiber-optics. The sample was placed in a square tube of quartz glass (in-house-designed).

III. Results and Discussion

Spectroscopic studies involving Am^{3+} in glass matrices are limited. When doped in fluorozirconate glasses, Am^{3+} was found to display four emission maxima upon excitation to the $^5\text{D}_2$ state³⁴. The photo-luminescence spectra of Am^{3+} in borosilicate glasses is shown in Figure 1. The 457

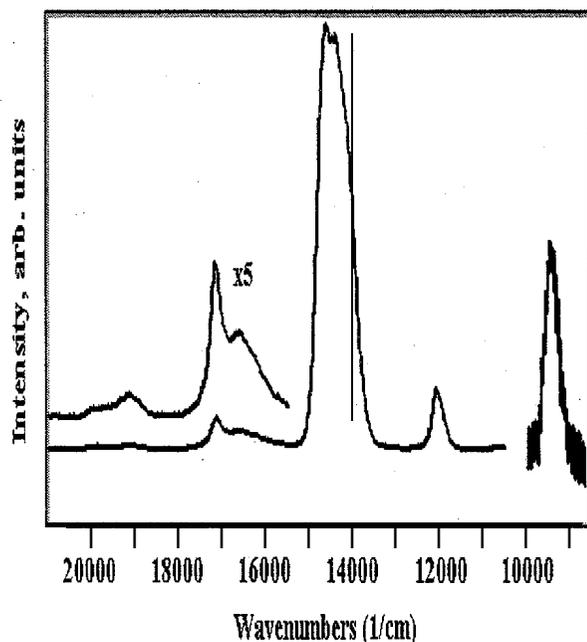


Fig. 1 Emission spectra of Am^{3+} in boro-silicate glass for excitation with 457 nm argon laser line.

nm laser line, which is in near resonance with the $^5\text{D}_2$ excited-state, was used in these excitations. The Am^{3+} spectra consist of a series of five emission bands that originate from two different excited states. The first of these features is observed at -19100 cm^{-1} and corresponds to the $^5\text{L}_6 \rightarrow ^7\text{F}_0$ transition. A weak shoulder appears at the high energy side of this band.

The second emission maximum is a combination of a sharp band overlaying a weak, broad feature. The sharp band centers at -17100 cm^{-1} and corresponds to the $^5\text{D}_1 \rightarrow ^7\text{F}_0$ transition, while the weaker broad shoulder at -16500 cm^{-1} corresponds to the $^5\text{L}_6 \rightarrow ^7\text{F}_1$ transition. The most intense band at -14600 cm^{-1} is accompanied by a broad shoulder at -14300 cm^{-1} . This region is known to consist

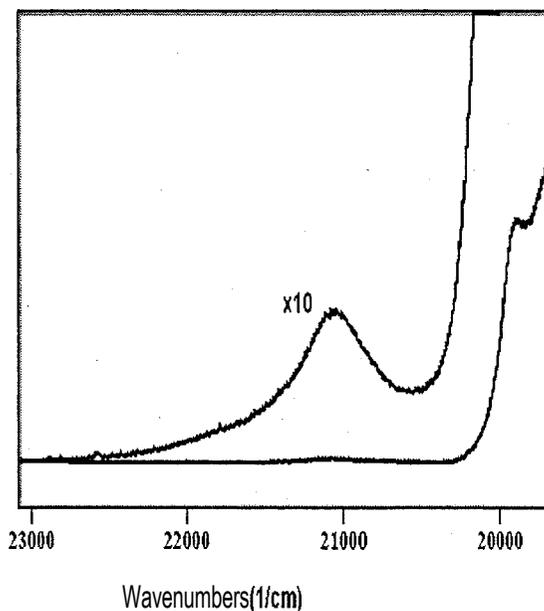


Fig. 2 Up-conversion emission from Am^{3+} in the anti-Stokes region of the 514.5 nm (19435 cm^{-1}) laser excitation.

of transitions originating from two different excited states. The higher energy side (at -14600 cm^{-1}) corresponds to contributions from the $^5\text{D}_1$ level, while the lower energy side mainly corresponds to contribution from the $^5\text{L}_6 \rightarrow ^7\text{F}_2$ transitions.

The second most intense band is observed at -12100 cm^{-1} and corresponds to the $^5\text{D}_1 \rightarrow ^7\text{F}_2$ transition. Finally, the infrared region of the spectrum consists of a broad band centering at -9500 cm^{-1} which belongs to the $^5\text{D}_1 \rightarrow ^7\text{F}_3$ transition. The overall spectral profile remains unchanged upon cooling the sample to liquid N_2 . No improvement in the resolution and/or sharpness of the bands were observed.

Several attributes, including excitation wavelength, laser power, and dopant-concentration were found to influence the overall spectral profile. An interesting feature is associated with a 514.5 nm (19435 cm^{-1}) excitation. As shown in Figure 2, anti-Stokes emissions have been observed at 19920 and 21100 cm^{-1} with a broad shoulder at -22000 cm^{-1} . The 514.5 nm laser, which is in near resonance with the $^5\text{L}_6$ state, is the only argon line that displays the up-conversion phenomenon. The 488 and/or 457 nm laser lines provide no band in the anti-Stokes region, although strong emission bands were observed in the Stokes region.

Insight into the energy up-conversion process has been gleaned from studying the dependence of the anti-Stokes emissions on the incident laser power. These studies were conducted using standard techniques, and involved laser

powers from 200 to 1800 mW. The samples had 2 - 5 atom % Am^{3+} , and yellow to amber physical-appearances. The laser power was measured by locating a power meter in front of the sample. The lack of detectable anti-Stokes emission within the first few hundred mW laser power indicates that the up-conversion proceeds via an inefficient mechanism. The log-log plot of the emission intensity vs laser power provided a slope of 3.7. The value is larger than a quadratic relationship expected for a direct or sequential two photon absorption scheme. The higher value of the slope implies that the up-conversion proceeds via a non-trivial mechanism.

One would hope to gain some insight into the mechanism of the up-conversion process by examining the concentration dependent behavior of the system. Several samples were prepared containing nominally 0.1, 0.5, and 1 atom % Am^{3+} . It is interesting to note that none of the samples with dopant levels of less than 1 atom % displayed the up-converted emission that was expected in the anti-Stokes region, even at the highest laser power. The Stokes region, on the other hand, displayed the characteristic bands of the Am^{3+} f - f transitions, although the spectral features were influenced by the dopant concentration. The dependence of the up-converted emission on the Am^{3+} content indicated that a single chromophore effect may not describe the process adequately. Hence, a mechanism involving multiple excitations of isolated Am^{3+} centers has been ruled out. The process then should involve transfer of excited-energy between neighboring ions.

The up-conversion process leading to the anti-Stokes emission starts with absorption of the 514.5 nm radiation and excitation to the $^5\text{L}_6$ state. Part of this excitation decays radiatively to the various ground state manifolds, while the other part populates the next lower $^5\text{D}_1$ state. Both the $^5\text{L}_6$ and $^5\text{D}_1$ are emitting states, although the relative intensities of the emissions originating from these states are dependent on the Am^{3+} concentration. At a higher Am^{3+} content it was found that, the relative intensity of the emission band originating from the $^5\text{D}_1$ state decreases as compared to the one originating from the $^5\text{L}_6$ state. For example, a comparison is shown in Figure 3 for the two emission bands located at 19100 and 17100 cm^{-1} and corresponding to the $^5\text{L}_6 \rightarrow ^7\text{F}_0$ and $^5\text{D}_1 \rightarrow ^7\text{F}_0$ transitions, respectively. The spectrum in Figure 3a corresponds to the sample doped with higher Am^{3+} content (5 atom %). The $^5\text{L}_6 \rightarrow ^7\text{F}_0$ transition located at 19100 cm^{-1} is more intense in the spectrum, and the ratio of the integrated peak area of this band to the 17100 cm^{-1} peak is 2. In contrast, the spectrum in Figure 3b corresponds to an Am^{3+} content of 0.1 atom %, and the ratio is significantly reduced (< 0.03). It can be concluded that emission originating from the $^5\text{D}_1$ state is dominant at low Am^{3+} levels. These changes clearly reflect the different influence concentration has on the two emitting states.

The increased ratio of the $^5\text{L}_6 \rightarrow ^7\text{F}_0$ to $^5\text{D}_1 \rightarrow ^7\text{F}_0$ emission intensity at first tempts one to attribute to a reduced

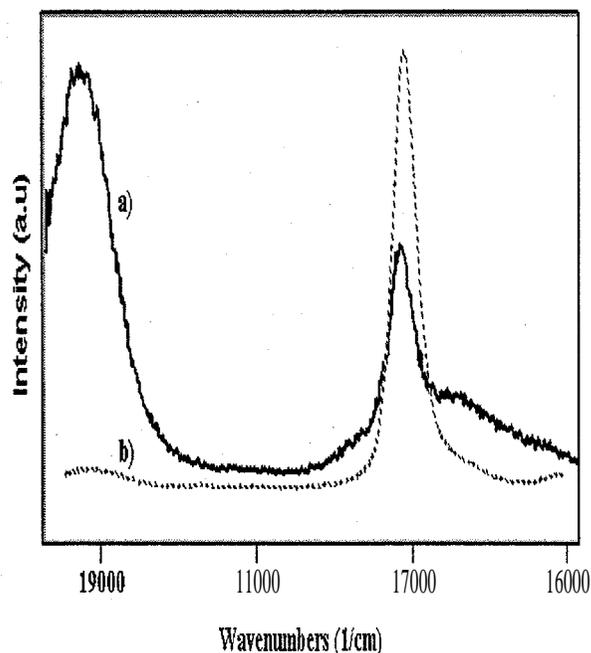


Fig.3 Emission spectra obtained with 514.5 nm excitation for Am^{3+} concentration of a) 5 atom %. Ratio of the integrated peak areas for the 19150 cm^{-1} to 17050 cm^{-1} bands is 2; b) 0.1 atom %. The comparable peak ratio is 0.03. Absolute emission intensities in the two spectra are not directly comparable due to variations in instrumental set-up and sample orientation, etc. The figures a and b are shown 6 and 12 times of their original intensities, respectively.

non-radiative relaxation of the higher $^5\text{L}_6$ excited state. However, this is inconsistent with the general understanding⁷), that changes in matrix type (low-phonon matrices) and/or low-temperature are the primary cause for increased quantum efficiency of higher excited levels. For example, although the $^5\text{L}_6$ state of Am^{3+} in solid-state (low-phonon) matrices is known to be strongly luminescent, the situation in aqueous solution is different in that high $\nu_{\text{O-H}}$ vibrational manifolds quench these emissions. As a result, emission from the lower $^5\text{D}_1$ state is more significant in aqueous media^{14, 15}). In our studies, both the boro-silicate matrix and the temperature remained unchanged, and a reduction in non-radiative de-excitation rate should not be anticipated with concentration. Rather an opposite effect should be expected with concentration.

Hence, a more likely explanation for the observed results may involve increased non-radiative relaxation at the lower $^5\text{D}_1$ state. The decrease in the relative emission intensity originating from the $^5\text{D}_1$ state (as compared to the emission

originating from the 5L_6 state) is indicative of an additional non-radiative relaxation process operating at this excited state at higher concentrations. One such process which could effectively quench an excited state emission is cross relaxation. As a non-radiative optical transition between excited and neighboring ground-state ions, cross-relaxation depends on the average separation between the species, hence on concentration¹⁵). Hence, the reduced emission originating from the 5D_1 state (relative to the 5L_6 state) is indicative of non-radiative de-population of the state due to cross-relaxation with a ground-state ion. It is important to note that a similar conclusion has been reached in prior studies involving the 5D_1 state of Am^{3+} doped in fluoride glasses¹³.

Upon consideration of various energy match-ups that might allow resonate interactions, the $[(^5D_1, ^7F_0)(^7F_6, ^7F_2)]$ scheme is suggested for cross-relaxation process. Under this scheme, the ion at the 5D_1 state would relax to the 7F_6 state, while the ground state ion is excited to the 7F_2 level. The two transitions are nearly in resonance and any mismatch in energy could easily be bridged by lattice phonons. Fast non-radiative de-excitation processes would bring both ions to the 7F_1 level, where additional photons are absorbed and excitation to the 5D_2 and/or 5G_2 level attained. The up-converted emission displayed in this matrix corresponds to the $^5D_2 \rightarrow ^7F_6$ transition. Additional data involving the dynamics of these transitions, including lifetime measurements, which will help further delineation of the process are currently in progress and will be published elsewhere¹⁶.

IV. Conclusion

The behavior of Stokes and anti-Stokes emissions exhibited by Am^{3+} in boro-silicate matrix is reported. Several attributes were found to influence the overall spectral profile including excitation wavelength, laser power, and dopant-concentration. Energy up-conversion was observed at 21100 and 19920 cm^{-1} upon excitation with the 514.5 nm (19435 cm^{-1}) argon ion laser line. The up-conversion proceeds through a multi-photon scheme and its efficiency increases with increased dopant level. Based on concentration dependent studies, the up-conversion involves

the cross relaxation, $[(^5D_1, ^7F_0)(^7F_6, ^7F_2)]$, process between neighboring americium ions.

Acknowledgement

This research was sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

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