



Emission profile of Bk(III) in a silicate matrix: anomalous dependence on excitation power

Z. Assefa^{a,*}, R.G. Haire^a, N.A. Stump^b

^aChemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6375, USA

^bWinston-Salem State University, Department of Physical Sciences, Winston-Salem, NC 27110, USA

Abstract

We have been conducting spectroscopic investigations of the transuranium elements in silicate glasses. These studies included spectroscopic monitoring of the decay profiles of selected short-lived actinides. Although the latter are not candidates for immobilization hosts, their half-lives make them attractive for probing certain fundamental issues. One facet of these studies has been spectroscopic investigations of Bk in a silicate matrix. Optical spectroscopy has shown that the trivalent state of Bk is the stable state in this matrix, and Bk(III) exhibits primarily two emission bands, centered at 15 340 and 13 475 cm^{-1} . The relative intensities of these two bands exhibit an unusual dependence on excitation power. At low power levels, the 13 475 cm^{-1} emission dominates; with increased power levels, the emission intensity of the 13 475 cm^{-1} band decreases at a greater rate than the band at 15 340 cm^{-1} . As a result, this latter band dominates at higher excitation powers. A similar dependence of these two Bk(III) emission bands with temperature has also been noted. Details of the emission profile of Bk in this matrix and the basis for the observed power dependence are discussed. © 1998 Elsevier Science S.A.

Keywords: Actinide; Berkelium; Glass; Luminescence; Spectroscopy

1. Introduction.

Absorption spectroscopy has been an important tool for investigating f-element ions in general, and the transplutonium species in particular. The major focus of such investigations has been the determination of the 5f electronic levels and the identification of oxidation states. Compared to absorption studies, luminescence techniques have received less attention in investigations of the higher transcurium elements. Most of the luminescence studies that have been reported on transcurium species have involved self-luminescence [1], and only in a few cases have photo-luminescence studies been reported [2,3]. This is despite the fact that, except for Pu and Np, the transuranium species (e.g. Am–Es) are all known to exhibit photoluminescence.

The dynamic nature of the 5f states has been largely unexplored spectroscopically. Although excited-state dynamics and energy transfer processes have been reported for tetravalent Cm and Bk ions in CeF_4 [4], little is published regarding the trivalent ions or ions of other oxidation states. In contrast, excited-state interactions for

the 4f species have been widely investigated and is an active area of research [5].

We have been conducting spectroscopic investigations of the transuranium elements in silicate glasses. These studies included spectroscopic monitoring of the decay profiles of selected, short-lived actinides. Although the latter are not candidates for immobilization hosts, their half-lives make them attractive for probing certain fundamental issues. One facet has been spectroscopic investigations of Bk in a silicate matrix. In this paper we present a detailed study involving the dynamic nature of the 5f excited-states for Bk(III) in a glass matrix. The Bk(III) spectrum consists of two primary emission bands which exhibit different behavior with intensity of the incident radiation and the temperature.

2. Experimental

2.1. Materials

The glass matrix used in this study had the following composition (mole percentage): SiO_2 (50%); B_2O_3 (18%); Na_2O (24%); CaO (3%). A glass stock without f elements

*Corresponding author. Fax: +1 423 5744987; e-mail: zaf@ornl.gov

was prepared by grinding thoroughly the components and heating until dissolution was complete (850°C). The molten material was slowly cooled to room temperature to provide a transparent glass. The actinides were incorporated into this base matrix by remelting the glass together with the actinide compound (e.g. oxide, halide, etc.) in a small platinum heater of local design. The actinide concentration was nominally 2 mol% for spectroscopic studies. Incorporation of the Bk in the glass provided a light green Bk(III) product, which eventually turned light brown with time due to radiation effects: similarly, Bk samples generated from the decay of Es-253 in this matrix also acquired a light brown color. The coloration is believed to reflect a radiation effect on the glass rather than oxidation state.

2.2. Spectroscopy

The emission studies were conducted using argon ion lasers (Models 306 and 90, Coherent) as the excitation sources, and a double meter-spectrophotometer (Raman Model HG.2S, Jobin-Yvon) using the procedure described previously [6]. Absorption spectra of the samples were obtained using an Instrument SA's optical system, which consisted of a 1000 M monochromator equipped with CCD, PMT and IR detectors. A 400-W Xe lamp was used as the light source. The sample, contained on an in-house designed square quartz tube, was placed under a microscope objective and analyzed with the light from the Xe lamp delivered via a fiber optic system. The transmitted light, collected with a second fiber, was directed into the monochromator. Spectramax for Windows software (Instruments SA) was used for data acquisition, while Spectra Calc 386 software (Galactic Industries) was used for data analysis.

3. Results and discussion

Both emission and absorption spectroscopy have been employed in our studies of Bk-249 in a silicate-based, glass matrix. The goals of these investigations were to explore the spectroscopic behavior of Bk in general, as well as to advance the fundamental and technological science of actinides in such glass matrices. The results reported here are a part of a larger spectroscopic project that involves several transcurium elements in different host materials.

The Bk-249 was incorporated both directly and indirectly in this glass matrix. Directly, by dissolution of either BkCl_3 or BkO_2 in the molten glass; indirectly, from the decay of Es-253 that had been incorporated previously into the glass. In all cases, Bk(III) was the oxidation state that was observed in this glass matrix.

Fig. 1 shows the excitation power dependence of the Bk(III) emissions from the glass. The spectra were re-

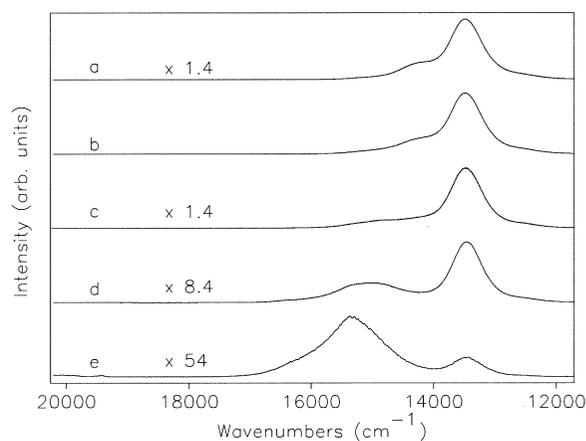


Fig. 1. Excitation power dependence of the emission profile of Bk(III) in borosilicate matrix: (a) 0.1; (b) 0.25; (c) 0.5; (d) 1; (e) 1.75 W. The spectra were recorded a few weeks after preparation; the 488-nm argon ion laser line was the excitation source. The intensities of the spectra in (a) and (c)–(e) are shown relative to (b) after multiplying the intensities of the original data with the numbers shown.

corded using the argon laser's 488-nm line as the excitation source. The power levels of the excitation radiation used in these measurements range from 0.1 to 1.75 W. These measurements were conducted on samples prepared with Bk that contained <5% of the Cf(III) daughter. As shown in Fig. 1a,b, at low excitation powers the emission at $13\,775\text{ cm}^{-1}$ dominates the spectra. A broad shoulder is also evident at the higher-energy side of this band. The intensity of the $13\,775\text{ cm}^{-1}$ emission band increases initially with increased incident radiation. For example, comparison of Fig. 1a and Fig. 1b shows that the intensity at 0.25 W (Fig. 1b) is larger by a factor of 1.4 compared to the emission intensity with 0.1 W (Fig. 1a). In Fig. 1c–e, the initial increase in intensity of the $13\,775\text{ cm}^{-1}$ band is followed by a sharp decrease when the exciting radiation power is increased further. Comparison of the intensities in Fig. 1b,d shows that the ratio at 0.25 vs. 1 W of exciting power is approximately 8.

The emission at $15\,340\text{ cm}^{-1}$, which appears only as a shoulder at low power, becomes a prominent, well-defined band at a laser power level of approximately 1 W. Although, the overall emission intensities of both bands decreased with excitation power, the band at $15\,340\text{ cm}^{-1}$ showed a smaller rate of reduction. As a result, the $15\,340\text{ cm}^{-1}$ band appears as the more dominant band in the spectrum shown in Fig. 1e, recorded with a laser power of 1.75 W.

Fig. 2 shows the excitation power dependence of Bk(III) emissions obtained from older samples of Es-253 glasses and 514 nm excitation. The spectra in Fig. 2 are shown at power levels ranging from 0.1 to 3 W. The overall spectral profile shown in Fig. 2 is similar to those observed in Fig. 1, in that an initial increase in the emission intensity of the $13\,775\text{ cm}^{-1}$ band is followed by a sharp decrease as power of the incident radiation is

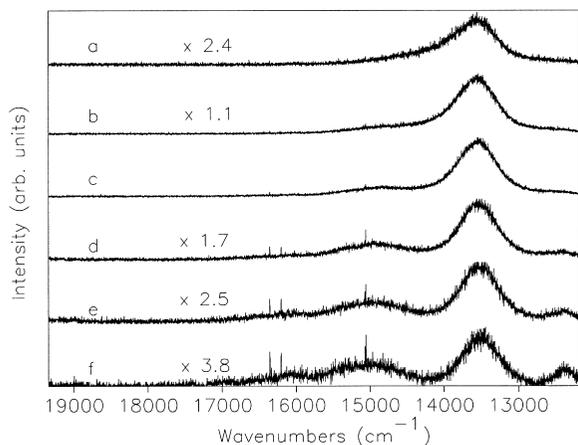


Fig. 2. Excitation power dependence of Bk(III) obtained through the in situ decay of Es. The 514-nm laser line was used for excitation: (a) 0.1; (b) 0.5; (c) 1.0; (d) 2.0; (e) 2.5; (f) 3.0 W. The intensities of the spectra in (a), (b), and (d)–(f) are shown relative to (c) after multiplying the intensities of the original data with the numbers shown.

increased. The broad, high-energy band at $15\,340\text{ cm}^{-1}$ (in Fig. 1) is slightly red shifted in Fig. 2 and appears at approximately $14\,900\text{ cm}^{-1}$.

Fig. 3 shows the temperature dependency of the emission profile for Bk(III). These measurements were conducted about a year after the sample's preparation, where about 60% of the original Bk(III) had converted to Cf(III). The power of the incident radiation was kept constant at 1 W, and the temperature of the samples varied from 34 to 207°C . As seen in Fig. 3a, the emission band at $13\,475\text{ cm}^{-1}$ has a maximum intensity at lower temperatures. With higher temperatures, a sharp decrease in this band's intensity occurs. Although a similar decrease in the intensity of the higher-energy ($15\,340\text{ cm}^{-1}$) band with temperature is also evident, the effect is less significant

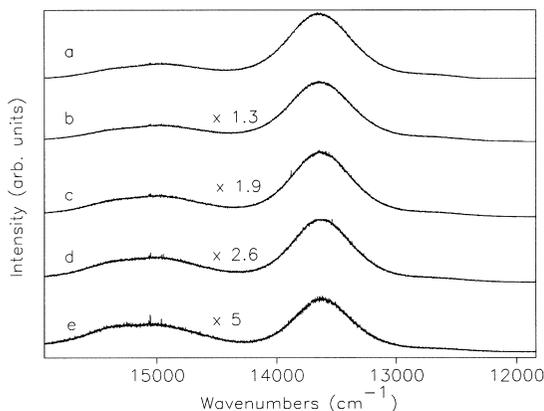


Fig. 3. Temperature dependence of the emission profile of Bk(III) in a borosilicate matrix: (a) 34°C ; (b) 71°C ; (c) 118°C ; (d) 155°C ; (e) 207°C . The low-energy band at $13\,475\text{ cm}^{-1}$ is quenched faster than the high-energy band with temperature. The laser power in these experiments was constant.

than for the low-energy band. As a consequence, the ratio of the intensities of the low-energy to the high-energy bands for Bk decreases with temperature. The overall effect of temperature on the emission profile is very similar to that found with increasing power of the incident radiation. The sharp decrease in the intensity of the $13\,475\text{ cm}^{-1}$ emission band, both with power and temperature increases, indicates the presence of a thermal quenching phenomenon that depopulates the excited-state from which the emission originates. Other possible explanations include cross relaxation and energy transfer between the neighboring ions. Efforts to understand the origins, and the dynamic behavior of the emissions, are currently underway and will also be investigated with freshly prepared Bk samples.

Another aspect of this study involved assessment of spectral changes accompanying the decay of $^{249}\text{Bk} \rightarrow ^{249}\text{Cf}$, and the potential effect of radiation on the matrix. Over a 1-year period, it became increasingly difficult to observe the 'quenching' of the $13\,475\text{ cm}^{-1}$ band's intensity with increased exciting power. In the first few weeks following sample preparation this 'quenching' of the $13\,475\text{ cm}^{-1}$ band occurred at lower power levels of the incident radiation than after 9–12 months of aging. In Fig. 1, for example, the maximum intensity for the low-energy ($13\,475\text{ cm}^{-1}$) band was attained at a laser power $<0.5\text{ W}$.

Although inconsistencies in focusing precluded quantitative comparison of data for the different time periods, it was evident that aged samples required higher laser powers to observe the expected reduction in the intensity of the $13\,475\text{ cm}^{-1}$ band. For example, in samples stored for over 9 months, the $15\,340\text{ cm}^{-1}$ band never dominated the spectrum, despite the fact that this band is easily observable in freshly prepared samples. This observation was initially thought to be related to radiation damage (e.g. darkening of the glass); hence, the temperature-dependent experiments were conducted. The data shown in Fig. 3 were maintained (only with minor variations) when the spectra were recorded during the cooling cycle of the sample. The maintenance of the emission intensities, both during the heating ($34\text{--}207^\circ\text{C}$) and cooling ($207\text{--}34^\circ\text{C}$) cycles, is inconsistent with the behavior expected from thermal effects resulting from radiation-induced defects or color centers.

Prior photoluminescence studies involving Bk(III) are limited. Carnall et al. [2] have reported that Bk(III) in aqueous solution exhibits a broad emission band centered at $15\,460\text{ cm}^{-1}$, when excited with $25\,575\text{ cm}^{-1}$ radiation. Photoluminescence studies of Bk(III) doped into single crystals of LaCl_3 have indicated three emission bands: one originating from the $^3\text{H}_6$ excited level to the $^7\text{F}_6$ ground level at $15\,430\text{ cm}^{-1}$; and two other bands originating from the $^5\text{D}_4$ level to the lowest $^7\text{F}_4$ and $^7\text{F}_5$ levels at $15\,128$ and $14\,493\text{ cm}^{-1}$, respectively [3]. Other studies have reported the self-luminescence of Bk(III) [1], as well as photoluminescence properties of Bk(IV) [7,8]. There

has been no previous study of the luminescence properties of Bk(III) in a glass matrix.

Evidence exists to suggest that the emission bands and the overall spectral profile reported above correspond to transitions within Bk(III) electronic levels. This assignment is supported by the fact that, of the actinide species (Am–Es) we have investigated, only Bk(III) samples displayed the emission profile discussed here. Differences in sample preparation (either directly or in situ via decay of Es-253) did not alter the spectral profile. In addition, the spectral profile has not been altered by the decay products of Bk. As shown in Fig. 4, Cf(III) shows a distinctively different spectral profile than Bk(III) samples (Fig. 1). Thus, we have dismissed the glass matrix as being a viable source of the observed emissions. As discussed earlier, other causes (e.g. radiation damage, color centers) have also been discounted as a source for the observed emissions. Thus, we have concluded that the emission profile is due to Bk(III).

While it has been possible to assign the emission to Bk(III), assigning unequivocally the bands to specific f–f transitions has been difficult with only the present data. The difficulty arises because the band at $13\,475\text{ cm}^{-1}$ has been observed for the first time in this study. Analysis of the electronic levels of Bk(III) indicates that, energetically, there are several transitions that could match this emission energy (e.g. $^3P_2 \rightarrow ^7F_{2,3}$, $^5D_4 \rightarrow ^7F_5$, etc.). Thus, additional data and lifetime measurements would be essential for assigning the emission bands to specific transitions.

The possibility of excited-state energy transfer between Bk(III) and Cf(III) has been considered in this study. As shown in Fig. 4, Cf(III) doped in borosilicate glasses shows a weak emission band at ca. $14\,600\text{ cm}^{-1}$, corresponding to the $^6H_{7/2} \rightarrow ^6H_{15/2}$ transition. Direct comparison (e.g. Figs. 1 and 4) of the emission exhibited by Cf(III)-doped glass showed no similarity with that of the

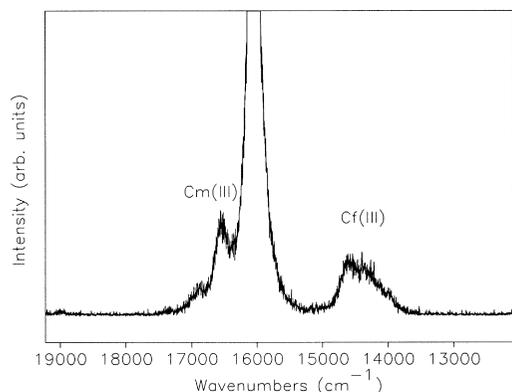


Fig. 4. Emission spectrum of Cf(III)-doped borosilicate glass. Note that the daughter Cm emission, at ca. $16\,100\text{ cm}^{-1}$, dominates the spectrum even though its content is small in the sample. The Cf(III) emission band corresponding to the $^6H_{7/2} \rightarrow ^6H_{15/2}$ transition is observed at ca. $14\,600\text{ cm}^{-1}$.

Bk-doped glass. Unlike the absorption spectra, where similarities between the absorption profiles of Bk(III) and Cf(III) precluded definitive identification and total assignment of the transitions to Bk(III) [9], spectral overlap does not exist between the emission bands of Cf(III) and Bk(III). Thus, we were able to follow the change in the spectral profile of Bk as it decays to Cf. Based on our detailed spectroscopic analysis, we have not found evidence to suggest significant excited-state interactions either between Bk and Cf, or between Bk and Cm ($^{249}\text{Cf} \rightarrow ^{245}\text{Cm} + \alpha$). We have, therefore, concluded that the effect of the ingrowth of Cf on the emission behavior of Bk(III) is minimal in our samples. Interestingly, the Cm-245 grand-daughter shows its characteristic emission bands within a year, even though the half-life of Cf-249 is 351 years, and the concentration of Cm present is small (0.2 atom % per year).

4. Summary

Spectral investigations of Bk in a silicate matrix were carried out using fresh Bk samples, as well as aged Es and Bk samples. Two major emission bands of Bk(III), believed to originate from f–f transitions, were observed at $15\,340$ and $13\,475\text{ cm}^{-1}$. The relative intensities of these two emission bands showed a dependence on the power of the excitation flux. At low power, the $13\,475\text{ cm}^{-1}$ emission band dominates; at higher levels the $13\,475\text{ cm}^{-1}$ emission band is ‘quenched’ relative to the $15\,340\text{ cm}^{-1}$ band. A similar quenching effect was also noted with temperature.

Acknowledgements

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation. The authors are indebted for the use of Bk-249 to the Office of BES, distributed through transplutonium element production program at Oak Ridge National Laboratory.

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