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ABSORPTION SPECTROPHOTOMETRIC CHARACTERIZATION OF Sm(II), Sm(III), AND Sm(II/III) BROMIDES AND Sm(III) OXYBROMIDE IN THE SOLID STATE*

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ABSTRACT

Absorption spectra obtained from $SmBr_3$, $SmBr_2$, and SmOBr were used in identifying the samarium species in several mixed-valence Sm(II/III) compounds produced by H_2 reduction of $SmBr_3$. The nature of the absorption of SmOBr made it possible to detect even traces of SmOBr in the Sm bromides.

INTRODUCTION

The results of a crystallographic study of phase equilibria in the samarium-bromine system have identified three intermediate or mixed-valence bromide compounds between the di- and trivalent ones (1,2). It is of interest to determine if the individual oxidation states, Sm(II) and (III), can be identified in these vernier compounds. If so, it would imply that separate crystallographic sites were occupied by individual Sm(II) and (III) ions; if not, the implication would be that electron exchange is occurring so rapidly that only an average species is present. The presence or absence of such individual Sm(II) and (III) ions cannot be determined by X-ray diffraction techniques but can be determined by absorption spectrophotometry if their individual spectra are known. In a recent crystallographic study of single crystals of U_2F_9, it was shown that the uranium atoms were all equivalent within the precision of the

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structural determination (3). Spectrophotometry was then applied to samples of U_2F_9, UF_4, and UF_5 to show that U_2F_9 exhibits spectral characteristics ascribable only to U(IV) and U(V) (3). In this paper we present absorption spectroscopic data for $SmBr_3$, $SmBr_2$, and two, mixed-valence compounds denoted here as $SmBr_x$ and $SmBr_{2+y}$. The absorption spectrum of SmOBr, a likely contaminant in samarium bromide samples, is also reported.

EXPERIMENTAL

All spectral studies described in this paper were made at room temperature by the use of a microscope-spectrophotometer of local design (4). Samples of $SmBr_2$ and $SmBr_x$ ($1.67<x<2.20$) were provided by J. M. Haschke (1). Although preliminary spectral data were obtained for both compounds, the $SmBr_2$ and $SmBr_x$ samples were relatively thick and so were opaque at wavelengths below 600 nm. Therefore, in-house preparation of Sm bromides was undertaken to produce thinner samples on which more complete spectral studies could be made.

Our methods of preparation of tri-, di-, and oxybromides on the μg scale are described elsewhere (4). All samples prepared at Oak Ridge were derived from the same source of Sm_2O_3, kindly supplied by R. G. Haire. Following hydrobromination of the oxide, cyclic hydrogen reductions of product $SmBr_3$ yielded $SmBr_2$. SmOBr was prepared by treatment of $SmBr_3$ with an HBr/H_2O gas mixture. The mixed-valence compound, $SmBr_{2+y}$, was produced by three consecutive thermal treatments (10 seconds each at about 500°C) of a $SmBr_3$ sample sealed under 575 torr H_2.

One sample of $SmBr_3$ was also examined by X-ray powder diffraction techniques. The LCR-2 program (5) was used to calculate the least-squares lattice parameters ($\pm\sigma$) including the Nelson-Riley correction. Line intensities were compared to those calculated by program POWD (6) assuming the atomic coordinates and thermal parameters of $CmBr_3$ (7) but not including a correction for sample absorption.

RESULTS AND DISCUSSION

The absorption spectra of $SmBr_2$, $SmBr_{2+y}$, and $SmBr_3$ are shown in Fig. 1. The spectrum of red $SmBr_2$ (top) is characterized by one broad band centered at 17×10^5 m^{-1} and a shoulder at 20×10^5 m^{-1}. No peaks are seen in the spectral region of 9 to 14×10^5 m^{-1}. In contrast the spectrum of light yellow $SmBr_3$ (bottom) exhibits a high energy tail of an absorption peak at 9×10^5 m^{-1} and a band of lower intensity at 10.3×10^5 m^{-1}. Additional features include three weak bands between 18 and 20×10^5 m^{-1} and a unique pattern of f-f transitions at still higher energies. The spectrum of $SmBr_{2+y}$ (middle)

exhibits the tribromide peaks at low wave numbers and the intense Sm(II) absorption peaks above 12 x 10^5 m^{-1}. This broad and intense absorption of Sm(II) prevents the observation of the weak f-f Sm(III) absorption peaks in the higher energy spectral region.

The absorption spectra of $SmBr_x$, SmOBr, and $SmBr_3$ are presented in Fig. 2. The spectrum of SmOBr can be distinguished easily from that of $SmBr_3$ in the spectral region of 9 to 11 x 10^5 m^{-1} on the basis of the number, position, and extreme sharpness of the SmOBr absorption peaks. Samples of the $SmBr_x$ compound did not yield useful spectra at energies greater than 17.5 x 10^5 m^{-1}. The more intense set of SmOBr peaks around 9 x 10^5 m^{-1} are present in the spectrum of $SmBr_x$. Haschke also pointed out that SmOBr was present (1). The absence of the $SmBr_3$ peak at 10.3 x 10^5 m^{-1} in the $SmBr_x$ spectrum of Fig. 2 cannot therefore be attributed to the opacity of the sample.

It is noteworthy that no spectral evidence for $SmBr_3$ is seen in the spectrum of $SmBr_x$ in contrast to its obvious presence (Fig. 1) in the spectrum of $SmBr_{2+y}$. This might mean that no uniquely $SmBr_3$ sites are present in the $SmBr_x$ compound, but more evaluation of such vernier compounds will be necessary to confirm this point. It has been reported that Cf(II) spectral peaks are seen in Cf(II)/Gd(III) halide compounds exhibiting the M_5X_{11} vernier structure (8). It is

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Figure 1. Absorption spectra of $SmBr_2$, $SmBr_{2+y}$, and $SmBr_3$.

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Figure 2. Absorption spectra of $SmBr_x$, SmOBr, and $SmBr_3$.

also possible that the presence or absence of individual cationic species in these compounds is not related to the vernier structure but only to the relative likelihood of electron transfer between the two cations. Additional work is necessary to resolve this question.

Not only can the sharp absorption peaks of SmOBr at 9×10^5 m^{-1} be seen in the $SmBr_x$ spectrum, but also they can be detected in the spectra of many of the samples of $SmBr_3$, $SmBr_2$, and mixed Sm(II/III) bromides (note the arrows in Figs. 1 and 2 pointing to this characteristic peak of SmOBr). This ability to detect even minor amounts of SmOBr attests to the sensitivity of this type of spectrophotometric analysis. The stability of $SmBr_2$ with respect to reaction with SiO_2 to form SmOBr has also been demonstrated; $SmBr_2$ sealed in SiO_2 was repeatedly heated, even to melting, with no resultant increase in the amount of SmOBr detected.

The powder pattern of one sample of $SmBr_3$ exhibited 36 lines out to $2\theta = 161°$. Following indexing on the basis of the $PuBr_3$-type orthorhombic structure, the lattice parameters were calculated to be $a_o = 0.4039(2)$ nm, $b_o = 1.2729(6)$ nm, and $c_o = 0.9140(3)$ nm. These values are in agreement with the recent values of Haschke (1).

The X-ray data obtained from the $SmBr_3$ sample confirmed its stoichiometry. Similar data collected from the $SmBr_2$ and $SmBr_{2+y}$ samples were not able to be indexed completely on the basis of the $SrBr_2$-type tetragonal and $M_5X_{11}/M_{11}X_{24}/M_6X_{13}$ vernier structures, respectively. These samples were macrocrystalline in character and produced low quality diffraction patterns. Thus, we have not confirmed the stoichiometries of these latter compounds.

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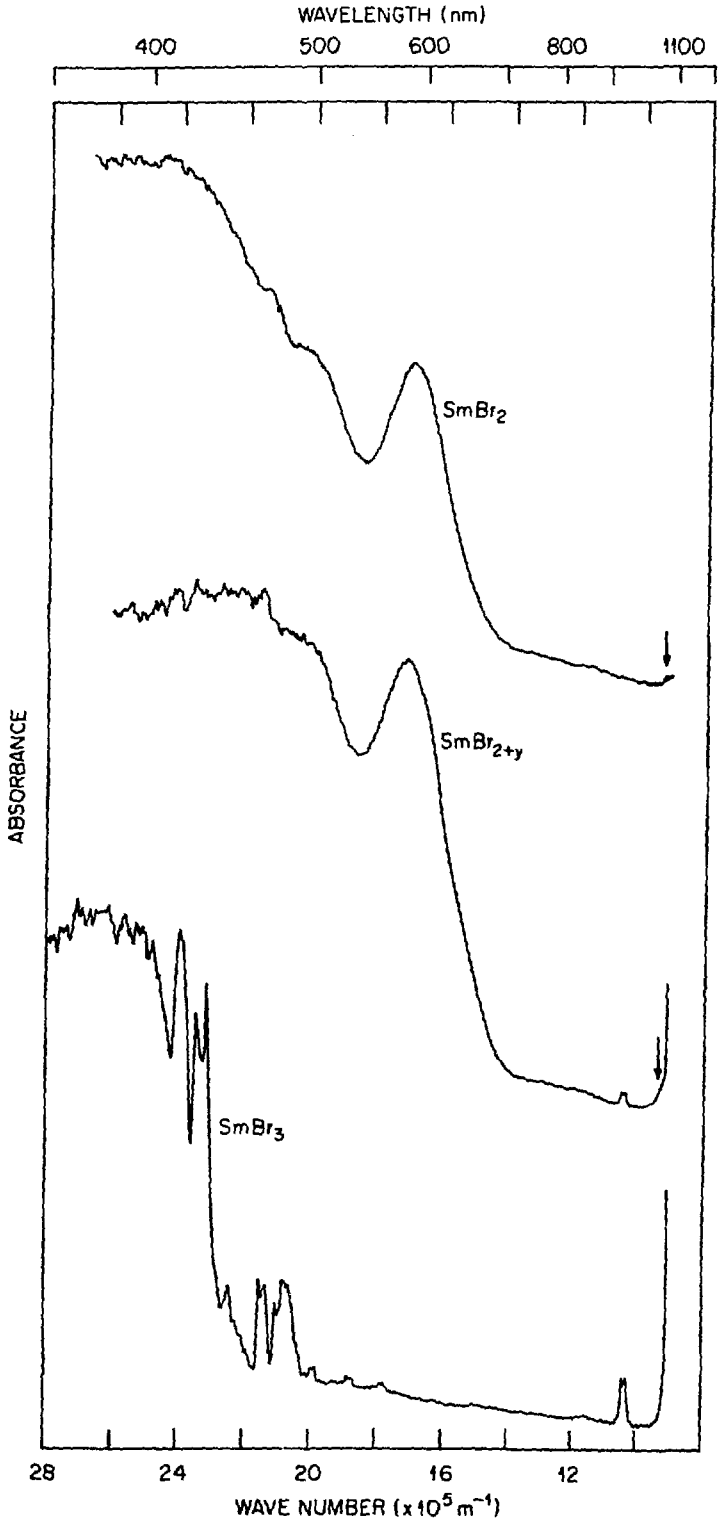
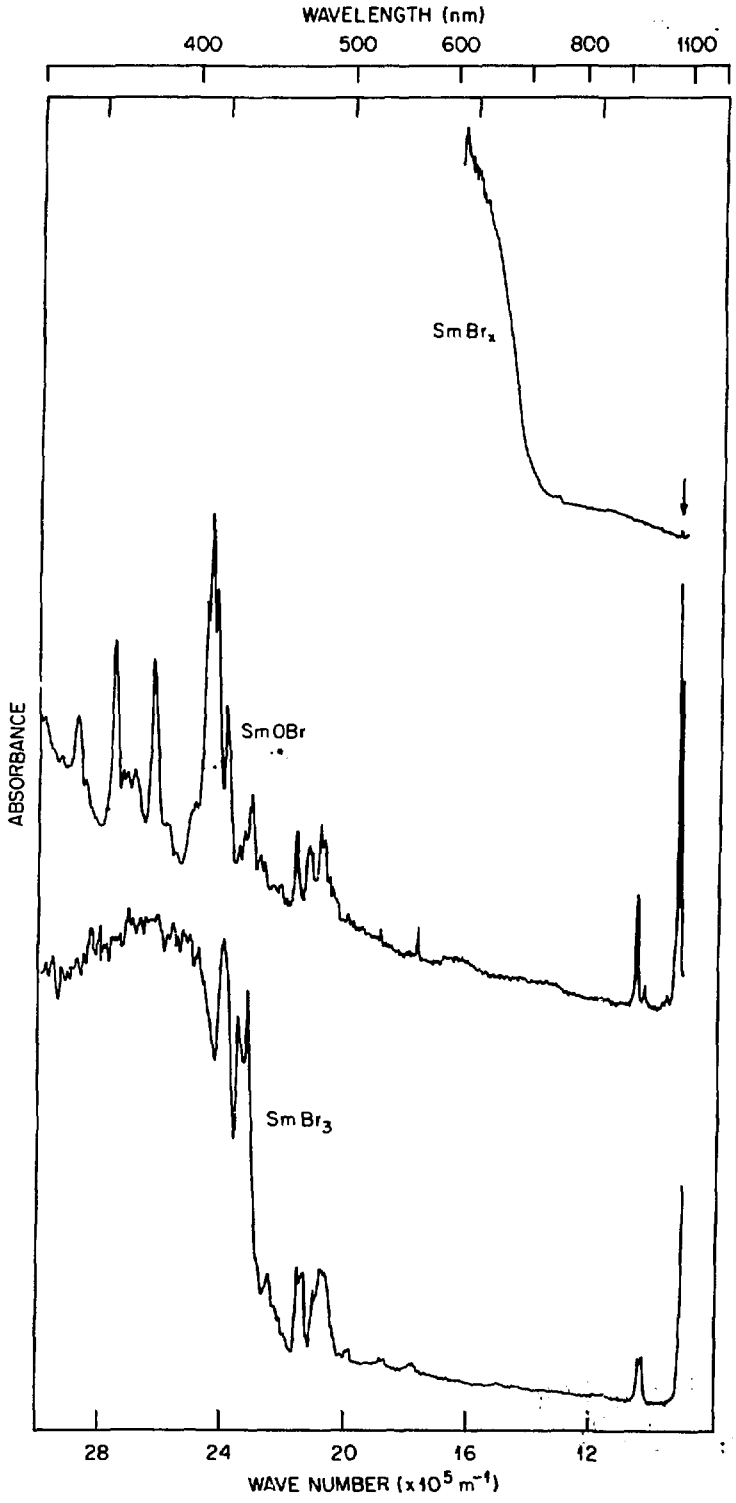
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