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MASS SPECTRA OF REFRACTORY MIXED-OXIDE COMPOUNDS WHICH CONTAIN AN ALKALINE EARTH

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ABSTRACT

The mass spectra of the high-temperature vapors over a series of barium tungstates have been measured. It is shown that the dominant vapor species over these mixed oxides is BaO(g); Ba(g) also is present as a minor vapor species over some of these oxides. The spectrum for Ba_2CaWO_6 shows Ca(g) in addition to BaO(g) and Ba(g). It appears that the BaO is formed by the solid state dissociation, e.g.

$Ba_3WO_6(c) \rightarrow 2\ BaO(c) + BaWO_4(l)$.

INTRODUCTION

There are increasing practical uses of refractory mixed-oxide compounds which contain at least one alkaline earth. An example of the use of this family of compounds is the thermionic emitter which is used in certain types of arc lamps [1,2]. There have been many studies reported on the physical properties of these mixed oxides, but there has been a paucity of studies on the high-temperature chemical behavior of the complex compounds. In particular, the high-temperature vaporization chemistry is of much interest since the application of these oxides is often determined by the thermal stability, as well as the vaporization mechanism. We have studied the high-temperature vaporization chemistry of these mixed-oxide compounds by Knudsen cell mass spectrometry, and also by X-ray analysis of the condensed phase.

EXPERIMENTAL

Materials preparation

All materials were prepared from high purity (at least 99.9%) raw materials, which included $BaCO_3$, $CaCO_3$, Y_2O_3, MoO_3, and WO_3. The preparation of the mixed oxides by a sintering process at temperatures up to 1600°C has been described previously [2]. The Ba_2CaWO_6 and the materials in the series $Ba_3Y_2WO_9$—$Ba_3Y_2(W_{0.2}Mo_{0.8})O_9$ all belong to the perovskite series, and were shown by X-ray diffraction to be of single phase [2].

Mass spectrometric measurements

The mass spectra of the high-temperature vapors were measured on a Bendix time-of-flight mass spectrometer, Model 12-101, with a Knudsen cell attachment supplied by Bendix. Measurements were made with the sample in contact with tungsten, platinum, or alumina (sapphire). The cell orifice diameters were 0.76, 1.02, and 1.27 mm, with a thickness of 0.076 mm. Approximately 0.3 g of sample was loaded into the cell for each measurement. After the loaded cell system was attached to the mass spectrometer, the cell was first radiantly heated to approximately 850°C over a period of 1—2 h. Subsequently, the cell was heated by electron bombardment. The lowest temperature by this heating mode was approximately 1000°C, and the maximum approximately 1650°C. The temperature measurements were made with a disappearing filament optical pyrometer which was focused on the cell orifice which served as the blackbody hole. The temperature was maintained to within ±7°C at a given heating power level.

The mass spectrum was visually scanned on the oscilloscope, at an electron accelerating energy of 20—30 eV, while the cell was being heated during any run. When a shutterable species emanating from the Knudsen cell was detected, the temperature was maintained constant while the spectrum was recorded on a strip chart. The relative intensity measurement as a function of sample temperature was generally made by focusing on the given peak, and recording the intensity over a period of 1—5 min to determine if there was a time dependence of the ion intensity. In some instances, the intensity of the line, such as that for the Ba^+ ion, was recorded at approximately 3 V above the appearance potential and also at approximately 30 V. The ion efficiency curves were determined for all species for which the intensities were of sufficient magnitude to allow satisfactory measurement. The appearance potentials of the positive ions were determined by comparison against those of H_2O^+ and N_2^+. The latter species were always present as a background in our spectra.

RESULTS AND DISCUSSION

Table 1 summarizes the mass spectrometric observations for all of the mixed oxides studied herein. In our Knudsen cell system, the lowest vapor pressure at which we can detect the species in the mass spectrum with any degree of accuracy is approximately 10^{-6} torr. It should be noted here that all of the materials, except Ba_3WO_6 and $BaWO_4$, changed to a deep blue color after heating above 1300°C. The $BaWO_4$ and Ba_3WO_6 retained their original white color after the heating.

In the mass spectra of the mixed oxides studied here, the positive ions which dominated the spectra were BaO^+ and Ba^+ in all of the materials, and

TABLE 1

Positive ions observed at 25—35 eV

Oxide	Crucible material	Ions	Temp. range (K)
$Ba_2CaWO_6(c)$	W, Al_2O_3	BaO^+, Ba^+, Ca^+, $BaWO_4^+$, $BaWO_3^+$, O^+	1709—1922
$Ba_3Y_2WO_9(c)$	W, Pt	BaO^+, Ba^+, $BaWO_4^+$, $BaWO_3^+$, O^+	1745—1821
$Ba_3Y_2(W_{0.8}Mo_{0.2})\ O_9(c)$	W	BaO^+, Ba^+, $BaWO_4^+$, $BaWO_3^+$, O^+	1690—1922
$Ba_3Y_2(W_{0.6}Mo_{0.4})\ O_9(c)$	W	BaO^+, Ba^+, O^+	1817—1912
$Ba_3Y_2(W_{0.4}Mo_{0.6})\ O_9(c)$	W	BaO^+, Ba^+, O^+	1798—1922
$Ba_3Y_2(W_{0.2}Mo_{0.8})\ O_9(c)$	W	BaO^+, Ba^+, O^+	1752—1862
$Ba_3WO_6(c)$	Pt, W	BaO^+, Ba^+	1608—1806
$BaWO_4(l)$	W	Ba^+, BaO^+, $BaWO_4^+$	1753—1853

also Ca^+ in the Ba_2CaWO_6. The $BaWO_4^+$ and $BaWO_3^+$ ions also began to appear in the spectra of Ba_2CaWO_6 at temperatures above 1500°C, but the intensities of these ions were appreciably lower than those of the other ions at the same temperature. As shown in Table 1, the $BaWO_3^+$ and the $BaWO_4^+$ ions were not observed in the spectra of all of the materials. In the case of $Ba_3Y_2(W_{0.4}Mo_{0.6})O_9$ and $Ba_3Y_2(W_{0.6}Mo_{0.4})O_9$, we probably did not observe the $BaWO_4^+$ and $BaWO_3^+$ ions because these ions appeared at temperatures above that which could be obtained in our instrument. Our maximum temperature limitation was about 1650°C. We did not observe the $BaWO_4^+$ and $BaWO_3^+$ ions over the $Ba_3Y_2(W_{0.2}Mo_{0.8})O_9$ in spite of the lower decomposition temperature of this oxide, and also in spite of the high relative vapor pressure of the Ba^+ and BaO^+ ions in the higher measuring temperature range. In most of the spectra, the O^+ ion was observed as one of the products of the dissociative vaporization of the oxides. However, we could not quantitatively assign a relative intensity to this ion because of the relatively high air background in our instrument, in spite of the spectrometer vacuum of 10^{-6} torr or lower. Table 2 shows the relative intensities of the major ions, Ba^+, BaO^+, and Ca^+ in the mass spectra.

As shown in Table 2, the BaO^+/Ba^+ ratio is essentially the same for the vapors over the $Ba_3Y_2WO_9$ and its derivatives, and this ratio remained constant over the temperature range studied for each of these oxide mixtures. Figure 1 shows the temperature dependence of the BaO^+ and Ba^+ ion intensities for $Ba_3Y_2WO_9$ which was contained in the tungsten crucible: here I is the ion intensity and T is the absolute temperature, and IT is proportional to the partial pressure. The measurement at 35 eV produced the same results from both the tungsten and the platinum crucibles. The enthalpy of vaporization at 35 eV was $\Delta H^\circ_{1783} = 97$ kcal mole^{-1}. Note that the slope for the Ba^+ ion measured at 8 eV, which was 3 eV above the appearance potential, was significantly higher than those of the other curves measured at 35 eV; the enthalpy of vaporization at 8 eV was 190 kcal mole^{-1}. The 8 eV measurement was not made in the platinum crucible. The temperature dependence of the BaO^+ and Ba^+ ions measured at 25 eV for the derivatives of $Ba_3Y_2WO_9$ was very similar to that shown in Fig. 1; we did not

TABLE 2

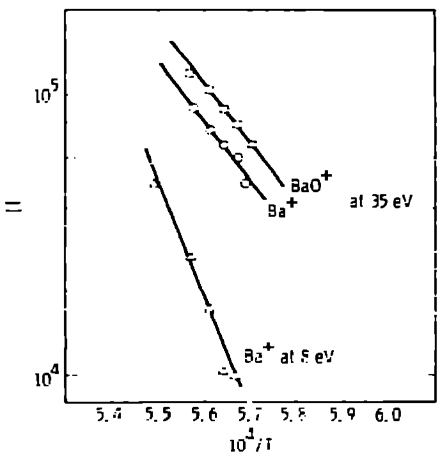
Relative intensities of ions at 1788 K

Oxide	Crucible Material	Energy (eV)	Relative intensity		
			Ba^+	BaO^+	Ca^+
$Ba_2CaWO_6(c)$	W, Al_2O_3	11	100	196	140
$Ba_3Y_2WO_9(c)$	W, Pt	35	100	135	
$Ba_3Y_2(W_{0.8}Mo_{0.2})\ O_9(c)$	W	25	100	133	
$Ba_3Y_2(W_{0.6}Mo_{0.4})\ O_9(c)$	W	25	100	124	
$Ba_3Y_2(W_{0.4}Mo_{0.6})\ O_9(c)$	W	25	100	134	
$Ba_3Y_2(W_{0.2}Mo_{0.8})\ O_9(c)$	W	25	100	140	
$Ba_3WO_6(c)$	Pt	30	100	220	
$Ba_3WO_6(c)$	W (at 1648°K)	30	100	~50	
$BaWO_4(l)$	W	30	100	74	

measure the temperature dependence for the Ba^+ ion at 8 eV for the derivative oxides.

Figure 2 shows the Clausius—Clapeyron plot for the Ba^+ and BaO^+ ions from Ba_3WO_6 measured at 30 eV from a platinum crucible. The enthalpy of vaporization of these ions was $\Delta H^{\circ}_{1710} = 105$ kcal mole^{-1}. We did not determine the temperature dependence of the mass spectra from the tungsten crucible but, as shown in Table 2, there is a drastic difference in the BaO^+/Ba^+ ratio between the two crucibles.

Figure 3 shows the temperature dependence of the BaO^+, Ba^+, Ca^+, and



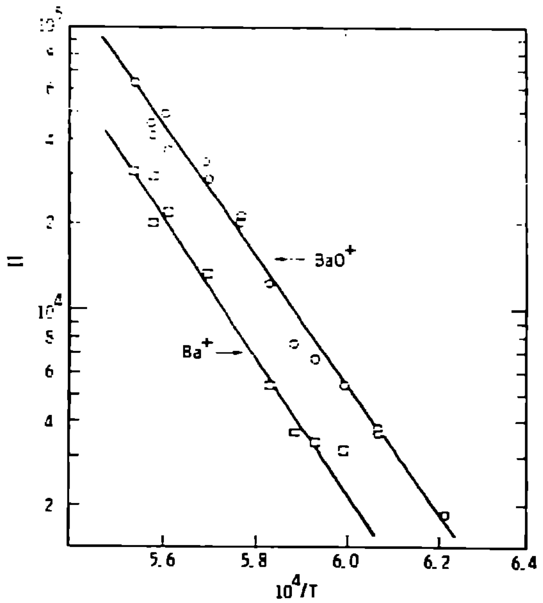


Fig. 1. Semilog plot of IT vs. $1/T$ for Ba^+ and BaO^+ from $Ba_3Y_2WO_9$ measured at 8 and 35 eV.

Fig. 2. Semilog plot of IT vs. $1/T$ for BaO^+ and Ba^+ from Ba_3WO_6 measured at 30 eV.

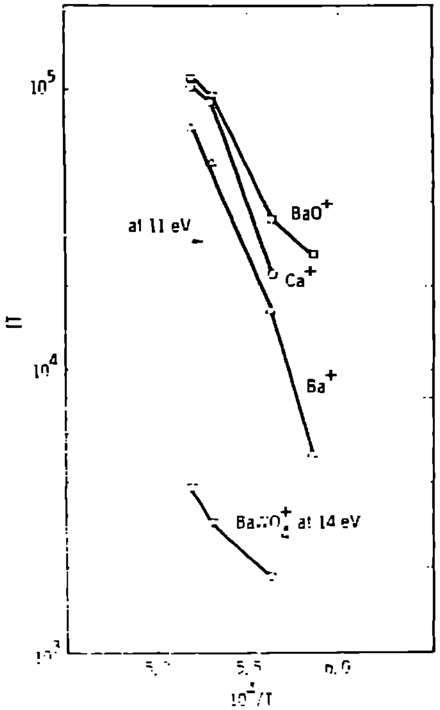


Fig. 3. Semilog plot of *IT* vs. 1/*T* for ions from Ba_2CaWO_6.

$BaWO_4^+$ ions over Ba_2CaWO_6, where the first three ions were measured at 11 eV and the $BaWO_4^+$ was measured at 14 eV. The $BaWO_3^+$ ion also was present at temperatures above 1550°C, but the ion intensity was too weak for even a reasonably accurate measurement. Admittedly, the temperature dependence data for this compound is quite poor, but the measurements show the predominance of the BaO^+, Ca^+, and Ba^+ ions in this spectrum. The BaO^+/Ba^+ ratio of 1.96 with this material was higher than that in the $Ba_3Y_2WO_9$; this difference is attributed to the difference in the electron accelerating energies at which the measurements were made.

The appearance potential (A.P.) for the Ba^+ ion in all of the materials studied here was between 4.9 and 6.0 eV, while the A.P. for the BaO^+ ion was between 6.4 and 7.5 eV. The A.P. for the Ca^+ ion from Ba_2CaWO_6 was 5.0 eV. All of the A.P. were measured to within ±0.5 eV by the linear extrapolation method. The A.P. for these three ions agree quite well with the ionization potentials of 5.2, 6.5 and 6.0 eV for Ba, BaO, and Ca, respectively [3]. However, examination of the efficiency curves suggests that the Ba^+ ion from all of the compounds has more than one parent.

Figure 4 shows the efficiency curves for the Ba^+, BaO^+ and Ca^+ ions from Ba_2CaWO_6. Also shown in this figure is the efficiency curve measured for the Ba^+ ion from barium metal. When we first determined the efficiency curves for the ions from Ba_2CaWO_6, we observed the anomalous hump at approximately 10 eV for the Ba^+ curve. This hump showed up more prominently in the curve for this ion from barium metal. This peaking in the ion intensity at ~10 eV has been determined to be an artifact of our particular spectrometer which we have not been able to eliminate. This peak is not present unless

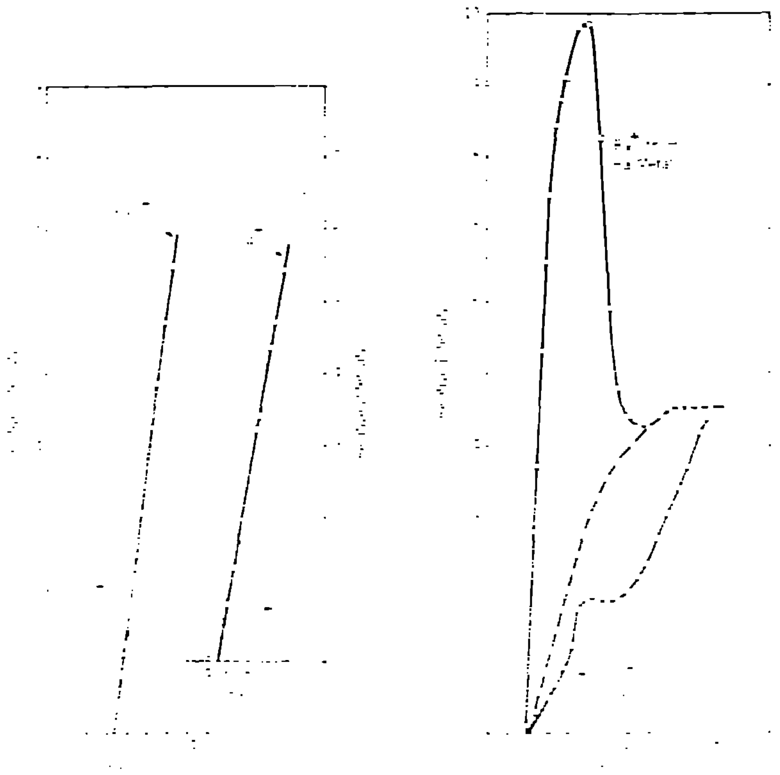


Fig. 4. Efficiency curves for BaO^+, Ca^+, and Ba^+ from Ba_2CaWO_6 at 1650 °C and for Ba^+ from barium metal at 700 °C.

there is an ion with a threshold below ~10 eV. For example, this anomalous peak is absent in the efficiency curves for H_2O^+ and N_2^+. The actual efficiency curve for the Ba^+ ion from barium metal should follow the broken curve in Fig. 4, and the intensity is seen to saturate above 19 eV. Because we cannot confidently correct for this anomalous peaking in the ion intensity at ~10 eV, we show the efficiency curves as they were measured. Examination of the curve for the Ba^+ ion from Ba_2CaWO_6 showed that there is more than a single source for this ion. The A.P. of 5.5 eV showed the contribution from Ba(g) in the vapor, but the continuously increasing intensity of the peak up to approximately 25 eV showed the contribution from a second source. The efficiency curve for the BaO^+ ion shows the predominant contribution from the ionization of BaO(g). The efficiency curve for the Ca^+ ion also suggests only a single source. Figure 5 shows similar efficiency curves for the Ba^+ and BaO^+ ions from $Ba_3Y_2WO_9$. All of these ions showed the anomalous peak at ~10 eV, but the straight lines in the region below 10 eV, and that above 10 eV, had the same slope. In addition, the intensities attained saturation at ~15 eV.

Figure 6 shows the efficiency curves for BaO^+ and Ba^+ from Ba_3WO_6 measured from the platinum crucible. The BaO^+ is clearly a parent ion from BaO(g). The Ba^+, however, appears to have at least two sources. The low threshold Ba^+ probably originates from Ba(g), but the ion appearing at 13 eV

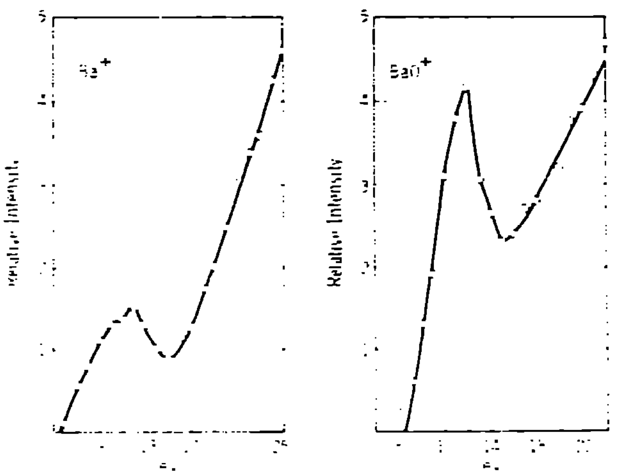


Fig. 5. Efficiency curves for Ba^+ and BaO^+ from $Ba_3Y_2WO_6$ at 1420°C.

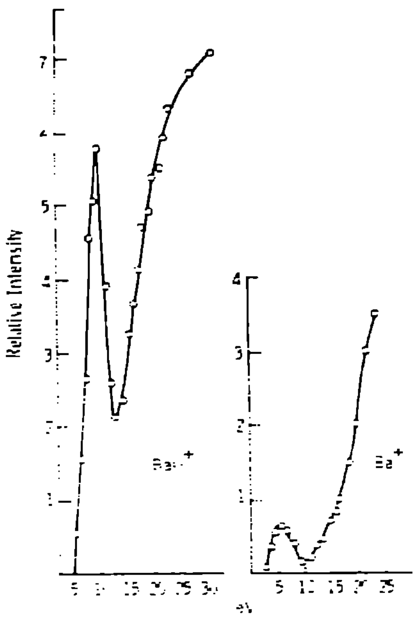


Fig. 6. Efficiency curves for BaO^+ and Ba^+ from Ba_3WO_6 at 1425°C.

is that formed by dissociative ionization of the BaO(g) [3].

The temperature dependence data for the BaO^+ ion, shown in Fig. 1, yielded an enthalpy of vaporization of 97 kcal mole^{-1} at 1783° K. The latter value is in good agreement with $\Delta H^{\circ}_{1700} = 102$ kcal mole^{-1} for the enthalpy of sublimation reported by Inghram et al. [4]. These authors also showed that the Ba^+ ion is formed by the dissociative ionization of BaO(g) by electron impact, and that the BaO^+/Ba^+ ion intensity ratio was approximately 9 at 30 eV electron bombardment energy. In our measurements on $Ba_3Y_2WO_6$ and its derivatives at 25—35 eV, the BaO^+/Ba^+ ratio was identical to that measured by Aldrich at 15 eV, and with the BaO contained in platinum [5]. It appears from our data that BaO is a product of the thermal decomposition of the mixed oxides. If CaO also is one of the products of decomposition of Ba_2CaWO_6, we would not have been able to observe this oxide in the vapor, nor the tungstates of calcium, in the temperature range of our measurements.

As shown in Fig. 1, the temperature dependence of the Ba^+ ion measured at 8 eV shows a very steep slope, with an enthalpy of vaporization of 190 kcal mole^{-1}. It appears that the Ba(g) arises mostly from the reduction of BaO(c) by tungsten according to

$$W(c) + 6\ BaO(c) \rightarrow 3\ Ba + Ba_3WO_6(c)$$

The enthalpy for this reaction is 177 kcal, compared with 249 kcal for the reaction

$$W(c) + 4\ BaO(c) \rightarrow 3\ Ba(g) + BaWO_4(c)$$

These enthalpies are based on the enthalpies of formation of $BaWO_4$(c) and Ba_3WO_6(c) reported by Rezukhina et al. [6] and the enthalpies of the BaO(c) and of Ba(g) reported in the JANAF Tables [7].

Previous authors have found that $BaWO_4$(g), $BaWO_3$(g), $CaWO_4$(g) and $CaWO_3$(g) are important vapor species, as detected by mass spectrometry over BaO and CaO in contact with tungsten crucibles [8]. We did not find this to be the case in the temperature range studied with the complex oxides. Nor did we observe any compounds of molybdenum or yttrium in the mass spectra over the mixed oxides which contained these elements. However, the thermal decomposition of $Ba_3Y_2WO_9$, and its derivatives, always resulted in Y_2O_3 and $BaWO_4$ as products.

It is difficult at the present time to speculate on all of the reactions which produce the vapor products observed in our measurements. However, it is clear that BaO(g) is the dominant species up to 1650° C, with Ca(g) and Ba(g) also present. The tungstates and tungstites, $BaWO_4$(g) and $BaWO_3$(g) respectively, were also vapor products over some of the materials, but these molecules made relatively small contributions to the vapor composition. It is clear that BaO is formed by the thermal decomposition of the complex oxides, and that the high vapor pressure of BaO dominates the equilibrium vapor.

We have observed that Ba_2CaWO_6, $Ba_3Y_2WO_9$ and the derivatives of the latter all become blue in color when these oxides are heated in vacuum above 1300° C. This color change, which suggests decomposition, takes place when the oxides are contained in tungsten, platinum, or alumina crucibles. This type of color change with decomposition in tungsten oxide is well known to be the result of the loss of oxygen with subsequent formation of suboxide. One source for the Ba(g), aside from the reduction of BaO by tungsten, may be from the reaction

$$\mathrm{BaO(g) + O \rightarrow Ba(g) + O_2}$$

with the O atom coming from the decomposition of the oxide.

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