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Abstract

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Mass-Spectrometric Study of the Composition of Vapor over Oxides of Rare-Earth Elements

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Chapka et al. ([1]) studied, by a mass-spectrometric method at high temperatures, the composition of vapor in equilibrium with lanthanum oxide and found that only lanthanum monoxide and atomic oxygen are present in the vapor; it was also shown that the saturated vapor pressure at 1860° K is $2.2 \cdot 10^{-7}$ atm. White, Goldstein, and Utny ([2]) measured, by an effusion method, the vapor pressure of the monoxides of lanthanum and neodymium over the corresponding sesquioxides in the temperature range 2230–2440° K. Comparing data on the formation energies of condensed oxides, on the sublimation enthalpies of the metals, and the few available values of the dissociation energies of gaseous monoxides, the authors come to the conclusion that the stability of gaseous MO molecules should decrease as the atomic number of the original element increases. M. Ackerman and Thorn ([3]), in their review, after considering the results of works ([1], [2]), assert that the value of the LaO vapor pressure measured by Chapka et al. is too high. Panish ([4]) reports the results of a mass-spectrometric investigation of the vapor composition over oxides of neodymium, praseodymium, samarium, and europium, paying special attention to preventing interaction of the substance under study with the container material, for which inserts of iridium and thorium oxide were used. He found a change in the principal evaporation product on going along the series from PrO to Eu; in small amounts over praseodymium oxide, gaseous PrO_2 was also found.

We investigated the composition of vapor over the oxides of all rare-earth elements with the exception of thulium. The investigations were carried out on an MI-1305 mass spectrometer. Figure 1 shows a diagram of the ion source. The substance under study is applied in a thin layer to the central part of the iridium ribbon evaporator (1), to which a thermocouple (2), made of tungsten-rhenium alloys containing respectively 5 and 20% rhenium ([5]), is spot-welded. Calibration of the thermocouple was carried out with the aid of a first-class optical pyrometer in the High-Temperature Laboratory of the All-Union Scientific Research Institute of Metrology named after Mendeleev. The deflecting plates (3) prevent ions, which may be formed by surface ionization of the oxides under study, from entering the ionizer box (4). The design of the source makes it possible to operate at ribbon-evaporator temperatures up to 2100°.

Fig. 1. Diagram of the ion source

Figure 1: Fig. 1. Diagram of the ion source

Fig. 2. Vapor pressure over rare-earth oxides

Figure 2: Fig. 2. Vapor pressure over rare-earth oxides

In interpreting the results of the mass-spectrometric investigation in order to obtain quantitative data on the ratio of the partial pressures of the vapor components, special attention must be paid to the possibility of the simultaneous formation of ions of equal mass through direct ionization of neutral particles and, in addition, through dissociative ionization of heavier molecules. Panish ([4]) assumes that the ratio of ion currents in the mass spectrum, studied at an ionizing voltage of 20 V, corresponds to the ratio of the concentrations of the corresponding neutral molecules in the vapors. This assumption seems to us unfounded–

data, since with an arbitrary choice of electron energy, on the one hand, dissociative ionization may proceed to a considerable extent, while on the other hand the ionization efficiency of individual molecules, especially of the MO_2 type, may already be very small. For all the oxides studied we estimated the appearance potentials of ions; the ionizing-voltage scale was corrected according to the known ionization potentials of argon and mercury. We then extrapolated the initial portions of the ionization-efficiency curves from the moment of onset of fragment-ion formation to the maximum of the ion current, where the magnitude of the current depends little on the electron energy. The ratio of the ion currents at the maximum of ionization efficiency, with a correction for the ratio of the effective ionization cross sections ([6]), most closely corresponds to the ratio of the concentrations of neutral particles in the vapors over the given oxide.

Fig. 1. Diagram of the ion source

The results of our study of the composition of the vapor over rare-earth oxides are presented in Table 1; it includes data on the mass spectra of the vapors obtained at ionizing voltages of 45 and 10 V; the

Fig. 2. Vapor pressure over rare-earth oxides.
a –data of Inghram et al. ([1]); *b* –data of White et al. ([2]); *c* –our data

largest ion current in each case was taken as unity. For different oxides the measurements were carried out at temperatures that ensured attainment of a vapor pressure of the main component of the order of 10^{-5} mm Hg. Using a variant of the Langmuir method previously described by us ([7]), we determined the vapor pressure of gaseous monoxides over lanthanum and neodymium oxides. For the remaining oxides the vapor pressure was estimated during simultaneous evaporation of equimolecular quantities of the oxide under study and lanthanum

oxide. Figure 2 presents data on the vapor pressure of monoxides of rare-earth elements, both our own and those obtained by other investigators ([1,2,4]). Over europium and ytterbium oxides the vapor pressure of the metals was measured.

Consideration of the experimental material shows that the volatility of rare-earth oxides in high vacuum, as well as the composition of their vapors, differs substantially for the oxides of different elements. A general tendency in the lanthanoid series is a decrease in the strength of gaseous monoxides on gradual transition from La compounds to Lu, the consequence of which is an increase in the ratio M^+/MO^+. This regularity is observed—

shows a distinct periodicity: the ratio M^+/MO^+ is greatest for the oxides of those elements that exhibit valence +2 (Eu, Yb) and have the lowest enthalpy of sublimation of the metal; these oxides also have an increased volatility. In the vapors over the oxides of elements exhibiting valence +4, we detected molecules of gaseous dioxides (CeO_2, PrO_2, TbO_2).

Table 1

Mass spectrum of vapors over rare-earth oxides

Oxide	45 V M^+	45 V MO^+	45 V MO_2^+	10 V M^+	10 V MO^+	10 V MO_2^+
La_2O_3	0.16	1.0	–	–	1.0	–
CeO_2	0.28	0.6	1.0	–	1.0	0.95
Ce_2O_3	0.18	0.91	1.0	–	1.0	0.3
Pr_2O_3	0.36	1.0	0.2	–	1.0	0.01
Nd_2O_3	0.25	1.0	–	–	1.0	–
Sm_2O_3	1.0	0.99	–	1.0	0.77	–
Eu_2O_3	1.0	0.2	–	1.0	0.15	–
Gd_2O_3	0.3	1.0	–	1.0	0.83	–
Tb_2O_3	0.2	1.0	0.01	0.9	1.0	–
Dy_2O_3	0.5	1.0	–	1.0	0.59	–
Ho_2O_3	1.0	0.77	–	1.0	0.45	–
Er_2O_3	1.0	1.0	–	1.0	0.72	–
Yb_2O_3	1.0	0.01	–	1.0	–	–
Lu_2O_3	1.0	0.9	–	1.0	0.60	–

In control experiments we obtained an analogous result by evaporating Tb_2O_3 from a tungsten ribbon, since the ion currents Ir^+ and TbO_2^+ are not separated by our mass spectrometer. Cerium dioxide, when heated in vacuum, dissociates to a composition close to $CeO_{1.80}$–$CeO_{1.67}$ ([8]). On evaporation, this oxide gives CeO and CeO_2 molecules in the vapor. The ratio of the ion currents CeO^+/CeO_2^+ does not remain constant, but gradually increases as the amount of material on the evaporator decreases, from 0.5 : 1.0 at the beginning of the experiment to 0.8 : 1.0 at the end (ionizing voltage 45 V). The mass spectrum

of cerium oxide vapor also contains CeO^+ and CeO_2^+ ions, and the ratio of these ion currents under the conditions of our experiments (the residual pressure in the mass spectrometer at the experimental temperature was $6\text{–}8 \cdot 10^{-7}$ mm Hg) is close to 0.95 : 1.0 and does not change as the sample evaporates. Thus, Ce_2O_3 evaporates congruently with a solid-phase composition close to $CeO_{1.6}$. In no case did we observe the formation of ions of the type $M_2O_3^+$ or polymeric ions $(MO)_n$.

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Note: Figure translations are in progress. See original paper for figures.