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Mechanisms for anion emission from the Eu_2O_3 matrix

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Abstract

A model is proposed to explain the mechanism for the experimentally observed, relatively intense, thermal emission of certain anions (ReO_4^- and the halides) from matrices where the anion is paired with an alkaline earth counter ion and embedded in a rare earth oxide in a +3 oxidation state. The primary mechanism is hypothesized to be that the −1 anion migrates much faster than the +2 cation through the +3 rare earth oxides. The anions migrate to the surface and sublime; the counter ion does not. This causes a concentration gradient that causes more anions to continue to migrate to the surface, followed by sublimation. Furthermore, explanations are offered as to why Eu_2O_3 and Yb_2O_3, which are used in the +3 oxidation state and are the only rare earths with readily accessible +2 oxidation states, are more efficient as anion emitting matrices than the other rare earth oxides with +3 oxidation states. The mechanism that can explain the significance of the +2 oxidation state of Eu_2O_3 and Yb_2O_3 matrices involves the following type of chemical reduction: $Ba(ReO_4)_2 + Eu_2O_3 + 2e^- = 2ReO_4^- + 2EuO +$ BaO. The reduction of europic to europus frees an oxygen atom that can combine with the Ba counter ion left as perrhenate migrates, satisfying the bonding requirements of the Ba counter ion and preventing the build up of charge imbalance in the matrix, which in turn should allow anions to continue to migrate and ultimately to sublime from the surface. A similar equation can be written for the halide emitters. It is probable that the two stages of the proposed process occur nearly simultaneously; otherwise the lattice energy would increase to unrealistic levels. (Int J Mass Spectrom 178 (1998) 9–17) © 1998 Elsevier Science B.V.

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1. Introduction

It was demonstrated in 1987 that rare earth oxides in the +3 oxidation state are effective thermal emitters of the perrhenate anion [1] when perrhenate is synthesized from Re metal in an oxidation reaction. It was later demonstrated that when the +3 rare earth has a readily accessible +2 oxidation state there is a considerable enhancement of ion emission [2] when the perrhenate anion is presynthesized and blended into the rare earth oxide as a minor component. It was also demonstrated that the counter ion to perrhenate had to be an alkaline earth element rather than an alkali element (Ba as opposed to Cs). The rare earths with the most stable +2 oxidation states are europium (Eu) and ytterbium (Yb). Eu has the most stable +2 oxidation state and is also the most efficient perrhenate emitter. In this earlier work [2] it was speculated that the enhancement effect might be due to an ability of the rare earth oxide to function as an oxidizing agent able to keep Re in its fully oxidized form (+7) as perrhenate.

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Dedicated to the memory of Al Nier.

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Since this earlier work was published, an ion/neutral mass spectrometer system has been developed that permits a much more detailed analysis to be conducted of these perrhenate anion emitting systems, the results of which do not support the concept that Eu_2O_3 functions as an oxidizing agent under these circumstances. Additional studies have been performed that demonstrate that halide ions are also effectively emitted from these materials and specifically when barium iodide is substituted for barium perrhenate an efficient iodide emitter is produced. Because the halides are the fully reduced forms of the halogens and are stable in these matrices, oxidation plays no role. An alternate explanation is needed to account for the enhanced ion emission observed with these materials.

2. Experimental

The ion/neutral mass spectrometer [3], described in detail elsewhere, measures the positive ions subliming from the surface of the hot emitter (positive surface ionization or PSI), then the negative ions subliming from the surface (negative surface ionization or NSI), and then the neutral particles via electron impact (EI) ionization, in sequence, with a repetition rate of 2–4 minutes for each of the three operating modes. The only significant change in the instrument since the earlier publication is the addition of negative ion measurement capabilities, which was accomplished by the addition of a dynode to convert negative ions to positive ions, which are in turn detected by the multiplier. An upper sample temperature limit to the operation of this instrument has not been established, but samples have been taken as high as 1300°C. This permits the development of a detailed history of all major species subliming from the emitters, positive ions, negative ions, and neutral particles (via EI) as a function of temperature. The perrhenate emitters based on Eu_2O_3 and Nd_2O_3 reported previously [2] were studied with this instrument. These are blends of 16 parts of the rare earth oxide to 1 part (by weight) of barium perrhenate. These matrices were chosen because Eu_2O_3 was the matrix that was the most efficient emitter of perrhenate, and Nd_2O_3 was the matrix that was the least efficient in the earlier study [2], thus offering the greatest contrast. Pure barium perrhenate pressed into a rhenium tube was also analyzed.

In the course of various experiments, it was noted that significant chloride and bromide anion beams were generated from a contaminated perrhenate emitter. This observation led to a series of experiments in which Eu_2O_3 was blended with BaI_2, with a weight ratio of about 16:1. There are four reasons for using iodide instead of chloride or bromide: (1) the reduced chance of contamination because of the lower natural abundance of iodine, (2) the heavy mass of the iodide ion is of greater interest as the primary ion in secondary ionization mass spectrometry (SIMS) guns, (3) iodine has only a single isotope, which simplifies application to time-of-flight (TOF)-SIMS, and (4) iodide is the most easily oxidized halide and hence the best choice for testing the concept of Eu_2O_3 being an oxidizing matrix. These emitters were pressed into Re tubes and spot welded onto filament posts as with the previous perrhenate emitters [2]. An additional experiment was conducted with a blend of barium iodide and lanthanum hexaboride (LAB6). The LAB6 experiment was conducted because LAB6 has found some use as an iodide emitter [4] in the isotope ratio measurement of fission product iodine. It was soon discovered that these emitters did not maintain emission levels for more than a few hours and the experiment was terminated early.

The same National Bureau of Standards (NBS) mass spectrometer designed for the measurement of isotope ratios that was used in the earlier studies [1, 2] was used to establish the ion emission properties of the iodide emitters. The tests were conducted at staged temperatures as in the earlier work [2], operating for 7 days.

Exact measurement of the emitter temperature remains a problem. An experiment was performed in which an emitter was set up such that both the front and rear of the tube containing the emitter could be viewed with an optical pyrometer. The rear of the tube is all that can be viewed when the emitter is installed in an ion gun. As an example, in one test the rear of the tube, which is a Ta plug, was at 950°C, the front edge of the tube was at 880°C, and the face of the emitter was at 820°C. The tube is supported and heated by filaments that are welded to the rear of the tube. Because heat is supplied to the rear of the tube, this explains why it is hotter than the front. The surface area of the emitter (a pressed powder) will be much higher than that of the Ta plug or the Re tube, causing it to radiate more heat and consequently to be cooler, as observed. As a consequence, the actual temperature of the emitter surface that produces ions will be lower than the reported measurement. Correcting for this error is complicated by the fact that the surface area of the emitters will vary with the particle size of the emitters before pressing and the degree of pressing. The temperatures listed are therefore uncorrected and approximate. The true temperature of the emitter is estimated to be 150–200°C lower than the measured temperatures.

3. Results

3.1. Perrhenate emitters

Perrhenate thermal emitters based on both Eu_2O_3 and Nd_2O_3 were studied with the ion/neutral mass spectrometer, and Eu_2O_3 was by far the most efficient matrix for ion emission, in agreement with the earlier results [2]. The only Re species observed for either emitter matrix was the perrhenate anion and minor amounts of ReO_3^- from NSI. This contrasts with the results in Delmore [1] where perrhenate was synthesized in situ and there was appreciable ReO_3^-. When the perrhenate species is presynthesized as opposed to produced in situ by a chemical reaction, the dominant species is ReO_4^-, as opposed to a mixture of ReO_4^- and ReO_3^-. Neither material had any Re species in the cation spectrum from PSI or EI. Ions that did not contain Re were readily observable in both the PSI mode (alkali metals and other less intense species) and EI modes (carbon dioxide, oxygen, and other less intense species) with excellent sensitivity, confirming that the instrument was operating properly. Heavily oxidized rhenium filaments were operated in the instrument in a separate experiment, and a variety of rhenium oxides were sublimed as neutral molecules and readily observed in the EI mode ($Re_2O_7^+$, ReO_2^+, ReO^+) at temperatures well below those used in the tests of the emitters themselves. If the perrhenate species were being reduced in the neodymium based emitter, we would expect to see these lower oxides of rhenium subliming as neutral molecules and being detected in the EI mode. If the main reason for the reduced efficiency of the Nd_2O_3 based emitter were the reduction of perrhenate to lower oxidation states, it would be expected that these species in lower oxidation states would volatilize and be detected in the EI mode. Because these species could not be observed the conclusion is that perrhenate is not reduced in either matrix.

Special attention was given to examining the spectra from all three modes to see whether the counter ion to perrhenate, barium, was vaporizing in any form. There was no evidence of barium in any of the spectra for any of the three modes, even at levels approaching the noise of the detector. If Ba were to migrate to the surface as an ionic species it is probable that ion emission from PSI would be observed because of the relatively low ionization potential (5.21 eV). Thus, the conclusion is that Ba is nonvolatile and possibly nonmigratory in these matrices. If excess Ba were tied up as the oxide, which is highly refractory, none would vaporize in any form at these temperatures. It would be expected that because Ba has a $+2$ charge and perrhenate and iodide have -1 charges, the rates of migration of these anions would be much higher than for Ba^{+2} for a given temperature.

The analysis of pure barium perrhenate gave quite different results. At typical operating temperatures with 900°C measured at the rear of the tube there were no perrhenate anions from NSI, no Ba cations from PSI, and strong Ba^+ and BaO^+ (but no Re containing species) spectra from EI. This temperature is many hundreds of degrees below where BaO would be expected to exhibit appreciable vapor pressure. This is interpreted as barium perrhenate vaporizing as some species, perhaps as the intact molecule, and dissociating under EI to give these less complex species. Because barium has a relatively low ionization potential, it is logical that when the parent molecule fragments under EI that the charge will be carried by the fragment that contains Ba. This implies that the Re containing molecular fragments are neutral and thus not detected. Indeed, there were no detectable species containing Re. Thus, the pure barium perrhenate is not an ion emitter at all, but appears to vaporize as a molecule that fragments on electron impact to give Ba^+ and BaO^+ and various neutral Re containing molecules. This illustrates the need for a matrix to serve as a diffusion medium to fractionate the anions from the cations, as in solid state chromatography. The rare earth oxides in the +3 oxidation state apparently are able to accomplish this fractionation.

In our earlier work [2] we observed a small exotherm in the differential thermal analysis at approximately 950 K, suggesting shrinkage in lattice constants, coupled with a possible phase change. On the basis of published work in the area of solid state ionics [5–8], it is possible that such a phase transition corresponds to a disordering of the oxide lattice, which allows the rapid conduction of perrhenate anions. However, x-ray powder diffraction patterns showed that the blends were amorphous powders both before and after sintering, and thus no definitive structural changes could be ascribed to the sintering on the basis of the x-ray analysis. In any event, confirmatory proof will be difficult to obtain because the amount of Eu in the lower oxidation state will be very small. This was made evident from an attempt to analyze the emitter material using x-ray photoelectron spectroscopy (XPS), which was unsuccessful because of the small percentage of EuO and the resolving capability of the instrument. Proof of the exact mechanism is beyond the scope of this article.

3.2. Iodide emitters

The iodide emitters were not tested as extensively for extended lifetimes in the NBS mass spectrometer as the perrhenate emitters reported in Delmore et al. [2], with only the Eu_2O_3 and Nd_2O_3 based emitters synthesized and tested. The same trends were observed, with the Eu_2O_3 based ion emitter having at least an order of magnitude higher integrated ion emission than the Nd_2O_3 based ion emitter. Table 1 contains the emission lifetimes of these tests in the same format as in Delmore et al. [2]. Studies conducted with both of these materials in the ion/neutral mass spectrometer demonstrated that the iodide anion from NSI was the only observable species containing iodine. Neither the PSI nor the EI modes had any species containing iodine, and again noniodine species were observed in good abundance in both modes to verify proper instrument operation. All three of these ion emission modes were monitored from room temperature to 900°C, but no oxidized iodine species were observed. If these matrices had appreciable oxidizing capability, it is expected that these materials would produce some oxidized iodine species that could be observed, but this was not the case. Also, if appreciable oxidation of iodide were occurring, the emission of iodide anions would have been depleted much sooner than occurred.

Table 1
Integrated intensities of I^- emission from Nd_2O_3 and Eu_2O_3 matrices and correlation with the III/II reduction potentials (from the literature)

Rare earth oxide/BaI_2	10^{-9} A h of I^-	III/II reduction potentials
Eu_2O_3	280	−0.43
Nd_2O_3	8.4	Too unstable to measure

The ion source imaging instrument used in earlier studies was used to image one of the iodide emitters [9]. An image from this iodide emitter is shown in Fig. 1. This photograph gives an image of the face of the material, demonstrating the surface topography and that ion emission is from the surface of the emitter itself, and not from an interfacial or gas phase process. Immediately after this experiment, this ion emitter was cooled, removed from the imaging instrument, and mounted in the ion/neutral mass spectrometer. This instrument was then used to verify that ion emission was in excess of 99% I^-, with the remaining ion emission being Cl^-. Thus, the photograph in Fig. 1 is that of I^- from the surface of the emitter. This seems like an obvious result, but there is nothing more fundamental than the knowledge of where the ions are originating if the ion emission process is to be

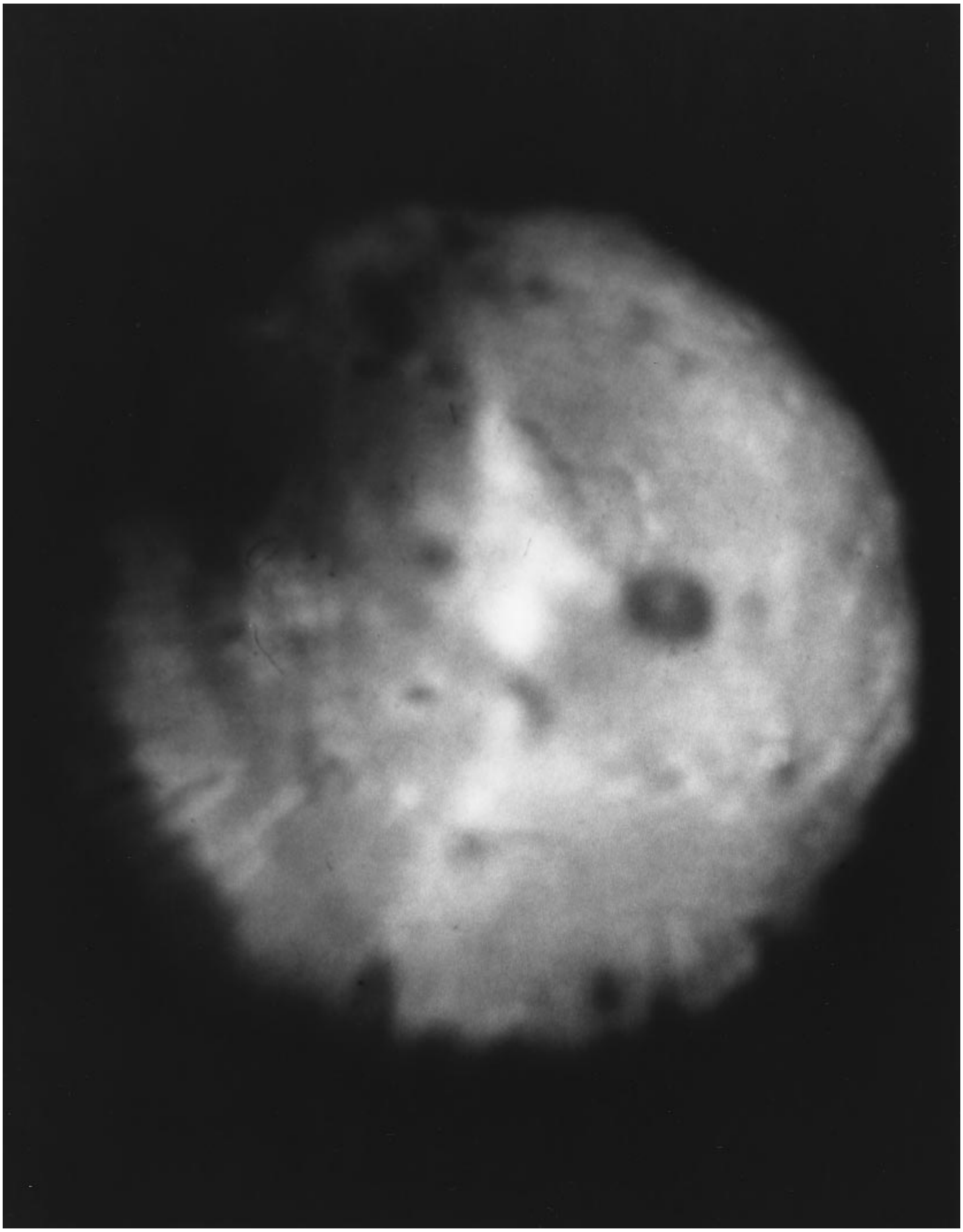

Fig. 1. Image of I^- ion from the face of an iodide emitter.

understood. If the ions were coming from an interfacial region, these materials would not be ion emitters at all and the ion formation mechanism would be very different.

Special attention was also given to the examination of the spectra from these iodide emitters in all three modes for any evidence of barium. Again, no evidence of any barium containing species could be detected at any level, demonstrating that the barium ion is nonvolatile in this matrix at the temperatures used, just as with the perrhenate emitter. If a Ba containing species were volatilizing it would be expected to fragment under electron bombardment and that the fragment containing Ba would carry the charge and be detected.

One of these iodide anion guns has been installed in a triple quadrupole secondary ion mass spectrometer and used to generate secondary ion mass spectra from a variety of heavily insulating samples. On the basis of preliminary data, the iodide anions appear to function well in this application. Pulsed extraction [10] combined with the iodide (127 Da) anion beam allowed abundant positive and negative secondary ion mass spectra to be generated from these insulating samples, including molecular anions, which are the most difficult ions to detect from insulators using SIMS. These iodide emitters have operated at pressures ranging from 10^{-5} to 10^{-7} Torr, in contrast to guns that use elemental iodine [11], and perhaps could operate even under ultrahigh vacuum (UHV) conditions without raising the pressure in the vacuum system. The perrhenate emitters have operated at 10^{-8} Torr without any measurable increase in pressure when heated from room temperature to 900°C after first aging for about 1 hour at temperature. Subsequent cooling and reheating to this temperature did not produce a measurable pressure rise, so UHV operation should be possible.

Perrhenate emitters in both Eu_2O_3 and in Nd_2O_3 matrices have been used extensively in the primary ion gun in SIMS instruments, with the result that the europium based perrhenate emitter had a useful integrated current lifetime of about 100 times or more than that of the neodymium based emitter (2 years at 200 pA versus 2 weeks at 50 pA). This compares to about a factor of 10 in the integrated lifetime studies of Delmore et al. [2]. The operational difference causing this difference in lifetime is thought to be the temperature of the emitter and the corresponding anion emission current, with tests in Delmore et al. [2] pushing the emitters to higher intensities at higher temperatures than for operation of the emitters in the SIMS guns. This was done to complete a single test in 1 week in Delmore et al. [2], whereas operation in the ion guns was for use in static SIMS analyses where 50–200 pA were required. These are "after the fact" observations that were not initially intended to be scientific comparisons of the emitters, but nevertheless, indicate that the more modest the operating conditions, the greater the difference between the two types of emitters in regards to the integrated ion current.

4. Discussion

A model is being proposed that is consistent with these results. There are two major features to this model. The first feature is that perrhenate (or the halides) migrate within the hot matrix and sublime from the surface much more readily than Ba, allowing for the charges to begin to segregate. If continued for long, this separation of charges would become thermodynamically untenable. The second feature is a mechanism for "healing" the matrix of lattice defects that arise from this separation of charges. Lattice defects resulting from the selective migration of ions away from the counter ion could have the effect of shutting down further migration. Thus, the requirement to "heal" the matrix. It is probable that these two steps occur nearly simultaneously, because any appreciable buildup of electrostatic charge of either polarity is thermodynamically improbable. These materials are nominally electrical insulators at room temperatures, but at ion emission temperatures are expected to have sufficient electrical conductivity (via electron conduction) to compensate for the emitted ion current. Electrons by themselves cannot simply replace an anion because this cannot satisfy the bonding requirements of the remaining cation. In this case, simple replacement of the anion with an electron would produce barium metal, not a feasible situation in an oxide matrix. Another anion is required to replace the perrhenate anion in order to prevent the occurrence of a charge (or color) center.

As the temperature of these emitters is increased, the embedded species will be more prone to migrate. This migration is in totally random directions unless there is some gradient driving a given species in a certain direction. When the temperature gets high enough for the more mobile -1 species to sublime from the surface, the concentration of that species at the surface will decrease and provide a concentration gradient to drive the migrating species toward the surface. This is the process that is hypothesized for the $+3$ rare earth oxides. Barium is not observable in the gas phase at levels many orders of magnitude below where perrhenate (or iodide) is observed. This supports the concept that the -1 species migrate away from the $+2$ species and sublime selectively. The matrix then serves as a diffusion medium for separating the anions and the cations. Without a suitable diffusion medium in which the cations and anions can segregate, there is no means by which to fractionate the anions from the cations so that selective sublimation of a single polarity ion can occur. This is demonstrated by the lack of ion emission from pure barium perrhenate.

There is a scarcity of data published in journals demonstrating that the tendency to migrate in high temperature oxide materials is dependent on the charge state of the ion. There is, however, considerable work performed and published in government reports on the topic of fission product migration in oxide based nuclear fuels. These studies clearly demonstrate that Cs migrates much more readily than Ba, and that Nd migrates little if at all. Hence, for a high temperature UO_2 matrix, the tendency to migrate is $Cs^{+1} \gg Ba^{+2} \gg Nd^{+3}$. This information is not documented in any one location, and was never meant to prove this issue, but does give an indication that the tendency to migrate in a high temperature oxide matrix is dependent to a considerable degree on the charge state of the ion. The interested reader can start with the 1973 US AEC publication of Maeck et al. [12] and references therein. It must be stated, however, that the tendency to migrate as a function of charge state in rare earth oxide matrices is not a proved fact, even though it does help to explain the experimental observations.

These results also give strong evidence that both the perrhenate and the iodide species are stable in both the europium and the neodymium oxide matrices, even at the ~900°C temperatures used in these studies. Thus, because both the fully oxidized (perrhenate) and the fully reduced (iodide) presynthesized anion species seem to be stable in both emitters, an explanation other than the concept of Eu_2O_3 being an oxidizing agent able to maintain rhenium as perrhenate (which is in its maximum oxidation state of $+7$) offered in the earlier work [2] is needed to explain the difference in anion emission levels. When the perrhenate anion emitters produced from both Eu_2O_3 and Nd_2O_3 are first brought up to emission temperature, the difference in ion emission is not great, but as the emitters age the differences become much more pronounced. Because repetitive studies that span thousands of hours would be required to quantitatively define these parameters, such studies have not been conducted, but the anecdotal evidence from operation of these emitters in SIMS guns is available. This indicates that if the emitter is not pushed to high intensities (200 pA as opposed to 10 nA), as with the studies in Delmore et al. [2], that a useful intensity will be maintained much longer, and the integrated total intensity will be much higher from the Eu_2O_3 based matrix than if the ion emission is pushed to very high levels.

These results are consistent with the concept that the more efficient matrix may be able to “heal” itself of damages that may occur from the loss of ions. The following chemical reaction is offered as an explanation for these observations:

$$Ba(ReO_4)_2 + Eu_2O_3 + 2e^-$$

$$= 2ReO_4^- \text{ (gas phase)} + 2EuO + BaO \text{ (reaction 1)}$$

This chemical reaction involves the reduction of the europic (or $+3$) oxidation state to the europus (or $+2$) oxidation state, thus freeing an oxygen anion to combine with barium to satisfy its bonding requirements. The power supply heating the filament can easily supply the electron current required to balance this reaction. If the bonding requirements of the counter ion are not satisfied, there will be a lattice defect with a charge (or color) center at each position from which a perrhenate anion has migrated. An electron by itself cannot satisfy the bonding requirements of the barium ion, but the oxygen anion does. If a sufficient number of these sites develop within the emitter, it is possible, or even probable, that further ion migration will be cut off, although we are not aware of independent studies that prove this point. This explanation accounts for the striking difference between the rare earths with readily accessible +2 oxidation states and the rare earths that have a +2 oxidation state that is difficult or impossible to access.

If this type of mechanism is actually occurring, it is probable that an intermediate and more complex reaction, or set of reactions, is taking place where only one of the perrhenate anions migrates from a $Ba(ReO_4)_2$ molecule. This would give a more complex barium oxy-perrhenate species such as:

$$2Ba(ReO_4)_2 + Eu_2O_3 + 2e^- = 2ReO_4^- + 2EuO + Ba_2O(ReO_4)_2 \quad \text{(reaction 2)}$$

A comparable reduction reaction can be written for the iodide emitter:

$$BaI_2 + Eu_2O_3 + 2e^- = 2I^- + 2EuO + BaO \quad \text{(reaction 3)}$$

Again, a more complex barium oxy-iodide species may be more probable.

This type of chemical reduction reaction can account for the striking improvement in operation of these anion emitters when a rare earth with a reasonably stable +2 oxidation state (Eu and Yb) is used as the anion emitting matrix. Without a reduction reaction of this type, the lattice will build up an electrical charge imbalance that will present a high energy barrier to further ion migration. Definitive proof of this chemical mechanism remains for another type of experiment.

There are three possible scenarios concerning the sequence of these steps. If the reduction reaction occurs first, it would create a negative charge imbalance within the lattice. If migration were to occur first, there would be a positive charge. In reality, there would be a large energy barrier to any significant charge imbalance in either direction. Hence, it is probable that the process proceeds with very little electrical imbalance of either polarity, and this may be one of the secrets of building an efficient thermal ion emitter.

An argument against this model is that if all of the $Ba(ReO_4)_2$ at the surface were to be converted to BaO, the cation sites required for additional anion migration might be cut off because BaO could not function effectively as a transfer center for the anions because of the bonds being saturated. This is where the more complex reaction can come into play. Only half of the Ba bonding would be tied up as an oxide, the other half remaining free to function as a transfer station for passing anions on to the next cation center.

Our knowledge of the high temperature chemistry of ion emitters is limited, but these experiments are yielding some insights. There are six criteria that can be hypothesized that are consistent with the results of these experiments:

1. The singly charged ion to be emitted needs to be presynthesized, paired with a suitable nonmigratory counter ion (in actual practice this means a higher charge state), and embedded in a matrix that enhances ion emission by causing the different polarity ions to fractionate by migrating at much different rates. The pure material by itself will not be an ion emitter.
2. The ion of interest also obviously needs to be stable in the matrix. This places various requirements on redox properties of the matrix, which could change with the ion being emitted.
3. The ion of interest must be able to migrate. Singly charged ions are thought to migrate much more readily than doubly charged ions, and the only ions measured are singly charged.
4. The counter ion needs to be nonvolatile and presumably nonmobile. If it is not, the entire neutral

molecule can migrate and sublime, bypassing the channel for producing gas phase ions. Stated another way, the ion of interest needs to migrate from one counter ion to the next until it eventually reaches the surface from which it can sublime.

5. There needs to be some mechanism available to satisfy the bonding requirements of the counter ion left after the ion of interest migrates and sublimes. The hypothesized reduction reaction can satisfy these bonding requirements. At the same time the cations must not have their bonds totally saturated because there must be some capability to function as "transfer stations" to facilitate anion migration.
6. It is probable that migration and reduction occur nearly simultaneously, because any appreciable electrical charge imbalance within the lattice would increase the lattice energy such that any further ion migration would be thermodynamically unfavorable.

5. Conclusions

A model is proposed in which a thermal (or surface) emitter will include a singly charged presynthesized ion to be emitted, paired with a multiply charged counter ion, and embedded as a minor component in a thermally stable matrix. When heated to a sufficient temperature, the singly charged ion migrates from its original counter ion on to an adjacent counter ion, and continues the process until it reaches the surface and sublimes. This presynthesized singly charged ion needs to be stable in the matrix and to sublime after it migrates to the surface. The matrix needs to have a redox reaction capable of generating an ion of the same polarity as the ion being emitted to satisfy the bonding requirements of the counter ion left as the ion migrates. An anion emitter will require a reduction reaction to generate an anion capable of satisfying the bonding requirements of the remaining cation, and a cation emitter will require an oxidation reaction to generate a cation to satisfy the bonding requirements of the remaining anion. This can be thought of as "healing" the matrix of the damage that occurs from the migration and sublimation of the ion. It is probable that the ion migration and the redox reaction occur nearly simultaneously because to do otherwise the energy of the lattice would be increased to unrealistic levels because of electrical charge imbalance. At the same time, the counter ion must not have its chemical bonds totally saturated, because then it could not function as a "transfer station" for conveying other ions out to the surface. This model is based on two types of successful anion emitters, and are contrasted to other emitter matrices studied that are much less successful or do not emit ions at all. This is not a sufficiently broad experimental base to try to state basic principles for preparing all ion emitters, but it does offer a few new perspectives and gives targets against which to design additional experiments. It also is suggestive that the design of highly efficient solid state ion emitters could be developed into a topic in synthetic inorganic chemistry.

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References

[1] J.E. Delmore, J. Phys. Chem. 91 (1987) 2883.
[2] J.E. Delmore, A.D. Appelhans, E.S. Peterson, Int. J. Mass Spectrom. Ion Phys. 146/147 (1995) 15–20.
[3] J.E. Delmore, T. Huett, J.E. Olson, A.D. Appelhans, Int. J. Mass Spectrom. Ion Phys. 155 (1996) 149–162.
[4] J.E. Delmore, Int. J. Mass Spectrom. Ion Phys. 43 (1982) 273–281.
[5] A. Bunde, Ber. Bunsenges. Phys. Chem. 87 (1983) 249.
[6] L. Lam, A. Bunde, Z. Physik B 30 (1978) 65.
[7] H. Schmalzried, Progr. Solid State Chem. 13 (1980) 119.
[8] H. Schmalzried, Chemical Kinetics of Solids, VCH, 1995, Chap. 15.
[9] J.E. Delmore, A.D. Appelhans, J.E. Olson, Int. J. Mass Spectrom. Ion Phys. 140 (1994) 111–122.
[10] A.D. Appelhans, D.A. Dahl, J.E. Delmore, Anal. Chem. 62 (1990) 1679–1686.
[11] I. Rachidi, J. Monte, J. Pelletier, C. Pompt, F. Rinchet, Appl. Phys. Lett. 28 (1976) 292.
[12] W.J. Maeck, R.L. Larsen, J.E. Rein, Burnup Determination For Fast Reactor Fuels, U.S. DOE Report TID-26209, UC-79c-TID-4500.