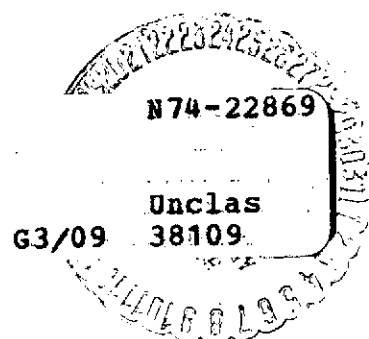


NASA TECHNICAL MEMORANDUM

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NASA TM X-71549

(NASA-TM-X-71549) HIGH-EFFICIENCY,
LOW-TEMPERATURE CESIUM DIODES WITH
LANTHANUM-HEXABORIDE ELECTRODES (NASA)
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HIGH-EFFICIENCY, LOW-TEMPERATURE CESIUM DIODES WITH LANTHANUM-HEXABORIDE ELECTRODES

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ABSTRACT

Lanthanum-hexaboride electrodes in 1700 K cesium diodes may triple power outputs compared with those demonstrated for nuclear thermionic space applications. Still greater relative gains seem possible for emitters below 1700 K. Further improvements in cesium-diode performance should result from the lower collector temperatures allowed for earth and low-power-space duties. Decreased temperatures will lessen thermal-transport losses that attend thermionic-conversion mechanisms. Such advantages will add to those from collector-Carnot and electrode effects. If plasma ignition difficulties impede diode temperature reductions, recycling small fractions of the output power could provide ionization. So high-efficiency, low-temperature cesium diodes with lanthanum-hexaboride electrodes appear feasible.

HIGH-EFFICIENCY, LOW-TEMPERATURE CESIUM DIODES WITH LANTHANUM-HEXABORIDE ELECTRODES

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SUMMARY

Emitters and collectors of lanthanum hexaboride may increase efficiencies of 1700 K cesium diodes by a factor of 3 over those previously obtained in nuclear thermionic space power programs. Even greater relative gains appear possible for emitter temperatures below 1700 K. Additional improvements in cesium-diode performance should result from the freedom allowed in selecting collector temperatures for terrestrial applications and low-power space duty. Such decreased temperatures will, of course, diminish the parasitic thermal-transport processes that accompany the productive thermionic-conversion mechanisms. These advantages will add to those of the collector-Carnot and electrode effects. The slight concentrations of cesium required for low lanthanum-hexaboride work functions also lessens thermal-conduction, electric-resistance, and collisional-deionization losses in the plasma. And when plasma-generation problems block further diode temperature reductions, various methods of recycling small fractions of the power output could provide the necessary cesium ions. So high-efficiency, low-temperature cesium diodes with lanthanum-hexaboride electrodes should be attainable in principle.

Combinations of reference information and NASA experience indicate that fabrication of thermionic-converters with lanthanum-hexaboride electrodes is feasible. This metallic compound causes no major problem in machining, brazing, electron-beam welding, or polishing. Vapor deposition is a demonstrated fact for similar metallides and should adapt to forming cylindric lanthanum-hexaboride electrodes. Because the electric resistance of lanthanum-hexaboride is comparable with that of the refractory metals, no special conductor designs are required. In addition, the anticipated low operating temperatures for these thermionic

converters should ease material and processing problems in general and extend service lifetimes. As a result of the summation of these observations, cesium diodes with lanthanum-hexaboride electrodes appear to offer significant potentialities in direct energy conversion.

METALLIDES IN THERMIONIC CONVERSION

Lanthanum hexaboride (LaB_6) emits electrons exceedingly well, produces very low surface potentials in cesium (Cs) vapor, and has a high melting point (refs. 1 to 3). For these and other reasons lanthanum-hexaboride electrodes in cesium-filled thermionic converters should yield much greater power outputs and operate effectively at lower temperatures than conventional metal emitters and collectors. Such improvements can mean much in land, sea, and space applications of direct energy conversion.

Lanthanum hexaboride is one of the metallides with characteristics suitable to exploit in the closely related energy-conversion and sensor applications. Compilations of properties for such metal compounds appear in references 1 to 12, which cite great numbers of publications related to this subject.

These references reveal many other metallides with high-temperature, electric, and electronic capabilities worthy of consideration for cesium-diode emitters: Metallic borides, carbides, nitrides, and silicides often have higher melting points and somewhat lower bulk conductivities than those of the refractory metals. For example, titanium diboride (TiB_2) melts at 3250 K and conducts electricity 0.5 to 0.7 times as well per unit volume as tungsten (W) - between 400 and 2400 K. But on a weight basis its conductivity is 2.0 to 2.8 times greater than that of tungsten over the same temperature span. Work-function values, which are very important in thermionic conversion, vary from 2.1 to 6.6 eV for borides, 2.0 to 4.9 for carbides, 2.9 to 4.0 for nitrides, and 2.5 to 4.3 for silicides. The preceding ranges are similar to the work-function spread for all metals, not just the refractory ones.

Such characteristics encouraged evaluations of metallides as electrodes in cesium thermionic converters in the early 1960's (typified by

refs. 13 and 14). However, metallic compounds are complex; their manufacture often yielded inhomogeneties and incomplete reactions, and their phases and compositions sometimes alter with large temperature changes. So the quickest path to predictability and quality control in cesium diodes led toward high-purity refractory metals.

But specific metallides still look too good to ignore for thermionic applications. And at present, lanthanum hexaboride leads this category: It serves as an excellent electron emitter in vacuums with work functions reported generally from 2.4 to 2.9 eV and with a melting point near 2800 K; it also reaches surface potentials as low as 0.8 V with adsorbed cesium (refs. 1, 2, 3, and 15). These properties imply more current, higher output voltages, and smaller plasma losses for cesium diodes with lower emitter and collector temperatures. The remainder of the present paper explores this potentiality in greater detail.

LANTHANUM-HEXABORIDE CHARACTERISTICS RELATED TO THERMIONIC CONVERSION

From recent careful work on lanthanum hexaboride between 1735 and 1954 K the authors of reference 15 conclude that the work function is 2.4 eV with a Richardson constant of $40 \text{ A/cm}^2 \text{ K}^2$. These values compare with 2.66 eV and $29 \text{ A/cm}^2 \text{ K}^2$ from references 16 to 18, 2.68 and 73 from reference 19, and 2.76 and 50 from reference 20. Reference 15 researchers attribute the "better" work-function determination to the absence of impurities introduced by binders and substrates in previous studies. The results of reference 21 support this view: There the work functions of hexaborides of samarium and europium change with alterations of the metals used as bases for the cathode coatings. In addition the workers of reference 15 observe that large differences in the Richardson constant can result from variations in density of the coated or sintered samples of lanthanum hexaboride used in previous studies. Thus their 2.4-eV work function and $40\text{-A/cm}^2 \text{ K}$ Richardson constant seem to be good values for dense pure randomly oriented polycrystalline lanthanum hexaboride.

But because these numbers are averages for contributions of various crystal planes, one or more of the monocrystal faces of lanthanum hexaboride would undoubtedly exhibit even better thermionic-emissive properties.

In addition to the expected improvement in thermionic characteristics with selected single-crystal surfaces, adsorption of cesium further reduces the work function of lanthanum hexaboride: Reference 3 indicates a 2.2-eV work function for cesium on lanthanum hexaboride at 1700 K without adsorptive optimization. And references 2 and 22 report a 0.8-eV work function for lanthanum hexaboride with optimum cesiation. Reference 2 omits the assumed $3\text{-A/cm}^2\text{ K}^2$ Richardson constant used by reference 22 probably because this is an unlikely value. If a $40\text{-A/cm}^2\text{ K}^2$ Richardson constant had been used, a 0.91-eV work-function minimum would have resulted for cesiated lanthanum hexaboride. For $120\text{-A/cm}^2\text{ K}^2$ the value would have been 0.96 eV. So a very conservative interpretation of reference 22 data still indicates a surface potential below 1.0 eV for optimum cesium adsorption on lanthanum hexaboride.

Obviously the cesium, substrate interactions are not the same for lanthanum hexaboride and metals: With metals, higher-work-function surfaces, like the most densely packed crystal faces of tungsten, rhenium, and iridium, retain cesium better and produce smaller surface potentials and greater emission. Lanthanum hexaboride, though, has approximately half the work-function value of these refractory metals, yet reaches much lower surface potentials with optimum cesium adsorption.

Reference 17 hypothesizes that the low work-functions for rare-earth hexaborides result from diffusion of metal atoms from the inner boron lattice to the surface. Ultimately, however, this proposed mechanism should create a superficial layer of metal - with a 3.3-eV work function in the lanthanum-hexaboride instance (ref. 2). Such a low metallic work function, according to the previously described relationship for cesium interactions with metals, means poor cesium adsorption and high optimum surface potentials. Of course, this deduction opposes the facts. Furthermore, recent publications confirm that lanthanum dispensing (ref. 17) is not the cause of the low work function of lanthanum

hexaboride (refs. 15, 23, and 24). In fact, the authors of reference 15 state that lanthanum hexaboride does not disperse lanthanum, that the so-called activation process previously thought to free lanthanum is really a removal of poisoning impurities, that lanthanum hexaboride not lanthanum evaporates from the surface at high temperatures, and that the low work function is indeed that of lanthanum hexaboride and not lanthanum.

Reference 23 also compares ion production from interactions of alkali-metal contaminants with high-work-function refractory metals and with low-work-function lanthanum hexaboride:

The desorbing species from rhenium and lanthanum hexaboride coated filaments were found to be identical. Initially at low temperatures extensive hydrocarbons were observed to desorb, and at higher temperatures positive ions of K and Na were emitted by the filaments. The relative magnitude of these two types of desorbing ions was found to be very dependent on time and temperature. If the filaments were raised to sufficiently high temperatures (about 1500° C), the intensity of these ion signals fell permanently below the detection limit of the experiment (5×10^3 ions/sec). . . .

Probably the most interesting aspect of the results is the extreme similarity of the thermodynamics of desorption of positive ion impurities from two surfaces differing so distinctly in their electronic characteristics (work function of rhenium = 4.9 eV; lanthanum hexaboride = 2.6 eV). Only in the kinetics of desorption were the ions coming from these two found to differ to any extent.

The assumption of a simple surface ionization process based on donation of the valence electrons of the alkali metal impurities to the surface before desorption makes these results extremely difficult to understand. The first ionization potentials of K and Na are 4.3 and 5.1 eV, respectively, [sic] this suggests that simple ionization by donation to the low

work-function lanthanum hexaboride is extremely implausible. In an attempt to eliminate the possibility of desorption of alkali impurities occurring from any small portions of rhenium metal exposed, the coated filaments were examined at $\times 500$ magnification using an optical microscope before being mounted in the apparatus. No evidence was obtained to suggest any flaws in the boride coating, either before or after the experiments. The possibility of microscopic patch fields with large differences in work function cannot however be overruled.

Based on electron emission lanthanum hexaboride has a low work function that is probably even lower for selected crystal planes. But lanthanum hexaboride also retains adsorbed cesium well and reaches optimum cesiated surface potentials considerably below those attained by the most effective metals, those with high bare work functions. And finally lanthanum hexaboride ionizes alkali metals in a manner similar to that of rhenium, which has one of the highest metal work functions.

One explanation for such concurrent phenomena might be that lanthanum hexaboride crystals have regions of much more widely varying work functions than those of metals. The very-low-work-function areas would emit electrons readily. The very-high-work-function zones would ionize alkali metals efficiently, adsorb and hold cesium well, and produce greatly diminished optimum cesiated surface potentials. These combined results are observed for lanthanum hexaboride. However scanning electron microscopy (ref. 15) indicates uniform electron emission over the whole surface of a "hot-pressed high-density lanthanum-hexaboride rod" with no evidence of low-work-function patches. Thus, if the preceding patch model applies, the regions of widely varying work functions must be considerably smaller than the "1000 Å linear dimensions . . . which can be clearly seen" (ref. 15).

In any event lanthanum hexaboride is indeed an interesting prospect for both emitters and collectors of cesium thermionic converters.

PROBABLE REDUCTIONS IN CESIUM-DIODE LOSSES WITH LANTHANUM-HEXABORIDE ELECTRODES

Internal losses for cesium thermionic converters developed for high-power space applications total approximately 0.5 V for emitters near 1700 K (ref. 25). This voltage drop results partially from the high cesium pressures needed to lower emitter work functions and produce effective electron emission. Another part of the losses derives from electron-collection or double-sheath effects caused by elevated collector (radiator) temperatures required for high-power generation in space. The latter is approximately 0.2 V, which leaves 0.3 V for the plasma generation alone (ref. 25).

As reference 25 states, this collector effect disappears at temperatures low enough to yield negligible back emission. For the land, sea, and low-power-space uses of high-efficiency, low-temperature thermionic converters, collector temperatures of 600 K and less, rather than 900 to 1100 K, are practical and often desirable. So back emission and the collector loss are not necessary evils. Without these problems the 0.3-V plasma drop represents all internal losses for these cesium diodes.

At this point, selecting 0.4 V for the plasma generation loss in a subsequent performance estimate for cesium thermionic converters with lanthanum-hexaboride electrodes appears conservative. And observing that recycling a small part of the diode power output in any of several ways could result in more efficient plasma generation adds to the conservatism.

But other interesting possibilities for reduction of internal losses arise with the prospect of lanthanum-hexaboride electrodes in cesium thermionic converters.

Lanthanum-hexaboride emitters need almost no cesium to produce low work functions and high electron emission. For example, the latest exacting determination placed the work function for bare lanthanum hexaboride at 2.4 eV between 1954 and 1735 K (ref. 15). In contrast, work functions of cesiated metal emitters in nearly optimized thermionic diodes for high-power space applications seldom fall to 2.4 eV (ref. 25).

Thus lanthanum-hexaboride emitters should allow better electron emission at much lower cesium pressures in thermionic converters. In addition to reducing electron transport resistance, diminished cesium concentrations decrease collisional recombination processes that consume plasma ions. These two effects mean lower plasma losses with lanthanum-hexaboride emitters. Of course, an emitter that yields greater electron current densities with reduced temperatures and much less cesium also cuts parasitic thermal radiation and conduction across the interelectrode gap.

At the same time external losses caused by radiation to the surroundings and by thermal conduction and electric resistance in the electrode leads drop with diminishing temperatures for both space and earth applications. And environmental conduction and convection decrease for land and sea uses of thermionic converters.

So lanthanum-hexaboride electrodes should allow significant reductions in cesium-diode losses to augment the more obvious electron-emission and output-voltage gains that result directly from lower work functions.

POWER-DENSITY ESTIMATES FOR CESIUM THERMIONIC CONVERTERS WITH LANTHANUM-HEXABORIDE ELECTRODES

The preceding information allows a simplified approximation of the power output for a cesium thermionic converter with lanthanum-hexaboride electrodes. The conditions selected for this purpose are a 1700 K emitter with a 2.3-eV work function and a $40\text{-A/cm}^2\text{ K}^2$ Richardson constant, a 600 K collector with a 1.0-eV work function and a $40\text{-A/cm}^2\text{ K}^2$ Richardson constant, and internal losses equivalent to a 0.4-V drop. As the cited references and discussion indicate, these are conservative characteristics. But even such conservatism leads to calculated results of approximately 18 A/cm^2 for the emitter, negligible back emission (0.06 A/cm^2) from the collector, and 0.9 V for the electrode voltage. Thus, a conservative estimate places the output at over 16 W/cm^2 .

Using a 2.2-eV emitter work function (ref. 22), which is still far above the value for optimum cesium absorption on lanthanum hexaboride, nearly doubles (1.98) the 1700 K-emitter current density. In addition a 0.3-V plasma drop (ref. 25), which can probably be reduced farther according to the arguments of the last section, and a 0.8-eV collector work function (refs. 2 and 22) increase the output voltage by 0.3 V. So with strict adherence to referential numbers an approximate output of over 42 W/cm^2 results.

Even the conservative estimate of over 16 W/cm^2 is nearly three times better than the best cesium diodes with clean 110-tungsten emitters and niobium collectors developed for high-power space applications: 5.4 W/cm^2 at 0.3 V for a 1700 K emitter (fig. 4 of ref. 26, also refs. 27 and 28).

The comparisons are for 1700 K because values for lanthanum-hexaboride work functions with and without adsorbed cesium are available for that temperature. But as the discussions of the previous section imply, the relative advantages of lanthanum-hexaboride electrodes in cesium thermionic converters should be greater at lower temperatures.

Of course, the preceding estimates depend entirely on the validity of published values for emission characteristics and plasma losses. Only tests of actual cesium thermionic converters with lanthanum-hexaboride emitters and collectors will reveal how close these approximations are to reality.

ASPECTS OF LANTHANUM-HEXABORIDE FABRICATION

In some past work at the NASA Lewis Research Center, technicians have cut, turned, shaped, smoothed, and lapped lanthanum hexaboride using precision machining techniques. They have also brazed lanthanum-hexaboride emitters and collectors to bases for variable-gap planar cesium diodes with miniature electrodes (diminiodes: refs. 26 and 29). However, the low-vapor-pressure fillers used were those for brazing refractory-metal electrodes in diminiodes (refs. 29 and 30), and the lanthanum-hexaboride compatibilities of these brazes are not established.

Other filler materials which prevent lanthanum-hexaboride, refractory-metal interactions (refs. 31 and 32) are available and preferred (refs. 1, 33, and 34). The compounds for brazing lanthanum-hexaboride electrodes to refractory-metal bases are themselves metal-lides: molybdenum disilicide, MoSi_2 ; tungsten carbide, WC; and the chromium carbide, Cr_7C_3 . Molybdenum disilicide apparently gives the best bond between lanthanum hexaboride and tantalum and provides an effective barrier to prevent undesirable interfacial reactions as well (ref. 35). In addition, graphite (refs. 17, 31, and 36), tantalum carbide (refs. 17 and 37), thoria (ref. 38), and rhenium (refs. 24 and 39 to 41) act as lanthanum-hexaboride-resistant coatings or bases - generally below 1500°C .

Incidentally reference 17 indicates strong vaporization of lanthanum hexaboride at 1500°C . But that paper gives a 2210°C melting point for lanthanum hexaboride, where later values all appear to be above 2500°C (refs. 42 to 45). Reference 43 states that the 2210°C melting point observed by reference 17 was probably that of boron. This rationalization in turn implies that the lanthanum-hexaboride composition of reference 17 was a combination of at least boron, lanthanum tetraboride, and lanthanum hexaboride. And although lanthanum hexaboride evaporates stoichiometrically (refs. 15, 42, 44, and 46), lanthanum tetraboride decomposes with heat and preferentially loses lanthanum (refs. 42, 44, and 46). So both the melting point and vaporization rates revealed by reference 17 for lanthanum hexaboride are somewhat in doubt.

Finally, reference 47 records that "the precipitation of the boride during the thermal decomposition of borohydrides has been used to produce borides of a number of metals . . ." Other metal-lides have also been deposited on substrates as results of high-temperature thermal and chemical reactions. Such vapor-deposition processes should adapt to forming cylindric emitters and collectors of lanthanum hexaboride. Thus, no insurmountable barriers appear to preclude the fabrication and testing of practical cesium thermionic converters with lanthanum-hexaboride electrodes.

FUTURE CESIATED METALLIC-BORIDE ELECTRODES

Although little is known about cesium interactions with lanthanum-hexaboride surfaces, enough information is available to predict excellent performance for low-temperature cesium thermionic converters with lanthanum-hexaboride electrodes. In fact the large current densities and output voltages and the diminished internal and external losses inferred from published data imply cesium-diode electrode efficiencies for lanthanum hexaboride several times those for the best refractory metals. Furthermore lanthanum-hexaboride fabrication presents no overwhelming difficulties. Methods also exist to prevent destructive lanthanum-hexaboride, metal reactions. And the anticipated operating temperatures below 1700 K should help to preclude such interactions and produce long service-life times.

In short, all prospects seem good. Apparently definition of the problems involved in using lanthanum-hexaboride electrodes in cesium thermionic converters must await the building and evaluation stages.

While lanthanum-hexaboride data are meager, results for cesium adsorption on other metallic hexaborides are nil. But these compounds have potentials worth considering. For example, reference 1 emphasizes yttrium hexaboride and ". . . the possibility of preparing cathodes from it, which are more efficient than those of lanthanum hexaboride, with a reduction of the working temperatures by 100^o-150^o C." Moreover, the physicochemical comparability of these two metallides (refs. 1 and 2) indicates probable similarities in their cesiated effects. Then, on the basis of bare thermionic capabilities alone (refs. 1 and 2), the hexaborides of cerium, gadolinium, terbium, and yttrium deserve screening in cesium diodes. And the combination of thermionics and ready availability makes calcium hexaboride, and perhaps its strontium counterpart, of interest too. Worthy of consideration also are the very-high-melting, chemically resistant diborides of tantalum, titanium, tungsten, and possibly scandium with published work-function values ranging imprecisely between 2.3 and 3.9 eV (ref. 2). However, neither cesiation data nor physical and chemical extrapolations from the hexaborides are available for this latter group of compounds. References 2 and 3 report

approximately 2.2-eV bare work functions for dodecaborides of cerium and lanthanum; the existence of such compositions as true compounds, though, is still unproven (refs. 2, 42, and 43). The tetraboride of cerium has a very low work function too - between 2.07 and 2.42 eV, as noted in reference 1.

Thus a cursory examination of metal borides in general reveals possibilities for cesiated electrodes other than lanthanum hexaboride. And these more promising metallides are candidates not only for thermionic diodes but also for electrodes of magnetohydrodynamic converters. Of course, different conditions prevail in magnetohydrodynamic applications utilizing cesium seeding. These combustion products often add to the chemical activity of cesium. In light of this environmental difference for the electrodes, a brief statement on the thermochemical properties of metallic borides seems in order (ref. 48):

The metal borides are characterized by general chemical inertness toward non-oxidizing acids (Mg_3B_2 , MnB are exceptions). Many are stable in air even to comparatively high temperatures. Strong oxidizing agents such as chlorine, fluorine, nitric acid, or hydrogen peroxide cause decompositions in most cases. The compounds are particularly susceptible to attack by alkaline materials, especially by fused alkalis under oxidizing conditions (e.g., with Na_2O_2 , PbO_2). The inertness of the MB_6 -type borides is striking, particularly in comparison with the ease with which nitrides and carbides of these same elements are hydrolyzed. Thus, these compounds are not attacked by acids such as hydrochloric, hydrofluoric, or dilute sulfuric, although they are decomposed by hot concentrated sulfuric acid or nitric acid.

The initially listed texts on metallides, such as reference 7, also testify to the high-temperature oxidation resistance of metallic borides. Reference 1 specifically indicates no lasting negative effects from oxygen as well as cesium adsorption on lanthanum-hexaboride emitters. However, interactions of combustion products and cesium on hot surfaces of lanthanum hexaboride or other metal borides may be another matter. How close does this last condition approximate the "attack by alkaline materials" mentioned by reference 48? Certainly an answer to that question

is a prime prerequisite for studies of cesiated metallic-boride electrodes for magnetohydrodynamic applications.

In any event, the potentialities discussed here appear to justify immediate screening of lanthanum hexaboride and several other metal borides to determine cesiated-electrode performances and life-times under conditions for thermionic and magnetohydrodynamic energy conversion.

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