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TITLE: Thermionic Topping of a Solar Power Plant Using Converters Containing Lanthanum Hexaboride Electrodes.*

AUTHOR(S): Edmund Storms

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los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

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Introduction

The efficiency of thermionic conversion, as described in the previous paper, has increased as the processes occurring at the electrode surfaces have been better understood. The discovery that surface oxygen improves the behavior of a tungsten electrode made an important contribution and now the W-O-Cs electrode is the standard against which further progress is measured. Unfortunately, there are only a limited number of variables which can be manipulated to improve the performance of such electrodes. Consequently, efforts are being made to find other electrode materials having a sufficiently low vaporization rate for atoms while retaining a high emission rate for electrons in the presence of Cs, a fairly unusual combination of properties. Finding such materials is expensive and the low level of funding has not given much urgency to progress in this area. Recently, however, some success has resulted from using a thermionic emitter which has found application in other areas.

Several workers have demonstrated that a significant increase in converter efficiency is possible, using lanthanum hexaboride electrodes. Russian experience, which leads the U.S. in this area, has added confidence to this approach. While LaB_6 appears to be superior to W-O-Cs, further development requires understanding a behavior which is not present when elemental electrodes are used. This paper will discuss some of the important variables associated with LaB_6 and, indeed, with compounds in general.

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Discussion

The most important variable which determines the behavior of lanthanum hexaboride is its stoichiometry. This compound can exist over a composition range at high temperature as shown in the partial phase diagram in Fig. 1.(1) All of the properties change as the composition is changed across this rather narrow range. Because very little attention has been given to this variable in the past, most early work can only be used as a guide and must be repeated before the actual behavior is known.

For a thermionic application, where atom and electron vaporization rates are important, it is the surface composition which must be considered. When lanthanum hexaboride vaporizes in vacuum, the surface quickly acquires a composition which is different from the interior, unless the interior has the congruently vaporizing composition (CVC). Most samples used in either research or application will not be at this special composition and will, therefore, show an inconsistent behavior. Furthermore, this surface composition will change either by reaction with ambient gases, hot surfaces nearby or when the temperature is changed. Failure to consider this behavior has lead to the impression that LaB_6 was approximately 100 times more volatile than is actually the case. Naturally, this error gave little encouragement to the use of LaB_6 in an application needing a lifetime of many years.

Regardless of the interior composition, the surface will tend to approach a value near $LaB_{6.05}$. However, the surface will be on the boron rich side of this composition if the interior is on the boron rich side and the reverse is true if the interior is on the boron poor side. Figure 2 shows how the surface composition is related to the interior composition at 1700 K.

As the temperature is increased, the surface composition becomes less influenced by the interior composition, as can be seen in Fig. 3 for 2100 K. From these figures we can conclude that the surface composition will change with temperature and this effect is strongest for interior compositions which are boron poor compared to $LaB_{6.0}$.

How does this behavior apply to the use of LaB_6 in a thermionic converter? The answer to this question involves three properties: the vaporization rate of atoms, which determines the life; the work function, which determines the efficiency; and the effect of Cs on these two properties. Other gases besides Cs may be useful with LaB_6, but this will not be discussed here.

Attrition caused by atom vaporization in vacuum at 1700 K is changed when the interior composition is changed, as shown in Fig. 4. This behavior will be modified if the samples are impure or if oxygen containing molecules are in the ambient gas. Oxygen causes the volatility of lanthanum hexaboride to increase through the formation of $LaO_{(g)}$ and various gaseous oxides of boron. The data presented are typical of slightly impure LaB_6 of commercial quality. When the temperature is changed, the change in attrition rate also depends on the interior composition. Figure 5 shows this change for samples consisting of $LaB_4 + LaB_6$ and of $LaB_6 + LaB_9$. Again the presence of oxygen will change this behavior.

Work done in Russia (2) has shown that the vacuum work function is a strong function of composition. This explains in part why the various reported values are in such disagreement. Since the work function is sensitive to the surface composition and the surface composition will change if the temperature or interior composition is changed, the measurement of a meaningful value for the work function is no easy task. If the value is based on the slope of a Log I/T^2 vs $1/T$ plot, the changing composition will produce an error. On the other hand, if the effective work function is calculated using the Richardson-Dushman equation with a value of 120 A/cm^2T^2 for the constant, the result may be in error because the constant may not apply to such compounds. In any case, the work function value will change when the temperature is changed because the surface composition changes. Consequently, when the electron emission current at one temperature is calculated from a reported work function value obtained at a different temperature the result may be seriously in error. I mention this problem to show some of the difficulties in making decisions about the usefulness of such materials. Although the effect of composition makes accurate measurements difficult, it does give an additional variable which can be adjusted to improve the performance of a device.

The cesiated work function is expensive to measure and little information is available. Unpublished information suggests the compound behaves differently compared to the elements. The reactivity of Cs with lanthanum hexaboride will once again, be sensitive to the stoichiometry of the surface.

In spite of these sources of ignorance, the actual use of LaB_6 electrodes in a cesium diode has produced encouraging results. Shortly before the program was cancelled, Jim Morris and co-workers, at NASA Lewis, obtained the results shown in Fig. 6.(3) Nearly stoichiometric LaB_6 was used as the emitter and slightly boron rich material was used as the collector. Without making any attempt to optimize the Cs pressure or temperature, they obtained results which are a significant improvement compared to the W-O-Cs electrode.

I have attempted to summarize, in a brief and informal way, what is known about LaB_6. I have not discussed the increasing amount of information about the behavior of single crystals or the effects produced by impurities, such as carbon. Much work needs to be done, and, under the present approach, an application must be found to provide the financial support. While the use of this method in solar conversion is not the only, nor necessarily, the best application at this time, your appreciation of the potential of this technique can encourage the necessary support, and hopefully, lead to a diode which will be useful in the future.

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3. Morris, J., Private Communication (1978).

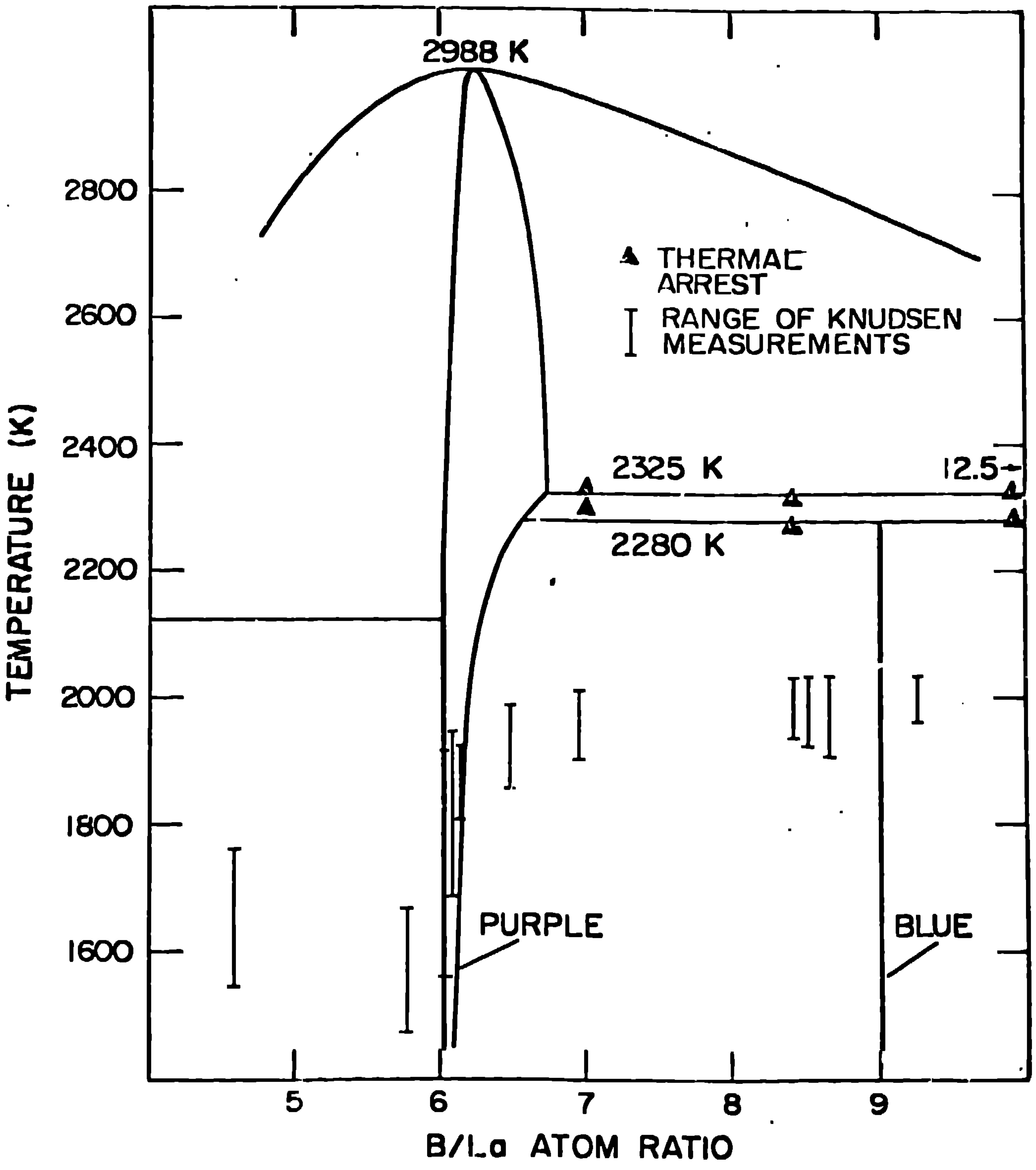

Figure 1. Partial Phase Diagram of the La-B System.

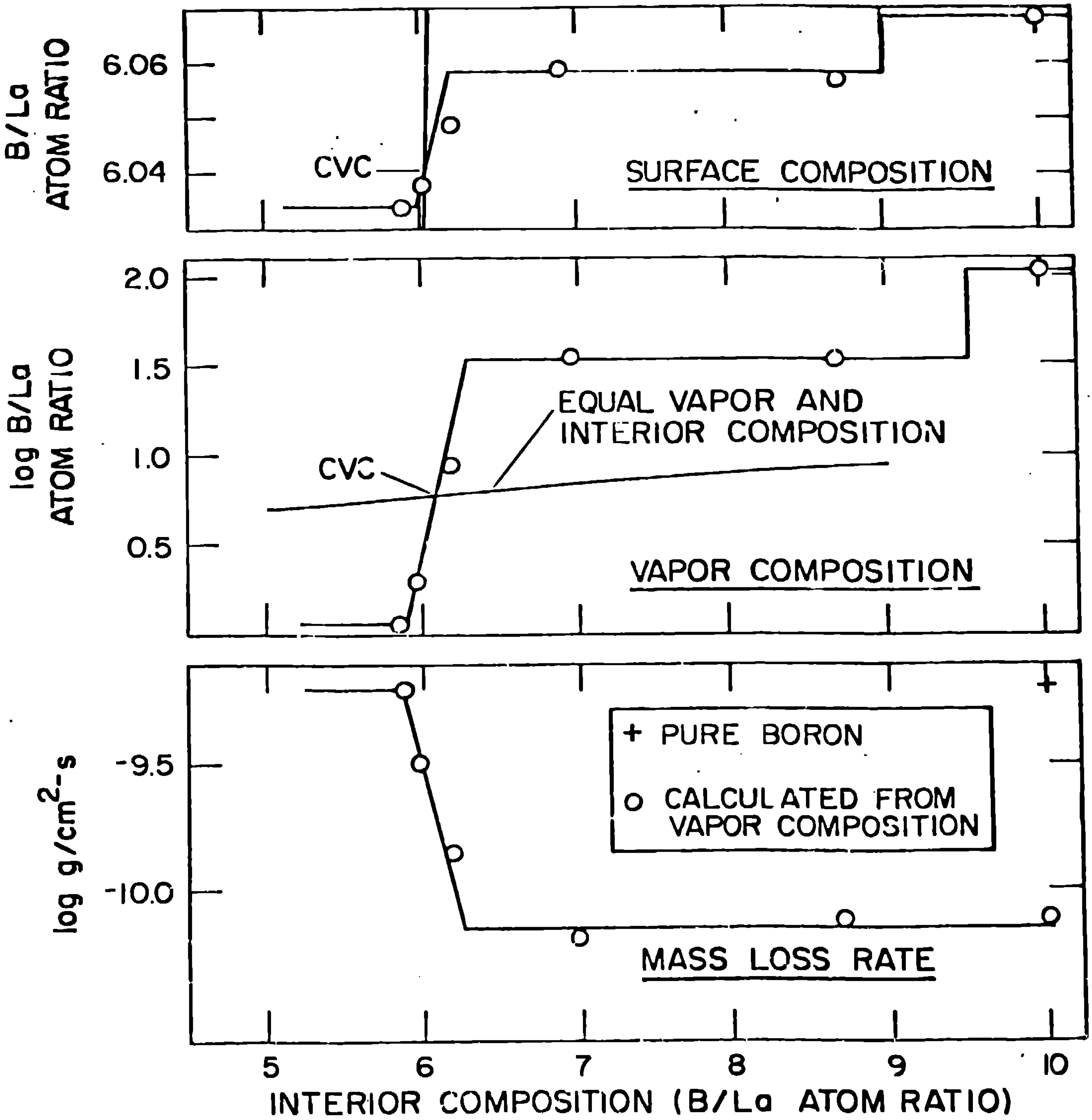

Figure 2. Relationship Between Surface Composition, Vapor Composition, and Mass Loss Rate as a Function of Interior Composition at 1700K for Freely Vaporizing Material.

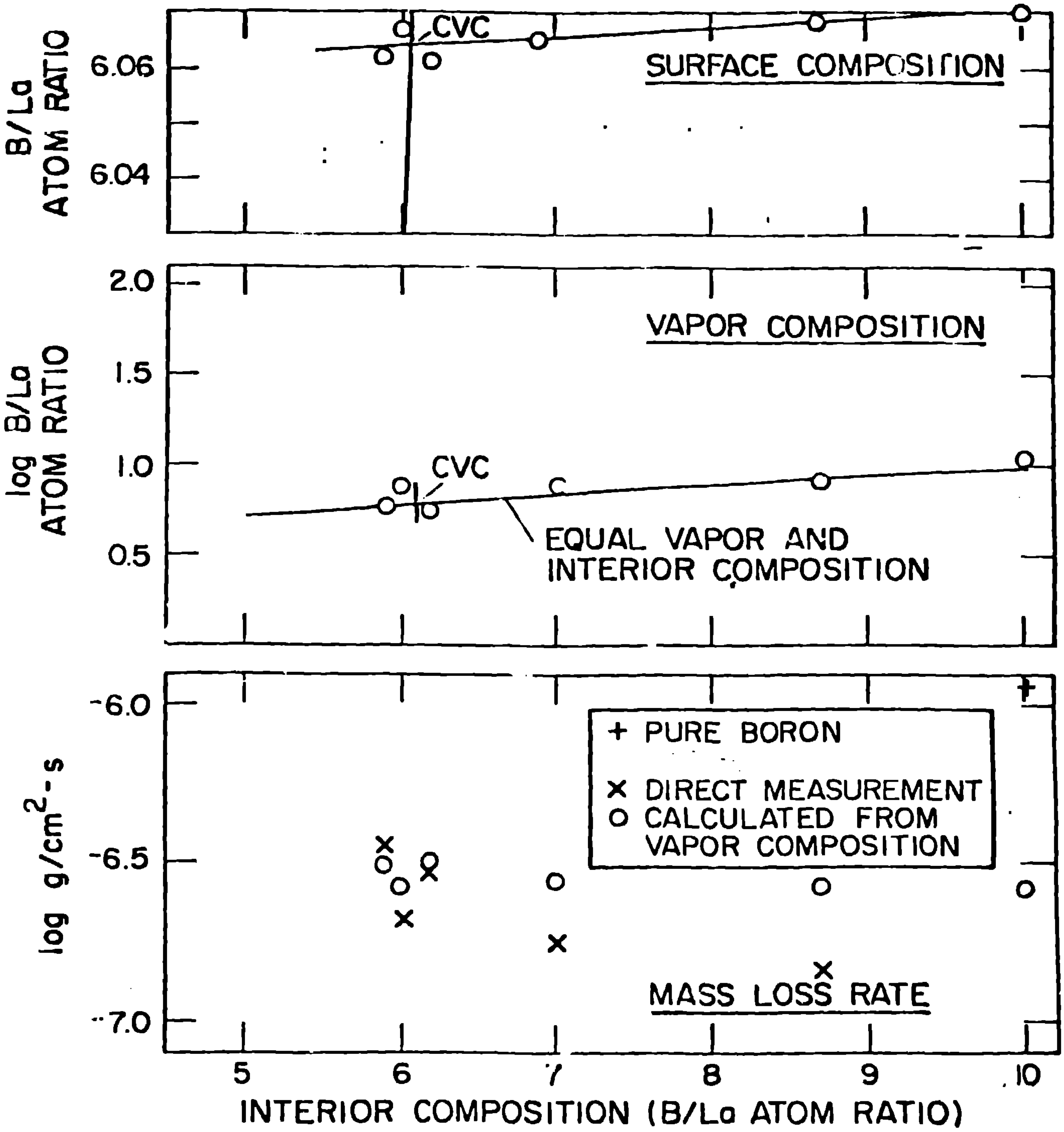

Figure 3. Relationship Between Surface Composition, Vapor Composition, and Mass Loss Rate as a Function of Interior Composition at 2100K for Freely Vaporizing Material.

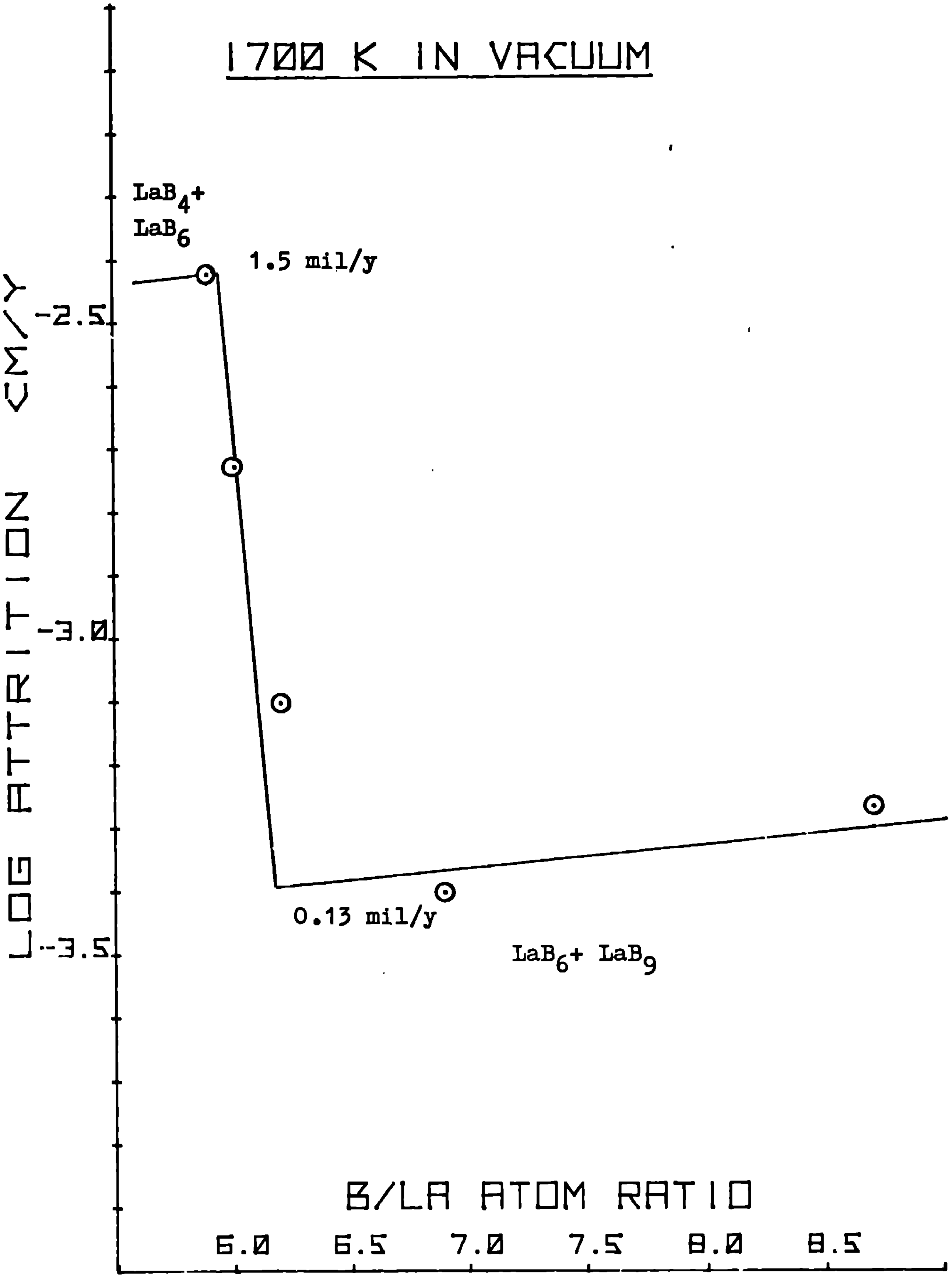

Figure 4. Attrition Rate for Various Compositions of Lanthanum Hexaboride at 1700K in Vacuum.

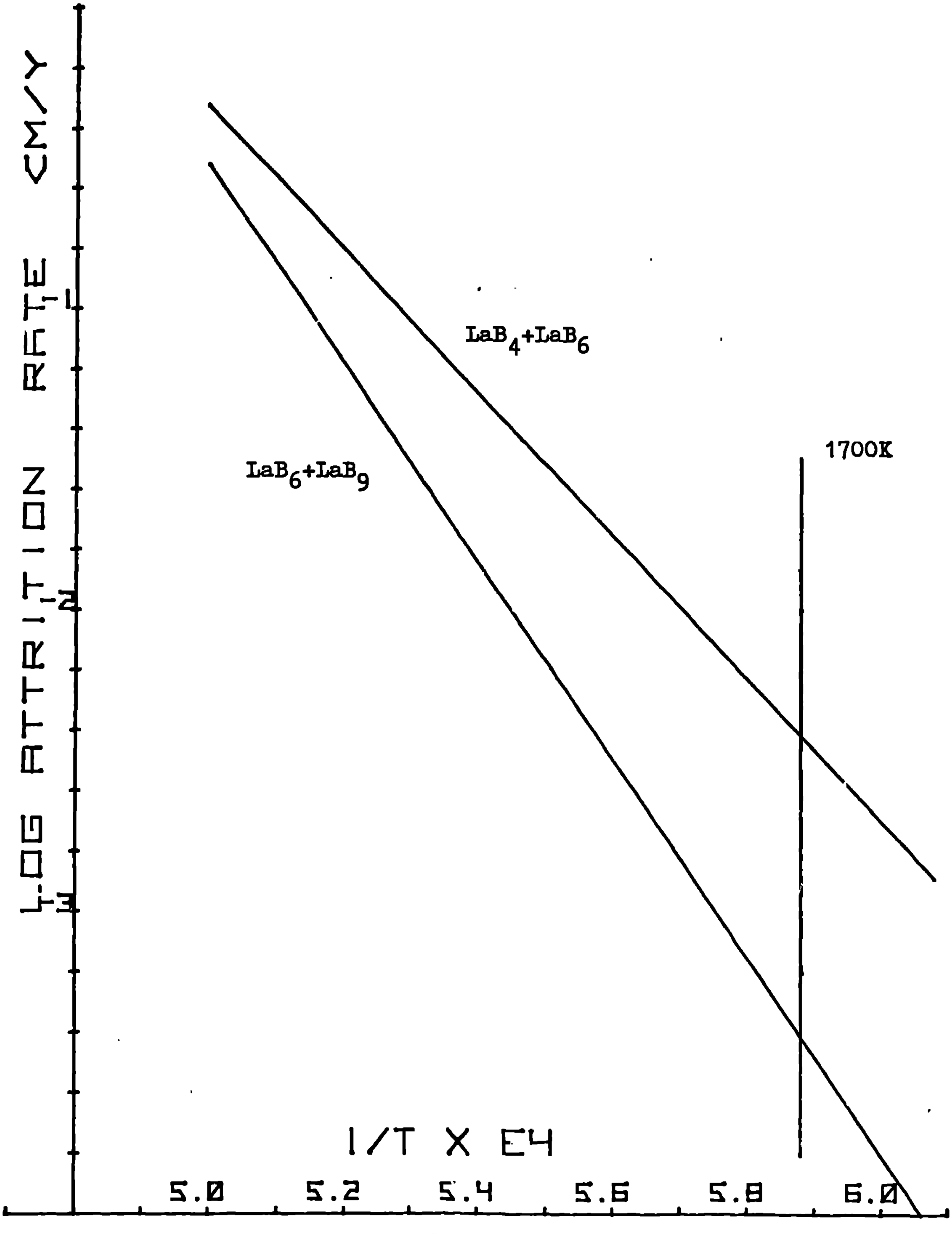

Figure 5. Attrition Rates for the Composition Extremes of Lanthanum Hexaboride vs 1/T.

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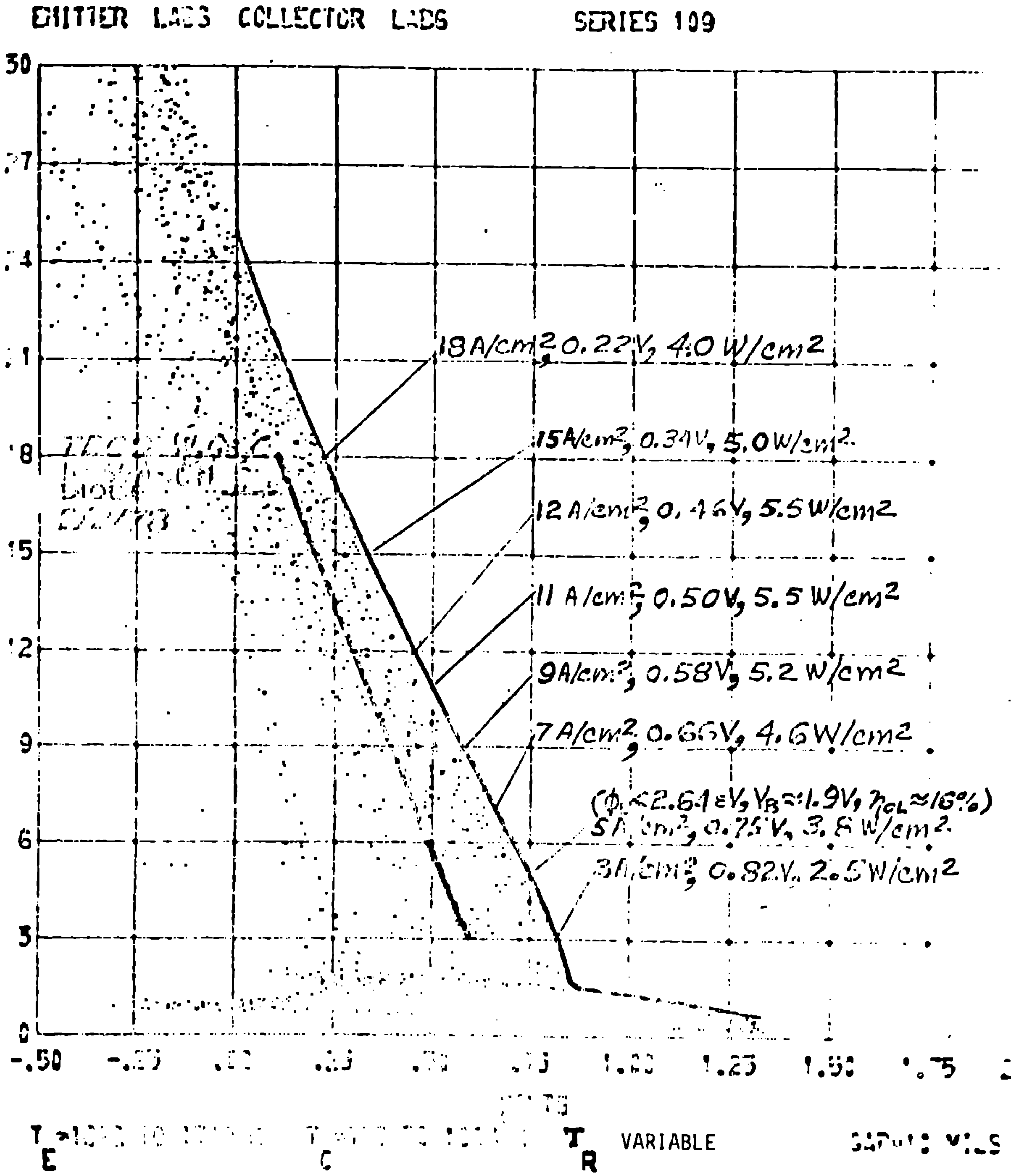

Figure 6. Preliminary Relationship between Generated Current and Voltage in a Cesium Diode using LaB_6 Electrodes. (Private Communication from Jim Morris, NASA Lewis)