

Calculation of composition in $\text{LaB}_6\text{--TiB}_2$ and $\text{LaB}_6\text{--ZrB}_2$ eutectics by means of pseudopotential method

D. Zakarian^a, V. Kartuzov^a, E. Kartuzov^a, A. Khachatryan^{a,*}, A. Sayir^b

^a Institute for Problems in Materials Science, NAS of Ukraine, Kyiv, Ukraine

^b NASA Glenn Center, USA

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Abstract

A method of aprioristic pseudo-potential and an internal energy of individual components of composite materials are introduced that allows prediction of eutectic composition for the eutectic invariant point of $\text{LaB}_6\text{--TiB}_2$ and $\text{LaB}_6\text{--ZrB}_2$ system. The numerical predictions agreed well with the experimental data for eutectic composition. We determined the crystal lattice parameters and demonstrated the insolubility of the constituent phases of $\text{LaB}_6\text{--TiB}_2$ and $\text{LaB}_6\text{--ZrB}_2$ eutectic systems. The experimental results validated the predictions for the lattice constants of the constituent phases. The transferability of these potentials by including kinetic energy components has been discussed.

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1. Introduction

Lanthanum hexaboride LaB_6 has a very high melting point and possesses a high density of free electrons. These unique combinations of properties make LaB_6 the primary candidate material for electron emission application. The electron emission has to be carried out at elevated temperatures and this application necessitates significant demands on the mechanical properties of LaB_6 . Lanthanum hexaboride is intrinsically brittle and thus the fracture toughness and tensile strength at elevated temperatures are of essential importance. A systematic study was undertaken to enhance the mechanical properties of the lanthanum hexaboride with the aim to improve reliability and life cycle. Yet, the improvement of mechanical properties of LaB_6 was limited due to the brittle characteristic of single crystals. We adopted a composite structure approach to produce unique microstructures to improve electron emission and mechanical properties concurrently. We used directional solidification process to fabricate dual phase structure by forming diborides of transition metals from groups IV–VI within the LaB_6 phase.^{1,2}

The directional solidification approach is not a new subject in the material community and metal–metal eutectics have been investigated in some detail.³ Most of the previous investigations on directionally solidified eutectic systems were experimental studies of metal eutectics. The continuum scale models were focused on solidification conditions of metal eutectics systems⁴ and provided some insight about the structure. In contrary to metal eutectic systems, the understanding of ceramic eutectic systems is in its infancy.⁵ The pioneering work by Ordanyan et al.^{1,2} and Paderno et al.^{6–8} provided guidance for the LaB_6 containing boride eutectic systems but the understanding of boride–boride eutectics systems are further complicated by a lack of reliable physical property data. The processing of boride eutectics requires ultra high temperatures and this introduces additional hurdles, i.e., to identify new compositions and eutectic invariant points. In accordance with these challenges, we used pseudopotentials in solid-state electronic structure calculations and investigated the compositions and eutectic invariant point for $\text{LaB}_6\text{--ZrB}_2$ and $\text{LaB}_6\text{--TiB}_2$ systems. The first step in the reconstruction of compositional spectrum is to identify exact eutectic point for wide range borides. The results we present here are only a part of our larger study on the phase stability, mechanical performance and emission properties of boride eutectics relevant to ultra high temperature materials. In this effort, the internal energy of constituent phases and crystal lat-

* Corresponding author. Tel.: +380 44 424 0102; fax: +380 44 424 2131.
E-mail address: nasu@mail.ru (A. Khachatryan).

tice parameters were calculated for the first time by means of quantum-mechanical calculations. The eutectic compositions of $\text{LaB}_6\text{-ZrB}_2$ and $\text{LaB}_6\text{-TiB}_2$ systems were determined from the condition of minimum thermodynamic potential at the equilibrium state and to our knowledge this approach is a pioneering approach for eutectic systems.

2. Results and discussion

The investigation of physico-mechanical properties of composite materials by means of quantum mechanics requires calculation of internal energy of crystals from the information about crystal structure of both hexaboride and diboride phases. Lanthanum hexaboride LaB_6 has a cubic structure and crystallizes in CaB_6 structure, where in a simple cubic lattice structure the lanthanum metal atoms are centered by octahedron from boron atoms. Diborides of transition metals have hexagonal structure similar to AlB_2 in which boron atoms form graphite-like networks, perpendicular to c -axis of unit cell. Thus, the diboride structure is built by the alternating layers of metal atoms and layers of boron network. The lanthanum atoms are positioned in hexagonal units of the lattice with a small ratio c/a and boron atoms form a hexagonal two-dimensional network.⁹

To derive state equation for the eutectic $\text{LaB}_6\text{-ZrB}_2$ or $\text{LaB}_6\text{-TiB}_2$ system requires judicious selection of an elementary cell for this composite structure that consists of LaB_6 and ZrB_2 or TiB_2 phases. We make use of experimental facts, that La, B, Zr (Ti) atoms do not build ternary or intermediate compounds, and the interface of eutectic phases was constructed through sharing of boron atoms between LaB_6 and ZrB_2 (or TiB_6) phases.⁷

2.1. Energy consideration of binary system

The macroscopic state of the system can be described through thermodynamic equation of state, i.e., when all internal properties are fixed. The thermodynamic function of state is expressed as

$$F = U_S - TS \quad (1)$$

where U_S is the internal energy of system, T is the absolute temperature, and S is the entropy. In principle, the microscopic state can be described from the knowledge of masses (velocities and moments), positions, all modes of motion of all of the constituent particles in a system. In the absence of such detailed knowledge as is required to determine state of the system, we utilize the properties based on different statistical theories on elementary models of interatomic interactions.¹⁰ An internal energy of each phase can be presented as $U_S = U + U_T$, where U is the energy of crystal lattice at absolute zero temperature, and U_T is the energy of thermal fluctuations at given temperature. The fluctuation of energy due to thermal field does not depend on state of the phase as a first approximation. Therefore, thermal energy contribution may be neglected for the analysis of energy balance and U_S may be replaced instead of U .

To carry out calculations from the first principles, we used a pseudo-potential method that has been described previously.¹¹

The matrix phase of eutectic consisted of single crystal LaB_6 phase and associated pseudo-potential can be represented as

$$V_{\text{LaB}_6}(q) = \frac{1}{\Omega_1} \left[\Omega_{\text{La}} V_{\text{La}}(q) + \Omega_{\text{B}} V_{\text{B}}(q) \sum_{i=1}^6 \exp(-i\vec{q}\vec{\tau}_i) \right] \quad (2)$$

In an analogous manner, the pseudo-potential for borides of transition metals MeB_2 (ZrB_2 or TiB_2) may be expressed by

$$V_{\text{MeB}_2}(q) = \frac{1}{\Omega_2} \left[\Omega_{\text{Me}} V_{\text{Me}}(q) + \Omega_{\text{B}} V_{\text{B}}(q) \sum_{i=1}^2 \exp(-i\vec{q}\vec{\tau}_i) \right] \quad (3)$$

Here Ω_{La} , Ω_{Me} and Ω_{B} are the volumes of atoms La, Me (Zr, Ti) and B; $\vec{\tau}_i$ are the radii vectors of boron atoms in an elementary cell; Ω_1 and Ω_2 are the volumes per one molecule LaB_6 and MeB_2 , respectively; \vec{q} is a wave vector.

The energy of electron-ion pairs for the constituent components of eutectic system can be described using pseudo-potential method of second order of perturbation theory and can be expressed as⁹:

$$U = \frac{1}{N} \sum_{i,j} \Phi(R_i - R_j) \quad (4)$$

$R_i - R_j$ is the interatomic distances, and N is the number of atoms in representative volume.

The sum of energy of constant molecular volume depends on type of structure and could be approximated as a sum of electrostatic energy and interfacial energy of eutectic structure. This can be expressed as a sum of pair intermolecular (interatomic) potentials;

$$\Phi(r) = \frac{z^2}{r} + \frac{2\Omega}{8\pi^3} \int \exp(i\vec{q}\vec{r}) \Phi_0(q) d\vec{q}, \quad (5)$$

where

$$\Phi_0(q) = V^2(q) \chi(q) \varepsilon(q) \quad (6)$$

Here functions $\varepsilon(q)$ and $\chi(q)$, describing shielding and correlation of electrons in the component are determined in Ref. 12; $r = |\vec{R}_i - \vec{R}_j|$ is the distance between atoms; Ω is the volume per one molecule, and $V(q)$ full pseudo-potential of components, z is the number of valence electrons of pair of interacting atoms.

2.2. Calculation of internal energy of LaB_6 and MeB_2 eutectic systems

The general form for the intermolecular potential for a pair of molecules i and j that placed from each other in a distance of R_{ij} , has the form

$$\Phi(R_{ij}) = \frac{2\Omega_0}{8\pi^3} \int \left[\Phi_0(\vec{q}) + \frac{2\pi}{\Omega_0 q^2} \left(z_1 \frac{\Omega_1}{\Omega_0} + z_2 \frac{\Omega_2}{\Omega_0} \sum_n \exp(-i\vec{q}\vec{\delta}_n) \right)^2 \right] \exp(i\vec{q}\vec{R}_{ij}) d\vec{q} \quad (7)$$

Here z_1, z_2 is the number of free electrons of atoms that formed the molecular composition. In addition, the energy of molecule interaction can be presented as a sum of pair intermolecular potentials:

$$U_{AA} = \frac{1}{N_0} \sum_{i,j} \Phi(\vec{R}_{ij}) \quad (8)$$

where N_0 is the number of molecules in representative cell.

The values of internal energies U_{AA} and U_{BB} corresponding to the energy of interaction between identical molecules (LaB_6 – LaB_6) or (MeB_2 – MeB_2) components of the eutectic composite and are calculated by formula (8). The crystal lattice parameters of the constituent phases, LaB_2 and MeB_2 , have been computed from the conditions of minimum energy criteria. To calculate the energy of interaction of various molecules A and B, we choose a representative cell in virtual crystal lattice with average volume and charge as follows:

$$\bar{\Omega} = \frac{1}{2}(\Omega_A + \Omega_B); \quad \bar{z} = \frac{1}{2}(z_A + z_B) \quad (9)$$

where Ω_A, z_A and Ω_B, z_B represents volume and charge of molecules A and B. We can write $\Phi_0(q)$ term in the form

$$\Phi_0(q) = V_A(q)V_B(q)\bar{\chi}(q)\bar{\varepsilon}(q) \quad (10)$$

Here V_A and V_B pseudopotentials of molecules of type A and B, but $\bar{\chi}(q)$ and $\bar{\varepsilon}(q)$ functions accounting for exchange-correlation effects and screening of free electron gas of averaged volume. Pair intermolecular potential for two types of molecules located on the distance R_{ij} can be written as:

$$\Phi_{AB}(R_{ij}) = \frac{2\bar{\Omega}}{(2\pi^3)} \int_0^{2k_F} \left[\Phi_0(q) + \frac{2\pi}{\bar{\Omega}q_0^2} \bar{z}^2 \right] \exp(i\vec{q}_0 \vec{R}_{ij}) d\vec{q} \quad (11)$$

Here \vec{q}_0 is the wave vector of mixed structure. The averaging is made through numerical integration on q_0 in interval $[0-2k_F^0]$ (k_F^0 is the Fermi impulse for averaged volume). The energy of interaction between molecules of types A and B would be written as follows:

$$U_{AB} = \frac{1}{N} \sum_{l,j} \Phi_{AB}(\vec{R}_{lj}) \quad (12)$$

Pair interatomic potentials for the investigated materials were calculated in terms of an approximation of the first coordination sphere. Energy of electron–ionic interactions was calculated for single LaB_6 and ZrB_2 (TiB_2) phases and for binary LaB_6 – ZrB_2 (TiB_2) eutectic system. The lattice constants were computed from the minimum of energy considerations and results are summarized in Table 1. The calculated values of energy of interaction between components in the system LaB_6 – TiB_2 (ZrB_2) are presented in Table 2. The comparison of energy of interactions shown in Table 2 reveal that molecular interaction between same type molecules is stronger than its polytype. This finding provides explanation for the formation of binary eutectic phases rather than a continuous solid solution.

Table 1

Calculated lattice constants of the constituent phases of eutectic and line compounds.

Material	The periods of lattice a,c (nm)			
	Pure compounds		Phases in alloy of eutectic structure	
	Calculations	Experiments	Calculations	
			LaB_6 – TiB_2	LaB_6 – ZrB_2
LaB_6	0.4153	0.4204	0.421	0.427
TiB_2	0.30259	0.302	0.3024	
	0.3232	0.3246	0.325	
ZrB_2	0.3195	0.317		0.311
	0.34808	0.353		0.345

2.3. Calculation of characteristic parameters of LaB_6 and MeB_2 eutectic systems

If C is the concentration of component A (LaB_6), then for U_S we obtain

$$U_S = C^2 U_{AA} + (1 - C)^2 U_{BB} + C(1 - C) U_{AB}, \quad (13)$$

where U_{AA} , U_{BB} , and U_{AB} are the energies of interaction between components A–A (LaB_6 – LaB_6), B–B (MeB_2 – MeB_2), and A–B (LaB_6 – MeB_2) respectively.

The fluctuation of energy due to thermal field does not depend on state of the phase as a first approximation. Therefore, thermal energy contribution may be neglected for the analysis of energy balance and U_S may be replaced instead of U . When $T=0$, as a second order of approximation of the pseudo-potential and taking into consideration of Eqs. (1) and (4), we may write the following expression for free energy:

$$F = C^2 U_{AA} + (1 - C)^2 U_{BB} + C(1 - C) U_{AB} \quad (14)$$

Proceeding from these assumptions, a functional dependence of thermodynamic potentials (14) for the system LaB_6 – MeB_2 versus LaB_6 concentration is obtained when $T=0$. The thermodynamic potential has a negative second derivative that shows evidence of low energy of bonding between the constituent phases of eutectic system (Table 2).^{10,11} Such a function for the internal energy change can be written in the form

$$\Delta U = U_{AB} - 0.5 \cdot (U_{AA} + U_{BB}) \quad (15)$$

which defines a type and a measure of stability of phase (solid or liquid, or as in this case two different solid phases).⁹ In case

Table 2

Internal energy of interaction between components in system LaB_6 – MeB_2 .

Characteristics		Energy (a.e.)
U_{AA}	LaB_6	0.84145
U_{BB}	TiB_2	2.18914
U_{BB}	ZrB_2	1.6979
U_{AB}	LaB_6 – TiB_2	0.2233
U_{AB}	LaB_6 – ZrB_2	0.2076

$\Delta U < 0$, then an interaction of atoms of diverse components is stronger than an interaction of atoms of the same component; thus they form a continuous number of solid solution. For the case $\Delta U > 0$, there is a disintegration on two solid solutions of different concentrations.

For the system $\text{LaB}_6\text{--TiB}_2$ we obtained $\Delta U = 1.64$ eV and for $\text{LaB}_6\text{--ZrB}_2$ $\Delta U = 1.06$ eV indicating the formation of two solid solutions of different concentrations. It is possible to define eutectic concentration of component LaB_6 in system $\text{LaB}_6\text{--MeB}_2$ from a condition $dF/dC = 0$

$$2c_E U_{AA} - 2(1 - c_E)U_{BD} + 2(1 - 2c_E)U_{AB} = 0 \quad (16)$$

Here c_E is the eutectic concentration of LaB_6 phase. In the system $\text{LaB}_6\text{--TiB}_2$ $c_E = 0.72$, and in $\text{LaB}_6\text{--ZrB}_2$ $c_E = 0.652$. For transition to volumetric concentration, we use the following ratio:

$$\Omega_0 = c_E \Omega_{\text{LaB}_6} + (1 - c_E) \Omega_{\text{MeB}_2}, \quad (17)$$

where Ω_0 is the system volume and Ω_{LaB_6} and Ω_{MeB_2} are the component volumes.

Volumetric concentration:

$$C_{\text{MeB}_2} = (1 - c_E) \frac{\Omega_{\text{MeB}_2}}{\Omega_0} \times 100\% \quad (18)$$

Finally we obtain $C_{\text{TiB}_2} = 10.948\%$ and $C_{\text{ZrB}_2} = 17.223\%$.

The experimental investigations proceeded this *ab initio* investigations has been done by Paderno^{3–5} on both $\text{LaB}_6\text{--ZrB}_2$ and $\text{LaB}_6\text{--TiB}_2$ binary systems by means of electron microscopy and microprobe analysis. This pioneering work has determined that the quasibinary $\text{LaB}_6\text{--ZrB}_2$ system has an invariant eutectic point at 16.3 at.% diboride composition. Likewise, $\text{LaB}_6\text{--TiB}_2$ binary systems had a eutectic invariant point at 10.4 at.% TiB_2 concentration. In spite of frozen-core approximation and lack of exact mathematical contributions of thermal energy fluctuations, the result of eutectic composition (Eq. (15)) is very close to the experimentally determined values. We anticipate to transfer the method used in this present investigation to construct pseudopotentials to predict different eutectic systems.

In future work, we plan to incorporate several factors that have not been accurately incorporated into our methodology. First, we plan to take into account the influence of temperature of system, i.e., to calculation system entropy proceeding from energy of atoms at nonzero temperature, by means of calculating eutectic temperature for the invariant point of both $\text{LaB}_6\text{--ZrB}_2$ and $\text{LaB}_6\text{--TiB}_2$ systems. We also plan to consider a wider class of diborides of transition metals (not only Ti and Zr, but also Hf, V, Cr, Nb, etc.) so that one can design of new class of eutectic materials. In addition, the analysis of interfacial energy (interface energy of interphases) of eutectic systems will be carried out.

2.4. Conclusions

1. The parameters of crystal lattices LaB_6 , TiB_2 , ZrB_2 calculated by means of the method of pseudo-potentials differ no

more than 1.2% (LaB_6) and 0.8% (ZrB_2) from the experimental values.³

2. The results of computer experiment carried out on the basis of pseudo-potential approach confirmed complete mutual insolubility of strengthening components (diborides of transition metals) in lanthanum hexaboride matrix.
3. The calculated concentration of LaB_6 phase in $\text{LaB}_6\text{--TiB}_2$ and $\text{LaB}_6\text{--ZrB}_2$ eutectic systems differs from those values obtained in the experiment^{9–11} less than 5.4%.

The numerical model developed in this work could be considered highly successful. The use of the method of pseudo-potential in approximation of the first coordination sphere described the eutectic temperature and invariant point of quasibinary alloys that consist of lanthanum hexaboride matrix reinforced by diborides of transition metals. In accordance with our results, the possibility of constructing transferable and separable pseudopotentials for use in conventional electronic-structure calculation can be used to predict of new eutectic systems.

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