

## Online Supporting Information (SI) for “Structural and chemical analysis of second-row impurities in liquid lead-bismuth eutectic by first-principles molecular dynamics”

### Appendix

#### A Comparison of Bader charges for typical molecules

The Bader charges of several typical molecules in a vacuum were calculated and related to their EN differences (John R. Rumble, ed., CRC Handbook of Chemistry and Physics, 99<sup>th</sup> edition (Internet Version 2018), CRC Press / Taylor & Francis, Boca Raton, FL.) in Table A. The bonding types were simply categorized according to the typical criteria of the EN difference: covalent if the EN difference  $< 0.4$  eV, ionic if the EN difference  $\geq 1.7$  eV, and polar covalent otherwise (Phillip Manning, “Chemical Bonds”, Infobase Publishing, 2009, p. 55.). The results are displayed in Table A.

First, in the case of LiF, which is categorized as an ionic molecule, Li and F exhibit a charge state of approximately  $0.8e$ . This means that both atoms are virtually fully charged. In LBE, Li indicates a similar charge to that in the LiF molecule, whereas F is somewhat less charged. This is possibly because the CN of F in LBE is insufficiently small to fully charge F. Next, in the case of BeO and BeH<sub>2</sub>, Be is largely positively charged even in BeH<sub>2</sub>, categorized as a polar-covalent molecule. Because the charge of Be is considerably smaller in LBE, it is highly expected that the Be-LBE interaction is covalent-wise, which is also expected from the EN.

For B, BN and BH<sub>3</sub> molecules were investigated. In BN, which is a polar-covalent molecule, B is largely charged although there is only one B-N bond. In BH<sub>3</sub>, which is a covalent molecule, B is less charged although there are three B-N bonds. The charge state of B in LBE is relatively similar to that in BH<sub>3</sub>, which implies covalent-wise B-LBE interaction. Similarly, the charge state of C in LBE is comparable to that in the CH<sub>4</sub> molecule, which also implies covalent-wise C-LBE interaction.

For N, the charge states of N in the Li<sub>3</sub>N, NH<sub>3</sub>, and NO<sub>2</sub> molecules were compared. The absolute charge of N decreases from  $2.40e$  to  $0.71e$  as the bonding type varies from ionic to covalent. Because the charge state of N in LBE is approximately  $0.9e$ , it is considered that the N-LBE interaction is covalent-wise. Lastly, the charge states of O in the NO<sub>2</sub>, H<sub>2</sub>O, and MgO molecules were examined. The absolute charge of O increases from  $0.34e$  to  $1.48e$  as the bonding type varies from covalent to ionic. Similar to N, it is assumed that the O-LBE interaction is covalent-wise. However, compared to those of C and N, the charge of O in LBE is more negative, whereas the CN is less. Thus, the ionicity in the impurity-LBE interaction should be greater in the case of O compared to those of C and N.

Table A Comparison of Bader charges for typical molecules.

Molecule	EN difference	Bonding type	Positive charge	Negative charge
LiF	3.00	Ionic	+0.86 (Li)	-0.83 (F)
BeO	1.87	Ionic	+1.52 (Be)	-1.48 (O)
BeH <sub>2</sub>	0.63	Polar covalent	+1.62 (Be)	-0.79 (H)
BN	1.00	Polar covalent	+1.25 (B)	-1.22 (N)
BH <sub>3</sub>	0.16	Covalent	+0.56 (B)	-0.18 (H)
CH <sub>4</sub>	0.35	Covalent	+0.20 (H)	-0.76 (C)

Li <sub>3</sub> N	2.06	Ionic	+0.84 (Li)	-2.40 (N)
NH <sub>3</sub>	0.84	Polar covalent	+0.42 (H)	-1.22 (N)
NO <sub>2</sub>	0.40	Covalent	+0.71 (N)	-0.34 (O)
H <sub>2</sub> O	1.24	Polar covalent	+0.56 (H)	-1.10 (O)
MgO	2.13	Ionic	+1.47 (Mg)	-1.48 (O)

## B Charge density visualization

To further confirm the impurity-LBE interaction suggested in the main body, the charge densities for Be, C, O, and F were visualized (Fig. B) for the wave function whose energy levels correspond to the bonding peaks in Fig. 13 and Fig. 14 (Be-2s: -4.2 eV, C-2p: -3.9 eV, O-2p: -4.4 eV, and F-2p: -4.5 eV).

As expected from pDOS, 2s-6p and 2p-6p covalent interactions are observable for Be and C, respectively. The Be-2s orbital has a spherical shape, and the resultant Be-LBE interaction is relatively isotropic because of the isotropy of the 2s orbital. This observation is consistent with Fig. 2 and Table 1, which indicate that the CN of Be is not as low as the 2p elements. Conversely, the interaction between C-2p and LBE-6p orbitals clearly exhibit directional dependence owing to the anisotropy of the 2p and 6p orbitals.

For O and F, the charge density of impurity-2p orbitals rather than LBE-6p orbitals are dominantly observed as expected from pDOS. We analyzed the isosurface by changing the charge density and determined that the contribution from the LBE-6p orbitals is considerably less compared to those from the O-2p and F-2p orbitals. It was confirmed that the bonding orbitals of the impurity-LBE interaction are contributed to primarily from the impurities in the case of O and F, and thus the interaction is expected to be relatively ionic.

The visualization result is consistent with the analysis results given in the main body.

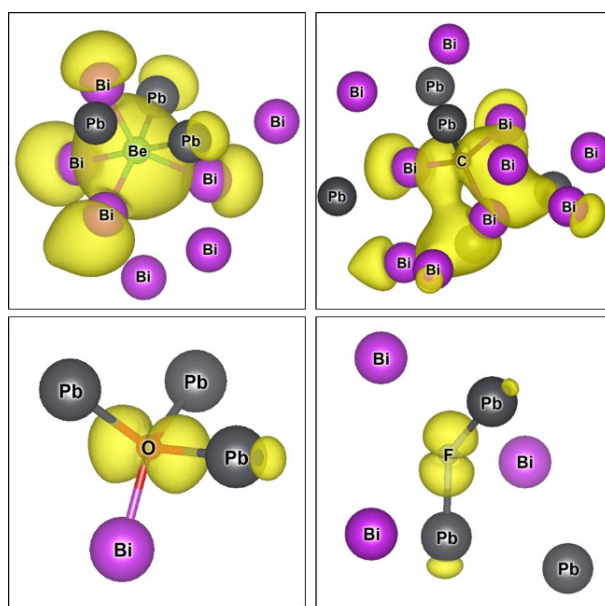


Fig. B Visualized charge density for selected 2s and 2p orbitals by construction of an isosurface. Charge densities of isosurfaces are set as follows: Be=0.0008, C=0.0008, O=0.005, and F=0.008 (electrons/Å<sup>3</sup>).

### C Energy differences among systems with different FNAs

It needs to be confirmed if the system energy difference according to the FNA composition displayed in Fig. 8 can cause visible preference. Here, we consider what we call “energy effect” and “configurational entropy effect.” The energy effect reflects the change in the potential energy depending on the FNA composition. The configurational entropy effect reflects the probability for a certain configuration of FNAs to appear, considering the difference in the number of Pb and Bi atoms in the eutectic composition. For example, if there is no energy effect, we simply calculate the probability that an impurity atom is surrounded by three Pb and one Bi atoms and thus the Pb fraction in the FNAs is 0.75 as follows:

$$g_{0.75} = \frac{45}{101} \times \frac{44}{100} \times \frac{43}{99} \times \frac{56}{98} \times {}_4C_1 = 0.1946. \quad (\text{C-1})$$

Then, considering both effects by multiplying the two terms and normalizing over the summation, we have

$$\frac{g_i \exp\left(-\frac{E_i}{kT}\right)}{\sum_j^{\text{all-states}} g_j \exp\left(-\frac{E_j}{kT}\right)} \quad (\text{C-2})$$

as the probability for state- $i$  to appear, where  $i$  and  $j$  represent the Pb fraction in the FNAs. For an impurity of which the CN is four, for example,  $i$  and  $j$  can be 0, 0.25, 0.5, 0.75, or 1. Table C summarizes the calculation results for several different CNs. It is demonstrated that if the energy difference between a system where all FNAs are Pb and a system where all FNAs are Bi is approximately 0.5 eV, a clear preference can be observed. For example, the expected percentage of Pb in the FNAs is less than 25% for the energy difference of 0.5 eV. Except for Be, energy differences greater than approximately 0.5 eV are observable in Fig. 8. Thus, we conclude that the energy differences displayed in Fig. 8 are sufficient to cause visible interaction preferences of the impurities.

Table C Expected Pb percentage in FNAs as function of energy difference and coordination number.

		Energy difference [eV]						
		-1	-0.5	-0.25	0	+0.25	+0.5	+1
Coordination number	2	99.6	93.5	77.2	44.6	16.0	4.3	0.2
	3	97.4	84.3	67.5	44.6	23.7	10.7	1.7
	4	93.3	76.7	61.9	44.6	28.4	16.4	4.5
	5	88.5	71.1	58.4	44.6	31.5	20.8	7.8
	6	83.7	66.9	56.0	44.6	33.6	24.2	11.1

### D Effects of SOC

The effect of SOC on the results of the present study is discussed in this section. In our previous study for 3d transition-metal impurity atoms in liquid LBE, a non-negligible change was induced by SOC in the pDOS for the Bi-6p band, whereas not in the pDOSs for the 3d transition-metal impurity atoms<sup>8</sup>. Similarly, the pDOS of the second-row impurities is not significantly changed by SOC as indicated in

Fig. D. Further, the changes in the relative energies and atomic forces for the eight second-row impurities over the three tested configurations are not large: 1.3 meV/atom and 0.054 eV/Å as the standard deviation, respectively. These values are comparable with the numerical errors caused by the plane wave cutoff and the k-point sampling grid size. The magnetic moments are virtually zero even with SOC for all impurities. Moreover, in the Bader analysis, the average changes induced by SOC in the atomic charges are  $-0.03e$  for Pb,  $+0.02e$  for Bi,  $+0.03e$  for B/C/N,  $+0.01e$  for O, and less than  $\pm 0.01e$  for the other impurities. Consequently, we conclude that the same findings with the present study can be achieved even if the calculations including SOC are performed.

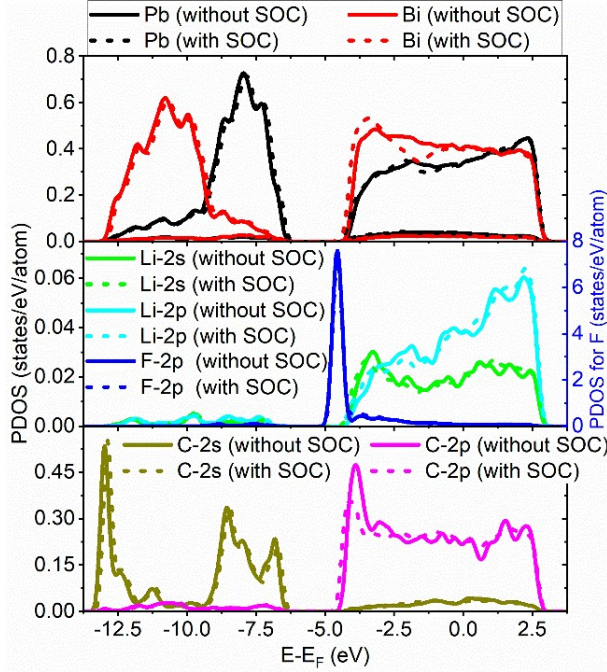


Fig. D Effects of SOC on pDOS of liquid LBE systems containing Li, C, and F impurity atoms at 1000 K.

### E Possible explanation for the interaction preferences of impurities

The observed interaction preferences in Section 3.4 can be explained with (i) the charge state of an impurity atom and (ii) the relative energy levels of the impurity 2s and 2p orbitals to that of the LBE-6p band.

First, with respect to the charge state, Pb is a minimally positively charged (approximately  $+0.11e$ ), whereas Bi is a minimally negatively charged (approximately  $-0.09e$ ) in liquid LBE owing to the EN difference. Then, it is reasonable that N, O, and F, which have negative charges, prefer Pb, whereas Li, which has a positive charge, prefers Bi because of attractive electrostatic forces. However, in the case of 3d transition-metal impurities in liquid LBE, although Fe is virtually neutral and Cr and Ni are positively ( $+0.3e$ ) and negatively ( $-0.3e$ ) charged, respectively, all these impurities have a preferences for Bi<sup>8</sup>. Thus, the impurity charge state should not be the main cause for the interaction preference, at least when the charge is relatively small.

Next, with respect to the electronic energy levels, Bi contributes more to the lower energy side of the LBE-6p band, whereas Pb contributes more to the higher energy side in liquid LBE (Fig. 13 and Fig. 14). Because the 2p orbital energy levels of N, O, and F are less than the 6p band energy level of LBE, the energy gain is greater if electron transfer occurs to the impurity from Pb rather than from Bi. Conversely, because the 2s orbital energy level of Li is greater than the 6p band energy level of LBE,

the energy gain is greater if the electron transfer occurs from the impurity to Bi rather than to Pb. This means that, in the case of the ionic interaction with LBE, negatively charged impurity atoms prefer Pb and positively charged impurity atoms prefer Bi.

Conversely, in the case of a covalent interaction with LBE, the 2s/2p-6p covalent interaction becomes stronger if an impurity 2s/2p energy level is better overlapped with the LBE-6p band below the Fermi level, which is mainly composed of the Bi-6p band. This is the cases for Be (2s-6p), B (2p-6p), and C (2p-6p). Although B and C are negatively charged according to their Bader charges, they do not demonstrate a preference for Pb. The preference of the 3d transition metals for Bi can be explained in the same manner: the 4s-6p and 3d-6p covalent interactions cause the preferences for Bi.

Tentatively, we assume that the explanation using the relative energy levels of impurity orbitals to the LBE-6p band is more reasonable, considering the better agreement with the FPMD results, although further studies are required for a conclusion.

## **Additional SI**

### **INCAR of the VASP code used for first-principles MD**

```
INCAR: MD for the system Pb(45)+Bi(56)+O(1) at 1000K
ALGO = Fast
PREC = Normal
ENCUT = 300 // cutoff energy for plane wave basis set (eV)
EDIFF = 1E-6
EDIFFG = -0.005

IBRION = 0 // MD
POTIM = 2 // time step (fs)
SMASS = 14 // Nose canonical ensemble
ISMEAR = 1 // 1st-order Methfessel-Paxton smearing
SIGMA = 0.2 // smearing width (eV)

ISIF = 0
ISPIN = 1 // not spin-polarized
ISYM = 0
NBLOCK = 1
NSW = 500 // number of steps

LREAL = A
MAXMIX = 40
NBANDS = 600 // number of bands
NELMIN = 4
NWRITE = 2
NPAR = 8

TEBEG = 1000
TEEND = 1000
LORBIT = 11
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End of online SI.