Analysis of Bulk Metallic Glass Formation Using a Tetrahedron Composition Diagram that Consists of Constituent Classes Based on Blocks of Elements in the Periodic Table

Akira Takeuchi¹, Budaraju Srinivasa Murty², Masashi Hasegawa¹,
Srinivasa Ranganathan³ and Akihisa Inoue¹

¹*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

²*Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Madras, Chennai 600 036, India*

³*Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India*

The formation of bulk metallic glasses (BMGs) has been analyzed with a tetrahedron composition diagram, which is comprised of constituent classes from blocks of elements in the periodic table. When Al and Ga are involved in the BMG composition environment, they are assumed to correspond to either s- or p-block elements. The analysis under the assumption reveals the presence of a composition band that connects the composition regions over different classes of BMGs. The diagram has a topological simplicity, is applicable to any multi-component alloy system, and can be analyzed from the bonding nature of the atomic pairs. Thus, this diagram is an important tool for analyzing and developing BMGs. [doi:10.2320/matertrans.MF200604]

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1. Introduction

Recently, bulk metallic glasses (BMGs) have received increasing attention in the field of non-equilibrium metallic materials because metallic glasses have been successfully fabricated in bulk shapes, which were a couple of millimeters or more.¹⁾ Because metallic glasses and BMGs are in a non-equilibrium state, there is a minimum cooling rate necessary to form the glassy phase when they are produced from a liquid. The critical cooling rate to form BMGs from a liquid is on the order of $100 \text{ K}\cdot\text{s}^{-1}$ or less, which is much slower than that of metallic glasses, which is on the order of $10^6 \text{ K}\cdot\text{s}^{-1}$ or more. BMGs can be produced in a bulk form due to the low critical cooling rate, which is close to the cooling rate required to form crystalline alloys in an equilibrium state. The formation of metallic glasses and BMGs from a liquid is related to the stabilization of the liquid phase, which is accompanied by the presence of an eutectic reaction in the alloy system.

Metallic glasses and BMGs have been discovered by selecting appropriate combinations of constituents for alloy systems and subsequently finding the appropriate alloy compositions to form a glassy phase in a solid state. In other words, metallic glasses and BMGs have been developed by finding alloy systems with a eutectic reaction and an alloy composition near where the eutectic reaction occurs. The appropriate combinations and fractions of the constituents have been reported as the classification of metallic glasses and BMGs. For instance, Hafner²⁾ has classified the glass-forming binary metallic systems into six classes, T-M, S-S, S-T, S-R, T-R and T-T, based on the chemical nature of their constituents where S, T, R, and M are abbreviations for simple metal, transition metal, rare-earth metal, and metalloid, respectively. Masumoto³⁾ has focused on the periodic table to show that there are important combinations of metal-

metal and metal-metalloid constituents that form amorphous alloys by a rapid-quenching technique.

Inoue⁴⁾ has extended this classification concept. In 2000, he classified BMGs into five classes according to the chemical species and atomic size differences of the constituents. In 2005, Takeuchi and Inoue⁵⁾ modified this BMG classification⁴⁾ by considering an additional factor, which is the period of the elements in the periodic table. They classified BMGs into seven classes;⁵⁾ the new classes of BMGs are represented by Cu-Ti-Zr and Ca-Mg-Zn BMGs, which were discovered between 2000 and 2005, have been added to the five original classes previously reported.⁴⁾ Besides the studies mentioned above, analyses on BMG formation have also been conducted using a topology approach⁶⁾ and a Mendeleev number approach⁷⁾ based on the concept of a Pettifor Map.⁸⁾

Current researchers have treated the constituent classes of BMGs differently. For instance, Sn has been assigned to the constituent class of (Al, Ga, Sn) in one study,⁴⁾ but in another study assigned Sn to a different constituent class.⁵⁾ On the other hand, Miracle⁶⁾ and Ranganathan *et al.*⁷⁾ treated Mg as a different constituent from Ca, which differs from the chemistry approach of the previous studies of the present authors.^{4,5)} These constituent class differences suggest that the classification of BMG systems should consider supplemental factors in order to complete the classification series of BMGs. Accordingly, the present report focuses on supplemental factors, which include the characteristics of the electrons (electron configuration and electronegativity), because these characteristics are related to the periodic table, which is the origin of the chemistry approach. In addition, the supplemental factors may also be useful for determining general trends in the composition regions of BMGs. This approach should be useful in determining the composition criteria, which has yet to be established, necessary to analyze

Table 1 Constituent classes used to classify metallic glasses^{2,3)} and BMGs^{4,5)} in previous studies. Constituent classes in the same vertical row show a similar relationship to those observed in other studies.

Class of constituents					Reference
S(Al)	S	T,R	T	M	2)
—	Metal	Metal	Metal	Metalloid	3)
Al,Ga,Sn	Simple Metal	ETM,Ln	LTM	Metalloid	4)
Al,Ga	IIA	ETM,Ln	LTM,BM	Metalloid	5)

S: simple metal, T: transition metal, R: rare-earth metal, M: metalloid
 Simple Metal: Be, Mg, ETM: early transition metal (IIIA-VIA), LTM: late transition metal (VIII-IIB), Ln: lanthanide metal, Metalloid: non-metal
 IIA: IIA group element, BM: IIIB-VIIB metallic element

BMG formation because only a few studies have been separately conducted for Ca-based⁷⁾ and Zr-based BMGs.⁹⁾ The latter study was based on conduction electron concentration.

The purposes of the present study are to classify BMGs based on the constituent class, which is categorized from chemical and electronic points of view, and to identify BMGs in terms of their alloy composition regions and alloy systems.

2. Procedure

This study uses two different classes. One is a class of BMG systems and the other is a constituent class where the class indicates a set in mathematical terms, and the constituents indicate the components of the alloy in a free atom state. It is noted that the former is the class of alloys, whereas the latter is the class of atoms. The analysis was conducted using the following procedure. The constituents of the alloys and the constituent class were initially considered. Then the class of the BMG system was addressed by considering the combinations of constituent classes instead of combinations of the alloy constituents. Accordingly, the class, group, components, and other terms used in the present study do not deal with local atomic arrangements.

Table 1 summarizes the constituent class used to classify the metallic glasses and the BMGs in the previous studies.²⁻⁵⁾ The metallic glasses can be formed by selecting constituents from a couple of constituent classes. For instance, the appropriate combinations of constituents from four classes of constituents, S, T, R, and M, yield six classes of metallic glasses, which are T-M, S-S, S-T, S-R, T-R, and T-T types.²⁾ An example of a metallic glass and its composition for each class of the glass-forming binary metallic system has been reported²⁾ as Pd₈₀Si₂₀ for T-M, Mg₇₀Zn₃₀ for S-S, Ca₆₅Pd₃₅ for S-T, La₇₀Al₃₀ for S-R, Gd₆₇Co₃₃ for T-R, and Nb₆₀Ni₄₀ for T-T. On the other hand, two constituent classes of metals and metalloids yield the metal-metal and metal-metalloid classes of metallic glasses.³⁾ Similarly, the constituents from five constituent classes, (1) Simple Metal, (2) Early Transition Metal (ETM) and Lanthanide Metal (Ln), (3) Late Transition Metal (LTM), (4) aluminium-gallium-tin (Al, Ga, Sn), and (5) Metalloid, have been reported by Inoue⁴⁾ to give five BMG classes. Here, these five constituent classes contain the following elements: (1) Be and Mg, (2) IIIA-VIIA elements and La to Lu, (3) VIII-IIB elements, (1) (5) B, C, Si,

Table 2 Some constituents for forming BMGs listed along with the constituent classes used in the present study and the period in the periodic table.

Period in the periodic table	Class of constituents			
	s	d _{EF}	d _{Lp}	p
2	Be	—	—	B,C
3	Mg,Al* ¹ (s)	—	Al* ² (p)	Si,P
4	Ca,Ga* ¹ (s)	Ti	Fe,Ni,Cu,Zn,Ga* ² (p)	Ge
5	—	Y,Zr	—	—
6	—	La	—	—

*¹(s), *²(p): Assumed to be a constituent, which is in the s- or d_{Lp}-class, respectively.

P, and Ge. Inoue⁴⁾ has reported representative BMG systems for each BMG class as (C-1) (ETM,Ln)-(Al,Ga,Sn)-LTM exemplified by La-Al-Ni, (C-2) (LTM)-(ETM,Ln)-Metalloid by Fe-Zr-B, (C-3) (LTM)-(Al,Ga,Sn)-Metalloid by Fe-(Al,Ga)-(P,C,B), (C-4) Simple Metal-LTM-(ETM,Ln) by Mg-Cu-Y, and (C-5) LTM-Metalloid by Pd-Ni-P BMG systems. Here, the symbol “C” in C-1 to C-5 designates the abbreviation of the class of the BMG system. In addition, the classification of BMGs reported by Takeuchi and Inoue⁵⁾ that modify the constituent classes, Simple Metal and LTM, in a previous study⁴⁾ to IIA and (LTM, BM), respectively, gives the seven classes of BMG systems where IIA is a IIA group element and BM is a IIIB-VIIB metallic element, which are both from the periodic table. The seven classes of BMG systems reported by Takeuchi and Inoue⁵⁾ consist of five classes of BMG systems, which correspond to the previous results by Inoue⁴⁾ and two new classes of BMG systems. The two classes of BMG systems are (C-6) LTM-(ETM,Ln), which is represented by Cu-Zr-Ti, and (C-7) IIA-(LTM,BM), which is represented by Ca-Mg-Zn. Table 1 shows that the constituent class is determined on the basis of the groups in the periodic table, which is the key to the chemical approach for classifying BMGs.

Table 2 summarizes some of the constituents used to form BMGs, which are listed in accordance with the constituent classes used in the present study and the period in the periodic table. The constituent classes in Table 2 are s, d_{EF}, d_{Lp}, and p, whose symbols are determined by the abbreviations of s-, d-, f-, and p-blocks in the periodic table and early (E) and late (L) transition metals, which contain elements of IIIA-VIIA and VIII to IIB elements, respectively. It should be noted that the lower-case s- is different from the capital S used in the previous study²⁾ because s- and others (d-, f-, and p-) are due to the outer electronic configuration of the elements. The classes of s- and p-mostly correspond to those of IIA and Metalloid in Table 1, respectively, and the latter was used in our previous study.⁵⁾ Furthermore, the classes of d_{EF} and d_{Lp} mostly correspond (2) to ETM,Ln and LTM,BM⁵⁾ in Table 1, respectively, where BM indicates IIIB-VIIB metallic elements.

In Table 2 we assume that Al and Ga can be constituents in either the s- or d_{Lp}-constituent class (Al*(s) or Al**(p), Ga*(s) or Ga**(p)) and that the class depends on the compositional environment of the BMG. The validity of this assumption is discussed in Section 4. With this assumption, the constituent classes used to form BMGs and their

Short Long	0	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIIB
	18	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Class of constituents		s	Al, Ga ← d _{ef} → Al, Ga										p					
			d _{lp}															
Block		s	d										p					

		s block																				p block				
		1	2																			1	2	3	4	5
H (2.1)	He	2 s (1.0)	Li (1.5)	Be (1.5)																	2 p (2.0)	B (2.5)	C (3.0)	N (3.5)	O (4.0)	F (4.0)
				d block																3 p (1.5)	Al (1.8)	Si (2.1)	P (2.5)	S (3.0)	Cl (3.0)	
Ne	Ar	3 s (0.8)	Na (1.0)	Mg (1.2)	3 d (1.3)	Sc (1.5)	Ti (1.6)	V (1.6)	Cr (1.5)	Mn (1.8)	Fe (1.8)	Co (1.8)	Ni (1.8)	Cu (1.9)	Zn (1.6)	4 p (1.6)	Ga (1.6)	Ge (1.6)	As (2.0)	Se (2.4)	Br (2.8)					
Kr	Xe	5 s (0.8)	Rb (1.0)	Sr (1.0)	4 d (1.2)	Y (1.4)	Zr (1.6)	Nb (1.8)	Mo (1.9)	Tc (2.2)	Ru (2.2)	Rh (2.2)	Pd (2.2)	Ag (1.9)	Cd (1.7)	5 p (1.7)	In (1.8)	Sn (1.8)	Sb (1.9)	Te (2.1)	I (2.5)					
Rn		6 s (0.7)	Cs (0.9)	Ba (0.9)	5 d (1.2)	Lu (1.3)	Hf (1.5)	Ta (1.7)	W (1.9)	Re (2.2)	Os (2.2)	Ir (2.2)	Pt (2.4)	Au (1.9)	Hg (1.9)	6 p (1.8)	Tl (1.8)	Pb (1.8)	Bi (1.9)	Po (2.0)	At (2.2)					
				f block																						
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Fig. 2 Classification of metallic glasses based on the constituent classes of the s-block elements (s), early transition metals and f-block elements (d_{Ef}), late transition and p-block metals (d_{Lp}) and metalloids (p). The numbers in the circles designate the number of BMG classes (C-1 to C-7), which corresponds to those in our previous study.⁵⁾ The class of the BMG systems and the combinations of constituent classes for each class of the BMG system are tabulated together.

Table 3 Class of the BMG system, representative alloy system, and principal constituents summarized by the constituent class. Atomic symbols in bold are the main constituent in each alloy system.

Class of BMG system	Representative system	Class of constituents			
		s	d _{Ef}	d _{Lp}	p
C-1	Zr-Al-Ni	Al ^{*1} (s)	Zr(La)	Ni,Cu	—
	Zr-Ti-Ni-Cu-Be	Be	Zr,Ti	Ni,Cu	—
C-2	Fe-Zr-B	—	Zr	Fe	B
C-3	Fe-(Al,Ga)-(P,B,C)	Al ^{*1} (s), Ga ^{*1} (s)	—	Fe	B,C,P,Si,Ge
C-4	Mg-Cu-Y	Mg	Y	Cu	—
C-5	Pd-Ni-P	—	—	Pd,Ni	P
C-6	Cu-Zr-Ti	—	Ti,Z	Cu	—
	Cu-Zr-Ga	—	Zr	Cu,Ga^{*2}(p)	—
	Cu-Hf-Al	—	Hf	Cu,Al^{*2}(p)	—
C-7	Ca-Mg-Cu	Ca(Mg)	—	Cu	—
	Ca-Mg-Zn	Ca(Mg)	—	Zn	—
	Ca-Mg-Al	Ca(Mg)	—	Al ^{*2} (p),Ag,Cu	—

^{*1}(s), ^{*2}(p): Assumed to be either a s- or d_{Lp}-class of constituent, respectively.

Table 4 shows the BMG system class, the alloy system, the alloy composition with reference number, and the s-d_{Ef}-d_{Lp}-p description of the alloy composition for representative BMGs. The alloy composition listed in Table 4 is rewritten as the s-d_{Ef}-d_{Lp}-p descriptions in order to use the s-d_{Ef}-d_{Lp}-p description in the composition diagram. For instance, La₅₅Al₂₅Ni₂₀, which is in C-1, is described as (d_{Ef})₅₅s₂₅-(d_{Lp})₂₀, indicating that La, Al, and Ni correspond to d_{Ef}-s-, and d_{Lp}-constituent classes, respectively. Similarly, (Zr_{41.2}-Ti_{13.8})Be_{22.5}(Cu_{12.5}Ni_{10.0}) in C-1 is described as (d_{Ef})₅₅s_{22.5}-

(d_{Lp})_{22.5}, which indicates that Zr and Ti belong to d_{Ef}-, Be to s-, and Cu and Ni to d_{Lp}-. As exemplified by (Zr_{41.2}-Ti_{13.8})Be_{22.5}(Cu_{12.5}Ni_{10.0}) BMG, the parentheses are used for alloy composition that are in the same constituent class. Table 4 sums the resultant compositions with respect to each constituent class. Furthermore, the order of the atomic symbol and its composition in the alloy composition in Table 4 are changed from the original reference in order to maintain consistency with the s-d_{Ef}-d_{Lp}-p description of each alloy system.

Table 4 Class of BMG system, alloy system, alloy composition with reference number, and s-d_Ef-d_Lp-p description of the alloy composition for representative BMGs. The s-d_Ef-d_Lp-p descriptions of the alloy compositions change from the alloy compositions listed in the third row in Table 4 in order to simplify the s-d_Ef-d_Lp-p description with respect to the points of the order of symbol and its composition.

No.	Alloy system	Alloy composition Reference)	s-d _E f-d _L p-p description
C-1	Zr- and La-based BMG		(d _E f) ₅₅₋₆₅ (s _{7.5-27.5} (d _L p) _{17.5-27.5}
	Ln-Al-Ni	La ₅₅ Al ₂₅ Ni ₂₀ ⁽¹⁰⁾	(d _E f) ₅₅ (s ₂₅ (d _L p) ₂₀
	Zr-Al-Ni	Zr ₆₀ Al ₁₅ Ni ₂₅ ⁽¹¹⁾	(d _E f) ₆₀ (s ₁₅ (d _L p) ₂₅
	Zr-Al-Ni-Cu	Zr ₆₅ Al _{7.5} (Ni _{7.5} Cu ₂₀) ⁽¹²⁾	(d _E f) ₆₅ (s _{7.5} (d _L p) _{27.5}
	Zr-Ti-Be-Ni-Cu	(Zr _{41.2} Ti _{13.8})Be _{22.5} (Cu _{12.5} Ni _{10.0}) ⁽¹³⁾ (Zr _{46.8} Ti _{8.2})Be _{27.5} (Cu _{7.5} Ni _{10.0}) ⁽¹⁴⁾	(d _E f) ₅₅ (s _{22.5} (d _L p) _{22.5} (d _E f) ₅₅ (s _{27.5} (d _L p) _{17.5}
C-2	Fe-ETM based BMG		(d _L p) ₆₃₋₇₂ (d _E f) _{5.5-6} (p _{22-31.5}
	Fe-Zr-B	Fe ₇₂ Y ₆ B ₂₂ ⁽¹⁵⁾	(d _L p) ₇₂ (d _E f) ₆ (p ₂₂
	Co-Fe-Ta-B	(Co ₄₃ Fe ₂₀)Ta _{5.5} B _{31.5} ⁽¹⁶⁾	(d _L p) ₆₃ (d _E f) _{5.5} (p _{31.5}
C-3	Fe-(Al,Ga) based BMG		(d _L p) ₇₂ (s ₃₋₇ (p ₂₁₋₂₅
	Fe-(Al,Ga)-Metalloid	Fe ₇₂ (Ga ₂ Al ₅)(P ₁₁ C ₆ B ₄) ⁽¹⁷⁾ Fe ₇₂ Ga ₃ (P _{9.5} C ₄ B ₄ Si _{2.5}) ⁽¹⁸⁾	(d _L p) ₇₂ (s ₇ (p ₂₁ (d _L p) ₇₂ (s ₃ (p ₂₅
C-4	Mg-based BMG		s ₅₀₋₇₀ (d _L p) ₂₀₋₃₀ (d _E f) ₁₀₋₂₀
	Mg-Ln-Ni, Mg-Ln-Cu	Mg ₅₀ Ni ₃₀ La ₂₀ ⁽¹⁹⁾ Mg ₆₅ Cu ₂₅ Y ₁₀ ⁽²⁰⁾	s ₅₀ (d _L p) ₃₀ (d _E f) ₂₀ s ₇₀ (d _L p) ₂₀ (d _E f) ₁₀
C-5	Pd- and Pt-based BMG		(d _L p) _{80-83.5} (p _{16.5-20}
	Pd-Ni-P	(Pd ₄₀ Ni ₄₀)P ₂₀ ⁽²¹⁾ (Pd _{77.5} Cu ₆)P _{16.5} ⁽²²⁾	(d _L p) ₈₀ (p ₂₀ (d _L p) _{83.5} (p _{16.5}
	Pd-Cu-Ni-P	(Pd ₄₀ Cu ₃₀ Ni ₁₀)P ₂₀ ⁽²³⁾	(d _L p) ₈₀ (p ₂₀
C-6	LTM-based BMG		(d _L p) _{41-66.4} (d _E f) _{33.6-59}
	Cu-Zr-Ti	Cu ₆₀ (Zr ₃₀ Ti ₁₀) ⁽²⁴⁾	(d _L p) ₆₀ (d _E f) ₄₀
	Ni-Nb-Sn	(Ni _{59.5} Sn _{6.9})Nb _{33.6} ⁽²⁵⁾	(d _L p) _{66.4} (d _E f) _{33.6}
	Ti-Zr-Cu-Ni	(Ti ₃₄ Zr ₁₁)(Cu ₄₇ Ni ₈) ⁽²⁶⁾	(d _L p) ₄₅ (d _E f) ₅₅
	Ti-Ni-Cu-Sn	(Ni ₂₀ Cu ₂₅ Sn ₅)Ti ₅₀ ⁽²⁷⁾	(d _L p) ₅₀ (d _E f) ₅₀
	Ti-Cu-Ni-Mo-Fe	(Cu ₂₃ Ni ₁₁ Fe ₇)(Ti ₅₂ Mo ₇) ⁽²⁸⁾	(d _L p) ₄₁ (d _E f) ₅₉
	Cu-Hf-Al	(Cu ₄₉ Al ₉)Hf ₄₂ ⁽²⁹⁾	(d _L p) ₅₈ (d _E f) ₄₂
	Cu-Zr-Ga	(Cu ₅₀ Ga ₅)Zr ₄₅ ⁽³⁰⁾	(d _L p) ₅₅ (d _E f) ₄₅
C-7	Ca-based BMG		s _{66.5-90} (d _L p) _{10-33.5}
	Ca-Mg-Cu	(Ca ₇₀ Mg ₂₀)Cu ₁₀ ⁽³¹⁾	s ₉₀ (d _L p) ₁₀
	Ca-Mg-Zn	(Ca ₆₅ Mg ₁₅)Zn ₂₀ ⁽³²⁾	s ₈₀ (d _L p) ₂₀
	Ca-Mg-Al	(Ca ₆₀ Mg ₁₀)Al ₃₀ ⁽³³⁾	s ₇₀ (d _L p) ₃₀
	Ca-Mg-Al-Ag	(Ca _{56.5} Mg ₁₀)(Al _{28.5} Ag ₅) ⁽³³⁾	s _{66.5} (d _L p) _{33.5}
	Ca-Mg-Al-Cu	(Ca _{56.5} Mg ₁₀)(Al _{28.5} Cu ₅) ⁽³³⁾	s _{66.5} (d _L p) _{33.5}

Figure 3(a) shows a projection of a tetrahedron composition diagram, which corresponds to the plane figure drawn in Fig. 2. The BMGs along with their reference numbers are plotted in the tetrahedron composition diagram in accordance with their s-d_Ef-d_Lp-p descriptions shown in Table 4. Figure 3(b) shows the three-dimensional view of the composition diagram. The thin lines parallel to the coordinates of s-p, p-d_Lp, d_Lp-s, and so on in Fig. 3 are to guide the eye in order to evaluate the BMG compositions using the s-d_Ef-d_Lp-p description. The thick gray curves, which connect the BMG plots, show the relationships of BMGs. Figure 3 can be regarded as a conventional tetrahedron composition diagram when treated as a quaternary alloy system, consisting of constituents from the s-, d_Ef-, d_Lp- and p-constituent classes, which is exemplified by the Mg(s)-Zr(d_Ef)-Fe(d_Lp)-B(p) system. In Fig. 3(b), the constituent classes of s-, d_Ef-, d_Lp-, and p- are placed at the vertices, BMGs, which belong to C-1 to C-4,⁽¹⁰⁻²⁰⁾ are plotted on the faces, and those belonging to

C-5 to C-7⁽²¹⁻³³⁾ are plotted on the edges of the tetrahedron composition diagram. Accordingly, it is noted that the BMGs with reference numbers of 10 to 33 are plotted at the edges or on the faces in Fig. 3(b), although the tetrahedron composition diagram has the capacity for plots inside the diagram. The absence of BMGs inside s-d_Ef-d_Lp-p tetrahedron composition diagram can be regarded as a general trend of currently known BMGs.

Figure 3 also provides other general trends for forming BMGs. As mentioned above, the composition band of the composition regions is formed as a thick curve in Fig. 3. This composition band tends to smoothly connect the composition regions of representative BMGs in the order of the reference number of BMGs: C-6,⁽²⁵⁻²⁸⁾ C-1,⁽¹²⁻¹⁴⁾ C-4,^(19,20) C-7,⁽³¹⁻³³⁾ C-3,^(17,18) C-5,^(22,23) and C-2.^(15,16) This tendency to form a composition band indicates that there are general trends in the composition regions over the seven classes of BMG systems. The presence of the composition band is mainly due

Fig. 3 s-dEf-dLp-p Composition diagram, in its plane projection (a) and solid drawing (b) with plots of typical BMGs from the seven classes of the BMG system. The numbers 10–33 surrounded by small circles or typed near the plot correspond to the reference numbers. The thick gray curve, which connects the BMG compositions, is the composition band where BMGs are readily obtained. Figure 3(a) can be seen as a solid figure when dLp is placed under the page and placing the p-class of constituents in Fig. 3(b) under the page gives a clear implication of a solid figure. (Pd₄₀Ni₄₀)P₂₀²¹) is compensatory plotted with (Pd₄₀Cu₃₀Ni₁₀)P₂₀²³) due to the overlap in the s-dEf-dLp-p description: (dLp)₈₀p₂₀. The ternary system of Ca-Mg-Cu³³) and quaternary systems of Ca-Mg-Al-Ag³³) and Ca-Mg-Al-Cu³³) are distinguished as 33T and 33Q, respectively, based on the s-dEf-dLp-p descriptions in Table 4 in order to avoid duplications in their reference number.

to the absence of BMGs plotted (1) on the s-dEf-p face, (2) on the dEf-dLp-p face inside of which the dLp-composition is 70 at% or less, (3) on the s-dEf-dLp face inside of which the dLp-composition is 30 at% or more, and (4) due to the absence of BMGs plotted inside the s-dLp-p face, except for Fe-(Al,Ga) based BMGs (C-3). In other words, this tendency indicates that BMGs can be formed by avoiding atomic pairs of s-p and dEf-p, which possess a covalent bond-like characteristic instead of a pure metallic bond.

Another trend for forming BMGs can be seen in the dense plots of compositions in different BMG classes. For instance, BMGs, which belong to C-2 (Fe₇₂Y₆B₂₂¹⁵) and (Co₄₃-Fe₂₀)Ta_{5.5}B_{31.5}¹⁶), C-3 (Fe₇₂(Ga₂Al₅)(P₁₁C₆B₄)¹⁷) and Fe₇₂-Ga₃(P_{9.5}C₄B₄Si_{2.5})¹⁸), and C-5 ((Pd₄₀Ni₄₀)P₂₀,²¹) (Pd_{77.5}-Cu₆)P_{16.5}²²) and (Pd₄₀Cu₃₀Ni₁₀)P₂₀²³) are very close to each other in Fig. 3 near (dLp)₈₀p₂₀, although the main constituents are different: Pd- and Pt-based BMGs (C-5) and Fe-based BMGs (C-2 and C-3). Furthermore, La₅₅Al₂₅Ni₂₀,¹⁰) (Zr_{41.2}Ti_{13.8})Be_{22.5}(Cu_{12.5}Ni_{10.0}),¹³) and (Zr_{46.8}Ti_{8.2})Be_{27.5}-(Cu_{7.5}Ni_{10.0})¹⁴) are also close together in the diagram. The former and latter are regarded as Metal-Metalloid BMG³) and Zr- or La-based BMG, respectively. Each type of BMG has an independent number of constituents. Thus, the s-dEf-dLp-p descriptions in Table 4, and the resulting plots in Fig. 3 are helpful from a chemical point of view for evaluating the similarity in BMG compositions of the constituents.

4. Discussion

The discussion is organized as follows: First, factors that support Al and Ga as constituents of the s-class are discussed in Sections 4.1 and 4.2. Then the relationships of BMGs obtained in our previous studies^{4,5}) are introduced in Section 4.3. These relationships are used in Section 4.4. to determine the status of Al and Ga in the BMG composition environment. Finally, the significance of the tetrahedron composition diagram is discussed in Section 4.5.

4.1 Electronegativity

The electronegativities (χ) of Al and Ga are 1.5 and 1.6, respectively and are shown in Fig. 1, which is from the literature.³⁴) On the other hand, the range of χ for s-block elements is $\chi \leq 1.0$ (Ca, Sr), 1.2 (Mg), and 1.5 (Be), while χ for VIII to VIB metallic elements is 1.5 (Al), 1.6 (Ga, Zn) and 2.4 (Au). Accordingly, χ of Al is the same as that of Be, which has the largest χ value among the s-block elements, and Ga has the next smallest χ value among the III to VIB metallic elements. Thus, an intermediate value of χ , which ranges 1.5 to 1.6, allows Al and Ga to be treated as constituents of the s-class when they are involved in BMGs.

4.2 Aspects for forming ionic bonds

The following aspects, which are usually discussed when forming ionic bonds, must be considered in order to understand why Al and Ga can be constituents of the s-class, even though they have a metallic bonding nature in BMGs.

4.2.1 Diagonal relationships in the periodic table³⁵)

The diagonal relationships in the periodic table support the similarity in the characteristics between Be and Al.³⁵) This relationship, which can be applied to sets of atomic pairs such as Li and Mg, Be and Al, and B and Si, are due to the comparative ease in the ionization of elements that are diagonal on the periodic table, which results from the counteracting effects of the increased ease in the ionization down a group and the decreased in the ease of ionization from left to right in the periodic table. Thus, the diagonal relationship between Be and Al indicates that these elements are similar because they both are ions with the same ease.³⁵)

4.2.2 Inert pair effect³⁵)

This sub-section evaluates the validity of distinguishing Al and Ga from other p-block metallic elements using the inert pair effect to treat Al and Ga as part of the s-constituent class. The inert pair effect addresses the possibility of an element, which belongs to a heavier sub-group B in the periodic table, to form ions other than that with an 18-electron group structure, which is the expected ionic structure.³⁵) These

Group (Block)	2	3	4	5	6	7
Period	(s or d)	(p)				
2	Be	B	C	N	O	F
3	Mg	Al	Si	P	S	Cl
4	Zn	Ga	Ge	As	Se	Br
5	Cd	In	Sn	Sb	Te	I
6	Hg	Tl	Pb	Bi	Po	At

Metalloid (non-metallic element)
inert pair effect type
s-block element
d-block element

Fig. 4 Part of the short-periodic table summarized with the group, block, and period.³⁵⁾ A thick line separates the upper-left and lower-right types. The elements in the lower-right types are the elements in which inert pair effect works.³⁵⁾ Among these elements, Al and Ga are the only p-block metallic elements that are independent of inert pair effect.

unexpected ions have a charge of two units less than that of the expected ions. For instance, although Pb^{4+} is predicted from the periodic table, Pb^{2+} is more stable. This Pb example differs from Al and Ga, which belong to lighter sub-group B, because Al and Ga form Al^{3+} and Ga^{3+} .³⁶⁾ In general, the inert pair effect works for p-block elements in the lower-right part of the periodic table (Cl, As, Se, Br, In, Sn, Sb, Te, I, Hg, Tl, Pb, and Bi)³⁵⁾ as shown in Fig. 4. Al and Ga are highlighted from the other metallic elements in Fig. 4 because Al and Ga are the only p-block elements with a non-inert pair type effect. Be, Mg, Zn, and Cd also display the non-inert pair effect type, but Be and Mg belong to the s-block, while Zn and Cd belong to the d-block.

4.3 Relationship between the main constituent and the classification of BMGs⁵⁾

The following relationships for BMGs were obtained in our previous⁵⁾ and the present study was partially used to determine the status of Al and Ga in Section 4.4. It has been reported⁵⁾ that BMGs found to date exhibit relationships between the BMG system class and the type of main constituent and the relative atomic radius of the main constituents. For instance, the main constituents of ternary C-1 (Zr- and La-based), C-5 (Pd- and Pt-based) and C-7 (Ca-based), ternary C-2 (Fe-based) and C-4 (Mg-based), and ternary C-6 (LTM-based) BMGs are the largest, intermediate, and smallest atomic radius, respectively. In addition, BMGs that belong to C-6 change their main constituent with the atomic radius from the smallest to the larger size as the glass-forming ability increases by multi-component alloying of ternary alloys. The minimum number of constituent classes necessary to form BMGs are two for C-5 to C-7 and three for the others (C-1 to C-4), which are identical to the results obtained in the present study (Fig. 2).

4.4 Determining the status of Al and Ga in a BMG composition environment

This sub-section discusses the status of Al and Ga in

BMGs in terms of the composition environment of the main constituent in the following four cases: (1) a d_{ef} -rich environment (C-1), (2) an s-rich environment (C-7), (3) a d_{Lp} -rich without a p environment (C-6), and (4) a d_{Lp} -rich with a p environment (C-3). We selected these four cases from Tables 3 and 4, which show that Al and Ga are constituents of BMGs belonging to C-1, C-3, C-6, and C-7, and that the main constituent, which is designated with a bold letter in Table 3 for these classes of BMGs, is a constituent in the d_{ef} -(C-1), d_{Lp} -(C-3), d_{Lp} -(C-6) and s-(C-7)-constituent classes. Furthermore, Table 3 shows that the presence of a metalloid (P, C, P, Si, Ge) in the p-class of constituents helps to distinguish the BMGs in C-3 from those in C-6 because both BMGs can be described as d_{Lp} -rich environments. In particular, we discuss the status of the s-constituent class of Al and Ga, which appears in (1) a d_{ef} -rich environment (C-1) and (4) a d_{Lp} -rich with a p composition environment (C-3), because the status of the s-constituent class for Al and Ga contradicts the fact that Al and Ga are p-block elements in the periodic table. In the next sub-section, we discuss this by hypothetically assuming that Al and Ga are constituents of the d_{Lp} -class, which is the opposite treatment for BMGs in C-1 and C-3 shown in Table 3.

4.4.1 d_{ef} -Rich environment (C-1)

Assuming Al is in the d_{Lp} -constituent class for a BMG in C-1 reduces the minimum number of constituents from three to two. For instance, Zr-Al-Ni in Table 3 would be described as (d_{ef} - d_{Lp}) instead of (s- d_{ef} - d_{Lp}) due to the shift in the constituent class of Al from s- to d_{Lp} -. This shift is inconsistent with the relationships obtained in the previous study, which is described in Section 4.3 and states that the minimum number of constituent classes for BMGs in C-1 is three. Moreover, assuming Al is a constituent in the d_{Lp} -constituent class would make $\text{Zr}_{60}\text{Al}_{15}\text{Ni}_{25}$ (Table 4) part of the d_{ef} - d_{Lp} class of BMG (C-6), but would maintain that the main constituent is Zr, which has the largest atomic radius (Zr: 0.162 nm, Al: 0.143 nm, Ni: 0.125 nm⁵⁾). This finding is inconsistent with the relationship that the main constituent of BMGs in C-6 is the constituent with the smallest atomic radius. These counter-examples support the status of Al as a constituent of the s-constituent class.

4.4.2 d_{Lp} -Rich with a p environment (C-3)

As shown in Table 4, $\text{Fe}_{72}(\text{Ga}_2\text{Al}_5)(\text{P}_{11}\text{C}_6\text{B}_4)^{17)}$ and $\text{Fe}_{72}\text{Ga}_3(\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5})^{18)}$ are the BMGs that belong to C-3. The constituents of these BMGs indicate that Ga is the primary constituent and Al is the supplemental constituent because $\text{Fe}_{72}\text{Ga}_3(\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5})^{18)}$ is formed in the BMG without Al. Accordingly, in this sub-section, the $\text{Fe}_{72}\text{Ga}_3(\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5})^{18)}$ BMG is initially discussed, and then the status of Al in BMGs is treated the same as BMGs with Ga for the $\text{Fe}_{72}(\text{Ga}_2\text{Al}_5)(\text{P}_{11}\text{C}_6\text{B}_4)$ BMG because the present approach does not allow the statuses of Al and Ga to be separately discussed in the $\text{Fe}_{72}(\text{Ga}_2\text{Al}_5)(\text{P}_{11}\text{C}_6\text{B}_4)$ BMG.

In Table 3, assuming Ga as an s-constituent class instead of as a constituent in the d_{Lp} -class makes $\text{Fe}_{72}\text{Ga}_3(\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5})$ BMG, which would be described as d_{Lp} -p (C-5) while maintaining the main constituent of Fe, which has an intermediate atomic radius (Fe: 0.124 nm, Ga: 0.124 nm, P: 0.109 nm, C: 0.077 nm, B: 0.090 nm⁵⁾). This result weakly affirms (5) the relationship of BMGs mentioned in Section

4.3, which indicates that the main constituent of BMGs in C-5 is the constituent with the largest atomic radius, because Fe and Ga have the same atomic radius. However, the BMG of $\text{Fe}_{72}(\text{Ga}_2\text{Al}_5)(\text{P}_{11}\text{C}_6\text{B}_4)$ contradicts the relationship mentioned in Section 4.3 with respect to the main constituent because Al, which has the largest atomic radius of 0.143 nm, is not the main constituent in the $\text{Fe}_{72}(\text{Ga}_2\text{Al}_5)(\text{P}_{11}\text{C}_6\text{B}_4)$ BMG. Thus, we concluded that Al and Ga are in the s-constituent class.

4.4.3 s-Rich (C-7) and d_Lp -rich without a p environment (C-6)

As shown in Table 3, Al and Ga in BMGs in C-7 and C-6 are part of the d_Lp -constituent class, which is expected because Al and Ga are p-block elements. Thus, in this subsection we explore this assignment by giving Al and Ga the hypothetical status as constituents in the s-constituent class BMGs in C-7 and C-6.

This assumption causes a discrepancy for the $(\text{Ca}_{60}\text{Mg}_{10})\text{Al}_{30}$ BMG (C-7), which is described as $s_{70}(d_Lp)_{30}$ in Table 4 because the hypothesis would make $(\text{Ca}_{60}\text{Mg}_{10})\text{Al}_{30}$ BMG part of the s_{100} constituent class. However, this type of BMG has yet to be discovered. On the other hand, applying this hypothesis to $(\text{Cu}_{49}\text{Al}_9)\text{Hf}_{42}$ and $(\text{Cu}_{50}\text{Ga}_5)\text{Zr}_{40}$ BMGs (C-6), which are in the $(d_Lp)_{58}(d_{Ef})_{42}$ and $(d_Lp)_{55}(d_{Ef})_{45}$ classes, respectively, in Table 4 would convert the classes to $s_9(d_Lp)_{49}(d_{Ef})_{42}$ and $s_5(d_Lp)_{50}(d_{Ef})_{45}$, respectively. Thus, BMGs in C-1 and C-4 should be s- d_Lp - d_{Ef} , as shown in Table 3, with the main constituent, Cu(d_Lp), unchanged. However, this contradicts the trend of BMGs described in Section 4.3, which is that the main constituents in C-1 and C-4 BMGs have the largest atomic radius. These examples of BMGs in C-7 and C-6 reveal that the hypothesis that Al and Ga are constituents in the s-constituent class BMGs in C-7 and C-6 does not satisfy the results obtained in the framework of previous studies.^{4,5)}

4.5 Significance of the tetrahedron composition diagram

As described in Section 3, the s- d_{Ef} - d_Lp -p tetrahedron composition diagram visually extracts similarities in the BMGs. For instance, it clearly shows that the BMGs are not formed in the s- d_{Ef} -p face of the diagram. Furthermore, the BMGs that belong to C-2, C-3, C-5 are plotted near the composition of $(d_Lp)_{80}p_{20}$ and are independent of the number of constituents necessary to form BMGs. Another similarity in the plots is exemplified by $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$,¹⁰⁾ $(\text{Zr}_{41.2}\text{Ti}_{13.8})\text{Be}_{22.5}(\text{Cu}_{12.5}\text{Ni}_{10.0})$,¹³⁾ and $(\text{Zr}_{46.8}\text{Ti}_{8.2})\text{Be}_{27.5}(\text{Cu}_{7.5}\text{Ni}_{10.0})$.¹⁴⁾ These examples imply the importance of BMG research on the different classes of BMGs as well as precise research for new alloy systems.

Furthermore, the discussion explored in Section 4.4 provides four types of composition environments for Al and Ga in BMGs: d_{Ef} -rich (C-1), s-rich (C-7), d_Lp -rich without a p-composition environment (C-6), and d_Lp -rich with a p environment (C-3). The results show that Al and Ga can be treated as constituents of the s-constituent class BMGs in a d_{Ef} -rich (C-1) and d_Lp -rich with a p-composition environment (C-3), but can be regarded as part of the d_Lp -constituent class in BMGs in an s-rich (C-7) and a d_Lp -rich without a p-composition environment (C-6). Thus, Al and Ga

belong to the p-block elements as free atoms, but they lose their p orbital characteristics when they are BMG constituents in the following cases: (1) when Al and Ga are in a d_{Ef} -rich (C-1) composition environment and are surrounded by solvent in the d_{Ef} class, and (2) when Al and Ga are in a d_Lp -rich with a p-(C-3) composition environment where a metalloid (P, C, B, Si, Ge) is also a constituent with Al and Ga. This interpretation exhibits the attractive and the repulsive interactions of Al and Ga, and the main constituent of BMGs. These observations should be related to the bonding nature of Al and Ga in each composition environment, which is governed by the main constituent, and should provide information on the electron structure of the BMGs.

Thus, the s- d_{Ef} - d_Lp -p composition diagram is of great importance for analyzing the characteristics of BMGs due to its simplicity and applicability to any multi-component alloy system. Furthermore, the composition diagram has potential for analyzing other non-equilibrium materials, such as quasicrystalline alloys and equilibrium alloys that contain intermetallic compounds. Combining the analyses of these metallic materials along with the s- d_{Ef} - d_Lp -p tetrahedron composition diagram should open a new approach for a better understanding of metallic materials.

5. Conclusion

The formation of bulk metallic glasses (BMGs) has been analyzed based on a chemistry approach assisted with the electron characteristics of the constituent elements. BMGs found to date have been classified into seven classes, which are comprised of constituent classes, s-, d_{Ef} -, d_Lp -, and p-, where these symbols are abbreviations for s-block elements (s), early transition metals and f-block elements (d_{Ef}), late transition and p-block metals (d_Lp), and metalloids (p). It is assumed that Al and Ga may be a constituent for either the s- or d_Lp -constituent class in order to reasonably plot the compositions of the BMG seven classes (C-1-C-7) in the s- d_{Ef} - d_Lp -p tetrahedron composition diagram. This supplemental approach, which considers the electron characteristics of the constituent elements associated with chemistry approach, solves the discrepancy in the classifications of BMGs in our previous studies with respect to Be-containing Zr-based BMGs, which were previously classified into a group other than a Zr-based system. The s- d_{Ef} - d_Lp -p tetrahedron composition diagram shows that a composition band exists in composition regions over the seven BMG classes. A prototype of the composition criteria to form BMGs on the basis of the chemistry approach has been obtained as the composition band of BMGs in a s- d_{Ef} - d_Lp -p tetrahedron diagram with a topological simplicity. This diagram is widely applicable to any multi-component alloy system and can be analyzed from the bonding nature of the atomic pairs.

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Appendix

Table A-1 Symbols used in the previous studies,^{2,4,5} their implication, representative constituents, and reference number.

Symbol	Implication	Representative constituents	Reference
S	<u>S</u> imple Metal	Be, Mg, Al, Ca, Zn	2)
T	<u>T</u> ransition Metal	Fe, Ni, Cu, Nb, W, Rh, Ta, Ir, Pd	2)
M	<u>M</u> etalloid	Si, P	2)
R	<u>R</u> are-Earth Metal	La, Ce, Gd	2)
ETM	<u>E</u> arly <u>T</u> ransition <u>M</u> etal	IIIA–VIIA metals	4,5)
LTM	<u>L</u> ate <u>T</u> ransition <u>M</u> etal	VIII–IIB metals	4,5)
Ln	<u>L</u> anthanide Metal	La to Yb	4,5)
Simple Metal	—	Be, Mg	4)
Metalloid	—	B, C, Si, P, Ge	4,5)
IIA	Alkaline Earth Metals, <u>IIA</u> Metals	Be, Mg, Ca	5)
BM	<u>IIIB–VIB</u> <u>M</u> etals	—	5)

Table A-2 Symbols and terms used in the present study and their explanation.

Symbol	Explanation
s-, d-, f-, p-block	Blocks in the periodic table (See Figure 1), which correspond to the mathematics term “set” to which the elements belong when the elements are free atoms.
Constituent	Component of the alloy that is present as an atom
Constituent class	The set to which a constituent belongs when alloyed
E, L	Abbreviations for <u>E</u> arly and <u>L</u> ate Transition Metals
s	Constituent class for IA and IIA metals
d _f f	Constituent class for IIIA–VIIA metals (<u>E</u> TM, necessary for <u>d</u> -block elements) and <u>f</u> -block elements
d _L p	Constituent class for <u>L</u> TM (<u>d</u> -block elements) and BM (<u>p</u> -block metallic elements)
p	Constituent class for non-metallic elements in <u>p</u> -block (Metalloid)
C-1 to C-7	<u>C</u> lasses of BMG systems