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**OVERVIEW**

# Classification of Bulk Metallic Glasses by Atomic Size Difference, Heat of Mixing and Period of Constituent Elements and Its Application to Characterization of the Main Alloying Element

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Bulk metallic glasses (BMGs) have been classified according to the atomic size difference, heat of mixing ($\Delta H^{mix}$) and period of the constituent elements in the periodic table. The BMGs discovered to date are classified into seven groups on the basis of a previous result by Inoue. The seven groups are as follows: (G-I) ETM/Ln-LTM/BM-Al/Ga, (G-II) ETM/Ln-LTM/BM-Metalloid, (G-III) Al/Ga-LTM/BM-Metalloid, (G-IV) IIA-ETM/Ln-LTM/BM, (G-V) LTM/BM-Metalloid, (G-VI) ETM/Ln-LTM/BM and (G-VII) IIA-LTM/BM, where ETM, Ln, LTM, BM and IIA refer to early transition, lanthanide, late transition, group IIIB–IVB and group IIA-group metals, respectively. The main alloying element of ternary G-I, G-V and G-VII, ternary G-II and G-IV, and ternary G-VI BMGs is the largest, intermediate and smallest atomic radius compared to the other alloying elements, respectively. The main alloying element of ternary BMGs belonging to G-I, G-V, G-VI and G-VII is an element in the atomic pair with the largest and negative value of $\Delta H^{mix}$ ($\underline{\Delta H}^{mix}_{L.N.}$), while the main element of ternary BMGs belonging to G-II and G-IV is independent of the atomic pair with $\underline{\Delta H}^{mix}_{L.N.}$. The characteristics of the main element derived for the ternary BMGs are directly applicable to multicomponent BMGs belonging to G-I, G-II, G-IV (Mg-based BMGs), G-V and G-VII. The main element can be the larger-sized element in the atomic pair with $\underline{\Delta H}^{mix}_{L.N.}$ or in the same group as the other elements for multicomponent BMGs belonging to G-III, G-IV (Be-containing Zr-based BMG) and G-VI. The main element of BMGs belonging to G-VI tends to change from the element with the smallest atomic radius in a ternary system to an element with a relatively large atomic size in a multicomponent system. The change is due to an increase in glass-forming ability through multicomponent alloying of BMGs belonging to G-VI. The results of the classification of BMGs obtained in the present study are important for further development of BMGs, with the results providing a road map for the development of new BMG compositions.

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***Keywords:*** *bulk metallic glass, mixing enthalpy, atomic radius, periodic table, main element, ternary system, multicomponent system, glass-forming ability, atomic configuration, interchangeability*

## 1. Introduction

It is widely known that metallic glasses are solid alloys exhibiting many superior properties to crystalline alloys. The unique properties originate from the random atomic arrangement of metallic glasses that contrasts with the regular atomic lattice arrangement found in crystalline alloys. Rapid quenching from the melt for the fabrication of metallic glasses is required since the random atomic arrangement is a non-equilibrium state. However, the size of metallic glass samples fabricated in this manner is constrained to less than one millimeter due to the high critical cooling rate required for the formation of conventional metallic glasses. Only a few metallic glasses have been reported to have been formed as bulk materials up until the early 1980s[1] due to the constraints on the sample size.

Since 1988, a number of alloys with a high glass-forming ability and able to be fabricated as bulk metallic glasses (BMGs) have been discovered in multicomponent Mg-,[2–4] La-,[5] Zr-,[6,7] Fe-,[8,9] and Pd-based[10,11] alloy systems. Subsequently, Inoue[12] succeeded in classifying the BMGs into five groups by focusing on the characteristics of the constituent elements with respect to the chemical species and their atomic size differences. This classification is useful for understanding the characteristics of BMGs. However, this classification is inadequate for the development of new BMGs for a number of reasons. First, an updated review of the classification system of BMGs is required as many BMGs have been discovered since the classification system by Inoue was proposed back in 2000. Second, the classification system describes the alloy system but not the range of glass-forming compositions in that system. For instance, it is widely accepted that the Zr-based Zr–Al–Ni alloy is a typical BMG, forming BMGs when the composition is Zr-rich. The previous classification system organizes the Zr–Al–Ni system into a single group of BMGs, even though BMGs fabricated to date in the system comprising Zr, Ni and Al are neither Al-based nor Ni-based BMGs. Furthermore, the Zr–Al–Ni system has a wide composition range for the formation of metallic glasses[6] over the Ni-rich side and a separate composition range for formation of the amorphous phase[6] in the Al-rich side. Third, this classification of BMGs fails to include Pd- and Pt-based alloy systems, although these alloys are widely accepted as typical BMGs.

The inadequacies mentioned above illustrate that the classification system for BMGs is incomplete due to a lack of defining properties, aside from chemical species and atomic size differences. In other words, a more practical classification system for BMGs can be developed by taking into account important quantities, such as heat of mixing of the constituent elements.[12] In addition, it is reasonable to assume that the periodicity of the elements in the periodic table is also likely to be an important quantity since the atomic size and heat of mixing should be related to the period of the element.

The purposes of the present paper are to summarize the characteristics of the known BMGs in terms of the atomic size difference, heat of mixing and period of the constituent elements, and to propose a classification system for BMGs that could be used to assist with further development of BMGs.

Table 1 The values of $\Delta H^{mix}_{\{AB\}}$ (kJ/mol) calculated by Miedema's model for atomic pairs between the elements with atomic numbers of (a) 1 to 46 and (b) 46 to 94. The values of $\Delta H^{mix}_{\{AB\}}$ for atomic pairs containing H, C or N are treated as 0 kJ/mol in a previous study.[14)]

| (b) \ (a) | 1 | 3 | 4 | 5 | 6 | 7 | 11 | 12 | 13 | 14 | 15 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | (a) \ (b) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | H | Li | Be | B | C | N | Na | Mg | Al | Si | P | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | |
| 46 Pd | -27 | -40 | -8 | -24 | -32 | -62 | -15 | -40 | -46 | -55 | -36.5 | -9 | -63 | -86 | -65 | -35 | -15 | -23 | -4 | -1 | 0 | -14 | -33 | -42 | -43.5 | -36 | -9 | -61 | -84 | -91 | -53 | -15 | 4 | 6 | 2 | | Pd 46 |
| 47 Ag | -10 | -16 | 6 | 5 | -32 | -94 | 0 | -10 | -4 | -20 | -18.5 | 7 | -28 | -28 | -2 | 17 | 27 | 13 | 28 | 19 | 15 | 2 | -4 | -5 | -17.5 | -8 | 7 | -27 | -29 | -20 | 16 | 37 | 24 | 23 | 10 | -7 | Ag 47 |
| 48 Cd | -6 | -13 | 11 | 13 | -27 | -91 | -3 | -6 | 3 | -13 | -11.5 | 1 | -32 | -30 | -8 | 9 | 17 | 2 | 17 | 6 | 2 | 6 | 1 | 1 | -14.5 | -4 | 1 | -33 | -35 | -26 | 11 | 28 | 10 | 9 | -6 | -26 | Cd 48 |
| 49 In | -6 | -12 | 16 | 18 | -27 | -98 | -5 | -4 | 7 | -10 | -10.5 | -4 | -35 | -30 | -5 | 12 | 20 | 3 | 19 | 7 | 2 | 10 | 3 | 3 | -13.5 | -3 | -4 | -37 | -36 | -25 | 15 | 33 | 11 | 10 | -8 | -31 | In 49 |
| 50 Sn | -4 | -18 | 15 | 18 | -23 | -90 | -8 | -9 | 4 | -11 | -7.5 | -7 | -45 | -45 | -21 | -1 | 10 | -7 | 11 | 0 | -4 | 7 | 1 | 1 | -12.5 | -1 | -7 | -46 | -51 | -43 | -1 | 20 | 5 | 4 | -13 | -34 | Sn 50 |
| 51 Sb | -1 | -28 | 18 | 23 | -13 | -74 | -20 | -16 | 2 | -8 | 2.5 | -22 | -62 | -61 | -33 | -8 | 7 | -11 | 10 | 2 | -1 | 7 | -1 | -1 | -10.5 | 3 | -24 | -66 | -68 | -60 | -11 | 17 | 8 | 9 | -8 | -28 | Sb 51 |
| 55 Cs | -16 | 16 | 29 | 29 | -43 | -155 | 3 | 25 | 26 | -3 | -24.5 | 0 | 19 | 70 | 104 | 103 | 97 | 71 | 85 | 58 | 48 | 28 | 15 | 14 | -19.5 | -12 | 0 | 14 | 62 | 101 | 135 | 128 | 69 | 64 | 34 | -9 | Cs 55 |
| 56 Ba | -49 | 0 | -10 | -19 | -90 | -212 | -3 | -4 | -20 | -52 | -85.5 | 6 | 1 | 28 | 57 | 57 | 50 | 29 | 37 | 11 | 0 | -9 | -23 | -30 | -63.5 | -66 | 9 | 0 | 20 | 52 | 81 | 73 | 11 | 6 | -21 | -62 | Ba 56 |
| 57 La | -60 | 6 | -29 | -47 | -116 | -235 | 24 | -7 | -38 | -73 | -112.5 | 46 | 8 | 2 | 20 | 22 | 17 | 3 | 5 | -17 | -27 | -21 | -31 | -41 | -73.5 | -81 | 52 | 14 | 0 | 13 | 36 | 31 | -23 | -28 | -50 | -82 | La 57 |
| 58 Ce | -61 | 7 | -30 | -48 | -116 | -234 | 25 | -7 | -38 | -73 | -112.5 | 47 | 9 | 2 | 18 | 20 | 15 | 1 | 3 | -18 | -28 | -21 | -31 | -41 | -73.5 | -81 | 53 | 15 | 0 | 12 | 34 | 29 | -25 | -30 | -52 | -83 | Ce 58 |
| 59 Pr | -61 | 7 | -31 | -49 | -117 | -233 | 26 | -6 | -38 | -73 | -112.5 | 49 | 10 | 1 | 17 | 18 | 13 | 0 | 1 | -20 | -30 | -22 | -31 | -41 | -72.5 | -81 | 55 | 16 | 0 | 10 | 32 | 26 | -27 | -32 | -53 | -83 | Pr 59 |
| 60 Nd | -61 | 7 | -31 | -49 | -116 | -235 | 26 | -6 | -38 | -73 | -112.5 | 49 | 10 | 2 | 17 | 18 | 13 | 0 | 1 | -20 | -30 | -22 | -31 | -40 | -101.5 | -80 | 55 | 16 | 0 | 10 | 32 | 26 | -27 | -32 | -53 | -83 | Nd 60 |
| 61 Pm | -61 | 8 | -33 | -51 | -118 | -233 | 28 | -6 | -39 | -74 | -114.5 | 51 | 11 | 1 | 15 | 16 | 10 | -2 | -2 | -23 | -32 | -23 | -32 | -41 | -73.5 | -81 | 57 | 18 | 0 | 9 | 29 | 23 | -30 | -35 | -56 | -86 | Pm 61 |
| 62 Sm | -61 | 8 | -32 | -50 | -117 | -202 | 28 | -6 | -38 | -74 | -113.5 | 50 | 11 | 1 | 15 | 17 | 11 | -1 | -1 | -22 | -31 | -22 | -31 | -40 | -72.5 | -80 | 56 | 17 | 0 | 9 | 30 | 24 | -29 | -34 | -54 | -84 | Sm 62 |
| 63 Eu | -45 | -1 | -12 | -19 | -87 | -231 | 0 | -5 | -19 | -49 | -79.5 | 10 | 0 | 21 | 48 | 49 | 43 | 23 | 30 | 7 | -3 | -10 | -21 | -27 | -58.5 | -60 | 13 | 0 | 14 | 42 | 69 | 63 | 6 | 2 | -24 | -61 | Eu 63 |
| 64 Gd | -61 | 8 | -32 | -50 | -117 | -232 | 28 | -6 | -39 | -73 | -113.5 | 50 | 11 | 1 | 15 | 17 | 11 | -1 | -1 | -22 | -31 | -22 | -31 | -40 | -72.5 | -80 | 56 | 17 | 0 | 9 | 30 | 24 | -29 | -34 | -54 | -84 | Gd 64 |
| 65 Tb | -61 | 9 | -33 | -51 | -118 | -232 | 29 | -6 | -39 | -74 | -113.5 | 52 | 12 | 1 | 14 | 15 | 9 | -3 | -3 | -23 | -32 | -23 | -31 | -40 | -72.5 | -80 | 58 | 18 | 0 | 8 | 28 | 22 | -30 | -35 | -56 | -85 | Tb 65 |
| 66 Dy | -61 | 9 | -32 | -51 | -117 | -231 | 29 | -6 | -38 | -74 | -112.5 | 51 | 12 | 1 | 14 | 15 | 9 | -3 | -3 | -23 | -32 | -22 | -31 | -40 | -71.5 | -80 | 58 | 18 | 0 | 8 | 27 | 22 | -30 | -35 | -55 | -84 | Dy 66 |
| 67 Ho | -60 | 8 | -32 | -50 | -116 | -229 | 28 | -6 | -38 | -73 | -111.5 | 51 | 11 | 1 | 14 | 16 | 10 | -2 | -2 | -22 | -31 | -22 | -30 | -39 | -71.5 | -79 | 57 | 18 | 0 | 9 | 28 | 22 | -29 | -34 | -54 | -83 | Ho 67 |
| 68 Er | -61 | 9 | -33 | -52 | -118 | -230 | 30 | -5 | -38 | -74 | -113.5 | 53 | 13 | 0 | 13 | 14 | 8 | -4 | -5 | -24 | -34 | -23 | -31 | -40 | -71.5 | -79 | 59 | 20 | 0 | 7 | 26 | 20 | -32 | -37 | -57 | -85 | Er 68 |
| 69 Tm | -61 | 9 | -33 | -52 | -117 | -229 | 30 | -5 | -38 | -74 | -112.5 | 52 | 13 | 0 | 12 | 13 | 8 | -4 | -5 | -24 | -34 | -23 | -30 | -39 | -71.5 | -79 | 59 | 20 | 0 | 7 | 25 | 19 | -32 | -37 | -56 | -85 | Tm 69 |
| 70 Yb | -45 | -1 | -14 | -22 | -88 | -199 | 2 | -6 | -20 | -51 | -80.5 | 12 | 0 | 16 | 41 | 43 | 37 | 19 | 25 | 2 | -7 | -12 | -21 | -27 | -58.5 | -59 | 16 | 1 | 10 | 36 | 61 | 55 | 1 | -4 | -28 | -62 | Yb 70 |
| 71 Lu | -61 | 10 | -35 | -54 | -119 | -231 | 31 | -5 | -39 | -75 | -114.5 | 55 | 14 | 0 | 11 | 11 | 5 | -6 | -7 | -27 | -36 | -24 | -31 | -40 | -71.5 | -80 | 61 | 21 | 0 | 6 | 23 | 17 | -35 | -40 | -59 | -87 | Lu 71 |
| 72 Hf | -63 | 30 | -37 | -66 | -123 | -218 | 63 | 10 | -39 | -77 | -117.5 | 92 | 39 | 5 | 0 | -2 | -9 | -12 | -21 | -35 | -42 | -17 | -24 | -34 | -65.5 | -75 | 98 | 50 | 11 | 0 | 4 | -4 | -47 | -52 | -63 | -80 | Hf 72 |
| 73 Ta | -46 | 48 | -24 | -54 | -101 | -173 | 89 | 30 | -19 | -56 | -89.5 | 119 | 60 | 16 | 1 | -1 | -7 | -4 | -15 | -24 | -29 | 2 | -3 | -10 | -37.5 | -45 | 125 | 73 | 27 | 3 | 0 | -5 | -35 | -39 | -45 | -52 | Ta 73 |
| 74 W | -24 | 50 | -3 | -31 | -60 | -103 | 97 | 38 | -2 | -31 | -46.5 | 124 | 57 | 9 | -6 | -1 | 1 | 6 | 0 | -1 | -3 | 22 | 15 | 11 | -7.5 | -9 | 129 | 70 | 24 | -9 | -8 | 0 | -7 | -10 | -9 | -6 | W 74 |
| 75 Re | -18 | 29 | 0 | -25 | -42 | -72 | 73 | 21 | -9 | -31 | -32.5 | 95 | 28 | -17 | -25 | -13 | -4 | -1 | 0 | 2 | 2 | 18 | 8 | 3 | -7.5 | -6 | 98 | 39 | -4 | -35 | -26 | -7 | 0 | -1 | 1 | 6 | Re 75 |
| 76 Os | -19 | 11 | -2 | -24 | -35 | -60 | 52 | 5 | -18 | -36 | -29.5 | 70 | 4 | -39 | -41 | -23 | -11 | -9 | -4 | 0 | 1 | 10 | -1 | -7 | -14.5 | -11 | 72 | 13 | -28 | -55 | -39 | -14 | 0 | 0 | 2 | 8 | Os 76 |
| 77 Ir | -20 | -9 | -5 | -26 | -32 | -54 | 28 | -13 | -30 | -43 | -30.5 | 42 | -23 | -62 | -57 | -34 | -18 | -18 | -9 | -3 | -2 | 0 | -13 | -21 | -24.5 | -19 | 44 | -16 | -53 | -76 | -53 | -21 | -2 | -1 | 1 | 6 | Ir 77 |
| 78 Pt | -24 | -33 | -10 | -28 | -30 | -52 | -1 | -35 | -44 | -53 | -34.5 | 9 | -55 | -89 | -74 | -45 | -24 | -28 | -13 | -7 | -5 | -12 | -29 | -38 | -37.5 | -31 | 9 | -50 | -83 | -100 | -67 | -28 | -3 | -1 | -2 | 2 | Pt 78 |
| 79 Au | -8 | -37 | 0 | -2 | -20 | -58 | -14 | -32 | -22 | -30 | -13.5 | -9 | -60 | -74 | -47 | -19 | 0 | -11 | 8 | 7 | 7 | -9 | -16 | -19 | -21.5 | -11 | -10 | -59 | -74 | -74 | -32 | 3 | 14 | 15 | 7 | 0 | Au 79 |
| 80 Hg | -3 | -19 | 15 | 19 | -20 | -81 | -11 | -10 | 4 | -10 | -4.5 | -10 | -43 | -37 | -10 | 10 | 21 | 4 | 22 | 12 | 8 | 8 | 1 | 1 | -11.5 | 0 | -11 | -45 | -43 | -31 | 11 | 32 | 18 | 18 | 2 | -18 | Hg 80 |
| 81 Tl | -3 | -15 | 23 | 27 | -19 | -91 | -11 | -3 | 11 | -4 | -1.5 | -13 | -40 | -28 | 2 | 22 | 31 | 11 | 31 | 18 | 13 | 15 | 6 | 6 | -9.5 | 3 | -14 | -44 | -35 | -19 | 26 | 46 | 25 | 24 | 5 | -21 | Tl 81 |
| 82 Pb | -1 | -21 | 25 | 30 | -13 | -82 | -18 | -8 | 10 | -2 | 4.5 | -21 | -52 | -40 | -8 | 15 | 28 | 7 | 29 | 17 | 13 | 15 | 5 | 5 | -7.5 | 6 | -23 | -56 | -48 | -33 | 17 | 42 | 26 | 25 | 6 | -18 | Pb 82 |
| 83 Bi | 0 | -23 | 26 | 31 | -12 | -80 | -20 | -10 | 10 | -2 | 5.5 | -24 | -56 | -46 | -14 | 10 | 24 | 3 | 26 | 14 | 10 | 15 | 4 | 4 | -7.5 | 7 | -26 | -61 | -54 | -40 | 12 | 38 | 23 | 23 | 3 | -21 | Bi 83 |
| 90 Th | -61 | 14 | -37 | -57 | -123 | -237 | 39 | -3 | -40 | -77 | -119.5 | 65 | 19 | 0 | 8 | 9 | 2 | -8 | -11 | -30 | -39 | -24 | -30 | -39 | -72.5 | -82 | 72 | 27 | 1 | 4 | 20 | 13 | -39 | -45 | -63 | -91 | Th 90 |
| 92 U | -53 | 30 | -27 | -54 | -105 | -189 | 65 | 14 | -30 | -66 | -98.5 | 93 | 37 | 3 | 0 | 1 | -3 | -5 | -11 | -23 | -29 | -7 | -15 | -25 | -52.5 | -60 | 99 | 48 | 11 | -3 | 4 | 2 | -31 | -36 | -46 | -59 | U 92 |
| 94 Pu | -54 | 21 | -25 | -50 | -102 | -188 | 49 | 6 | -33 | -66 | -95.5 | 72 | 24 | -1 | 2 | 4 | 2 | -4 | -6 | -19 | -25 | -9 | -20 | -29 | -56.5 | -62 | 77 | 33 | 4 | -3 | 9 | 8 | -26 | -30 | -42 | -58 | Pu 94 |
| (b) \ (a) | H | Li | Be | B | C | N | Na | Mg | Al | Si | P | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | (b) |
| | 1 | 3 | 4 | 5 | 6 | 7 | 11 | 12 | 13 | 14 | 15 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | (a) |

Table 2 The values of $\Delta H^{mix}_{\{AB\}}$ (kJ/mol) calculated by Miedema's model for atomic pairs between elements with atomic numbers (a) 1 to 45 and (b) 47 to 94. The values of $\Delta H^{mix}_{\{AB\}}$ for atomic pairs containing H, C or N are treated as 0 kJ/mol in a previous study.[14)]

| (b) \ (a) | 1 H | 3 Li | 4 Be | 5 B | 6 C | 7 N | 11 Na | 12 Mg | 13 Al | 14 Si | 15 P | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | (a) \ (a) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 47 Ag | H | -25 | 2 | 5 | -3 | -18 | -16 | -19 | -8 | -19 | 0.5 | -16 | -46 | -60 | -54 | -39 | -28 | -34 | -23 | -23 | -23 | -6 | -8 | -8 | -14.5 | -1 | -16 | -45 | -61 | -69 | -46 | -28 | -21 | -20 | -23 | H 1 |
| 48 Cd | -2 | Cd | | Li | -5 | -6 | -61 | -145 | 4 | 0 | -4 | -30 | -45.5 | 11 | -1 | 12 | 34 | 37 | 35 | 19 | 26 | 8 | 1 | -5 | -7 | -9 | -34.5 | -29 | 13 | 0 | 8 | 27 | 51 | 49 | 8 | 5 | -14 | Li 3 |
| 49 In | -2 | 0 | In | | Be | 0 | -15 | -39 | 18 | -3 | 0 | -15 | -3.5 | 27 | -14 | -36 | -30 | -16 | -7 | -10 | -4 | -4 | -4 | 0 | 4 | 5 | -3.5 | 7 | 28 | -10 | -32 | -43 | -25 | -7 | -3 | -3 | -6 | Be 4 |
| 50 Sn | -3 | 0 | 0 | Sn | | B | -10 | -28 | 18 | -4 | 0 | -14 | 0.5 | 27 | -22 | -55 | -58 | -42 | -31 | -32 | -26 | -24 | -24 | 0 | 4 | 6 | -0.5 | 10 | 28 | -18 | -50 | -71 | -54 | -34 | -25 | -24 | -25 | B 5 |
| 51 Sb | -4 | -2 | -4 | -1 | Sb | | C | -2 | -45 | -55 | -36 | -39 | -4.5 | -43 | -89 | -118 | -109 | -82 | -61 | -66 | -50 | -42 | -39 | -33 | -32 | -33 | -29.5 | -14 | -44 | -87 | -117 | -131 | -102 | -67 | -39 | -35 | -35 | C 6 |
| 55 Cs | 8 | 1 | -4 | -7 | -25 | Cs | | N | -141 | -134 | -92 | -81 | -24.5 | -152 | -201 | -224 | -190 | -143 | -107 | -119 | -87 | -75 | -69 | -84 | -88 | -95 | -78.5 | -59 | -154 | -206 | -232 | -233 | -174 | -115 | -68 | -61 | -63 | N 7 |
| 56 Ba | -28 | -36 | -42 | -51 | -72 | 12 | Ba | | Na | 10 | 13 | -11 | -26.5 | 1 | 1 | 34 | 68 | 73 | 71 | 49 | 62 | 41 | 32 | 16 | 6 | 5 | -21.5 | -14 | 2 | -2 | 28 | 59 | 93 | 93 | 47 | 44 | 19 | Na 11 |
| 57 La | -30 | -36 | -39 | -53 | -71 | 57 | 16 | La | | Mg | -2 | -26 | -39.5 | 20 | -6 | -3 | 16 | 23 | 24 | 10 | 18 | 3 | -4 | -3 | -4 | -4 | -26.5 | -21 | 23 | -4 | -6 | 6 | 32 | 36 | 3 | 0 | -17 | Mg 12 |
| 58 Ce | -30 | -36 | -38 | -52 | -70 | 59 | 17 | 0 | Ce | | Al | -19 | -20.5 | 23 | -20 | -38 | -30 | -16 | -10 | -19 | -11 | -19 | -22 | -1 | 1 | 1 | -14.5 | -6 | 25 | -18 | -38 | -44 | -18 | -5 | -20 | -21 | -32 | Al 13 |
| 59 Pr | -30 | -35 | -37 | -52 | -69 | 60 | 18 | 0 | 0 | Pr | | Si | -25.5 | -4 | -51 | -74 | -66 | -48 | -37 | -45 | -35 | -38 | -40 | -19 | -18 | -17 | -14.5 | -17 | -4 | -49 | -73 | -84 | -56 | -35 | -38 | -38 | -46 | Si 14 |
| 60 Nd | -29 | -35 | -37 | -51 | -69 | 60 | 18 | 0 | 0 | 0 | Nd | | P | -24.5 | -81.5 | -112.5 | -100.5 | -70.5 | -49.5 | -57.5 | -39.5 | -35.5 | -34.5 | -17.5 | -17.5 | -18.5 | -17 | -2.5 | -24.5 | -81.5 | -113.5 | -127.5 | -89.5 | -53.5 | -33.5 | -30.5 | -34.5 | P 15 |
| 61 Pm | -30 | -35 | -37 | -52 | -69 | 63 | 20 | 0 | 0 | 0 | 0 | Pm | | K | 12 | 58 | 94 | 96 | 91 | 66 | 81 | 55 | 45 | 25 | 13 | 12 | -19.5 | -11 | 0 | 7 | 50 | 88 | 123 | 120 | 65 | 60 | 31 | K 19 |
| 62 Sm | -30 | -35 | -36 | -51 | -68 | 62 | 20 | 0 | 0 | 0 | 0 | 0 | Sm | | Ca | 17 | 43 | 44 | 38 | 19 | 25 | 2 | -7 | -13 | -22 | -28 | -59.5 | -61 | 15 | 1 | 11 | 37 | 63 | 56 | 1 | -4 | -28 | Ca 20 |
| 63 Eu | -27 | -32 | -35 | -44 | -63 | 16 | 0 | 11 | 12 | 13 | 13 | 14 | 14 | Eu | | Sc | 8 | 7 | 1 | -8 | -11 | -30 | -39 | -24 | -29 | -38 | -69.5 | -77 | 64 | 25 | 1 | 4 | 18 | 11 | -39 | -44 | -61 | Sc 21 |
| 64 Gd | -29 | -35 | -36 | -51 | -68 | 62 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 14 | Gd | | Ti | -2 | -7 | -8 | -17 | -28 | -35 | -9 | -15 | -23 | -51.5 | -60 | 100 | 53 | 15 | 0 | 2 | -4 | -39 | -43 | -52 | Ti 22 |
| 65 Tb | -29 | -34 | -35 | -50 | -67 | 64 | 21 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 0 | Tb | | V | -2 | -1 | -7 | -14 | -18 | 5 | -2 | -8 | -31.5 | -35 | 100 | 54 | 17 | -4 | -1 | 0 | -21 | -25 | -29 | V 23 |
| 66 Dy | -29 | -34 | -35 | -50 | -67 | 63 | 21 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 0 | 0 | Dy | | Cr | 2 | -1 | -4 | -7 | 12 | 5 | -1 | -18.5 | -19 | 94 | 47 | 11 | -12 | -7 | 0 | -9 | -12 | -13 | Cr 24 |
| 67 Ho | -29 | -33 | -35 | -49 | -66 | 62 | 20 | 0 | 0 | 0 | 0 | 0 | 0 | 15 | 0 | 0 | 0 | Ho | | Mn | 0 | -5 | -8 | 4 | -6 | -13 | -31.5 | -31 | 69 | 27 | -1 | -15 | -4 | 5 | -8 | -11 | -16 | Mn 25 |
| 68 Er | -29 | -33 | -34 | -49 | -66 | 65 | 22 | 1 | 0 | 0 | 0 | 0 | 0 | 16 | 0 | 0 | 0 | 0 | Er | | Fe | -1 | -2 | 13 | 4 | -2 | -15.5 | -14 | 83 | 34 | -1 | -25 | -16 | -2 | -3 | -5 | -5 | Fe 26 |
| 69 Tm | -29 | -33 | -34 | -49 | -66 | 65 | 22 | 1 | 0 | 0 | 0 | 0 | 0 | 16 | 0 | 0 | 0 | 0 | 0 | Tm | | Co | 0 | 6 | -5 | -11 | -21.5 | -18 | 57 | 10 | -22 | -41 | -25 | -5 | 0 | -1 | -2 | Co 27 |
| 70 Yb | -28 | -31 | -34 | -43 | -61 | 19 | 1 | 8 | 8 | 9 | 9 | 11 | 10 | 0 | 10 | 11 | 11 | 11 | 12 | 12 | Yb | | Ni | 4 | -9 | -15 | -23.5 | -19 | 47 | -1 | -31 | -49 | -30 | -7 | 1 | 0 | -1 | Ni 28 |
| 71 Lu | -30 | -33 | -34 | -49 | -66 | 67 | 24 | 1 | 1 | 0 | 0 | 0 | 0 | 18 | 0 | 0 | 0 | 0 | 0 | 0 | 14 | Lu | | Cu | 1 | 1 | -11.5 | -3 | 27 | -9 | -22 | -23 | 3 | 19 | 8 | 7 | -2 | Cu 29 |
| 72 Hf | -13 | -19 | -18 | -35 | -50 | 104 | 54 | 15 | 14 | 13 | 13 | 11 | 11 | 44 | 11 | 10 | 10 | 10 | 9 | 9 | 38 | 8 | Hf | | Zn | 0 | -15.5 | -6 | 14 | -21 | -31 | -29 | -1 | 12 | -4 | -5 | -17 | Zn 30 |
| 73 Ta | 15 | 9 | 13 | -3 | -13 | 130 | 77 | 33 | 31 | 29 | 29 | 27 | 27 | 66 | 27 | 25 | 25 | 26 | 23 | 23 | 58 | 21 | 3 | Ta | | Ga | -15.5 | -6 | 13 | -27 | -40 | -40 | -8 | 7 | -10 | -11 | -25 | Ga 31 |
| 74 W | 43 | 33 | 38 | 27 | 25 | 132 | 74 | 32 | 29 | 26 | 26 | 23 | 24 | 64 | 24 | 21 | 21 | 22 | 19 | 19 | 56 | 16 | -6 | -7 | W | | Ge | -12.5 | -19.5 | -59.5 | -72.5 | -72.5 | -36.5 | -13.5 | -18.5 | -18.5 | -29.5 | Ge 32 |
| 75 Re | 38 | 25 | 29 | 20 | 23 | 101 | 42 | 3 | 0 | -2 | -2 | -5 | -4 | 34 | -4 | -7 | -7 | -5 | -9 | -9 | 28 | -12 | -30 | -24 | -4 | Re | | As | -12 | -61 | -80 | -85 | -44 | -16 | -15 | -14 | -24 | As 33 |
| 76 Os | 28 | 14 | 16 | 9 | 14 | 74 | 15 | -21 | -24 | -26 | -26 | -29 | -28 | 9 | -28 | -30 | -29 | -28 | -31 | -31 | 4 | -34 | -48 | -38 | -10 | -1 | Os | | Pb | 10 | 56 | 95 | 130 | 125 | 67 | 62 | 33 | Rb 37 |
| 77 Ir | 16 | 0 | 0 | -5 | 1 | 45 | -14 | -48 | -50 | -52 | -51 | -55 | -53 | -18 | -53 | -55 | -55 | -53 | -56 | -56 | -22 | -59 | -68 | -52 | -16 | -3 | -1 | Ir | | Sr | 17 | 48 | 76 | 69 | 10 | 5 | -22 | Sr 38 |
| 78 Pt | -1 | -18 | -21 | -25 | -17 | 10 | -50 | -80 | -81 | -82 | -82 | -85 | -84 | -51 | -83 | -85 | -84 | -83 | -86 | -85 | -54 | -88 | -90 | -66 | -20 | -4 | 0 | 0 | Pt | | Y | 9 | 30 | 24 | -29 | -34 | -54 | Y 39 |
| 79 Au | -6 | -11 | -11 | -10 | -4 | -9 | -60 | -73 | -73 | -73 | -73 | -75 | -74 | -58 | -74 | -74 | -74 | -72 | -74 | -74 | -59 | -75 | -63 | -32 | 12 | 20 | 18 | 13 | 4 | Au | | Zr | 4 | -6 | -53 | -59 | -72 | Zr 40 |
| 80 Hg | -1 | 0 | -1 | 0 | -1 | -11 | -49 | -45 | -44 | -43 | -43 | -43 | -43 | -43 | -43 | -42 | -42 | -41 | -41 | -41 | -42 | -41 | -23 | 9 | 38 | 33 | 23 | 9 | -9 | -4 | Hg | | Nb | -6 | -36 | -41 | -46 | Nb 41 |
| 81 Tl | 3 | 2 | 0 | 2 | -1 | -15 | -49 | -38 | -37 | -36 | -36 | -35 | -35 | -41 | -35 | -34 | -34 | -33 | -33 | -32 | -39 | -32 | -11 | 24 | 52 | 44 | 30 | 14 | -8 | -2 | 1 | Tl | | Mo | -11 | -14 | -15 | Mo 42 |
| 82 Pb | 3 | 2 | -1 | 2 | 1 | -25 | -62 | -51 | -50 | -49 | -49 | -49 | -48 | -53 | -48 | -47 | -46 | -46 | -45 | -45 | -50 | -45 | -23 | 15 | 49 | 44 | 32 | 16 | -5 | 2 | 1 | -1 | Pb | | Tc | 0 | 0 | Tc 43 |
| 83 Bi | 2 | 1 | -1 | 1 | 1 | -27 | -68 | -58 | -57 | -56 | -55 | -55 | -54 | -58 | -54 | -53 | -53 | -52 | -52 | -51 | -55 | -51 | -30 | 9 | 45 | 40 | 29 | 14 | -8 | 2 | 1 | -1 | 0 | Bi | | Ru | 1 | Ru 44 |
| 90 Th | -29 | -32 | -31 | -48 | -65 | 78 | 30 | 3 | 2 | 2 | 2 | 1 | 1 | 23 | 1 | 1 | 1 | 1 | 1 | 1 | 18 | 0 | 6 | 18 | 12 | -16 | -39 | -64 | -94 | -78 | -39 | -28 | -41 | -48 | Th | | Rh | Rh 45 |
| 92 U | 0 | -8 | -7 | -23 | -34 | 104 | 52 | 15 | 14 | 12 | 12 | 10 | 11 | 43 | 11 | 10 | 9 | 10 | 8 | 8 | 36 | 7 | -2 | 3 | 1 | -17 | -33 | -50 | -68 | -43 | -10 | 1 | -9 | -15 | 4 | U | | (a) |
| 94 Pu | -6 | -16 | -16 | -30 | -42 | 81 | 36 | 7 | 6 | 5 | 5 | 4 | 4 | 29 | 4 | 3 | 3 | 3 | 2 | 2 | 24 | 1 | -1 | 8 | 8 | -10 | -26 | -44 | -63 | -45 | -18 | -10 | -20 | -26 | 0 | 1 | Pu | |
| (b) \ (b) | Ag 47 | Cd 48 | In 49 | Sn 50 | Sb 51 | Cs 55 | Ba 56 | La 57 | Ce 58 | Pr 59 | Nd 60 | Pm 61 | Sm 62 | Eu 63 | Gd 64 | Tb 65 | Dy 66 | Ho 67 | Er 68 | Tm 69 | Yb 70 | Lu 71 | Hf 72 | Ta 73 | W 74 | Re 75 | Os 76 | Ir 77 | Pt 78 | Au 79 | Hg 80 | Tl 81 | Pb 82 | Bi 83 | Th 90 | U 92 | Pu 94 | (b) \ (b) |

Table 3 Conventional table for the values of $\Delta H^{mix}_{\{AB\}}$. Tables 1 and 2 are prepared using the symmetry of the table. The square part surrounded by thick lines corresponds to Table 1. The triangle parts surrounded by thick lines with (a,b) coordinates of (1-45,1-45) and (47-94,47-94) correspond to the upper right and lower left parts of Table 2, respectively.

| (a) | | 1 | 3 | 4 | 5 | ⋯ | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | ⋯ | 83 | 90 | 92 | 94 | (a) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (b) | | H | Li | Be | B | ⋯ | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | ⋯ | Bi | Th | U | Pu | | (b) |
| 1 | H | | -25 | 2 | 5 | | -28 | -21 | -20 | -23 | -27 | -10 | -6 | -6 | -4 | | 0 | -61 | -53 | -54 | H | 1 |
| 3 | Li | -25 | | -5 | -6 | | 49 | 8 | 5 | -14 | -40 | -16 | -13 | -12 | -18 | | -23 | 14 | 30 | 21 | Li | 3 |
| 4 | Be | 2 | | | 0 | | -7 | -3 | -3 | -6 | -8 | 6 | 11 | 16 | 15 | | 26 | -37 | -27 | -25 | Be | 4 |
| 5 | B | 5 | -6 | 0 | | | -34 | -25 | -24 | -25 | -24 | 5 | 13 | 18 | 18 | | 31 | -57 | -54 | -50 | B | 5 |
| ⋮ | ⋮ | | | | | | | | | | | | | | | | | | | | ⋮ | ⋮ |
| 42 | Mo | -28 | 49 | -7 | -34 | | | -11 | -14 | -15 | -15 | 37 | 28 | 33 | 20 | | 38 | 13 | 2 | 8 | Mo | 43 |
| 43 | Tc | -21 | 8 | -3 | -25 | | -11 | | 0 | 0 | 4 | 24 | 10 | 11 | 5 | | 23 | -39 | -31 | -26 | Tc | 44 |
| 44 | Ru | -20 | 5 | -3 | -24 | | -14 | 0 | | 1 | 6 | 23 | 9 | 10 | 4 | | 23 | -45 | -36 | -30 | Ru | 44 |
| 45 | Rh | -23 | -14 | -6 | -25 | | -15 | 0 | 1 | | 2 | 10 | -6 | -8 | -13 | | 3 | -63 | -46 | -42 | Rh | 45 |
| 46 | Pd | -27 | -40 | -8 | -24 | | -15 | 4 | 6 | 2 | | -7 | -26 | -31 | -34 | | -21 | -91 | -59 | -58 | Pd | 46 |
| 47 | Ag | -10 | -16 | 6 | 5 | | 37 | 24 | 23 | 10 | -7 | | -2 | -2 | -3 | | 2 | -29 | 0 | -6 | Ag | 47 |
| 48 | Cd | -6 | -13 | 11 | 13 | | 28 | 10 | 9 | -6 | -26 | -2 | | 0 | 0 | | 1 | -32 | -8 | -16 | Cd | 48 |
| 49 | In | -6 | -12 | 16 | 18 | | 33 | 11 | 10 | -8 | -31 | -2 | 0 | | 0 | | -1 | -31 | -7 | -16 | In | 49 |
| 50 | Sn | -4 | -18 | 15 | 18 | | 20 | 5 | 4 | -13 | -34 | -3 | 0 | 0 | | | 1 | -48 | -23 | -30 | Sn | 50 |
| ⋮ | ⋮ | | | | | | | | | | | | | | | | | | | | ⋮ | ⋮ |
| 83 | Bi | 0 | -23 | 26 | 31 | | 38 | 23 | 23 | 3 | -21 | 2 | 1 | -1 | 1 | | | -48 | -15 | -26 | Bi | 83 |
| 90 | Th | -61 | 14 | -37 | -57 | | 13 | -39 | -45 | -63 | -91 | -29 | -32 | -31 | -48 | | -48 | | 4 | 0 | Th | 90 |
| 92 | U | -53 | 30 | -27 | -54 | | 2 | -31 | -36 | -46 | -59 | 0 | -8 | -7 | -23 | | -15 | 4 | | 1 | U | 92 |
| 94 | Pu | -54 | 21 | -25 | -50 | | 8 | -26 | -30 | -42 | -58 | -6 | -16 | -16 | -30 | | -26 | 0 | 1 | | Pu | 94 |
| (b) | | H | Li | Be | B | ⋯ | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | ⋯ | Bi | Th | U | Pu | | (b) |
| | (a) | 1 | 3 | 4 | 5 | ⋯ | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | ⋯ | 83 | 90 | 92 | 94 | (a) | |

## 2. Data Used for Analysis

### 2.1 Heat of Mixing

The values of heat of mixing were quoted as enthalpy of mixing ($\Delta H^{mix}_{\{AB\}}$)[13] of the binary liquid in an A–B system at an equi-atomic composition. From the Miedema's model,[13] one can deal with $\Delta H^{mix}_{\{AB\}}$ for TM–TM and TM–NTM atomic pairs (except for those of gaseous elements) where TM and NTM are a transition metal and non-transition metal containing metalloid, respectively. In addition, values of $\Delta H^{mix}_{\{AB\}}$ for a total of 1053 atomic pairs including NTM–NTM atomic pairs were quoted[14] for ternary alloy systems listed in a databook for the formation of amorphous alloys.[15] On the basis of a previous report,[14] $\Delta H^{mix}_{\{AB\}}$ was calculated for 2628 atomic pairs from 73 elements; that is, the atomic pairs that can be dealt with by Miedema's model. Tables 1 and 2 summarize the values of $\Delta H^{mix}_{\{AB\}}$, while Table 3 explains how to read the values of $\Delta H^{mix}_{\{AB\}}$. In Tables 1 and 2, it should be noted that the values of $\Delta H^{mix}_{\{AB\}}$ containing NTM (H, B, C, N, P, Si and Ge) are modified[14] from the original values of $\Delta H^{mix}_{\{AB\}}$ [13] due to the subtraction term required for NTMs to transform to metallic elements[13] ($\Delta H^{trans}_{i}$). The values of $\Delta H^{trans}_{i}$ (i = H, B, C, N, P, Si and Ge) are 100, 30, 180, 310, 17, 34 and 25 kJ/mol, respectively.[13] The subtraction term for a binary A–B system with an equiatomic composition is $\Delta H^{trans}_{i}/2$ for TM–NTM and $(\Delta H^{trans}_{i} + \Delta H^{trans}_{j})/2$ for NTM–NTM, where $i$ and $j$ refer to the two elements ($i \neq j$) in NTMs. It is noted that values of $\Delta H^{mix}_{\{AB\}}$ for atomic pairs containing H, C or N are treated as 0 kJ/mol in a previous study.[14]

### 2.2 Atomic Size

The atomic size of an element is quoted from a databook[16] as the atomic radius which is taken as half of the interatomic distance in a crystalline state. Figure 1 illustrates the atomic radius of elements and the relationship with their position in the periodic table, together with the numerical values of atomic radius.

### 2.3 Previous Classification of BMGs[12]

Figure 2 illustrates the previous classification system for BMGs as considered by Inoue.[12] From Fig. 2, it is evident that the four groups (G-I to G-IV) of the BMGs are composed of three in five groups of elements: an early transition metal (ETM), lanthanide metal (Ln), late transition metal (LTM), simple metal, metalloid and group of elements (Al,Ga,Sn). An exception to this rule is BMGs of G-III that are reported[12] to form as multicomponent systems comprising several constituent elements as illustrated by the Fe–(Al,Ga)–(P,C,B) system.[7] Another exception to this rule is BMGs of G-V consisting of elements from two groups of elements (LTM and Metalloid). This is exemplified by Pd–Ni–P BMG that Pd and Ni belong to LTM, and P belongs to Metalloid. This type of BMG is designated by "line type" in the present paper.

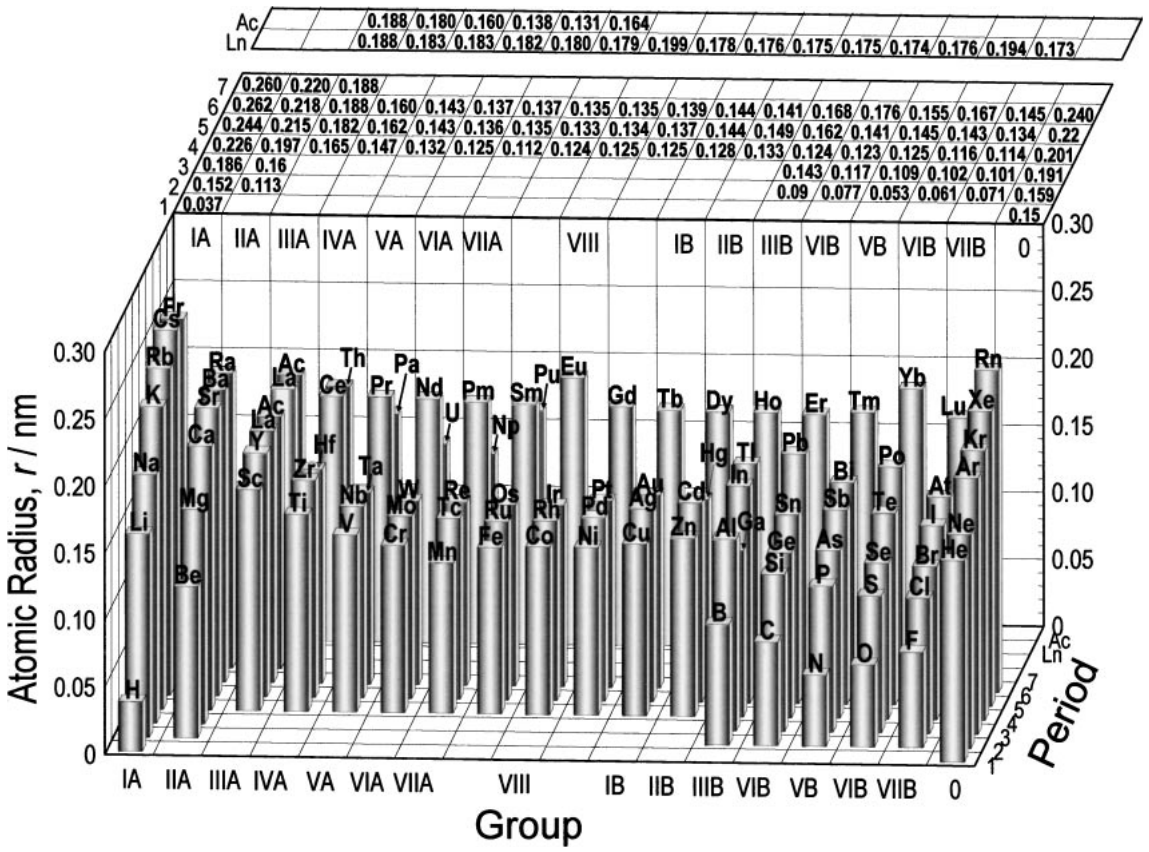



Fig. 1 Atomic radii[16] of elements plotted as a 3-D bar graph over the periodic table. The numerical values of the atomic radii (nm) for the elements are also shown at the top. Atomic radius of Lanthanide (Ln) and Actinide (Ac) metals, which are belonging to IIIA, are plotted separately. Half the interatomic distance is regarded as the atomic radius.[16] The interatomic radius is determined by metallic, covalent and van der Waals bondings in metals, non-metals and rare gases, respectively. The elements in the metal-nonmetal region of the periodic table and elements with polymorphous transformations have the following atomic radii (nm) (C: 0.071, Mn: 0.150, Zn: 0.148, Ga: 0.138, Cd: 0.166, In: 0.168, Sn: 0.151, Hg: 0.158, Tl: 0.170, U: 0.150, Np: 0.148).

### 2.4 The BMGs discovered after 2000

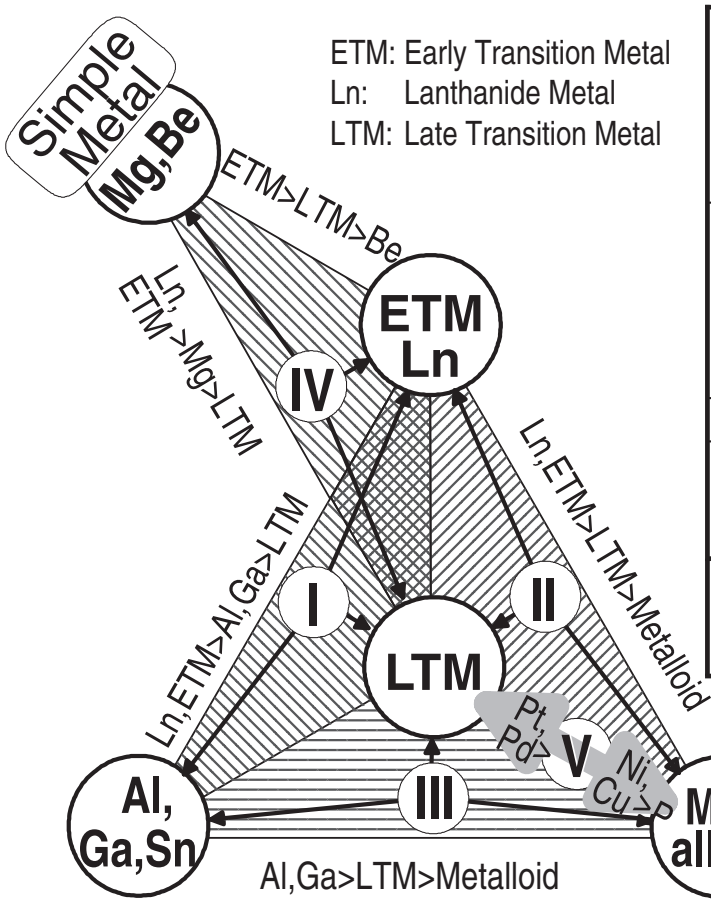
Several BMGs have been discovered since the proposed classification system for BMGs by Inoue in 2000, including the Cu–Zr–Ti,[17] Ca–Mg–Cu,[18,19] Ca–Mg–Zn,[20] Ni–Nb–Sn,[21] Ni–Nb–Ta,[22] Ti–Cu–Ni based system[23] and Ti–Cu–Ni–Mo–Fe system.[24] These new BMGs are also analyzed in the present study.

## 3. Results

Figure 3 shows the result of classifying BMGs based on BMGs from previous results[12] and new BMGs as described in Section 2. It is noted that there are differences in element groups between Figs. 2 and 3. The element group of Al–Ga–Sn in Fig. 2 is modified as Al–Ga in Fig. 3. Simple metals (Be,Mg) are extended to alkaline earth metals (IIA: Be,Mg, Ca). In addition, LTM are extended to LTM containing the IIIB–IVB metals (LTM/BM). The reason for differences in the groups of elements between Figs. 2 and 3 will be discussed in Section 4. As a result, BMGs discovered to date can be classified into seven groups based on the constituent elements belonging to the groups of elements in Fig. 3. These groups are G-I: ETM/Ln-LTM/BM-Al/Ga, G-II: ETM/Ln-LTM/BM-Metalloid, G-III: Al/Ga-LTM/BM-Metalloid, G-IV: IIA-ETM/Ln-LTM/BM, G-V: LTM/BM-Metalloid, G-VI: ETM/Ln-LTM/BM, and G-VII: IIA-LTM/BM. The representative alloy systems for each of these groups are also tabulated in Fig. 3. The BMGs belonging to G-V, G-VI and G-VII are drawn as a line type in Fig. 3 as a result of the present classification.

It should be noted that Fig. 3 is a projection of Fig. 4, which is a solid figure with Fig. 3 at the base and with a perpendicular axis corresponding to the period as well. In Fig. 4, all of the BMGs within each group form either a triangle, polygon or polyhedron with three or more elements which are located at the period axis of each group of elements. Accordingly, the groups G-V to G-VII, which are discerned as a line type combining two kinds of groups of elements in Fig. 3, can form either a triangle, polygon or polyhedron in Fig. 4, which explains why the Pd–Ni–P BMG belongs to G-V. Thus, the period of the constituent elements that compose BMGs is also an important quantity for the formation of a BMG.

Figure 5 illustrates the relationship between the atomic size difference, heat of mixing of the constituent elements ($\Delta H^{\mathrm{mix}}$) and main element of the ternary BMGs. Figure 5(a) shows the atomic radius of elements plotted in a sequence from the smallest (H) to the largest (Cs), followed by Fig. 5(b), which is drawn by tracing the locations of the elements in Fig. 5(a) horizontally for the constituent ele-




| | | |
|---|---|---|
| I | Zr-Al-Ni | Ln-Al-Ni |
| | Zr-Al-Cu | Ln-Al-Cu |
| | Zr-Al-Ni-Cu | Ln-Al-Ni-Cu |
| | Zr-Ti-Al-Ni-Cu | Ln-Ga-Ni |
| | Zr-Ga-Ni | Ln-Ga-Cu |
| II | Fe-Zr-B | |
| | Fe-Hf-B | |
| | Fe-Zr-Hf-B | |
| | Fe-Co-Ln-B | |
| | Co-Zr-Nb-B | |
| III | Fe-(Al,Ga)-metalloid | |
| IV | Mg-Ln-Ni | |
| | Mg-Ln-Cu | |
| | Zr-Ti-Be-Ni-Cu | |
| V | Pd-Ni-P | |
| | Pd-Cu-Ni-P | |
| | Pt-Ni-P | |

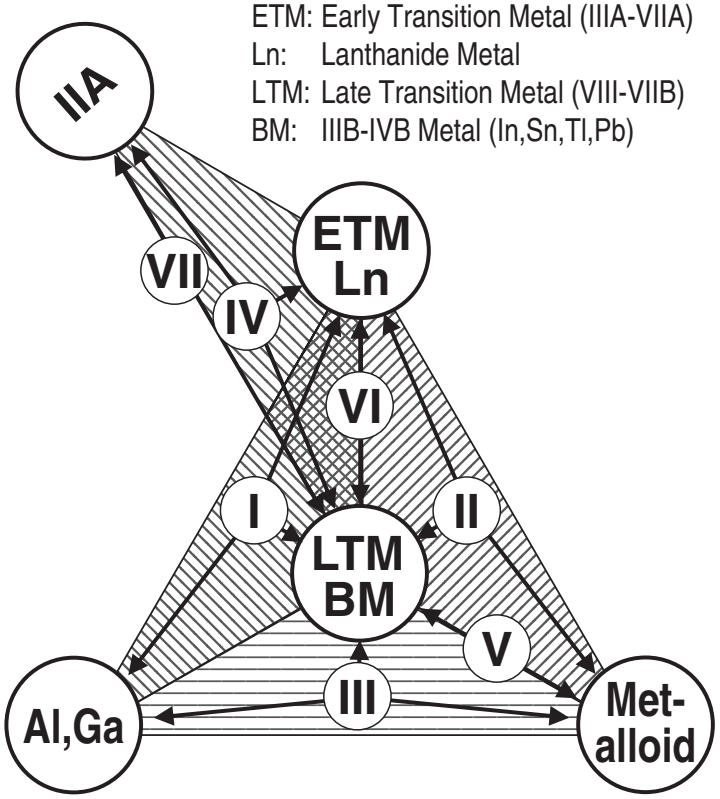
Fig. 2 Previous BMG classification system proposed by Inoue.[12)]

ments of the representative ternary BMGs belonging to each of the seven groups. The following ternary alloys were chosen as representative BMGs from each of the seven groups: Zr–Al–Ni[6)] and La–Al–Ni[5)] for G-I, Fe–Zr–B[9)] for G-II, Mg–La–Ni[4)] and Mg–Cu–Y[3)] for G-IV, Pd–Ni–P[11)] and Pd–Ni–Si[1)] for G-V, Ni–Nb–Sn,[21)] Ni–Nb–Ta[22)] and Cu–Ti–Zr[17)] for G-VI, and Ca–Mg–Cu[18)] and Ca–Mg–Zn[20)] for G-VII. In addition, the relationship between $\Delta H^{\mathrm{mix}}$ and typical compositions of ternary BMGs are summarized in Fig. 5(c). Figure 5 shows the characteristics of a ternary BMG with a composition of $A_aB_bC_c$, and corresponding atomic radii of $r_A$, $r_B$ and $r_C$ (where $r_A > r_B > r_C$) and mixing enthalpies of mixing of $\Delta H^{\mathrm{mix}}_{\{AB\}}$, $\Delta H^{\mathrm{mix}}_{\{BC\}}$ and $\Delta H^{\mathrm{mix}}_{\{CA\}}$, respectively. The largest, negative enthalpy of mixing ($\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$) is underlined with the symbol $\underline{\Delta H}^{\mathrm{mix}}_{\{AB\}}$ and its numerical value. The main constituent elements with the highest composition in a system are illustrated with closed circles and white lettering. This is exemplified by $Zr_{60}Ni_{25}Al_{15}$ BMG in Fig. 5(c) that Zr with 60 at% , which is the main element in the system, is illustrated with closed circles and white lettering and that $\underline{\Delta H}^{\mathrm{mix}}_{\{ZrNi\}}$ value of $-49$ kJ/mol, which is the largest, negative enthalpy of mixing in the system, is underlined.

From Fig. 5, it is obvious that the main element of a BMG has the largest radius for G-I, G-V and G-VII, smallest radius for G-VI, and an intermediate radius for G-II and G-IV. It is noted that Pd and Ni in $Pd_{40}Ni_{40}P_{20}$ BMG are equal in their stoichiometry, such that Ni could also be considered to be the main element. However, Pd is regarded as the main element in this work. The details will be discussed in Section 4–6. The important point to note for $\Delta H^{\mathrm{mix}}$ is that BMGs belonging to G-II and G-IV have $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ for the C-A atomic pair consisting of the largest and the smallest constituent elements ($\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}} = \underline{\Delta H}^{\mathrm{mix}}_{\{CA\}}$). Figure 5 shows that the ratios of $\Delta H^{\mathrm{mix}}_{\{AB\}}/\Delta H^{\mathrm{mix}}_{\{BC\}}$ or $\Delta H^{\mathrm{mix}}_{\{BC\}}/\Delta H^{\mathrm{mix}}_{\{AB\}}$, and $|\underline{\Delta H}^{\mathrm{mix}}_{\{CA\}}|/\{|\Delta H^{\mathrm{mix}}_{\{AB\}}| + |\Delta H^{\mathrm{mix}}_{\{BC\}}|\}$ of the G-II and G-IV BMGs for the Fe–Zr–B, Mg–La–Ni and Mg–Cu–Y systems are in the range of 1–2 and 1.1–2.4, respectively. In contrast, the main element is independent of the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ for BMGs belonging to G-I, G-V and G-VII.

## 4. Discussion

The classification of BMGs depends on the element groups of the constituent elements. Thus, the following items will be discussed in terms of the element groups: (1) Sn in the group of elements of LTM/BM, (2) extension of an element group as a function of the period, (3) Ca in the group of elements of IIA with simple metals (Be,Mg), and (4) BMGs containing constituent elements in the same group in the periodic table. In addition, (5) applicability of the characteristics of the main element in BMGs based on multicomponent systems, (6) exchangeability of constituent elements in multicomponent BMGs, and (7) significance of the classification of BMGs will be discussed.




| | |
|---|---|
| I | Zr-Al-Ni, Ln-Al-Ni |
| | Zr-Al-Cu, Ln-Al-Cu |
| | Zr-Al-Ni-Cu, Ln-Al-Ni-Cu |
| | Zr-Ti-Al-Ni-Cu |
| | Zr-Ga-Ni, Ln-Ga-Ni Ln-Ga-Cu |
| II | Fe-Zr-B, Fe-Hf-B |
| | Fe-Zr-Hf-B |
| | Fe-Co-Ln-B |
| | Co-Zr-Nb-B |
| | Co-Fe-Ta-B |
| III | Fe-(Al,Ga)-Metalloid |
| IV | Mg-Ln-Ni, Mg-Ln-Cu |
| | Zr-Ti-Be-Ni-Cu |
| | Ti-Cu-Ni-Sn-Be |
| | Ti-Cu-Ni-Sn-Be-Zr |
| V | Pd-Ni-P |
| | Pd-Cu-Ni-P |
| | Pt-Ni-P |
| VI | Cu-Zr-Ti |
| | Ni-Nb-Ta, Ni-Nb-Sn |
| | Ti-Zr-Cu-Ni |
| | Ti-Ni-Cu-Sn |
| | Ti-Cu-Ni-Mo-Fe |
| VII | Ca-Mg-Cu |
| | Ca-Mg-Zn |

Fig. 3 Classification of BMGs discovered to date, showing seven groups denoted by G-I to G-VII. The ETM and LTM represent the transition metals belonging to groups IIIA–VIIA and VIII–IIB in the periodic table, respectively.

### 4.1 Sn in the element group of LTM/BM

As shown in Fig. 2, Inoue previously classified Sn in the group of elements of Al, Ga, Sn on the basis of reports that a BMG is formed in the Ti–Ni–Cu–Sn system[25]—the only known BMG containing Sn prior to 2000. Subsequently, BMGs containing Sn have been discovered for the following systems: Ni–Nb–Sn,[21] Ti–Cu–Ni–Sn,[23] Ti–Cu–Ni–B–Si–Sn,[26] Ni–Ti–Zr–(Si,Sn),[27] $Cu_{47}Ti_{33}Zr_{11}Ni_8X_1$ (X = Fe, Si, Sn, Pb)[28] and $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$.[29]

The reason for shifting Sn from (Al,Ga,Sn) to the LTM/BM group of elements is due to the following considerations. First, the main element depends on the type of BMG as for ternary BMGs in Fig. 5. Second, the characteristics of a BMG are determined by the major constituent elements with respect to composition. In other words, minor elements or additional elements scarcely change the characteristics of BMGs. This leads to the third consideration that similar BMGs should be classified into the same group of BMGs.

The first consideration is supported if Sn is placed in the LTM/BM group of elements, which leads to Ni–Nb–Sn BMGs being classified as G-VI BMGs. In addition, the $Ni_{59.5}Nb_{33.6}Sn_{6.9}$ BMG[25] satisfies the characteristics of the main element of the BMGs belonging to G-VI. That is, the smallest element (Ni) is the main element. On the other hand, if Sn is placed in the element group of (Al,Ga,Sn)—the element group used for the analysis of the characteristics of BMGs in the previous study[12]—the $Ni_{59.5}Nb_{33.6}Sn_{6.9}$ BMG is classified as a G-I BMG. The element with the largest atomic radius (Sn) may be the main element for BMGs belonging to G-I, which is at variance with $Ni_{59.5}Nb_{33.6}Sn_{6.9}$ BMG in which Ni is the main element. The second consideration is proven by the similarities between $Ni_{59.5}Nb_{33.6}Sn_{6.9}$ and $Ni_{60}Nb_{30}Ta_{10}$[22] BMGs in terms of composition, atomic radius and $\Delta H^{mix}$ of the constituent elements. For example, the differences in composition of each of the constituent elements are within 4 at%. In addition, both BMGs have a common $\Delta H^{mix}_{\{Ni-Nb\}}$ and one atomic pair with a $\Delta H^{mix}$ that is almost zero. For example, $\Delta H^{mix}_{\{Nb-Sn\}}$ and $\Delta H^{mix}_{\{Nb-Ta\}}$ are $-1$ and 0 kJ/mol, respectively, and $\Delta H^{mix}$ for Ni–Sn and Ni–Ta atomic pairs are negative values. Furthermore, the atomic radii of Sn and Ta are 0.137 and 0.145 nm, respectively, which is quite similar to Ni and Nb with atomic radii of 0.125 and 0.143 nm, respectively. From these two considerations, one can observe the similarities between $Ni_{59.5}Nb_{33.6}Sn_{6.9}$ and $Ni_{60}Nb_{30}Ta_{10}$ BMGs, satisfying the third consideration that similar BMGs should be classified into the same group.

If Sn is placed in the LTM group of elements, it is possible to classify various Sn-containing BMGs as follows: Ti–Cu–Ni–Sn[24] in G-VI, Ti–Cu–Ni–B–Si–Sn[26] in G-II, Ni–Ti–Zr–Sn[27] in G-VI, $Cu_{47}Ti_{33}Zr_{11}Ni_8X_1$ (X = Fe, Sn, Pb)[28] in G-VI, and $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$[29] in G-II. In stark contrast, the (Al,Ga,Sn) group of elements does not allow the placement of Ti–Cu–Ni–B–Si–Sn and $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ BMGs into any of the groups as shown in Fig. 3.

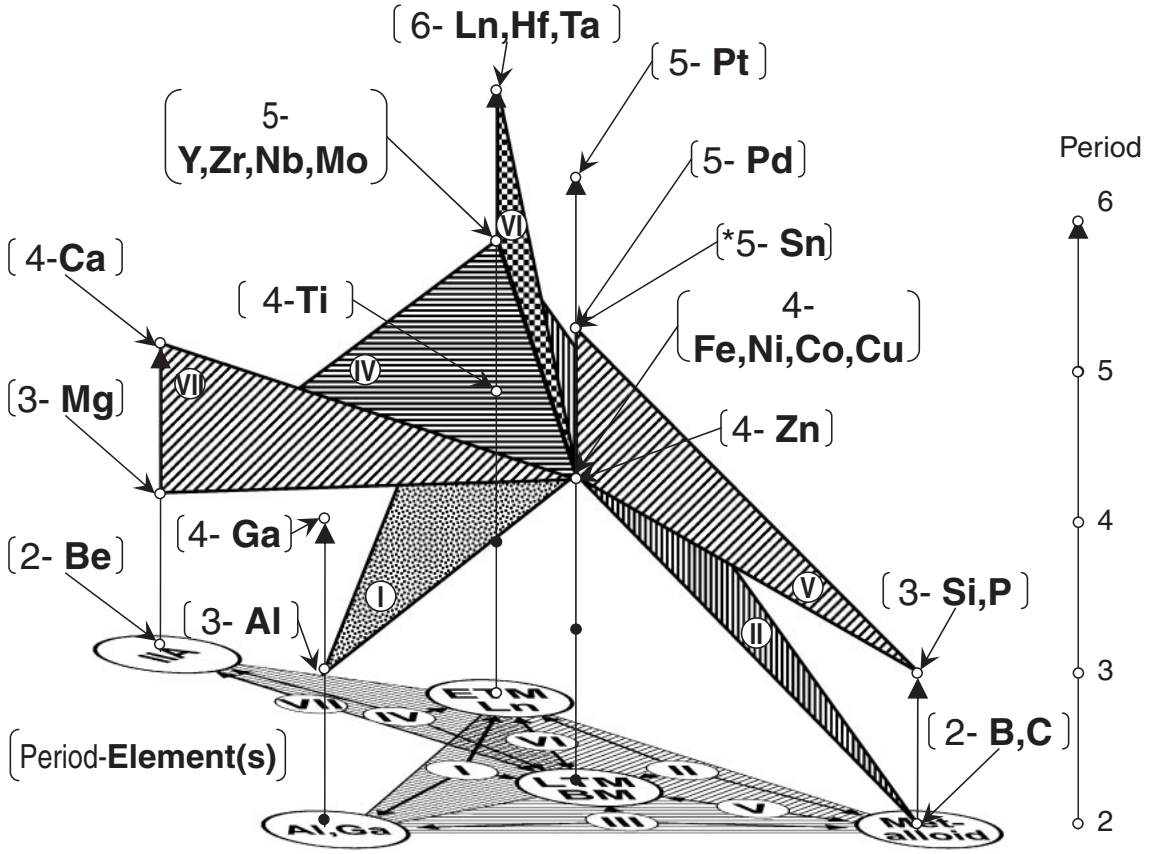



Fig. 4 A solid figure with a base of Fig. 3, and an extended axis of the period of the element in each group of elements. The representative ternary systems in each group of BMGs is drawn as a triangle for G-I: Zr–Al–Ni, G-II: Fe–Zr–B, G-IV: Mg–Cu–Y, G-V: Pd–Ni–P, G-VI: Ni–Nb–Ta, G-VII: Ca–Mg–Cu. The multicomponent BMGs with four or more elements can form a polygon or polyhedron in the solid figure. Asterisk denotes the element belonging to IB–IVB (BM). Closed circle in the period axis denotes the absence of elements.

### 4.2 Extension of element groups as a function of the period

As shown in Fig. 3, element group was extended as a function of the period by considering that Ni and Pd both belong to the LTM group of elements. This assumption is supported by the tendency for the atomic radii of transition metals to increase consideably between the fourth and fifth period in the periodic table. For instance, the atomic radii[16] of Ni, Pd and Pt, which belong to the fourth, fifth and sixth period, are 0.125, 0.137 and 0.139 nm, respectively, and that of Ti, Zr and Hf are 0.147, 0.162 and 0.160 nm, respectively. Thus, the difference in atomic radii is greater between transition metals in the fourth and fifth periods compared with those between the fifth and sixth periods. For other transition metals, this tendency is also shown in Fig. 6.

The extending of element groups as a function of the period is important for understanding the characteristics of BMGs. As described in Section 3, the Pd–Ni–P system forms a triangle in Fig. 4. However, it should be noted that BMGs with a thickness of several millimeters, described as a line type within the solid figure, have not been reported. For instance, LTM(4)-LTM(4)-Metalloid(3), where the numbers in the parentheses denote the period of the element, is not a BMG-forming system as demonstrated by the Ni–Fe–P system. On the other hand, the LTM(5)-LTM(4)-Metalloid(3) is drawn as a line in Fig. 3 and triangle in Fig. 4, and is typified by the Pd–Ni–P BMG system. In general, differences in atomic radius also correspond to a difference in group and period on the periodic table. Hence, the period of the constituent elements is also an important quantity for the formation of BMGs.

### 4.3 Ca in the IIA group of elements with Simple metal (Be,Mg)

The element groups of Simple metal (Be,Mg) in Fig. 2 is extended to IIA in Fig. 3. The reasons for grouping Be, Mg and Ca into IIA are as follows. First, the atomic radii[16] of Be, Mg and Ca are 0.113, 0.160, and 0.197 nm, respectively. Accordingly, the atomic radii of Be, Mg and Ca increase monotonously with increasing period, as is also apparent in Fig. 6(a). Second, one can discern the similarity with respect to atomic size differences and $\Delta H^{\mathrm{mix}}$'s for Ca–Mg–Zn and Mg–Cu–Y systems in Fig. 5. The atomic radii of Ca, Mg and Zn are 0.197, 0.160 and 0.133 nm, respectively. The atomic radii of Y, Mg and Cu are 0.182, 0.160 and 0.128 nm, respectively. In addition, only one value of $\Delta H^{\mathrm{mix}}$ is different among the atomic pairs with the intermediate and smallest radii. For instance, $\Delta H^{\mathrm{mix}}$ for Mg–Zn and Mg–Cu are $-4$ kJ/mol and $-3$ kJ/mol, respectively. However, Mg is the main element in the Mg–Cu–Y system (G-IV), while Ca is the main element in the Ca–Mg–Zn system (G-VII). From these observations, it is reasonable to include Ca in the IIA group of elements.

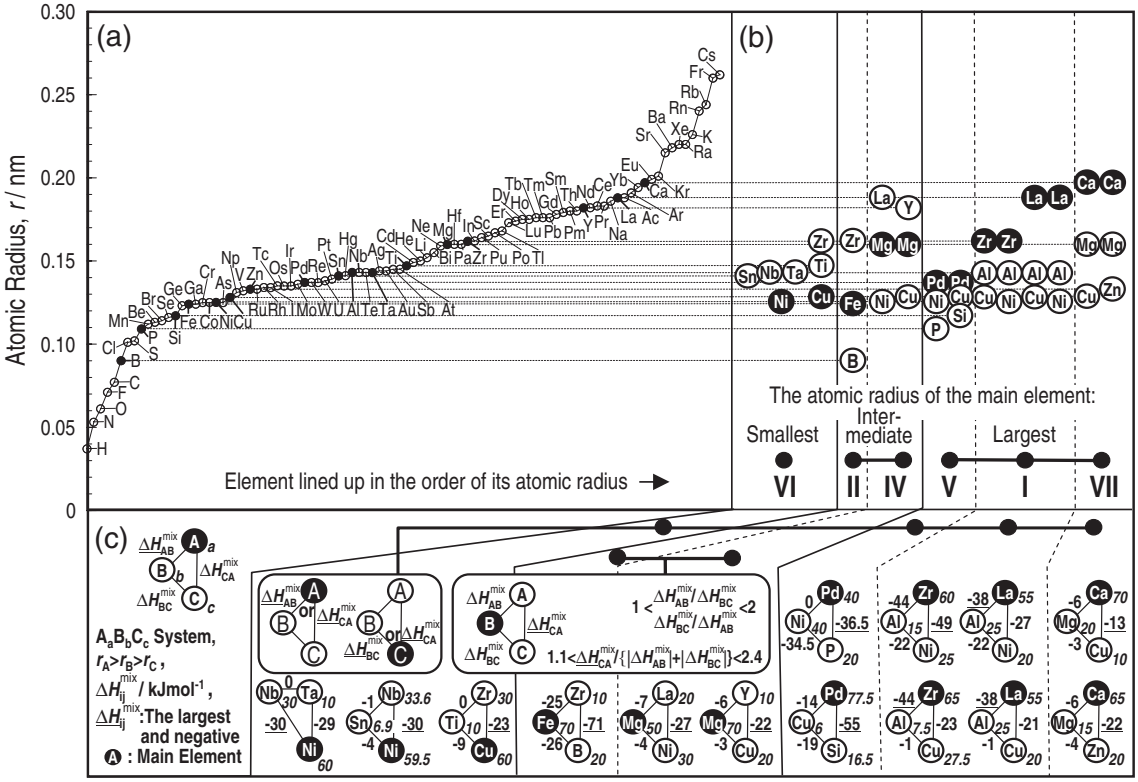



Fig. 5 The relationships between the atomic size differences, $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$ of the constituent elements and main element of ternary BMGs. (a) The atomic radius of elements plotted in sequence of their atomic radii from smallest (H) to largest (Cs). (b) The relationship of the atomic size difference of the constituent elements of representative ternary BMGs for the seven groups. The main elements are drawn in solid circles in which the symbol of the element is written in white. (c) The relationships of the $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$ and typical composition for the ternary BMGs. The largest, negative values of $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$ are underlined and the composition of the system is written in italics.

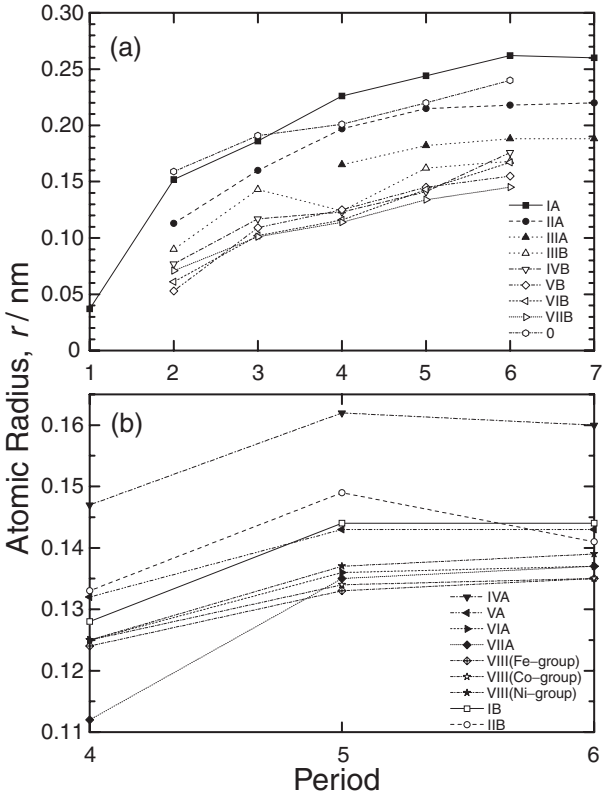



Fig. 6 Change in atomic radius as a function of the period in the periodic table. (a) IA to IIIA and IIIB to 0. (b) IVA to IIB. For the lanthanide (Ln) and actinide (Ac) metals, the atomic radii of La and Ac are plotted.

### 4.4 BMGs containing constituent elements in the same group in the periodic table

The BMGs placed in groups G-V to G-VII are characterized by having constituent elements that all fall into the same group in the periodic table. As a result, these BMGs are drawn as a line type in Fig. 3. The values of $\Delta H^{\mathrm{mix}}$ between atomic pairs are calculated to be 0 or nearly 0 kJ/mol for BMGs having their constituent elements in the same group in the periodic table. Examples are Nb–Ta, Ti–Zr and Ni–Pd atomic pairs (Fig. 5). Furthermore, the difference in atomic radii for elements within the same group in the periodic table is relatively small by comparison with elements from different groups. For instance, the atomic radii[16] of Ni, Nb and Ta are 0.125, 0.143 and 0.143 nm, respectively. Very little difference in atomic radius can be observed between Nb and Ta, although this system is BMG-forming. Thus, it is possible to conclude that the difference in the period is prior to the difference in atomic size in the case of BMGs consisting of elements in the same group of the periodic table.

### 4.5 Applicability of the characteristics of the main element of the BMGs in multicomponent systems

Within the seven groups of BMGs, G-III is considerably different from the other groups with respect to the number of necessary elements for BMG formation. For instance, the Fe–(Al,Ga)–(P,C,B) alloy system requires as many as six constituent elements to form as a BMG. Confirmation of

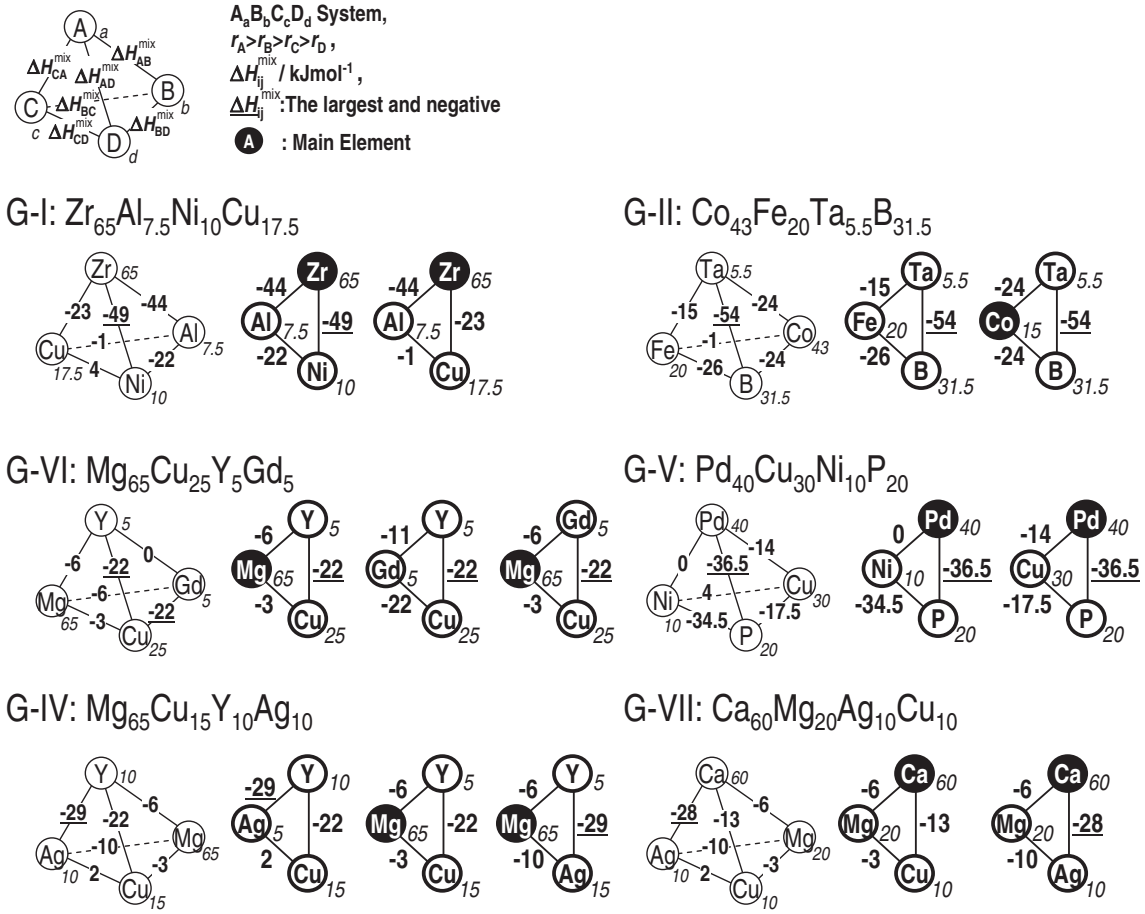



Fig. 7 The heat of mixing ($\Delta H^{\mathrm{mix}}_{\{AB\}}$) for atomic pairs of the quaternary BMGs belonging to G-I, G-II, G-VI, G-V and G-VII. The values of $\Delta H^{\mathrm{mix}}_{\{AB\}}$ (kJ/mol) are written with normal text. The value of $\Delta H^{\mathrm{mix}}_{\{AB\}}$ with the largest, negative value for each BMG is underlined. The main elements are marked with solid circles in white letters, and the compositions of the system are written in italics. In each alloy system, quasi-ternary systems are selected from all of the possible systems for the alloy, provided that the selected quasi-ternary system belongs to the group of BMGs from G-I to G-VII. The locations of the elements in the tetrahedron depend on the atomic radius ($r$) of the constituent elements.

the adoptability of the characteristics of the main element of BMGs as derived in Section 3 to multicomponent systems is required since typical BMGs are mostly based on quaternary systems.

Figure 7 shows $\Delta H^{\mathrm{mix}}$ for different atomic pairs for quaternary BMGs belonging to G-I ($Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$[30]), G-II ($Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$[31]), G-IV ($Mg_{65}Cu_{25}Y_5Gd_5$[32] and $Mg_{65}Cu_{15}Y_{10}Ag_{10}$[33]), G-V ($Pd_{40}Cu_{30}Ni_{10}P_{20}$[10]) and G-VII ($Ca_{60}Mg_{20}Ag_{10}Cu_{10}$[19]). The values of $\Delta H^{\mathrm{mix}}$ are drawn in a tetrahedron for each BMG together with the quasi-ternary systems, selected by taking three elements from the four, under the condition that the selected quasi-ternary systems belong to G-I to G-VII. For example, Zr–Al–Ni and Zr–Al–Cu quasi-ternary systems would be selected from Zr–Al–Ni, Zr–Ni–Cu, Zr–Al–Cu and Al–Cu–Ni if the Zr–Al–Ni–Cu quaternary system was to be considered. The Zr–Ni–Cu and Al–Cu–Ni quasi-ternary systems were excluded since these quasi-ternary systems do not belong to G-I to G-VII. In the same way, one can select quasi-ternary systems for the other quaternary BMGs. Here, it is noted that $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is found in the atomic pair of the selected quasi-ternary systems, and the characteristics of the main element analyzed for the ternary BMGs can be applied to these quaternary BMGs belonging to G-I, G-II, G-IV, G-V and G-VII. Moreover, the multicomponent BMGs in these groups with five or more constituent elements show the same characteristics for the main element.

In contrast, BMGs belonging to G-III, G-IV and G-VI have another tendency for the characteristic of the main element. Figure 8 shows the relationships of $\Delta H^{\mathrm{mix}}$'s between the atomic pairs for the multicomponent BMGs belonging to G-III ($Fe_{72}Al_5Ga_2P_{11}C_6B_4$[8]), G-IV ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$[7] and $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$[23]) and G-VI ($Ti_{50}Ni_{20}Cu_{25}Sn_5$,[25] $Ti_{34}Zr_{11}Cu_{47}Ni_8$[34] and $Ti_{52}Cu_{23}Ni_{11}Mo_7Fe_7$[24]). In each alloy system, quasi-ternary systems are selected in the same way as is described in Fig. 7. In Fig. 8, one can recognize the same tendency as is shown in Fig. 7, namely, that $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is also found in the atomic pair of the selected quasi-ternary systems for these BMGs. It is proposed an assumption that the main element of multicomponent BMGs has a larger atomic radius in the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$. This assumption is applied to determine the characteristics of the main element for BMGs belonging to G-III ($Fe_{72}Al_5Ga_2P_{11}C_6B_4$) due to the absence of fundamental ternary BMGs in this group. Permitting the assumption, one can detect Fe as the main element due to the facts that $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$

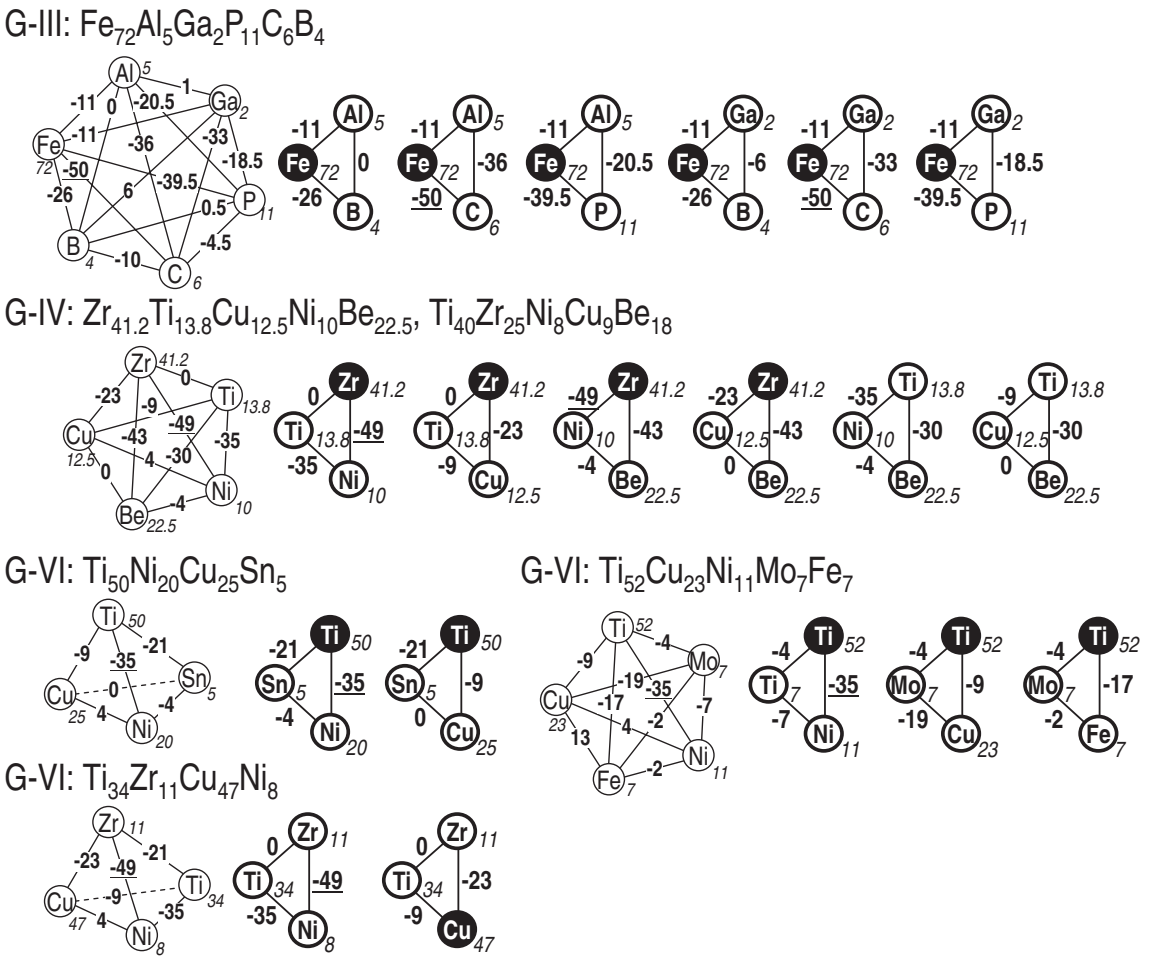



Fig. 8 The heat of mixing ($\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$) between the atomic pairs of the multicomponent BMGs belonging to G-III, G-IV, G-VI and G-VI. The symbols have the same meaning to those in Fig. 7. For the Zr–Ti–Cu–Ni–Be system in G-IV, $Zr_{46.5}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ is selected as the representative composition for showing the values of $\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$. The locations of the elements in the polyhedron depend on the atomic radius of the constituent elements.

is found in the Fe–C atomic pair and that the atomic radius of Fe is larger than C. Thus, the assumption mentioned above holds for the $Fe_{72}Al_5Ga_2P_{11}C_6B_4$ BMG.

The characteristics of the main element of multicomponent BMGs obtained under the assumption are applicable to the Ti–Ni–Cu–Sn and Ti–Cu–Ni–Mo–Fe systems belonging to G-VI. For instance, the largest element in these systems is Ti, which is the main element, and $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is found in the Ti–Ni atomic pair in both the Ti–Ni–Cu–Sn and Ti–Ni systems. From these results, one can identify Ti as the main element with respect to the atomic radius of the main element for Ti–Ni–Cu–Sn and Ti–Cu–Ni–Mo–Fe, coinciding with the experimental results. Attention should be paid to the fact that the main element of BMGs belonging to G-VI in a ternary system is the element with the smallest atomic radius. Thus, the main element of BMGs belonging to G-VI shifts from the smallest to the largest one due to this multicomponent alloying effect. It is widely accepted that the glass-forming ability of BMGs is enhanced by multicomponent alloying. Thus, this shift with respect to the size of the main element is due to the changes in the local atomic arrangement of BMGs. In other words, it can be interpreted to mean that the local atomic arrangement of BMGs belonging to G-VI become stable with increasing atomic radius of the main element.

Aside from G-VI BMGs, the main element of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG also exhibits the characteristics of the main element of multicomponent BMGs such that $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is found in the Zr–Ni atomic pair and the atomic radius of Zr is larger than Ni. However, it has recently been reported that $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$,[23] which has a different composition to $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, also forms a BMG, although both systems are in the same group of BMGs. The existence of a Ti-based Ti–Zr–Ni–Cu–Be BMG is at variance with the characteristics of the main element of multicomponent BMGs. However, the variance can be interpreted as the co-existence of BMG composition regions in a multicomponent system, which is found in the Ti–Zr–Cu–Ni system.[34] It is reported[34] that the Ti–Zr–Cu–Ni system has two BMG composition regions on the Ti- and Zr-rich sides owing to the near interchangeability between Ni and Cu. Interchangeability between Ni and Cu can take place in both Zr- and Ti-based BMGs since the Zr–Ti–Cu–Ni–Be system also has Ni and Cu. Thus, the characteristics of the main element for multicomponent BMGs are modified as follows: first, the main element of the BMGs was determined

by finding $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ and the larger element in terms of the atomic radius in an atomic pair, and then this element was extended to the same group of elements in the periodic table.

Finally, we focus on the Ti–Zr–Cu–Ni BMGs. According to the modified characteristics of the elements in a multicomponent systems, Zr is determined to be the main element, and then it is extended to Ti due to the interchangeability of Ni and Cu. However, the main element of the $Ti_{34}Zr_{11}Cu_{47}Ni_8$ BMG[34] is Cu, which has the second smallest atomic radius in the system. This result is at variance with all of the characteristics of multicomponent BMGs described in this section. However, the main element of this system can be regarded as having the smallest radius for the following reasons: (1) near equal atomic radii of Ni and Cu (Ni: 0.125 nm, Cu: 0.128 nm), (2) interchangeability[34] between Ni and Cu, and (3) the composition ratio between LTM(Cu,Ni) and ETM(Ti,Zr) of 55:45, implying that $Ti_{34}Zr_{11}Cu_{47}Ni_8$ BMG can be regarded as an LTM-based BMG. In addition to these reasons, it also should be noted that the Ti–Zr–Cu–Ni system has two BMG composition regions on the Zr- and Ti-rich side. It is reported[34] that the $Ti_{34}Zr_{11}Cu_{47}Ni_8$ BMG belongs to the Ti-rich side. Therefore, it is expected that further multicomponent alloying in this quaternary system will lead to the formation of Zr-based BMGs.

The main element of BMGs in G-VI can shift through the following three stages with increasing GFA of the systems: (1) LTM(Cu,Ni), (2) co-existence of LTM(Cu,Ni) and ETM(Ti,Zr), and (3) ETM(Ti,Zr), where the atomic radius of the element in the group of elements is generally described as $r_{\mathrm{ETM}} > r_{\mathrm{LTM}}$, as shown in Fig. 1. For the BMGs belonging to G-VI discovered to date, it is interpreted that the ternary Cu–Zr–Ti, quaternary $Ti_{34}Zr_{11}Cu_{47}Ni_8$, and quiternary $Ti_{52}Cu_{23}Ni_{11}Mo_7Fe_7$ BMGs are in the first, second and third stage, respectively.

### 4.6 Exchangeability of constituent elements in BMGs

As a result of the analysis of the main element of BMGs, it is found that multicomponent BMGs belonging to G-VI have a probability of having two or more main elements. A typical example is the $Ti_{34}Zr_{11}Cu_{47}Ni_8$ BMG[34] with BMG-forming composition ranges on both the Ti- and Zr-rich sides of the system, owing to approximate interchangeability between Ni and Cu.[34] It is assumed that either the interchangeability or some similar mechanism affects the composition of BMGs between elements in the same group in the periodic table. Under such an assumption, the atomic pairs of (Ni,Cu), (Ti,Zr), (Ni,Pd), etc. can change the composition in the BMGs. These sets of elements have a common characteristic in that they exhibit complete solid solubility at high temperatures according to their binary phase diagrams,[35] and are constituent elements in BMGs belonging to G-V and G-VI. It is possible to explain from these results the reason for $Pd_{40}Ni_{40}P_{20}$ BMG having the same composition between Pd and Ni as main elements.

### 4.7 Significance of the classification of BMGs

It is possible to obtain information about the main element and the composition of the alloy system required for formation of a BMG as a result of the characteristics determined for the ternary BMGs shown in Fig. 5 and their extension to multicomponent BMGs described in Section 4–5. The information enables a decrease in the tasks required for the development of BMGs to 25% for ternary systems when considering the Gibbs triangle for alloy compositions. The classification system for BMGs developed in the present study is of great importance to further development of BMGs since currently it is not possible to predict the optimal composition for BMG formation. In particular, the characteristics of the main element in multicomponent BMGs, as discussed in 4–5, can be used for the selection of additional elements in the case of multicomponent alloying.

## 5. Conclusions

On the basis of previous results by Inoue in 2000, bulk metallic glasses (BMGs) discovered to date are classified according to atomic size differences, heat of mixing ($\Delta H^{\mathrm{mix}}_{\{\mathrm{AB}\}}$) of A–B atomic pairs and period of the constituent elements. The main results obtained from the present study are as follows.

(1) It has been found that BMGs can be classified into seven groups (G-I to G-VII) represented by G-I: ETM/Ln-LTM/BM-Al/Ga, G-II: ETM/Ln-LTM/BM-Metalloid, G-III: Al/Ga-LTM/BM-Metalloid, G-IV: IIA-ETM/Ln-LTM/BM, G-V: LTM/BM-Metalloid, G-VI: ETM/Ln-LTM/BM, and G-VII: IIA-LTM/BM.

(2) The main alloying element in ternary G-I, G-V and G-VII, ternary G-II and G-IV, and ternary G-VI BMGs is the greatest, intermediate and smallest atomic radius among the other alloying elements, respectively. The main alloying element of ternary BMGs belonging to G-I, G-V, G-VI and G-VII is an element in the atomic pair with the largest negative value of $\Delta H^{\mathrm{mix}}$ ($\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$), while the main element of ternary BMGs belonging to G-II and G-IV is independent of the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$. The absolute value of $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is greater than that of the sum of the absolute values of $\Delta H^{\mathrm{mix}}$ for the other atomic pairs by a factor of 1.1 to 2.4, and the ratio of the $\Delta H^{\mathrm{mix}}$'s for the atomic pairs other than atomic pairs with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ is in the range of 1 to 2. In contrast, the main element is independent of the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ for BMGs belonging to G-I, G-V and G-VII.

(3) The characteristics of the main element derived for ternary BMGs are directly applicable to multicomponent BMGs belonging to G-I, G-II, G-IV (Mg-based BMGs), G-V and G-VII. For multicomponent BMGs belonging to G-III, G-IV (Be-containing Zr-based BMG) and G-VI, the main element can be the larger-sized element in the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ or an element in the same group with the element in the periodic table.

(4) In addition to differences in chemical species, (1) atomic size differences that accompany different periods in the periodic table and (2) differences in the periods of the constituent elements in the periodic table can also both be important for the formation of BMGs. The elements of Pd and Ni in Pd–Ni–P (G-VI) BMG are a typical example of the first case while Nb and Ta in Ni–Nb–Ta (G-VI) BMG are a typical example of the second case.

(5) BMGs belonging to G-VI change the characteristics of the main element with respect to its atomic radius and with increasing glass-forming ability due to multicomponent alloying. The main element changes from the smallest size for ternary BMGs to a larger atomic size in the atomic pair with $\underline{\Delta H}^{\mathrm{mix}}_{\mathrm{L.N.}}$ in multicomponent systems. This change occurs due to the interchangeability between elements in the same group in the periodic table.

(6) The classification system developed in the present study is important for further development of BMGs, as it helps predict the alloy systems that lead to formation of BMGs and appropriate composition of BMGs by also designating the main component of the system.

## Acknowledgements

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