Diverse densest ternary sphere packings

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Abstract

The exploration of the densest structures of multi-sized hard spheres under periodic boundary conditions is a fundamental problem in mathematics and a wide variety of sciences including materials science. We present our exhaustive computational exploration of the densest ternary sphere packings (DTSPs) for 451 radius ratios and 436 compositions on top of our previous study [Koshoji and Ozaki, Phys. Rev. E 104, 024 101 (2021)]. The unbiased exploration by a random structure searching method discovers diverse 22 putative DTSPs, and thereby 60 putative DTSPs are identified in total including the 38 DTSPs discussed by the previous study. Some of the discovered DTSPs are well-ordered, for example, the medium spheres in the (9-7-3) structure are placed in a straight line with comprising the unit cell, and the DTSP has the $P\overline{1}m3m$ symmetry if the structural distortion is corrected. At a considerable number of radius ratios, the highest packing fractions are achieved by the phase separations consisting of only the FCC and/or the putative densest binary sphere packings (DBSPs) for all compositions. The trend is becoming more evident as the small and medium spheres are getting larger, which suggests either the binary packings are actually the densest packings or that the dense ternary packings have unit cells larger than those in this study. On the other hand, the number of the DTSPs increase as the particle size of small spheres gets small. The structural diversity indicates that many unknown DTSPs may hide in a very narrow range of radius ratio where the size of small spheres is smaller due to the competition with respect to the packing fractions of many structural candidates. Finally, we discuss the correspondence of the DTSPs with real crystals based on the space group. Our study suggests that the diverse structures of DTSPs can be effectively used as structural prototypes for searching ternary, quaternary, and quinary crystal structures.

1. Introduction

The longstanding effort to the analytic identification of the densest unary sphere packing (DUSP) has been fulfilled in the 2000s despite the simpleness of the problem [1]. Likewise, analytic identification of the densest binary sphere packings (DBSPs) is also too difficult to prove, however, the development of computers has been enabling us to explore the DBSPs by computer simulations [2–10]. As a result, a total of 28 putative DBSPs are known at the present time [11].

If we only explore the periodic dense packings of spheres of $n$ different sizes by computer, the packing fraction at given sphere-composition ratio is maximized by filling the space with not more than $n$ kinds of periodic packings [9–11]. The necessity of the phase separation can be understood from a simple example: At a given composition, the periodic boundary condition limits the maximum packing fraction, and in many cases, it is less than the packing fraction of the FCC packing. In this case, the space-filling with the single periodic packing is sparser than the phase separation to the $n$ kinds of FCC packings. Furthermore, if we know a denser multinary sphere packing of any composition than the FCC packing, the phase separations including the multinary packing have higher packing fractions than that consisting of only $n$ kinds of FCC packings. The examples indicate that we must consider all possible mixtures of packings when identifying the densest multinary packings.
at a given composition and size ratio. In this context, we must construct the phase diagrams which show the densest phase separation at each radius and composition ratio.

However, previous studies on the dense ternary sphere packings [12–16] do not construct the phase diagrams. Note that the DBSPs are the candidates for the phase separation as well as the FCC packings of small, medium, and large spheres, so we have to know the precise packing fractions of the DBSPs to construct the phase diagrams of the densest ternary sphere packings (DTSPs). Accordingly, following the seminal studies which

Table 1. The number of generated structures for exploring DTSPs at each composition.

| Range of $N$ | Number of generated structures |
|--------------|--------------------------------|
| $3 \leq N \leq 5$ | 200,000 |
| $6 \leq N \leq 7$ | 700,000 |
| $8 \leq N \leq 10$ | 2,000,000 |
| $11 \leq N \leq 15$ | 10,000,000 |
| $16 \leq N \leq 20$ | 20,000,000 |
| $21 \leq N \leq 25$ | 40,000,000 |
| $26 \leq N \leq 30$ | 60,000,000 |
had constructed the phase diagram for binary system [9–11], we constructed the phase diagram for ternary systems at 45 kinds of radius ratios so as to find the DTSPs [17]. As a result, we successfully discovered the 37 putative DTSPs. The well-ordered DTSPs as exemplified in figure 1 tend to appear on the phase diagrams where the radius ratios of small and medium spheres are relatively large.

The well-ordered DTSPs may lead to promising structural prototypes for exploring materials under high pressure. In fact, the previous study [11] showed that many crystals can be understood as DBSPs. For example, the clathrate crystal of the LaH$_{10}$, which is one of the superhydrides synthesized under high pressure,
corresponds to the XY$_{10}$ structure that is one of the DBSPs. The hydrogen sublattice of the LaH$_{10}$ is responsible for high-temperature superconductivity [19–21], and the structural property can also be realized by some of the DTSPs such as the (13-2-1) structure [17] with replacing small spheres with hydrogen atoms. Although the previous study [17] reported that the correspondence of the DTSPs with crystals seems to be exceptional, we expect that the unique structural prototypes, which is difficult to design based on the perspectives of chemical bonds and/or local polyhedrons as found in coordination structures to transition elements, may enable materials to have functional properties under high pressure.

As shown in the previous studies [9–11], some of the DBSPs such as the (7-3) structure become the densest in very narrow radius ratios, and this is because several packings are competitive to each other with respect to packing fractions at every radius ratio. This complexity of the binary phase diagram indicates that some of the

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**Table 4.** The (4-3-1) structure [17] has the $P6_3/mmc$ symmetry if the structural distortion is corrected. Medium spheres constitute the kagome lattice, as shown in figure 1(c). This structure appears on the phase diagrams at the 22 radius ratios.

| Radius ratio | Radius ratio | Radius ratio |
|--------------|--------------|--------------|
| 0.29: 0.42: 1.00 | 0.29: 0.43: 1.00 | 0.29: 0.44: 1.00 |
| 0.29: 0.45: 1.00 | 0.29: 0.46: 1.00 | 0.29: 0.47: 1.00 |
| 0.29: 0.48: 1.00 | 0.29: 0.49: 1.00 | 0.29: 0.50: 1.00 |
| 0.30: 0.43: 1.00 | 0.30: 0.44: 1.00 | 0.30: 0.45: 1.00 |
| 0.30: 0.46: 1.00 | 0.30: 0.47: 1.00 | 0.30: 0.48: 1.00 |
| 0.30: 0.49: 1.00 | 0.30: 0.50: 1.00 | 0.31: 0.47: 1.00 |
| 0.31: 0.48: 1.00 | 0.31: 0.49: 1.00 | 0.31: 0.50: 1.00 |
| 0.31: 0.51: 1.00 |               |              |
unknown DTSPs are also the densest in very narrow radius ratios. Therefore, it is necessary to explore the DTSPs more precisely with respect to the radius ratios than the previous study [17] so that we can know the full picture of the ternary phase diagram uncovering unknown DTSPs.

In this study, to show the full picture of the ternary phase diagram with discovering unknown DTSPs following the previous study [17], we have additionally explored the DTSPs at 451 kinds of radius ratios and 436 kinds of compositions. The maximum number of spheres per unit cell is set to be 25 for most radius ratios, where the number is larger than that in the previous study [17]. As a result, we have additionally found 22 putative DTSPs including six structures identified as Semi-DTSPs (SDTSPs) in [17] and the (8-6-2)$_2$ structure that is the long-period structure of the (4-3-1) structure [17]. Since the minimum radius ratio of small spheres is set to be larger than in the previous study [17], the discovered DTSPs are well-ordered; for example, the (9-7-3)

![Figure 4. The phase diagrams at the radius ratios of 0.29: 0.45: 1.00 (a) and 0.29: 0.46: 1.00 (b) show that the (10-2-1)$_2$ structure (c) is the DTSP, and the packing fractions at the two radius ratios are 0.789 643 and 0.790 202, respectively. The (4-2-2)$_1$ structure plotted on the phase diagram (b) has the packing fraction of 0.773 744, and the structure is shown in figure 11(d). The (2-2-2)$_1$, (4-3-1), and (4-4-2) structures plotted on the phase diagrams are also the DTSPs shown in figures 1(a), 1(c), and 1(d), respectively.](image-url)
Figure 5. The phase diagram at the radius ratio of 0.29: 0.48: 1.00 (a) shows that the (6-6-4) structure (b) is the DTSP, and the packing fraction is 0.765610. If the structural distortion is corrected, this structure has the $I\bar{4}m$ symmetry. The (4-3-1) structure plotted on the phase diagram is the DTSP shown in figure 1(c).

Table 5. The (4-4-2) structure [17], which can be directly derived from the HgBr$_2$ structure as shown in figure 1(d), has the $Cmcm$ symmetry if the structural distortion is corrected. This structure appears on the phase diagram at the 16 radius ratios.

| Radius ratio | Radius ratio | Radius ratio |
|--------------|--------------|--------------|
| 0.29: 0.42: 1.00 | 0.29: 0.43: 1.00 | 0.29: 0.44: 1.00 |
| 0.29: 0.45: 1.00 | 0.29: 0.46: 1.00 | 0.29: 0.47: 1.00 |
| 0.30: 0.42: 1.00 | 0.30: 0.43: 1.00 | 0.30: 0.44: 1.00 |
| 0.30: 0.45: 1.00 | 0.30: 0.46: 1.00 | 0.30: 0.47: 1.00 |
| 0.31: 0.43: 1.00 | 0.31: 0.44: 1.00 | 0.31: 0.45: 1.00 |
| 0.31: 0.47: 1.00 |   |   |

Table 6. The unit cell of the (10-6-3) structure [17] are comprised of medium spheres as shown in 1(f). The (10-6-3) structure has the $Pm\bar{3}m$ symmetry if the structural distortion is corrected. This structure appears on the phase diagrams at the seven radius ratios.

| Radius ratio | Radius ratio | Radius ratio |
|--------------|--------------|--------------|
| 0.33: 0.52: 1.00 | 0.34: 0.50: 1.00 | 0.34: 0.51: 1.00 |
| 0.35: 0.49: 1.00 | 0.35: 0.50: 1.00 | 0.35: 0.51: 1.00 |
| 0.36: 0.49: 1.00 |   |   |
structure is comprised of the cubic unit cell constituted by medium spheres, and the DTSP has the \( \text{Pm}\bar{3}m \) symmetry if the structural distortion is corrected. In addition, our results show that at a considerable number of radius ratios, the highest packing fraction at each composition is achieved by the phase separations consisting of only the FCC and/or the DBSPs, and the trend is becoming more evident as the small and medium spheres are getting larger. On the other hand, in the case that \( \alpha_1 = 0.29 \), we find nine DTSPs; the discovery indicates that the phase diagrams around the area of 0.29 as the smallest radius are complex, which indicates that unknown DTSPs may hide in a very narrow range of radius ratio where the size of small spheres is smaller due to the competition with respect to the packing fractions of many structural candidates.

The paper is organized as follows: section 2 describes the conditions for the exhaustive exploration of the DTSPs; section 3 presents the discovered DTSPs with phase diagrams and discusses the results. In section 4, we summarize this study.

### 2. Computational methods and conditions

In this section, we summarize the method to explore the DTSPs and describe the exploration areas including radius ratios and compositions.

#### 2.1. Exploration method

Our previous study [11, 17] showed that the algorithm, which is based on the piling-up and iterative-balance methods, is effective enough to search the densest sphere packings (DSPs). The piling-up method is an approach to randomly generate initial structures for exploring DSPs. The random approach, which directly generates multilayered structures with modest overlaps, enables us to find a wide variety of packings due to the unbiased distribution of initial structures in the configuration space. The iterative balance method optimizes initial
Figure 7. The phase diagram at the radius ratio of 0.29: 0.51: 1.00 (a) shows that the (6-2-2) structure is the DTSP, and the packing fraction is 0.781 880. This structure has already been discussed in the previous study [17] as SDTSP. The (8-6-2) structure plotted on the phase diagram (a) has the packing fraction of 0.780 879, and the structure is shown in figure 12 (b). The (2-2-2) structure plotted on the phase diagram is also the DTSP shown in figures 1 (b).

Table 7. The (13-2-1) structure, which is shown in figure 1 (g), has the Fm3m symmetry if the structural distortion is corrected. The structure appears on the phase diagram at the eight radius ratios listed in table 7. Note that for 0.40 ≤ α₁ ≤ 0.64, we choose only 13 values of 0.40, 0.42, ..., 0.64, and let α₂ be chosen only from 18 values from 0.50, 0.52, ..., 0.74, as discussed in section 2.2.2.

| Radius ratio | Radius ratio | Radius ratio |
|--------------|--------------|--------------|
| 0.42: 0.62: 1.00 | 0.42: 0.64: 1.00 | 0.44: 0.62: 1.00 |
| 0.44: 0.64: 1.00 | 0.44: 0.66: 1.00 | 0.46: 0.60: 1.00 |
| 0.46: 0.62: 1.00 | 0.46: 0.64: 1.00 |               |

Table 8. The (13-3-1) structure, which is shown in figure 1 (h), has the Pm3m symmetry if the structural distortion is corrected. This structure appears on the phase diagram at the nine radius ratios.

| Radius ratio | Radius ratio | Radius ratio |
|--------------|--------------|--------------|
| 0.29: 0.41: 1.00 | 0.29: 0.42: 1.00 | 0.29: 0.43: 1.00 |
| 0.30: 0.40: 1.00 | 0.30: 0.41: 1.00 | 0.30: 0.42: 1.00 |
| 0.30: 0.43: 1.00 | 0.31: 0.41: 1.00 | 0.31: 0.42: 1.00 |
structures to dense packing structures by minimizing the volume of unit cells and the overlaps between spheres simultaneously by the steepest descent method under pressure with the hard-sphere potential. The method can find the most optimal structural distortion for high density since the pressure makes as many distances between spheres as possible converge to zero. Although a large number of optimization steps is necessary to find the local highest packing fractions accurately, the computational cost is low because of the efficiency of each step. Before the fine iterative balance optimization, we apply the pseudoannealing to optimize initial structures to packing structures with overlap. Besides, to reduce the computational cost, coarse iterative balance optimization is applied to reject sparse structures based on the rough estimation of the packing fraction. In this study, we apply the algorithm to the detailed exploration of the DTSPs, where all parameters of the exhaustive exploration and reoptimization for DTSPs are set to the default values given in [17].

Figure 8. The phase diagrams at the radius ratios of 0.29: 0.63: 1.00 (a) and 0.29: 0.64: 1.00 (b) show that the (4-2-2)_2 structure (c) is the DTSP, and the packing fractions at the two radius ratios are 0.764 640 and 0.762 837, respectively. This structure has already been discussed in the previous study [17] as SDTSP.
2.2. Exploration conditions.
We have exhaustively explored DTSPs at 451 kinds of radius ratios and 436 kinds of compositions. In this subsection, we detail the conditions.

2.2.1. Radius ratios
We write $\alpha_1$ and $\alpha_2$ as the radii of small and medium spheres, respectively, where we fix the radius of large spheres to be 1.0. For $\alpha_1$ and $\alpha_2$, we impose a restriction as

$$\alpha_1 + 0.1 \leq \alpha_2.$$  \hfill (1)

The radius ratios at which we explore the DTSPs are given below:

- For $0.29 \leq \alpha_1 \leq 0.38$, we choose ten values of 0.29, 0.30, \ldots, 0.38 for $\alpha_1$. Letting $\alpha_2$ be chosen from 36 values from 0.39, 0.40, \ldots, 0.74 under the constraint to $\alpha_1$ and $\alpha_2$ given in equation (1), the total number of radius ratios is 315.

- For $0.40 \leq \alpha_1 \leq 0.64$, we choose 13 values of 0.40, 0.42, \ldots, 0.64 for $\alpha_1$. Letting $\alpha_2$ be chosen from 18 values from 0.50, 0.52, \ldots, 0.74 under the constraint to $\alpha_1$ and $\alpha_2$ given in equation (1), the total number of radius ratios is 91.

- For $0.66 \leq \alpha_1 \leq 0.82$, we choose nine values of 0.66, 0.68, \ldots, 0.82 for $\alpha_1$. Letting $\alpha_2$ be chosen from nine values from 0.76, 0.78, \ldots, 0.92 under the constraint to $\alpha_1$ and $\alpha_2$ given in equation (1), the total number of radius ratios is 45.

Note that the condition by equation (1) is introduced to avoid DBSPs-type structures as the DTSPs, which will appear when two radius ratios are close. This is not a substantial discovery of DTSPs. The reason why the smallest radius is set to 0.29 is that we noticed that the phase diagrams are very complicated in the area where the
smallest radius is less than 0.29, and where it were not certain that our computational explorations searched the DTSPs properly. Thus, we restricted our searches the area where smallest radius is not less than 0.29.

2.2.2. Compositions
We write \( n_1, n_2, \) and \( n_3 \) as the numbers of small, medium, and large spheres per unit cell, respectively; the total number of spheres per unit cell is denoted by \( N \). We explore the DTSPs for all compositions which satisfy the three constraints shown below:

\[
3 \leq N \leq 25, \\
n_3 \leq n_2 \leq n_1, \\
n_1 \leq 5(n_2 + n_3).
\]
The number of compositions which satisfy equations (2), (3), and (4) is 436. Note that the constraint equation (4) excludes compositions that include too many small spheres; in case that the radius ratios of small spheres is large as 0.40 or 0.50, we can guess that the number of small spheres per unit cell is not be too large as the DBSPs [10, 11]. The exceptional cases are given below:

- For \( 0.40 \leq \alpha_1 \leq 0.64 \), \( N \) is set to be from 3 to 30. In this case, the number of compositions becomes 743.
- For \( \alpha_1 = 0.29 \), \( N \) is set to be from 3 to 20. In this case, the number of compositions becomes 227.

The number of generated structures at each composition in creating initial structures is given in Table 1. Note that the discovered DTSPs are named as \((n_1-n_2-n_3)\) structure. When the two DTSPs have the same composition, we distinguish them by an index \( p \) as \((n_1-n_2-n_3)_p\).

2.2.3. Phase separation

We denote the composition ratios of small, medium, and large spheres as \(x_1, x_2, x_3\), respectively, which are defined as

\[
x_j = \frac{n_j}{N},
\]

As discussed in previous studies [10, 11], for a given composition ratio \((x_1, x_2, x_3)\) of three kinds of spheres, the densest packing fraction can be achieved by the phase separation which consists of less than or equal to three structures when every candidate structure is periodic. Therefore, we must consider all possible mixtures of packings when identifying the DTSPs at a given composition and size ratio. In this context, we must construct the phase diagrams which show the densest phase separation at each radius and composition ratio. Note that we must know the accurate packing fractions of DBSPs at each radius ratio. For ease of visibility, only the 779 composition ratios that fulfill the conditions:

\[
n_3 \leq n_1 + n_2, \quad 3 \leq N \leq 20,
\]

are plotted on the phase diagrams shown in this study.
3. Result and discussion

In this section, we discuss the discovered DTSPs, constructed phase diagrams, the geometric features of the DTSPs, and the correspondence between DTSPs and crystals.

3.1. DTSPs on phase diagrams

In our exhaustive search for the DTSPs, we find the 22 kinds of unknown DTSPs including the six structures identified as SDTSPs in [17], and the (8-6-2)$_L$ structure that is the long-period structure of the (4-3-1) structure shown in figure 1(c). The discovered DTSPs are shown in figures 2 to 21 with the corresponding phase diagrams and the captions describing the basic structural information such as packing fraction and spacegroup. In all the figures showing structures, the lines between spheres do not necessarily correspond to the contact between spheres. The spacegroup is determined by the code Spglib [22] with correcting the structural distortions in each DTSP. Three-dimensional data of the discovered DTSPs are available online [23]. Note that it is not apparent whether there is at least one DTSP in the densest phase separation at any radius and composition ratio, since the densest packing fraction may consist of only the FCC structures and/or DBSPs.

The discovered DTSPs tend to be well-ordered, for example, the (9-7-3) structure shown in figure 19(c) has the $Pm3m$ symmetry if the distortion is corrected. Four medium spheres are placed on the edge of the cubic unit cell, one large sphere is placed at the center of each surface of the unit cell, and nine small spheres are placed into the cubic cell, and one of them is placed at the center. This structural property is similar to that of the (9-6-3) and (10-6-3) structures [17] shown in figures 1(e) and 1(f). The difference between the (9-6-3) and (9-7-3) structures is whether or not one medium sphere is placed at the vertex of the unit cell, while in (10-6-3) structure, one small sphere is placed at the vertex of the unit cell. These three packings are related to the perovskite structure, and in this sense, they are similar to the (13-3-1) structure shown in figure 1(h). The small difference of the radius ratios makes a change that which DTSPs are the densest.
As the (9-7-3) structure, some of the discovered DTSPs are relevant to the other DBSPs and DTSPs, for example, the (6-6-4) structure shown in figure 5 is composed of the local structures in the (6-1) and (16-4) structures that are the two of the DBSPs [9–11]. In fact, small spheres constitute a chain structure that can be seen in the (6-1) structure, and medium spheres constituting an octahedron are placed in a distorted rectangular consisting of large spheres as in the (16-4) structure. These local structures can be seen in crystals; the (16-4) structure corresponds to the crystal of the UB4, and the (6-1) structure corresponds to the crystal of the YH6 under high pressure [24], as discussed in [11]. Therefore, we can expect that the (6-6-4) structure might be realized by materials under high pressure. The chain structure of small spheres can also be seen in the (10-3-2) and (6-2-2) structure shown in figures 6 and 7, respectively. Besides, the kagome lattice of medium spheres can be seen in the (10-3-2) structure as well as the (4-3-1) structure shown in figure 1(c), and honeycomb lattice can be seen in not only the (6-2-2) structure but also the AuTe2 structure that is one of the DBSP [3, 9, 10]. Finally, the difference between the (5-4-3) and (6-4-3) structures shown in figures 14 and 15 comes from the absence or existence of one small sphere between the two medium spheres in the cluster. The resemblance among DTSPs indicates that there are dense local structures as discussed in the binary case [11]. Whether or not local structures can comprise the DTSPs is equivalent to whether or not it is possible to combine the local structures with periodicity so that there are no unnecessary voids or distortions.

This study also shows that the well-ordered DTSPs which have already been discovered in the previous study [17] appears on the ternary phase diagrams at many radius ratios. Tables 2 to 8 show the radius ratios at which the seven of the nine DTSPs shown in figure 1 appear on the phase diagrams. In addition, the (9-6-3) and (16-2-2) structures shown in figures 1(e) and 1(i), respectively, appear on the phase diagram at the radius ratio of 0.30: 0.55: 1.00 and 0.35: 0.45: 1.00, respectively. Finally, the (2-1-1) structure [17], whose unit cell is half of that of the corrected (4-2-2), structure, appears on the phase diagrams at the two radius ratios of 0.48: 0.74: 1.00 and 0.50: 0.70: 1.00.

Figure 13. The phase diagram at the radius ratio of 0.31: 0.47: 1.00 (a) shows that the (10-4-2) structure (b) is the DTSP, and the packing fraction is 0.783 260. If the structural distortion is corrected, this structure has the Cmcm symmetry. The (2-2-2), (4-3-1), and (4-4-2) structures plotted on the phase diagram are the DTSPs shown in figures 1(a), (c), and (d), respectively.
3.2. Full pictures of the ternary phase diagrams

In this study, we have exhaustively explored the DTSPs at 451 kinds of radius ratios, however, at a considerable number of radius ratios, the highest packing fractions are achieved by the phase separations consisting of only the FCC and/or the DBSPs for all compositions; the DTSPs appear at only 76 kinds of radius ratios. The trend is becoming more evident as the small and medium spheres are getting larger, in fact, we find no DTSPs for the case of \( \alpha_1 = 0.66 \). It suggests that either the DBSPs are actually the densest packings or the dense ternary local structures are getting complex as the small and medium spheres are getting larger, since the DTSPs seems to be composed of the combination of dense local structures such that there are no unnecessary voids or distortions. Accordingly, we cannot exclude the possibility that the DTSPs have unit cells larger than \( N = 25 \).

On the other hand, in the case that \( \alpha_1 = 0.29 \), we find nine DTSPs, which indicates that the phase diagrams are complex where the smallest radius is near 0.29. In fact, as denoted in section 2.2.1, since it is difficult to

![Figure 14. The phase diagrams at the radius ratio of 0.33: 0.44: 1.00 (a) and 0.33: 0.45: 1.00 (b) show that the (6-4-3) structure (c) is the DTSP, and the packing fractions at the two radius ratios are 0.771 081 and 0.768 801, respectively. If the structural distortion is corrected, this structure has the \textit{Immm} symmetry. This structure also appears on the phase diagram at 0.34: 0.45: 1.00 as shown in figure 16(a).](image)
certainly identify the DTSPs in the complex areas, we exclude the case of 0.28 as the smallest radius, but we seemed to find some DTSPs when we executed a preliminary exploration at the area. In general, the phase diagrams seems to be getting complex as the radii of small and medium spheres are getting smaller, in fact, the previous study \[17\] showed that there are seven putative DTSPs at the radius ratios of 0.20: 0.45: 1.00. This is because as the radii of small and medium spheres decreases, it becomes easier to fit the smaller particles, singly or as clusters, into the voids left by the large sphere packing, which indicate an assumption that there are many competitive structures with respect to the packing fraction in this area. The competitions cause the complexity of phase diagrams; we can expect that there are unknown DTSPs that appear on the phase diagrams in a very narrow range of radius ratio as the \((7-3)\) structure \[9–11\]. For the radius ratios of \(\alpha < 0.30\), more detailed research with respect to the radius ratios is necessary to get full pictures of the ternary phase diagrams in this area.

**Figure 15.** The phase diagram at the radius ratio of 0.34: 0.44: 1.00 (a) shows that the \((5-4-3)\) structure (b) and the \((7-2-1)\) structure (c) are the DTSPs. The packing fractions of these two DTSPs are 0.768 812 and 0.769 884, respectively. The \((5-4-3)\) structure, which has already been discussed in the previous study \[17\] as SDTSP, has the Imm2 symmetry if the slight distortion is corrected. Besides, if the structural distortion of the \((7-2-1)\) structure is corrected, it has the Amm2 symmetry.
3.3. Geometric features of discovered DTSPs

We analyze the structural properties, and accordingly, we classify the DTSPs by how the structural framework is constituted.

The structural framework of the (9-7-3) structure is composed of medium spheres as the cubic unit cell of the (9-7-3) structure is constituted by only seven medium spheres, as shown in figure 19(c). The (9-6-3) and (10-6-3) structures shown in figures 1(e) and 1(f) have the same structural features. One large sphere is placed at the center of each surface of the unit cell, and the large spheres constituting octahedrons enclose small spheres.

The structural frameworks of the (10-2-1), (10-2-1), (10-2-2) structures shown in figures 3(b), 4(c), and 20(b), respectively are constituted by clathrates of small and medium spheres that enclose one large sphere. The (7-2-1), (8-6-2), (8-6-2), and (10-4-2) structures, shown in figures 15(c), 2(b), 18(b), and 13(b), respectively, have the same structural features with the (13-3-1) and (16-2-2) structures which have already been discovered in [17], shown in figures 1(h) and 1(i).

For some DTSPs, structural frameworks are comprised of small spheres. In the (13-2-1) structure shown in figure 1(g), one large sphere is surrounded by 24 small spheres consisting of the truncated octahedron, where large spheres constitute the FCC structure without contact. Besides, one medium sphere in a tetrahedral site is also surrounded by 12 small spheres consisting of the truncated tetrahedron, and additionally, one small sphere in an octahedral site is surrounded by 12 small spheres consisting of the cuboctahedron. Since the radii of small and medium spheres are too large as listed in table 7 to be placed in tetrahedral and octahedral sites, the structural framework can be regarded as one of the unique small-sphere frameworks.

As the radii of small and medium spheres are getting small, structural frameworks tend to be constituted by large spheres; small and medium spheres are placed in voids among large spheres. For example, in the XYZ structure, which had already been discovered in [17], large spheres constitute the FCC structures with contact,
and small and medium spheres are placed in the tetrahedral and octahedral sites. The \((2-2-2)_1\) and \((2-2-2)_2\) structures shown in figures 1(a) and 1(b) are also composed of large-sphere frameworks; small and medium spheres are placed in the polyhedrons that are composed of large spheres. Besides, in the \((5-4-3)_1\) and \((6-4-3)_1\) structures shown in figures 15(b) and 14(c), respectively, clusters consisting of small and medium spheres are placed in voids among large spheres. However, some DTSPs might be better not to be classified as those. For example, in the \((4-2-2)_1\), \((4-2-2)_2\), \((4-2-2)_3\), \((4-2-2)_4\), \((6-3-2)_1\) and \((16-3-2)_1\) structures shown in figures 11(d), 8(c), 9(b), 10(c), 16(b), and 17(b), respectively, small and medium spheres are placed in voids comprised by large spheres, but simultaneously they loosely enclose the large spheres, as it were to say structural frameworks are constituted by three kinds of spheres. Besides, some DTSPs can also be understood as the cluster-type DTSPs, for example, the \((13-3-1)_1\) structure shown in figures 1(h) contains clusters constituted by 13 small spheres. This structure can be derived from a perovskite structure; one site is occupied by the cluster. Furthermore, as discussed in [17], some of DTSPs such as the \((4-3-1)_1\) and \((4-4-2)_1\) structures shown in figures 1(c) and 1(d), respectively, can be derived from the DBSPs.

The random approaches can find any type of structure without \textit{a priori} knowledge, but they are difficult to explore the complex structures consisting of large unit cells. An improved methodology to generate more promising initial structures based on the structural properties of the DTSPs are essential to explore the DTSPs composed of large unit cells.

3.4. DTSPs and crystal structures

In recent years, many algorithms are developed to predict crystal structures [25–35]. Those methods have successfully predicted many materials, but it is still difficult to find stable structures of ternary and quaternary materials since the size of the configuration space becomes explosively large. Then, we expect that the DTSPs give the unknown structural prototypes of materials under high pressure.
As discussed in [11], many crystals can be understood as DBSPs. The result implies that the DSPs can be effectively used as structural prototypes for crystal structures, especially for high-pressure phases. In this study, we also investigate the correspondence of the discovered DTSPs with crystals registered in ICSD [36]. As a result, we have discovered three correspondences; first, we confirm the correspondence between the (4-2-2)5 structure shown in figure 21(b) and the ternary Cu3Ti structure, but this correspondence have already been discussed in the previous study [17] as one of the SDTSPs; second, the (4-2-2)6 structure shown in figure 21(c) corresponds to the Cu2GaSr structure while this correspondence was also discussed in the previous study [17] as one of the SDTSPs; finally, the (2-1-1) structure [17], which is equal to the (4-2-2)6 structure with the correction of structural distortion, also corresponds to the Cu2GaSr structure. Note that we referred to the space group determined by the code Spglib [22] with correcting the structural distortions in each DTSP so that we determine the correspondence.

The correspondences of the DTSPs and the crystals seem to be exceptional, but future experiments may realize crystals isotypic to the DTSPs or quaternary and/or quinary structural prototypes in which some spheres in the DTSPs are replaced by fourth and/or fifth spheres. The (13-3-1) structure includes the cluster structures consisting of 13 small spheres, as shown in figure 1(h), but one small sphere in the cluster may be better for nature to be replaced by fourth sphere, where the cluster structure is similar to that constituted by 13 hydrogen atoms in the MgH13 under pressure, which possesses high predicted Tc [37]. Besides, if we replace a small sphere at the center in the (9-6-3) structure shown in figure 1(e) for a fourth sphere, we can get a quaternary structural prototype named (8-1-6-3) structure as shown in figure 22(a). Boron atoms sometimes constitute the octahedron as can be seen in in the UB4, so the medium spheres in the (8-1-6-3) structure might be realized by boron atoms. Similarly, regarding the (9-7-3) structure shown in figure 19(c), if we replace a small sphere at the center for a fourth sphere and the medium sphere at the vertex of the unit cell for a fifth sphere, we can get a quinary structural prototype named (8-1-6-1-3) structure shown in 22(b). The fourth and fifth spheres are surrounded

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**Figure 18.** The phase diagram at the radius ratio of 0.35: 0.48: 1.00 (a) show that the (8-6-2)2 structure is the DTSP, and the packing fraction is 0.764 043. If the structural distortion is corrected, this structure has the Pmmn symmetry.
by six spheres constituting octahedrons, respectively. Finally, the (14-1-1-3) structure, in which all the medium spheres in the (8-1-6-1-3) structure are replaced by small spheres, might be one of the promising structural prototypes for metal hydrides.

Otherwise, we can use the local structures in the DTSPs as prototype blocks for the design of unknown crystal prototypes. In fact, the (10-4-1) structure shown in figure 23 includes the tetrahedron consisting of small spheres in the tetrahedral sites comprised by large spheres, and the LaBeH$_8$ [38] also includes the tetrahedron consisting of hydrogen atoms in the tetrahedral sites. Note that one small sphere is placed at the center of the tetrahedron in the (10-4-1) structure, while no atom is placed there in the LaBeH$_8$. The similarity indicates that the dense local structures are preferred by materials under pressure. Therefore, local structures that sometimes appear in the DSPs may be building blocks in crystals. For example, we can guess that the octahedrons consisting

Figure 23. The phase diagrams at the radius ratios of 0.36: 0.47: 1.00 (a) and 0.37: 0.47: 1.00 (b) shows that the (9-7-3) structure (c) is the DTSP, and the packing fractions at the two radius ratios are 0.767 631 and 0.774 290, respectively. If the structural distortion is corrected, this structure has the $Pn\bar{3}m$ symmetry.
of eight spheres are preferred by materials under pressure since the octahedrons sometimes appear in the DSPs such as the \((16-4)\) \([11]\), \((6-6-4)\), and \((9-6-3)\) structures.

4. Conclusion

We exhaustively explored DTSPs for unit cells up to 25 spheres at 451 kinds of radius ratios and 436 kinds of compositions. As a result, we have additionally found 22 putative DTSPs, and besides, we successfully confirmed that some of the well-ordered DTSPs that have already been discovered in the previous study \([17]\) appear on the ternary phase diagrams at relatively many radius ratios. The 60 putative DTSPs have been identified in total in the previous \([17]\) and present studies. Our results show that at a considerable number of radius ratios, the highest packing fraction at each composition is achieved by the phase separations consisting of only the FCC and/or the DBSPs, and the trend is becoming more evident as the small and medium spheres are getting larger. The result suggests that either the binary packings are the densest packings possible or that the dense ternary packings have unit cells larger than \(N = 25\); to put the latter in different words, the densely-packed local structures composed of three kinds of spheres may be getting more complex as the small and medium spheres are getting larger.

Since the minimum radius of small spheres is set to be larger than in the previous study \([17]\), the discovered DTSPs are well-ordered and they tend to have high symmetries. We classify the discovered DTSPs based on how structural frameworks are comprised. Our random approach, which just generates multilayered initial structures, successfully found any type of structure without \textit{a priori} knowledge, but it seems to be difficult to find the DTSPs composed of larger unit cells than in this study. Therefore, it is necessary for finding the complex DTSPs to develop more effective approaches that create more promising initial structures.

Despite the great progress of the algorithms to predict crystal structures \([25–35]\), it is still difficult to search the stable structures of ternary and quaternary materials. Then, we expect that the DTSPs are effectively utilized as structural prototypes to explore the ternary materials under high pressure. Possibly, the quaternary and/or
quinary structural prototypes, in which some spheres in the DTSPs are replaced by fourth and/or fifth spheres, might be favorable structural prototypes for materials under high pressure.

Our exhaustive exploration of DTSPs reveals that packings of multi-sized hard spheres yield diverse periodic structures realized by subtle combinations with a large number of spheres, and indicates that further studies will disclose highly ordered structures in larger unit cells including many spheres more than those surveyed in this study. The explorations for the densest structures of the quaternary sphere packings and these higher dimensional cases will be interesting future directions.

Figure 21. The common phase diagram (a) at the seven radius ratios of 0.48: 0.64: 1.00, 0.48: 0.66: 1.00, 0.48: 0.68: 1.00, 0.48: 0.70: 1.00, 0.48: 0.72: 1.00, 0.50: 0.66: 1.00, and 0.50: 0.68: 1.00, shows that the (4-2-2), structure (b) is the DTSP, and the packing fractions at the seven radius ratios are 0.747 827, 0.758 687, 0.761 453, 0.758 173, 0.758 223, 0.758 050, and 0.769 880, respectively. This structure, which has already been discussed in the previous study \cite{17} as SDTSP, has the \textit{Pmnn} symmetry if the structural distortion is corrected. At the three radius ratios of 0.48: 0.68: 1.00, 0.48: 0.70: 1.00, and 0.48: 0.72: 1.00, the (4-2-2), structure (c) has the same packing fractions as those of the (4-2-2), structure. This structure, which has also already been discussed in the previous study \cite{17} as SDTSP, has the \textit{R3m} symmetry if the structural distortion is corrected. Note that the (4-2-2), structure is equal to the (2-1-1) structure, which was found in the previous study \cite{17}, if the structural distortion in the (4-2-2), structure is corrected enough to reduce the unit cell.
Acknowledgments

R K is financially supported by the Quantum Science and Technology Fellowship Program (Q-STEP) that is the University Fellowship program for Science and Technology Innovations, and the Grant-in-Aid for JSPS Research Fellow. The calculations was performed by the supercomputer, Ohtaka, in ISSP, the Univ. of Tokyo.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: http://www.samlai-square.org/.

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