Synthesis and TEM study of Ag—In—(Eu, Ce) ternary approximants

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Abstract. Ternary Ag—In—(Eu, Ce) 1/1 approximants are synthesized and their structures are studied by transmission electron microscopy (TEM). For both the approximants, superlattice spots are clearly observed at room temperature, and the superstructures of the Ag—In—(Eu, Ce) approximants are found to be similar to those of Cd5Eu4 and Cd57Ce6, respectively. The Ag—In—Eu 1/1 approximant has a double unit cell with space group $Fd\overline{3}$ while the Ag—In—Ce 1/1 approximant has a normal unit cell with space group $Pn\overline{3}$, both at room temperature. The results suggest that the tetrahedron at the center of the icosahedral cluster is ordered in the Ag—In—(Eu, Ce) approximants in the same manner as the corresponding binary approximants Cd6(Eu, Ce). Furthermore, TEM observations at high temperatures reveal that the Ag—In—(Eu, Ce) approximants undergo a phase transition to a $bcc$ lattice at an elevated temperature. The transitions are understood as a consequence of disordering of the tetrahedron located at the center of the icosahedral cluster.

1. Introduction

An occurrence of a phase transition has been observed at a low temperature for a series of Cd6M (M = Ca, Rare earth metals) 1/1 cubic approximants [1, 2, 3]. The phase transitions were attributed to an orientational ordering of the Cd4 tetrahedron located at the center of the icosahedral cluster, which builds up a $bcc$ lattice with additional glue atoms. Soon after the discovery of the binary Cd5.7M QCs [4, 5], Guo et al. have found that the Cd atoms can be replaced by equal atomic concentrations of Ag and In atoms for the Cd5.7M QCs as well as for the Cd6M approximants, and as a consequence a variety of ternary approximants have been obtained at the compositions Ag5In4M11 [6].

Concerning the ordering phenomena, one interesting fact is that the Eu and Ce containing systems behave in a different fashion among the Cd6M compounds. For instance, Cd52Eu4 possesses a $2a \times 2a \times 2a$ superlattice structure (space group $Fd\overline{3}$) and Cd57Ce6 possesses $P$-type structure (space group $Pn\overline{3}$) even at room temperature [7, 8]. Moreover, a recent X-ray diffraction experiment on the 1/1 Ag—In—Eu by Gomez et al. [9] has demonstrated that it also forms a superlattice at room temperature, the detailed structure of which has not been clear yet.

In the present study, we have prepared single phases of the Ag—In—(Eu,Ce) 1/1 approximants and performed transmission electron microscopy (TEM) observations at room temperature as well as at elevated temperatures in order to investigate their structures and their temperature evolution and, in particular, to obtain insight into the occurrence of a phase transition.

2. Experimental

Alloys of nominal compositions Ag42.5In42.5Eu15 and Ag48In37Ce15 were prepared by melting high purity elements of Ag (99.999 wt%), In (99.999 wt%), Eu (99.9 wt%) and Ce (99.9 wt%) in an Al2O3 crucible sealed inside a quartz tube under Ar atmosphere. The Ag—In—(Eu,Ce) alloys were then annealed at 823 K and 773 K for 100 h in order to obtain a homogeneous single phase.

TEM observations were performed for pulverized samples at various temperatures between 300 K and 700 K by using a JEM-2010F (JEOL) operating at 200 kV with heating holder EM-31050 (JEOL).

3. Results and discussion

Figures 1 and 2 present selected area electron diffraction patterns of Ag42.5In42.5Eu15 and Ag48In37Ce15 at room temperature along (a) [100], (b) [111] and (c) [110] zone axes. In Fig. 1(c), weak reflections marked by the triangles cannot be indexed as a conventional $bcc$ lattice. The indices of the weak reflections are given by $h + \frac{1}{2}k + \frac{1}{2}l = \text{even}$, which means that the formation of a double unit cell at room temperature. In addition, the reflections are found to satisfy $h + k + l = 4n$, which indicates the existence of $d$ glide. Therefore, it is concluded that Ag42.5In42.5Eu15 possesses a $fcc$ lattice with $d$-glide, which results in the space group $Fd\overline{3}$.
In the case of Ag\(_{48}\)In\(_{37}\)Ce\(_{15}\), it is noticed that weak reflections marked by the triangles (\(hkl; h + k + l = \text{odd}\)) which are not allowed in a bcc lattice appear. Therefore, the Ag–In–Ce approximant has a simple cubic lattice. In addition a condition \(0kl; k + l = \text{even}\) is satisfied, which suggests the existence of \(n\)-glide symmetry. It is noted that unallowed reflections such as 001 and 003 observed in Fig. 2(c) are due to multiple diffraction since these spots are absent in Fig. 2(a). Therefore, the Ag–In–Ce approximant possesses a primitive lattice with the space group \(Pn\bar{3}\).

Fig. 1. Electron diffraction patterns of Ag\(_{42.5}\)In\(_{42.5}\)Eu\(_{15}\) along (a) [100], (b) [111] and (c) [110] axes taken at room temperature. (d) Enlarged pattern of (c).

In the case of Ag\(_{44}\)In\(_{37}\)Ce\(_{15}\), it is noticed that weak reflections marked by the triangles (\(hkl; h + k + l = \text{odd}\)) which are not allowed in a bcc lattice appear. Therefore, the Ag–In–Ce approximant has a simple cubic lattice. In addition a condition \(0kl; k + l = \text{even}\) is satisfied, which suggests the existence of \(n\)-glide symmetry. It is noted that unallowed reflections such as 001 and 003 observed in Fig. 2(c) are due to multiple diffraction since these spots are absent in Fig. 2(a). Therefore, the Ag–In–Ce approximant possesses a primitive lattice with the space group \(Pn\bar{3}\).

Fig. 2. Electron diffraction patterns of Ag\(_{44}\)In\(_{37}\)Ce\(_{15}\) along (a) [100], (b) [111] and (c) [110] axes taken at room temperature. (d) Enlarged pattern of (c).

Fig. 3 shows the structure models obtained for (a) the Ag–In–Eu and (b) the Ag–In–Ce 1/1 approximants at room temperature. The ordering of the tetrahedra are determined by the \(d\)-glide and the \(n\)-glide symmetries observed for the Ag–In–Eu and the Ag–In–Ce approximants, respectively. The Ag–In–Eu approximant, Fig. 3(a) there are two symmetry-nonequivalent clusters. For the Ag–In–Ce approximant, the \(n\)-glide symmetry requires alternative ordering of the tetrahedron along the [110] direction. The superstructures of the Ag–In–(Eu,Ce) approximants are found to be similar to those of Cd\(_{25}\)Eu\(_4\) and Cd\(_{37}\)Ce\(_6\), respectively.

Figures 4 and 5 present selected area electron diffraction patterns of Ag\(_{42.5}\)In\(_{42.5}\)Eu\(_{15}\) and Ag\(_{44}\)In\(_{37}\)Ce\(_{15}\) along [110] axis at room temperature and at an elevated temperature. When Ag\(_{42.5}\)In\(_{42.5}\)Eu\(_{15}\) is heated up to 430 K, reflections at the positions marked by triangles are found to disappear and when the specimen is cooled down they are found to reappear again. We confirmed that the phenomenon occurs repeatedly with temperature variation across 430 K, which means a phase transition takes place reversibly at 430 K. In Fig. 4, all the reflections at 430 K can be indexed by considering a half unit cell, and in addition the condition \(bkl; h + k + l = \text{even}\) is satisfied, which means that the high temperature phase has an \(a \times a \times a\) bcc lattice. Therefore, it follows that the undergoes a phase transition at 430 K to a bcc phase with a half period.

Fig. 3. Schematic illustrations of the unit cell of (a) the Ag–In–Eu and (b) the Ag–In–Ce 1/1 approximants at room temperature with respect to the two kinds of icosahedral clusters and two differently-oriented tetrahedra, respectively.

Fig. 4. Electron diffraction patterns of Ag\(_{42.5}\)In\(_{42.5}\)Eu\(_{15}\) along [110] axis (a) at room temperature and (b) at 430 K.
On the other hand, in the case of Ag₄₇In₃₈Ce₁₅, reflections at positions marked by the triangles are found to disappear at 380 K and they reappear when the specimen is cooled down, which suggests that the phenomenon occurs repeatedly with temperature variation across 380 K. Therefore, a reversible phase transition also occurs in the Ag₄₇In₃₈Ce₁₅ at 380 K. As seen in Fig. 5(b), the reflections satisfy the condition $hkl; h + k + l = \text{even}$ above 380 K, which means that the high temperature phase has a bcc lattice. Thus, it is concluded that the Ag–In–Ce approximant undergoes a phase transition at 380 K to a bcc phase with the same period.

The present work has shown that the Eu and Ce bearing 1/1 approximants possess a superlattice structure at room temperature. TEM observation has revealed that both the approximants undergo a phase transition to a bcc lattice at an elevated temperature. The transitions are likely to be due to orientational disordering of the tetrahedron as in the cases of the Cd-based approximant: The superstructures of Cd₃₂Eu₄ and Cd₃₇Ce₆ are considered to be formed by an ordered arrangement of the tetrahedron located at the center of icosahedral cluster [7, 8].

4. Conclusion

Ternary Ag–In–(Eu, Ce) 1/1 approximants were synthesized and their structures were investigated by transmission electron microscopy at room temperature as well as at elevated temperatures. As a result, both the approximants have been found to form a superstructure at room temperature: The Ag–In–Eu 1/1 approximant has a double unit cell with $Fd\bar{3}$ while the Ag–In–Ce 1/1 approximant has a normal unit cell with $Pn\bar{3}m$. Moreover, the superlattice reflections were found to disappear at elevated temperatures for both the approximants, indicating an occurrence of a phase transition. The transitions can be understood as a consequence of orientational disordering of a tetrahedron located at the center of the icosahedral cluster.

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References