

Chemical Science

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: K. Matsumoto, M. Kudo, Y. Tatetsu, R. Sato, R. Takahata and T. Teranishi, *Chem. Sci.*, 2025, DOI: 10.1039/D5SC01754H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Atomic diffusion barriers and inter-element miscibility guide the development of unexplored crystal phases†

Kenshi Matsumoto^{*a}, Masaki Kudo^b, Yasutomi Tatetsu^c, Ryota Sato^a, Ryo Takahata^{a,d} and Toshiharu Teranishi^{*a,d}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Z3-Fe(Pd,In)₃ ordered alloy nanoparticles containing alternating layers of an L1₀ (CuAu-type)-like PdFePd trilayer and a Pd–In ordered alloy monolayer are formed by following the inter-element miscibility of In, which is miscible with Pd but immiscible with Fe. An understanding of the atomic diffusion processes based on inter-element miscibility is required to effectively synthesize such unknown crystal phases. In this study, we demonstrated that the temperature required for the formation of the Z3 structure largely depends on the diffusion path of Fe into PdIn_x or In into FePd₃ alloy nanoparticles. The results indicate that the design of the diffusion path should be considered to develop unexplored crystal phases, especially in alloy systems containing an immiscible pair of elements.

Introduction

The crystal structure is an important factor in determining the physical and chemical properties of metal nanomaterials;^{1,2} thus, the stabilization of unknown crystal structures is an attractive approach for discovering highly functional materials.³ In particular, alloy systems have the potential to exhibit various physical and chemical properties because numerous structures are geometrically allowed at specific compositions.⁴ However, the formation of crystal structures is governed by thermodynamics, and thus it is extremely difficult to develop crystal structures with thermodynamically unfavourable atomic arrangements. Although many metastable phases have been reported under specific conditions, such as high pressure,⁵ high temperature,⁶ nano-size^{7,8} and lattice strain,^{9,10} these phases were represented by well-known crystal structures. In contrast, the development of synthetic strategies for producing unprecedented crystal structures is relatively challenging.

Recently, we succeeded in synthesizing unprecedented Z3-Fe(Pd,In)₃ alloy nanoparticles (NPs), which consisted of alternating layers of an L1₀ (CuAu-type)-like PdFePd trilayer and a Pd–In ordered alloy monolayer (Figure 1a), using nanoparticulate precursors of A1 (face-centred cubic (fcc)-type solid-solution) PdIn_x@FeO_y core@shell (A1-PdIn_x@FeO_y) NPs.¹¹ In addition, it was both experimentally and theoretically confirmed that the inter-element miscibility of In, which is miscible with Pd but immiscible with Fe,¹² provided the driving

force for stabilizing the Z3 phase. Z3-Fe(Pd,In)₃ phase possesses not only ferromagnetic property with high coercivity¹¹ but also high potential as oxygen reduction reaction catalyst.³ Elucidating the formation mechanism of the Z3-Fe(Pd,In)₃ phase, specifically the atomic diffusion process, is necessary to expand the library of unexplored ordered alloy structures based on the inter-element miscibility of the third element.

NPs have two advantages for this investigation. One is to facilitate the atomic diffusion required to form an alloy with a homogeneous composition.¹³ The other advantage is the ease of structural transformation, considering that a disorder-order transformation of the crystal structure in alloys propagates from the particle surface to the core.^{14,15}

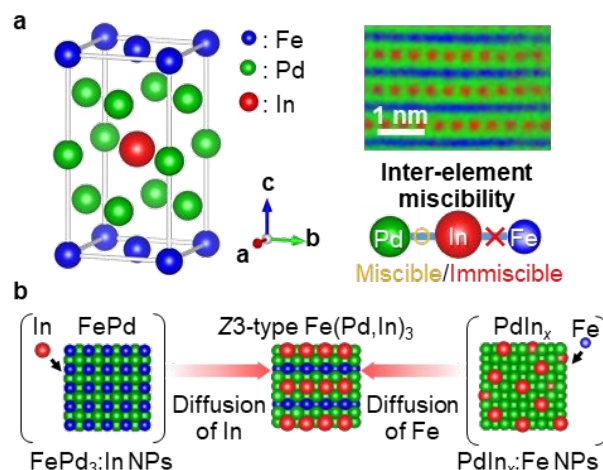


Fig. 1 (a) Unit cell of the unprecedented Z3-Fe(Pd,In)₃ structure, atomic-resolution EDX elemental mapping for [100] of the Z3 phase (red: In-L, blue: Fe-K, green: Pd-L), and inter-element miscibility of In with Pd and Fe (reproduced from ref. [11]). (b) Illustration depicting the thermal conversion of two well-designed precursor nanostructures into the Z3-Fe(Pd,In)₃ phase.

^a Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. E-mail: matsumoto.kenshi.3r@kyoto-u.ac.jp, teranishi@scl.kyoto-u.ac.jp

^b The Ultramicroscopy Research Center, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

^c Department of Health Informatics, Meio University, Biimata, Nago, Okinawa, 905-8585, Japan.

^d Department of Chemistry, Graduate School of Science, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

† Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



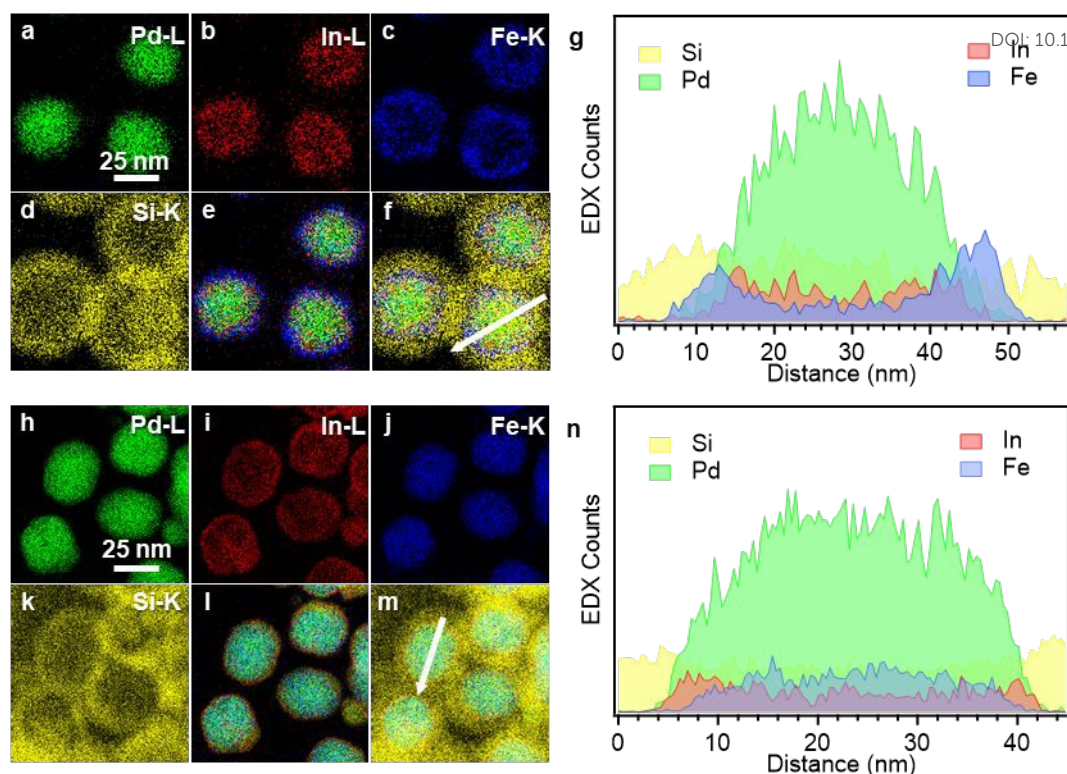


Fig. 2 (a–d, h–k) EDX elemental maps (Pd-L (a and h), In-L (b and i), Fe-K (c and j) and Si-K (d and k)) of $\text{FePd}_3\text{:In}$ (a–d) and $\text{PdIn}_x\text{:Fe}$ (h–k) NPs. (e, f, l, m) Overlay of a–c (e), a–d (f), h–j (l) and h–k (m). (g, n) EDX line profiles indicated by the white arrows in f and m.

In this work, we demonstrate the importance of designing precursor materials that consider the ease of atomic diffusion to synthesize NPs with unknown crystal phases like the Z3 phase. To investigate how the immiscibility between Fe and In affects their diffusion processes to form the Z3 phase, we designed two types of NPs, namely $\text{FePd}_3\text{:In}$ NPs (diffusion of In into the FePd_3 alloy) and $\text{PdIn}_x\text{:Fe}$ NPs (diffusion of Fe into the In-poor PdIn_x alloy; $17 < x < 23$ atomic % (at.%)), in which the atomic diffusion is promoted by reductive annealing to provide a Z3-Fe(Pd,In)_3 phase (Figure 1b). We found that the reductive annealing temperatures of the two NPs differ by 200 K during the formation of Z3-Fe(Pd,In)_3 . To clarify the diffusion paths of In and Fe, the intermediate phases obtained before the formation of the Z3-Fe(Pd,In)_3 phase were identified by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDX) and powder X-ray diffraction (XRD). The results indicate that the extent to which Fe and In occupy adjacent sites in the crystal structure during the diffusion process determines the formation temperature (i.e., inter-diffusion activation energy) of the Z3-Fe(Pd,In)_3 phase. Moreover, a theoretical approach based on first-principles calculations supports our claim that the differences in activation energies depending on diffusion paths can be qualitatively explained by the differences in formation energies of the intermediates leading to the Z3 phase. Therefore, the diffusion path must be considered in the design of precursor materials, to facilitate the discovery of unexplored crystal structures in ternary alloys containing immiscible elemental pairs.

Results and discussion

Synthesis of two types of nanoparticle precursors

Fe and In are an immiscible combination in a binary phase diagram.¹² To investigate how the diffusion path affects the formation temperature of the Z3-Fe(Pd,In)_3 NPs, two types of nanoparticle precursors with different distributions of Fe, Pd and In ($\text{FePd}_3\text{:In}$ and $\text{PdIn}_x\text{:Fe}$ NPs) were synthesized using step-by-step approaches.

$\text{FePd}_3\text{:In}$ NPs were synthesized as follows: (a1) synthesis of 23 nm Pd NPs,^{11,16} (a2) growth of FeO_y shells on Pd NPs (Pd@FeO_y core@shell NPs),^{11,16} (a3) growth of mesoporous SiO_2 shells on Pd@FeO_y NPs ($\text{Pd@FeO}_y\text{@SiO}_2$ NPs),¹⁷ (a4) transformation of $\text{Pd@FeO}_y\text{@SiO}_2$ NPs into $L1_2$ (Cu_3Au -type) $\text{FePd}_3\text{@SiO}_2$ NPs by reductive annealing and (a5) deposition of In on the $L1_2\text{-FePd}_3$ using InCl_3 in solution (see Supporting Information for details and Figure S1).

$\text{PdIn}_x\text{:Fe}$ NPs were synthesized as follows: (b1) synthesis of 23 nm Pd NPs,^{11,16} (b2) alloying Pd NPs with In (PdIn_x NPs),¹¹ (b3) growth of FeO_y shells on PdIn_x NPs ($\text{PdIn}_x\text{@FeO}_y$ NPs),¹¹ (b4) sequential growth of mesoporous SiO_2 shells on $\text{PdIn}_x\text{@FeO}_y$ NPs ($\text{PdIn}_x\text{@FeO}_y\text{@SiO}_2$ NPs)¹⁷ and (b5) transformation of $\text{PdIn}_x\text{@FeO}_y$ NPs into $\text{PdIn}_x\text{:Fe}$ NPs by reductive annealing (see Supporting Information for details and Figure S1).

In the above syntheses, SiO_2 shells were used to suppress inter-particle fusion during the annealing processes. The Pd/In/Fe ratios of $\text{FePd}_3\text{:In}$ and $\text{PdIn}_x\text{:Fe}$ NPs were 65/12/23 and 60/14/26 (at.%), respectively, which were previously confirmed to be within the



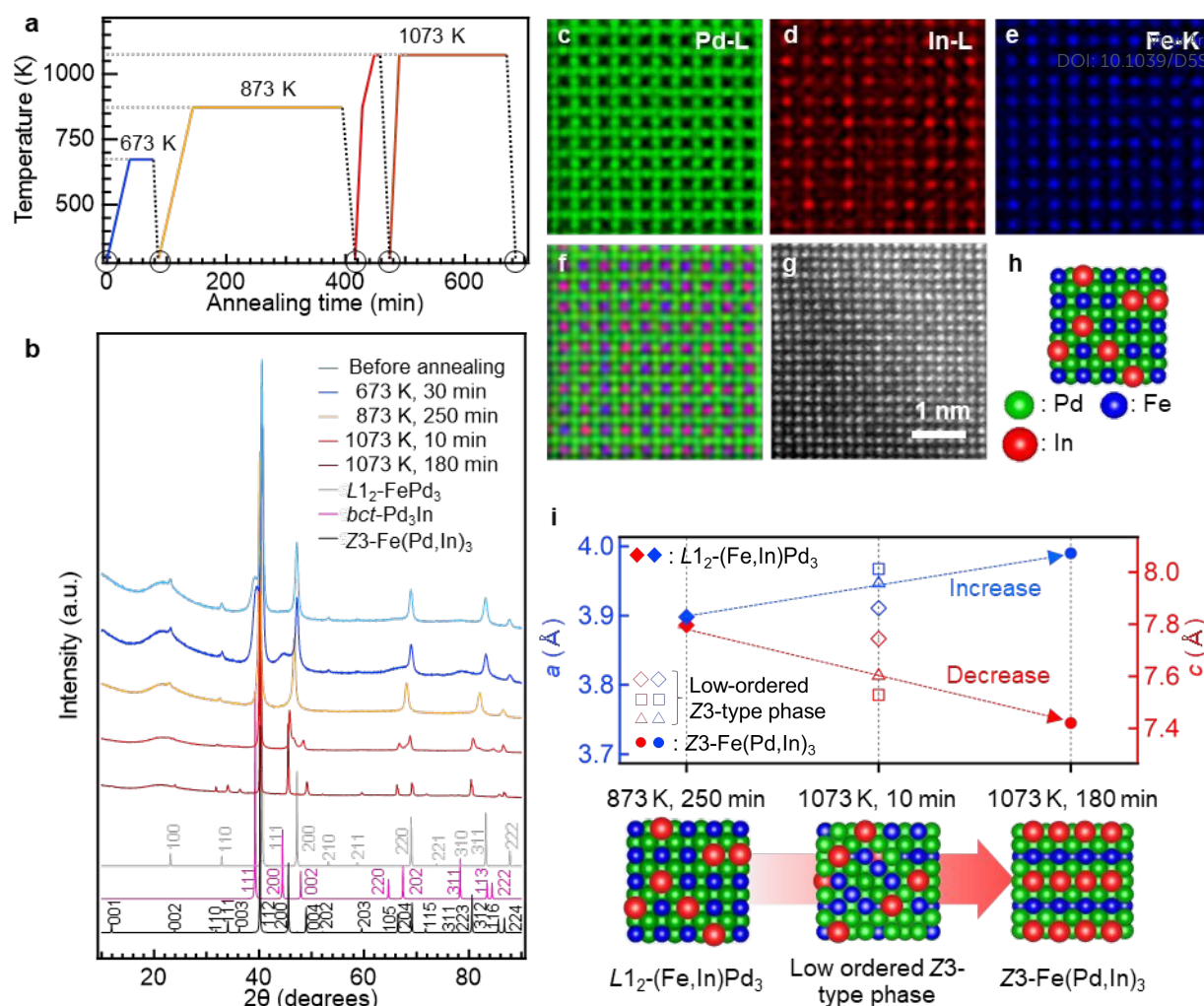


Fig. 3. (a) An annealing program, in which ex-situ characterizations—HAADF-STEM, EDX and powder XRD—were conducted at the conditions marked with open circles. (b) Powder XRD patterns for NPs obtained by reductive annealing at 673 K for 30 min, 873 K for 250 min and 1073 K for 10 and 180 min. Powder XRD patterns were measured at the X-ray wavelength of 1.542 Å. (c–g) Atomic-resolution EDX elemental maps (Pd–L (c), In–L (d) and Fe–K (e)), overlay of c–e (f) and the HAADF-STEM image (g) of NPs formed after reductive annealing at 873 K for 250 min. (h) Crystal phase model obtained from c–g. (i) Lattice parameters [a (blue) and c (red)] of major phase obtained by Rietveld refinements for b (Fig. S2†) (solid rhombi $\blacklozenge$: $L1_2$ -(Fe,In)Pd₃, open rhombi $\diamond$, squares $\square$ and triangles $\triangle$: three low-ordered Z3-type Fe–Pd–In, solid circles $\bullet$: Z3-Fe(Pd,In)₃) and crystal phase models obtained from the lattice parameters.

composition range required to form the Z3-Fe(Pd,In)₃ phase.¹¹ Rietveld refinements for powder XRD patterns and EDX elemental maps revealed that the FePd₃:In NPs have an $L1_2$ -FePd₃@body-centred tetragonal (bct)-type Pd₃In ($L1_2$ -FePd₃@ bct -Pd₃In) structure, whereas the PdIn_x:Fe NPs have an $A1$ - and bct -type PdIn_x@body-centred cubic (bcc)-type Fe (PdIn_x@ bcc -Fe) structure (Figures 2, S2, and S7).

Formation process of the Z3-Fe(Pd,In)₃ phase from FePd₃:In NPs

To not only confirm the formation of the Z3-Fe(Pd,In)₃ phase but also investigate the structure of intermediates formed from FePd₃:In NPs, reductive annealing was conducted at 673 K for 40 min and 873 K for 250 min (Figure 3a), and the obtained crystal phases were characterized at room temperature. Rietveld refinements for powder XRD patterns showed that the reductive annealing of FePd₃:In NPs at 673 K gave the $L1_2$ -FePd₃ and bct -Pd₃In phases, followed by transformation into the $L1_2$ -Fe–Pd–In and bcc -Fe phases by further reductive annealing at 873 K (Figures 3b and S2). HAADF-

STEM observation and EDX elemental maps of NPs obtained at 873 K for 250 min showed selective substitution of Fe with In in the $L1_2$ -FePd₃ phase to give homogeneous distributions of Fe, Pd and In (Figures 3c–h and S3), as observed in our previous work.¹¹ The Z3-Fe(Pd,In)₃ phase was not formed below 873 K when using FePd₃:In NPs as a starting material.

To confirm whether the Z3-Fe(Pd,In)₃ phase can be formed from FePd₃:In NPs, reductive annealing was conducted at 1073 K for NPs obtained at 873 K for 250 min (Figure 3a). The reductive annealing at 1073 K for 10 min provided the three tetragonal Fe–Pd–In phases, and further reductive annealing for 180 min (total time) gave the Z3-Fe(Pd,In)₃ single phase (Figures 3b and S2). Considering the changes in lattice parameters of all crystal phases formed through the reductive annealing process from 873 to 1073 K, the a -axis and c -axis lengths monotonically increased and decreased, respectively, with the increase in annealing temperature and time; that is, we observed a monotonical increase in tetragonality (a/c) (Figure 3i). This means that the highly symmetric $L1_2$ (cubic) phase formed at 873 K was



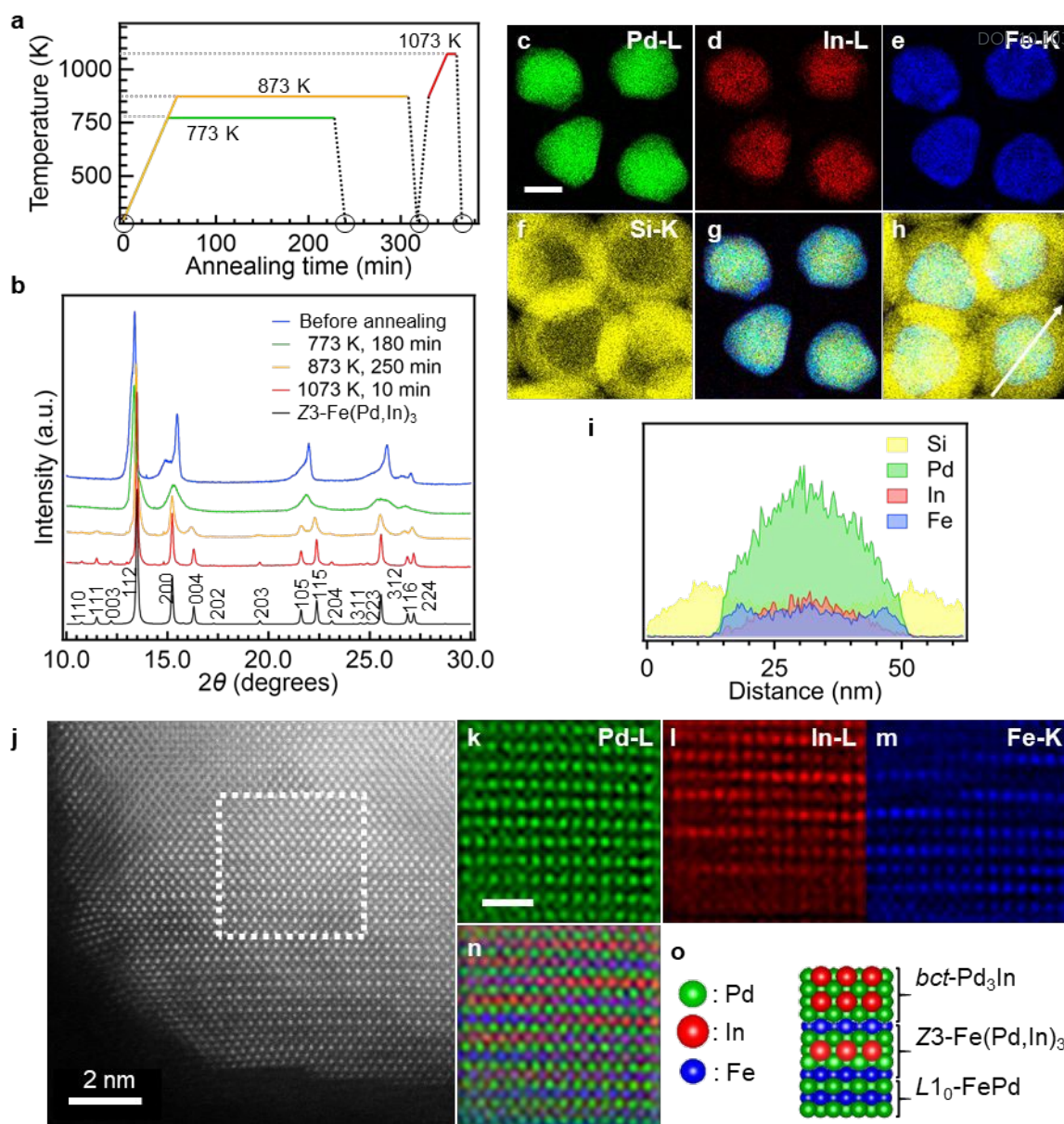


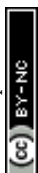
Fig. 4 (a) An annealing program, in which ex-situ characterizations—HAADF-STEM, EDX and powder XRD—were conducted at the conditions marked with open circles. (b) Powder XRD patterns for $\text{PdIn}_x\text{:Fe}$ NPs and NPs obtained by reductive annealing at 773 K for 180 min, 873 K for 250 min and 1073 K for 10 min. Powder XRD patterns were obtained using a synchrotron source with an X-ray wavelength of 0.5274 Å. (c–f) EDX elemental maps (Pd-L (c), In-L (d), Fe-K (e) and Si-K (f)) of NPs obtained by reductive annealing at 773 K for 180 min. (g, h) Overlays of c–e (g) and c–f (h). (i) EDX line profiles obtained along the white arrow in h. (j) HAADF-STEM image around the interface of Pd–In@Fe–Pd NPs obtained by reductive annealing at 773 K for 180 min. (k–m) Atomic-resolution EDX elemental maps (Pd-L (k), In-L (l) and Fe-K (m)) of the white square region in j. (n) Overlay of k–m. (o) Crystal phase model obtained from k–m.

converted into the low-ordered Z3-type (tetragonal) phase at 1073 K, as observed in the formation of the low-ordered tetragonal $\text{L1}_0\text{-FePt}$ phase from the higher symmetric cubic A1-FePt phase during the reductive annealing process.¹⁸ The HAADF-STEM observation and EDX elemental mapping also show that the low-ordered tetragonal phase was formed after reductive annealing at 1073 K for 10 min (Figure S4). In facts, we quantitatively evaluated the order degree (S) of low-ordered Z3-type phase by using the ordered peak of 111 (see Supporting Information for details), from which the S value of the low-ordered Z3-type phase showed the lower value (0.21) than that of Z3-Fe(Pd,In)_3 formed by the annealing at 1073 K for 10 min (0.94) (Figure S5). Consequently, in the case of $\text{FePd}_3\text{:In}$ NPs, the highly

ordered Z3-Fe(Pd,In)_3 phase was formed at 1073 K via the $\text{L1}_2\text{-(Fe,In)Pd}_3$ and low-ordered Z3-type phases.

Formation process of the Z3-Fe(Pd,In)_3 phase from $\text{PdIn}_x\text{:Fe}$ NPs

The formation of the Z3-Fe(Pd,In)_3 phase from $\text{FePd}_3\text{:In}$ NPs required the annealing temperature of 1073 K. Next, we used $\text{PdIn}_x\text{:Fe}$ NPs as a starting nanoparticulate precursor to investigate how the Fe diffusion into PdIn_x alloy NPs containing a small amount of In ($17 < x < 23$ at.%) affects the formation temperature of the Z3 phase. First, the reductive annealing of $\text{PdIn}_x\text{:Fe}$ NPs was carried out at 873 K for 250 min and 1073 K for 10 min (Figure 4a), and the resulting crystal



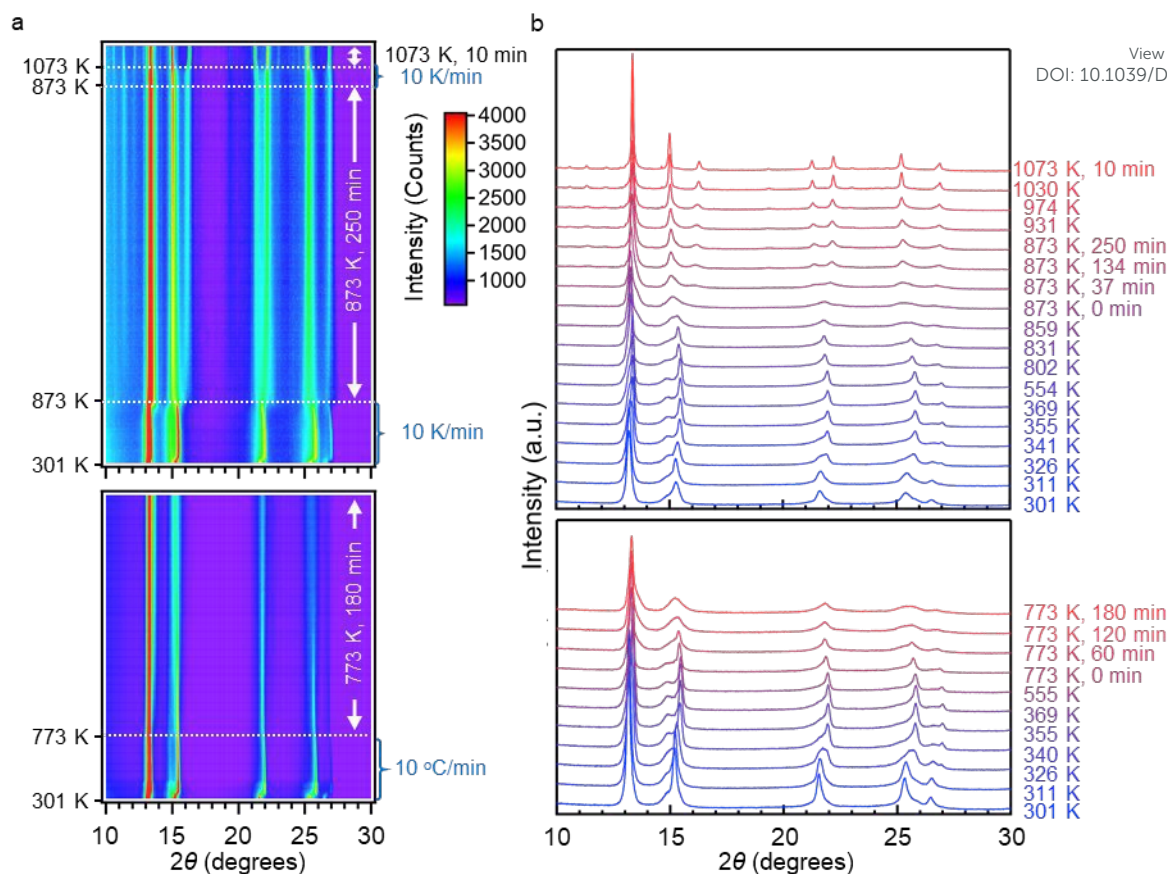


Fig. 5 (a) Two-dimensional plots of powder XRD patterns recorded during the reductive annealing of $\text{PdIn}_x\text{:Fe}$ NPs at the conditions marked with orange, red and green solid lines in Fig. 4a; (upper) heated to 873 K at 10 K/min, kept at 873 K for 250 min, heated to 1073 K at 10 K/min and kept at 1073 K for 10 min; (bottom) heated to 773 K at 10 K/min and kept at 773 K for 180 min. (b) Corresponding partial powder XRD patterns of the products.

phases were characterized at room temperature. Unlike the $\text{FePd}_3\text{:In}$ NPs, powder XRD patterns revealed that the Z3 phase was already formed at 873 K (Figure 4b). To clarify the detailed crystal structure change of $\text{PdIn}_x\text{:Fe}$ NPs, the reductive annealing of $\text{PdIn}_x\text{:Fe}$ NPs was conducted at 773 K for 180 min (Figure 4a). As expected, the resulting NPs possessed different diffraction pattern compared with both $\text{PdIn}_x\text{:Fe}$ and Z3- $\text{Fe}(\text{Pd},\text{In})_3$ NPs (Figure 4b), but it was difficult to determine the precise crystal structure from the diffraction pattern alone, owing to low crystallinity.

Then, a local structural analysis was conducted to identify this intermediate phase. EDX elemental maps revealed the formation of Pd-In@Fe-Pd NPs by the reductive annealing at 773 K, resulting in heterogeneous distributions of Fe, Pd and In (Figures 4c–i), in contrast to the homogeneous distributions in NPs obtained at 873 and 1073 K (Figures S6 and S7). Notably, HAADF-STEM and EDX showed the formation of the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase between the $L1_0\text{-FePd}$ and the $bct\text{-Pd}_3\text{In}$ phases (Figures 4j–o). Based on this structural information, Rietveld refinements for powder XRD patterns were performed to verify the Z3- $\text{Fe}(\text{Pd},\text{In})_3$, $L1_0\text{-FePd}$ and $bct\text{-Pd}_3\text{In}$ phases after the reductive annealing of $\text{PdIn}_x\text{:Fe}$ NPs at 773 and 873 K, as well as the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase obtained by reductive annealing at 1073 K (Figure S8). The results demonstrated that the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase was formed between the $L1_0\text{-FePd}$ and $bct\text{-Pd}_3\text{In}$ phases (Figure 4o).

In addition to the aforementioned structural characterizations at room temperature, in situ powder XRD measurements were adopted

for interrogating the products formed by the reductive annealing of $\text{PdIn}_x\text{:Fe}$ NPs (Figure 5). Below 326 K, the diffraction patterns already differed from that of $\text{PdIn}_x\text{:Fe}$ NPs owing to the hydrogen insertion into the A1- and bct -type PdIn_x phases (Figure S9).¹⁹ From 326 to 773 K, hydrogen atoms were released from the A1- and bct -type PdIn_x phases, and the diffraction patterns became similar to that of $\text{PdIn}_x\text{:Fe}$ NPs. Diffraction peaks with broader widths than those of $\text{PdIn}_x\text{:Fe}$ NPs were observed from 773 to 873 K, indicating the formation of the $L1_0\text{-FePd}/\text{Z3-Fe}(\text{Pd},\text{In})_3/bct\text{-Pd}_3\text{In}$ triphase, rather than other structures. This is because the phase-segregation in one particle inevitably decreases the crystalline size of each phase, unlike the formation of ternary solid-solution or ordered Fe-Pd-In alloy. Above 873 K, the diffraction pattern of the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase was confirmed. Therefore, in situ XRD measurements are consistent with the characterizations performed at room temperature, confirming the detection of the intermediate phases during the transition from $\text{PdIn}_x\text{:Fe}$ NPs to the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase. Ultimately, using $\text{PdIn}_x\text{:Fe}$ NPs as a nanoparticulate precursor, the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase was obtained as a main phase at 873 K via the formation of the $L1_0\text{-FePd}/\text{Z3-Fe}(\text{Pd},\text{In})_3/bct\text{-Pd}_3\text{In}$ triphase.

Dependence of the formation temperature of the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ structure on the atomic diffusion path

Surprisingly, there was a difference of 200 K in the temperature required to form the Z3 structure as the main phase between



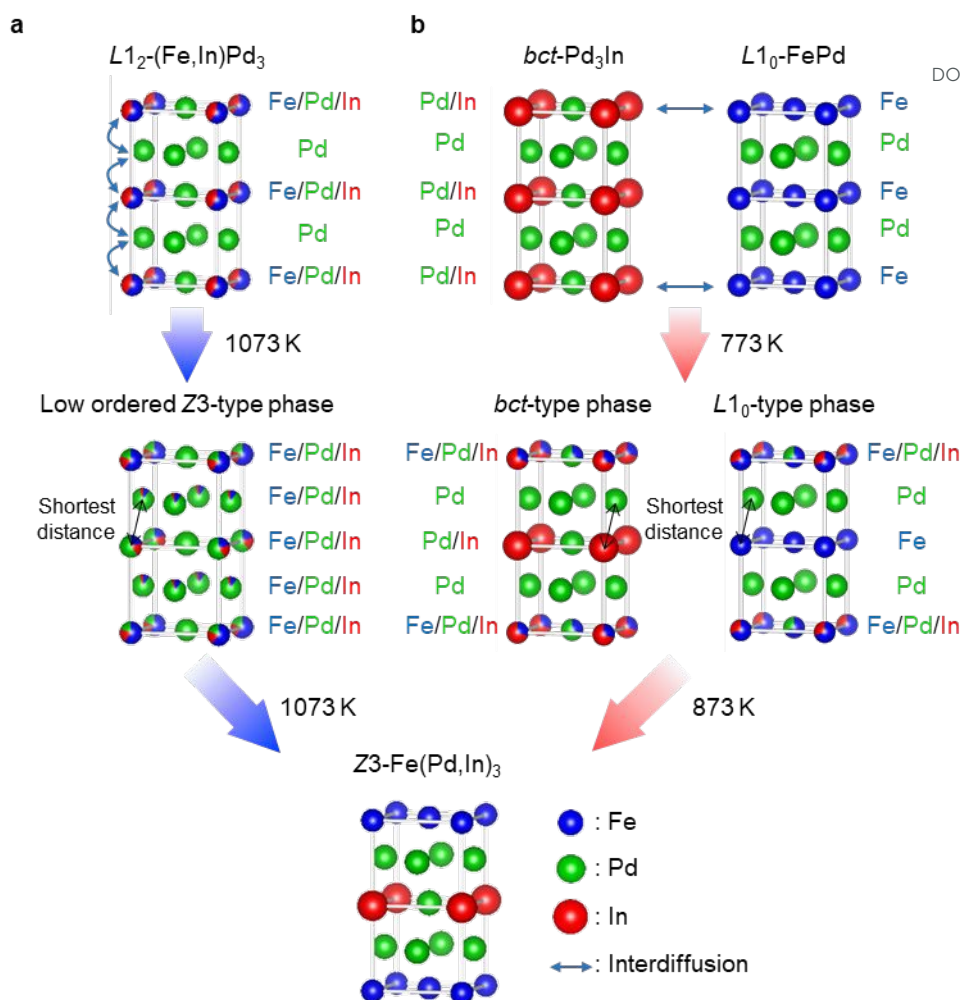


Fig. 6 (a, b) Illustrations of the formation processes for the Z3-Fe(Pd,In)₃ phase obtained from the L1₂-(Fe,In)Pd₃ (a) and L1₀-FePd/bct-Pd₃In diphases (b), which are the intermediate structures formed from FePd₃:In and PdIn_x:Fe NPs, respectively.

FePd₃:In and PdIn_x:Fe NPs within a practical time duration. However, understanding the origin of the formation temperature difference is important in the experimental exploration of novel ordered alloy structures.

Heights of activation barriers between the intermediates structures to form Z3 structures are considered the main factors for determining the formation temperature of the Z3 structure. To understand the origin of this formation temperature difference, we investigated the Fe and In substitution sites in intermediate phases formed from FePd₃:In and PdIn_x:Fe NPs. First, the intermediate phase formed after the reductive annealing of FePd₃:In NPs at 1073 K for 10 min is the low-ordered Z3-type phase (Figures 3 and S4). Formation of the low-ordered Z3-type phase, in which Fe and In were detected in all monolayers (Figure S4), results from the substitution of Fe or In with Pd in the Pd monolayer of L1₂-(Fe,In)Pd₃, leading to the occupation of In at the atomic sites closest to Fe (Figure 6a). Therefore, in the case of FePd₃:In NPs, Fe and In occupy the closest sites to induce the crystal phase change from L1₂-(Fe,In)Pd₃ to the more thermodynamically stable Z3-Fe(Pd,In)₃ phases.

Conversely, Fe and In atoms do not exist in Pd monolayers of the intermediate structure formed by the reductive annealing of PdIn_x:Fe NPs, or the L1₀-FePd/Z3-Fe(Pd,In)₃/bct-Pd₃In triphase (Figures 4j–o and S10); Fe and In are not close to each other in the triphase

because all the interplanar spacings between Pd monolayers in the L1₀-FePd, bct-Pd₃In and Z3-Fe(Pd,In)₃ phases are shorter than the corresponding *a*-axis lengths.^{11,16,20} By estimating the interatomic distances from the XRD pattern of L1₀-FePd/Z3-Fe(Pd,In)₃/bct-Pd₃In triphase, we found that the first and second neighbour distances were 0.272–0.278 and 0.280–0.285 nm, respectively (Figure S8). Note that this second neighbour distance is longer than the nearest neighbour distance (0.273–0.275 nm) of the low-ordered Z3-type phase derived from FePd₃:In NPs (Figure S2). In other words, there is a big difference in the interatomic distance between Fe and In in the intermediate phases formed from FePd₃:In and PdIn_x:Fe NPs.

Then, to confirm whether the Fe atoms avoid occupying the sites adjacent to the In sites in the diffusion process from the L1₀-FePd/Z3-Fe(Pd,In)₃/bct-Pd₃In triphase to the Z3-Fe(Pd,In)₃ single phase, HAADF-STEM and EDX of NPs with the L1₀-FePd/Z3-Fe(Pd,In)₃/bct-Pd₃In triphase were conducted during reductive annealing at 873 K. Fast Fourier transform images were obtained from HAADF-STEM images of the two NPs, showing the brighter 001 and 003 diffraction spots derived from Z3 structure with the increase in reductive annealing time (0, 10, 40 and 100 min), which indicates the increase in the volume ratio of the Z3 phase (Figure S11). Atomic-resolution EDX elemental maps for a particular area of one NP showed that the



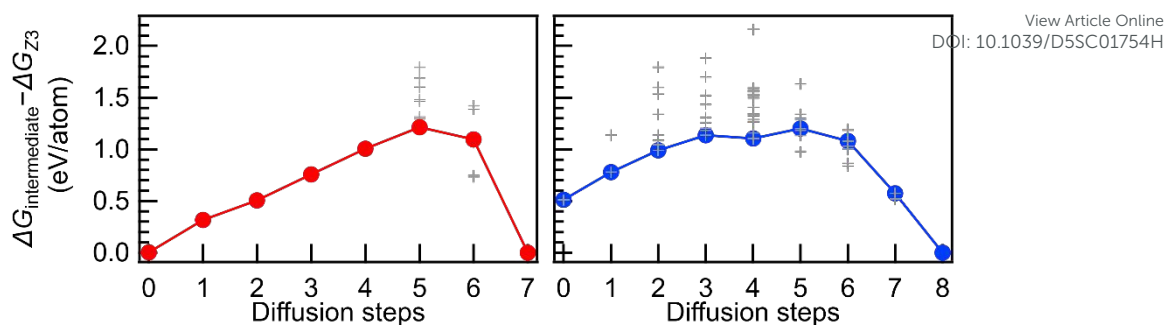


Fig. 7 Formation energies, or Gibbs free energies at 0 K, of intermediate structures ($\Delta G_{\text{intermediate}}$) compared with Z3- $\text{Fe}_8\text{Pd}_{20}\text{In}_4$ (ΔG_{Z3}), where the red and blue curves are the diffusion paths with the minimum formation energies formed from $\text{L}_{12}\text{-Fe}_4\text{Pd}_{24}\text{In}_4$ and $\text{L}_{10}\text{-Fe}_{16}\text{Pd}_{16}/\text{bct-Pd}_{24}\text{In}_8$, respectively, and the + mark represents other paths.

L_{10} , Z3 and *bct* triphase was epitaxially stacked along the [001] direction of the constituent three phases (Figure S12). In the NPs obtained by reductive annealing at 873 K for 0, 10 and 40 min, Pd monolayers in the triphase were sandwiched by two Fe–Pd–In alloy monolayers, which indicates selective occupation of Fe and In in certain atomic sites of the L_{10} and *bct* phases. Specifically, the NPs underwent substitution of Fe for Pd or In in the Pd–In monolayers of the *bct*- Pd_3In structure and substitution of Pd or In for Fe in the L_{10} -FePd structure (Figure 6b). Therefore, it was found that Fe and In diffuse while avoiding each other during the formation of the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ single phase from the $\text{L}_{10}\text{-FePd}/\text{Z3-Fe}(\text{Pd},\text{In})_3/\text{bct-Pd}_3\text{In}$ triphase.

By comparing the diffusion paths of In in FePd_3In NPs and Fe in PdIn_xFe NPs during reductive annealing, we found that the major difference is whether Fe and In occupy adjacent sites as the atomic diffusion proceeds. To evaluate the activation energies for atomic diffusion into Z3 phase, we calculated the formation energies of various intermediate phases from $\text{L}_{12}\text{-Fe}_4\text{Pd}_6\text{In}_4$ or $\text{L}_{10}\text{-Fe}_2\text{Pd}_2/\text{bct-Pd}_3\text{In}_1$ to Z3- $\text{Fe}_2\text{Pd}_5\text{In}_1$ phases (see Supporting Information for details, Figures 7 and S13 and Tables S1 and S2). Such an elementary process to form Z3 phase gives quasi-activation energies between intermediate structures because the activation energies are larger than the formation energies. Interestingly, intermediate phases from $\text{L}_{12}\text{-Fe}_4\text{Pd}_6\text{In}_4$ to Z3- $\text{Fe}_2\text{Pd}_5\text{In}_1$ phases showed the larger difference in the formation energies than that of $\text{L}_{10}\text{-Fe}_2\text{Pd}_2/\text{bct-Pd}_3\text{In}_1$ biphasic. Moreover, compared with $\text{L}_{10}\text{-Fe}_2\text{Pd}_2/\text{bct-Pd}_3\text{In}_1$ biphasic, the diffusion paths—corresponding to a frequency factor in Arrhenius equation—with small energy barriers are fewer because the intermediate structures with neighbouring Fe and In atoms are thermodynamically unstable (Table S1). Therefore, the phase stabilities determined by inter-element miscibility suggest that the unfavourable diffusion paths of In and Fe in FePd_3In NPs require a reductive annealing temperature that is 200 K higher to form the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phase.

Conclusions

We propose that the design of the diffusion path is important for experimentally exploring unknown ternary ordered alloys that contain a pair of immiscible elements at lower temperatures. Herein, we designed two types of diffusion paths, that is, introducing In into the FePd_3 alloy (FePd_3In) and

Fe into the In-poor PdIn_x alloy (PdIn_xFe) NPs, to investigate the diffusion path-dependent formation mechanism of the Z3- $\text{Fe}(\text{Pd},\text{In})_3$ phases. Reductive annealing converted FePd_3In NPs into $\text{L}_{12}\text{-(Fe,In)Pd}_3$ at 873 K and then into Z3- $\text{Fe}(\text{Pd},\text{In})_3$ at 1073 K via a low-ordered Z3-type structure. In contrast, PdIn_xFe NPs were converted into the $\text{L}_{10}\text{-FePd}/\text{Z3-Fe}(\text{Pd},\text{In})_3/\text{bct-Pd}_3\text{In}$ triphase at 773 K and then into Z3- $\text{Fe}(\text{Pd},\text{In})_3$ at 873 K. It was concluded that the difference in the formation temperature of the Z3 phase depended on whether In and Fe were close to each other during the diffusion process, considering the low miscibility of Fe with In. We expect that control over the diffusion process is necessary to discover unknown ordered alloy structures containing an immiscible elemental pair.

Author contributions

K.M., R.S., R.T. and T.T. conceived the study. K.M. and R.S. designed the synthesis scheme. K.M. performed the synthesis and characterizations. K.M. and R.S. measured and analyzed the powder XRD patterns obtained at SPring-8. M.K. collected the HAADF-STEM images and EDX elemental maps. K.M. and M.K. conducted the repeated HAADF-STEM and EDX observations of a specific particle. Y.T. calculated the formation energies. K.M., Y.T. and T.T. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

The authors declare no competing financial interests.

Data availability

The data supporting this article have been included as part of the ESI.†

Acknowledgements

Powder XRD measurements were performed using the BL02B2 beamline at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2021B1513 (K.M.), 2021B1708 (R.S.), 2022A1068 (R.S.)),



2022A1227 (K.M.) and 2022B1848 (K.M.)), which were experimentally supported by Dr. S. Kobayashi, Dr. Y. Mori and Dr. S. Kawaguchi. EDX elemental maps were obtained by Advanced Research Infrastructure and Nanotechnology in Japan, sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Proposal No. JPMXP09A21KU0397 (K.M.)). Preparation of annealed samples was supported by Prof. M. Yamauchi (Kyushu University). This work was supported by JST-CREST (Grant No. JPMJCR21B4) (T. T.), JSPS KAKENHI for Scientific Research (S) (Grant Nos. JP19H05634 and JP24H00053 (T.T.)), Scientific Research (B) (Grant No. JP18H01953 (R.S.)), Challenging Research (Exploratory) (Grant Nos. JP19K22231 (T.T.) and JP17K19178 (R.S.)) and Early-Career Scientists (Grant No. JP22K14554 (K.M.)). We thank Robert Ireland, PhD, from Edanz (<https://jp.edanz.com/ac>) for editing a draft of this manuscript.

Notes and references

- Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publisher, 1988.
- D. Wu, K. Kusada, S. M. Aspera, H. Nakanishi, Y. Chen, O. Seo, C. Song, J. Kim, S. Hiroi, O. Sakata, T. Yamamoto, S. Matsumura, Y. Nanba, M. Koyama, N. Ogiwara, S. Kawaguchi, Y. Kubota and H. Kitagawa, *ACS Mater. Au* 2022, **2**, 110.
- K. Matsumoto, R. Sato and T. Teranishi, *Trends Chem.* 2023, **5**, 201.
- R. V. Chepulskii, S. V. Barabash and A. Zunger, *Phys. Rev. B* 2012, **85**, 144201.
- G. Mettela, Y. A. Sorb, A. Shukla, C. Bellin, V. Svitlyk, M. Mezouar, C. Narayana and G. U. Kulkarni, *Chem. Mater.* 2017, **29**, 1485.
- M. Cui, C. Yang, S. Hwang, M. Yang, S. Overa, Q. Dong, Y. Yao, A. H. Brozena, D. A. Cullen, M. Chi, T. F. Blum, D. Morris, Z. Finrock, X. Wang, P. Zhang, V. G. Goncharov, X. Guo, J. Luo, Y. Mo, F. Jiao and L. Hu, *Sci. Adv.* 2022, **8**, eabm4322.
- K. Kusada, M. Yamauchi, H. Kobayashi, H. Kitagawa and Y. Kubota, *J. Am. Chem. Soc.* 2010, **132**, 15896.
- J. Pirart, A. Front, D. Rapetti, C. Andreazza-Vignolle, P. Andreazza, C. Mottet and R. Ferrando, *Nat. Commun.* 2019, **10**, 1982.
- P. Quarterman, C. Sun, J. Garcia-Barriocanal, M. DC, Y. Lv, S. Manipatruni, D. E. Nikonov, I. A. Young, P. M. Voyles and J.-P. Wang, *Nat. Commun.* 2018, **9**, 2058.
- A. Janssen, Z. Lyu, M. Figueras-Valls, H.-Y. Chao, Y. Shi, V. Pawlik, M. Chi, M. Mavrikakis and Y. Xia, *Nano Lett.* 2022, **22**, 3591.
- K. Matsumoto, R. Sato, Y. Tatetsu, R. Takahata, S. Yamazoe, M. Yamauchi, Y. Inagaki, Y. Horibe, M. Kudo, T. Toriyama, M. Auchi, M. Haruta, H. Kurata and T. Teranishi, *Nat. Commun.* 2022, **13**, 1047.
- T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak, *Binary Alloy Phase Diagrams*; ASM International, ed. 2, 1990.
- J. E. S. van der Hoeven, T. A. J. Welling, T. A. G. Silva, J. E. van den Reijen, C. L. Fontaine, X. Carrier, C. Louis, A. van Blaaderen and P. E. de Jongh, *ACS Nano* 2018, **12**, 8467.
- F. Li, Y. Zong, Y. Ma, M. Wang, W. Shang, P. Tao, C. Song, T. Deng, H. Zhu and J. Wu, *ACS Nano* 2021, **15**, 5284.
- X. Chen, S. Zhang, C. Li, Z. Liu, X. Sun, S. Cheng, D. N. Zakharov, S. Hwang, Y. Zhu, J. Fang, G. Wang and G. Zhou, *Proc. Natl. Acad. Sci. USA* 2022, **119**, e2117899119.
- K. Matsumoto, R. Sato, T. T. Trinh, N. Sakuma, T. Shoji, M. Haruta, H. Kurata and T. Teranishi, *Nanoscale Adv.* 2019, **1**, 2598.
- D.-S. Bae, K.-S. Han and J. H. Adair, *J. Mater. Chem.* 2002, **12**, 3117.
- J. P. Liu, K. Elkins, D. Li, V. Nandwana and N. Poudyal, *IEEE Trans. Magn.* 2006, **42**, 3036.
- H. Kohlmann, A. V. Skripov, A. V. Soloninin and T. J. Udovic, *J. Solid State Chem.* 2010, **183**, 2461.
- Q. Feng, S. Zhao, Y. Wang, J. Dong, W. Chen, D. He, D. Wang, J. Yang, Y. Zhu, H. Zhu, L. Gu, Z. Li, Y. Liu, R. Yu, J. Li and Y. Li, *J. Am. Soc. Chem.* 2017, **139**, 7294.



All data is available in the main text and in the ESI.

