Variation in crystal structure of $L n_2 N i_{1−x} C u_x O_{4+δ}$ ($L n$: La, Pr, Nd, Sm, Eu, and their solid solution) based on type of $L n$: Relationship between crystal structure and tolerance factor

Chengkun WANG¹, Haruki SOGA¹, Takao YUGI¹, Mamoru SAKAI¹, Takashi OKIBA¹ and Takuya HASHIMOTO¹,

¹Department of Physics, College of Humanities and Science, Nihon University, 3–25–40 Sakurajousui, Setagaya-ku, Tokyo 156–8550, Japan

The variation in the crystal structure of $L n_2 N i_{1−x} C u_x O_{4+δ}$, which has great potential as a new cathode material for solid oxide fuel cells, based on the type of $L n$ (La, Pr, Nd, Sm, Eu, and their solid solution), was investigated. For $L n$ with ionic radius larger than 1.21 Å (1 Å = 0.1 nm), a single-phase $K_2 N i F_4$ structure called T-phase was prepared for $0.0 ≤ x ≤ 1.0$. For $L n$ with ionic radius between 1.21 and 1.15 Å, the crystal structure changed from single T-phase to single Nd$_2$CuO$_4$ structure called $T'$-phase, through the mixture of T-phase and $T'$-phase, along with increasing Cu content. The range of Cu content, in which the mixture phase was obtained because of the miscibility gap, increased with the decreasing size of $L n$. The single T-phase was never prepared for $L n$ with ionic radius below 1.15 Å. Rough tendencies were observed, indicating that the single T-phase was obtained or was not prepared if the tolerance factor was above or below 0.865, respectively. The mixture of T-phase and $T'$-phase was obtained because of the miscibility gap by decreasing the tolerance factor slightly below about 0.865. The T-phase was never generated by decreasing the tolerance factor any further. The change of the crystal structure by Cu content and kind of $L n$ can also be explained by using Jahn–Teller effect of $Cu^{2+}$ ion.

Key-words: Ln$_2$Ni$_{1−x}$Cu$_x$O$_{4+δ}$, Crystal structure, Phase relationship, Miscibility gap, Tolerance factor

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1. Introduction

Mixed ionic and electronic conducting materials are applied to various technological devices, such as oxygen permeable membranes, oxygen pumps, oxygen sensors, and electrodes of solid oxide fuel cells (SOFCs). The search for new and superior mixed conducting materials is still in progress. For example, to increase energy conversion efficiency of SOFCs, materials with both high ionic and electronic conductivity are required for reducing the energy loss at the cathode. Currently, La$_{1−x}$Ca$_x$MnO$_{3+δ}$ or La$_{1−x}$Sr$_x$MnO$_{3+δ}$ with a perovskite structure are frequently employed as a cathode material; however, low oxide ion conductivity must be solved for improvement in the energy conversion efficiency. As a new cathode material, Ni-based layered perovskite compounds with a $K_2 N i F_4$-type crystal structure (T-phase), Ln$_2$NiO$_{4+δ}$ ($L n$: La, Pr, Nd, and so on), are gaining significant attention for their mixed conducting properties.¹-¹⁰ The crystal structure of Ln$_2$NiO$_4$ with T-phase can be described as an alternate accumulation of the perovskite-layer including [NiO$_6$] octahedra and rock-salt layer composed of Ln and oxide ions along the c-axis.¹¹-¹³ It was reported that the interstitial oxygen located in the rock-salt layer was an origin of oxide ion conduction and generation of holes, which was conducted within the perovskite layer.

For application of Ln$_2$NiO$_{4+δ}$ to cathode materials, some problems, such as instability at high temperature and low electrical conductivity must be solved. To overcome these problems, partial substitution of Cu for a Ni site was examined. Improvement of not only stability but also conductivity and oxygen permeation rate by the partial substitution was reported.¹⁵-²⁰ However, excess substitution causes generation of $T'$-phase, which is composed of a stacking of a [CuO$_2$] sheet without apical oxide ions and fluorite layer for a few types of $L n$. Singh et al. reported a crystal structure of La$_{1−x}$Cu$_x$O$_{4+δ}$ with $x = 0.0–0.9$ as T-phase, while Pr$_2$Ni$_{0.25}$Cu$_{0.75}$O$_{4+δ}$ was a mixture of T-phase and $T'$-phase.²⁹,³¹ Recently, we clarified

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† Corresponding author: T. Hashimoto; E-mail: takuya@chs.nihon-u.ac.jp
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that Nd$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ with 0.4 ≤ x ≤ 0.9 is a mixture of T-phase and T’-phase because of the miscibility gap. The electrical conductivity decreased with the generation of T’-phase; thus, variation in the obtained phase and crystal structure of Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ on not only the Cu content but also the type of Ln is an indispensable information for their application.

In this study, variation in the obtained phase and crystal structure of Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ based on different types of Ln was investigated. The examined Ln were La, Pr, Nd, Sm, and Eu, and the compositional range of x where T-phase was obtained was also examined. In addition, the size of Ln was controlled by employing a solid solution of lanthanoid as Ln. Dependence of x range, where T-phase was prepared, on the size of Ln was examined. It was revealed that the compositional range, in which T-phase was obtained, was successfully explained using the tolerance factor and Jahn–Teller effect of Cu$^{2+}$ ion.

2. Experimental

Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ was prepared using the Pechini method with Ln$_2$O$_3$ (Ln = La, Pr, Nd, Sm and Eu: 99.9%, Furuuchi Chemical Corp.), Ni(NO$_3$)$_2$:6H$_2$O (99.9%, Wako Pure Chemical Industries), and CuO (99.9%, Furuuchi Chemical Corp.) as the starting materials. The purity of Ni(NO$_3$)$_2$:6H$_2$O was evaluated based on the weight of NiO, which was present after heat treatment at 1000°C in air. Ln$_2$O$_3$ and CuO were dissolved in a mixture of dilute HNO$_3$ and hydrogen peroxide solution. Ni(NO$_3$)$_2$:6H$_2$O was dissolved in distilled H$_2$O. Each solution was mixed in a cation stoichiometric ratio. After addition of the citric acid and ethylene glycol, the mixture was heated at about 450°C until the residual materials caught fire, thereby resulting in a precursor. The obtained precursor was crushed into powder form and calcined at 700°C for 24 h in air, followed by pressing into a pellet and additional heating at 1000°C for 10 h in air, and subsequent reheating at 1200°C for 10 h in air. The specimens were then cooled at a rate of 300°C/h in air.

The synthesized specimens were crushed into powder form and analyzed by X-ray diffraction (XRD; Cu Ka: 50 kV, 250 mA, RINT-2500, Rigaku Co., Ltd.) to distinguish if a single phase had been obtained and to clarify the crystal system at room temperature in air. The lattice constants and molar volumes of the specimens were evaluated using the Bragg angles of 211 and 213 for the tetragonal T-phase; 313, 133, and 008 for the orthorhombic T-phase; and 211 and 008 for the tetragonal T’-phase.

For some specimens of Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, the lattice constants and the compositional ratios of the T-phase and T’-phase were analyzed by the Rietveld method using program RIETAN-FP. The morphology and cation distribution of the fractured cross section of Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ were evaluated by performing scanning electron microscopy-energy-dispersive X-ray (SEM-EDX) analysis (JEOL: JCM-5700 equipped with JED-2300). Before the analysis, the fractured surface was coated with carbon to avoid charging.

3. Results and discussion

3.1 Crystal structure of La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ at room temperature

It was reported that δ in La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ prepared in air decreased from 0.16 to 0.01 with increasing x from 0.0 to 1.0. Ideal, δ should be the same to clarify pure effect of Cu substitution on crystal structure, however, preparation with the same δ was considered to be impossible because range of δ variation drastically decreased with increasing Cu content. In addition, it was also reported that the variation of δ certainly affected space group of La$_2$Ni$_{4+\delta}$ but that T-phase was maintained irrespective of δ variation. Therefore, alignment of preparation atmosphere, which is important for application, was prioritized and effect of δ on crystal structure was approximated as negligibly small in this study.

The XRD patterns of La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ are shown in Fig. 1. The diffraction patterns of the specimens for 0.0 ≤ x ≤ 0.8 were successfully indexed as a single phase of the tetragonal T-phase with a space group of I4/mmm (No. 139). By increasing the Cu content from x = 0.8 to x = 0.9, single peaks, such as 213, split as shown in Fig. 1(b), thereby indicating variation in the crystal structure. The diffraction patterns of x = 0.9 and 1.0 were indexed as a single phase of an orthorhombic T-phase with Fmmm (No. 69). Being different from Nd$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ T’-phase was never observed, which showed an agreement with the results reported by Singh et al. The lattice constants and molar volume of La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ are shown in Fig. S1 in the supporting file. The c-axis monotonically increased with increasing x for all compositions, while the a-axis decreased for 0.0 ≤ x ≤ 0.8, thereby indicating a successful Cu substitution. The anisotropic change of lattice constants can be attributed to Jahn–Teller effect of Cu$^{2+}$ ion, as discussed later in 3.6. The molar volumes linearly increased with the increasing Cu content for 0.0 ≤ x ≤ 0.4, whereas saturation because of the decrease in a-axis was observed for 0.5 ≤ x ≤ 0.9. The abrupt increase from x = 0.9 and 1.0 can be ascribed to the structural phase transition from tetragonal to orthorhombic.

3.2 Variation of crystal structure of Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ by Cu content

For Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ (0.0 ≤ x ≤ 0.2) and Nd$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ (0.0 ≤ x ≤ 0.2), it was reported that δ slightly decreased from 0.146 to 0.116 and from 0.118 to 0.107, respectively, with increasing Cu content from 0.0 to 0.2, showing similar tendency with La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$. Certainly, variation of δ was considered to be an origin of structural change from orthorhombic to tetragonal in Nd$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ with increasing Cu content; however, T-phase was maintained irrespective of δ. Therefore, effect of δ on crystal structure was approximated as negligibly small at discussion below, like the discussion in 3.1.

The XRD patterns of Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ are shown in Fig. 2. The diffraction patterns of the specimens for 0.0 ≤ x ≤ 0.4 were indexed as a single phase of the orthorhomb-
bic T-phase with space group of $Fmmm$ (No. 69). For the diffraction patterns of the specimens with $0.5 \leq x \leq 0.9$, new peaks, represented by red Miller indices, were observed in addition to those assigned as the orthorhombic T-phase. The intensity of the new peaks increased and that of the peaks identified as the orthorhombic T-phase decreased with the increasing value of $x$ from 0.5 to 0.9, with little change of the Bragg angles of all peaks. For a specimen

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**Fig. 1.** (a) XRD patterns of $\text{La}_2\text{Ni}_1-x\text{Cu}_x\text{O}_4$. (b) Close up of (a) in the $2\theta$ range (53–59°). The blue and black Miller indices represent the tetragonal T-phase and orthorhombic T-phase, respectively.

**Fig. 2.** (a) XRD patterns of $\text{Pr}_2\text{Ni}_1-x\text{Cu}_x\text{O}_4$. (b) Close up of (a) in the $2\theta$ range (51–60°). The black and red Miller indices represent the orthorhombic T-phase and tetragonal T$\beta$-phase, respectively.
with \( x = 1.0 \), only the new peaks remained, which were identified as tetragonal \( T' \)-phase with a space group of \( I4/mmm \) (No. 139). Therefore, the specimens with \( 0.5 \leq x \leq 0.9 \) were concluded to be a mixture of the orthorhombic \( T \)-phase and tetragonal \( T' \)-phase. The results agreed with those reported by Singh et al., thereby insisting that \( \text{Pr}_2\text{Ni}_0.25\text{Cu}_0.75\text{O}_4 \) was mixture of \( T \)-phase and \( T' \)-phase.

One of the probable origins of the generation of the mixture is the miscibility gap for \( 0.5 \leq x \leq 0.9 \), as was reported in \( \text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) with \( 0.4 \leq x \leq 0.9 \). The constant lattice constants and satisfaction of the lever rule in molar ratio between \( T \)-phase and \( T' \)-phase should be observed if the miscibility gap exists. Rietveld analysis was performed for XRD patterns of \( \text{Pr}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) with \( 0.4 \leq x \leq 1.0 \), for minute evaluation of the lattice constants and molar ratio between the both phases. Figure 3 shows the results of Rietveld analysis of \( \text{Pr}_2\text{Ni}_0.2\text{Cu}_0.8\text{O}_{4+\delta} \) as a representative result. The optimized structural parameters, \( R \) (correlation coefficient) values, and \( S \) (goodness-of-fit indicator) are listed in Table 1. The results of the Rietveld analysis for XRD patterns of other compositions are shown in Figs. S2–S7 and Tables S1–S6 in the supporting file. A good agreement was observed between the experimentally observed and calculated XRD patterns in every specimen.

Figure 4 shows the lattice constants and molar volume of \( \text{Pr}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) at room temperature evaluated by Rietveld analysis. The \( c \)-axis and molar volume linearly increased with the increasing value of \( x \) for \( 0.0 \leq x \leq 0.5 \), thereby indicating a successful partial substitution of Cu for the Ni site. For \( 0.5 \leq x \leq 0.9 \), the lattice constants and molar volume of both \( T \)-phase and \( T' \)-phase were constant, thereby indicating a constant composition of both \( T \)-phase and \( T' \)-phase. Figure 5 shows the molar fraction of \( T' \)-phase of \( \text{Pr}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) evaluated by Rietveld analysis. A linear relationship between Cu content and molar ratio of \( T' \)-phase was observed for \( 0.5 \leq x \leq 0.9 \), thereby indicating the satisfaction of lever rule because of the miscibility gap. Figure 5 also shows the molar fraction of \( \text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) was slightly wider than that of \( \text{Pr}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \). The compositional range of the miscibility gap in \( \text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \) was slightly wider than that of \( \text{Pr}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \). Zheng and Świerczek reported that the amount of \( T' \)-phase in \( \text{Pr}_2\text{Ni}_{0.5}\text{Cu}_0.5\text{O}_{4+\delta} \)
was smaller than that in Nd$_2$Ni$_{0.5}$Cu$_{0.5}$O$_{4+\delta}$, thereby showing an agreement with the results shown in Fig. 5. To confirm phase separation because of the miscibility gap, SEM-EDX measurements were performed on the specimens with 0.4 ≤ x ≤ 0.9. Figure 6 shows EDX images of the fractured cross section of the specimens with x = 0.4, 0.6, and 0.8. The cation distribution in the specimen with x = 0.4 was homogeneous [depicted as (1)], whereas an additional phase with a different cation composition [depicted as (2)] was observed in the specimens with x ≥ 0.5. The fraction of the phase represented as (2) increased with the increasing value of x. Figure S8 shows the intensity of X-ray emitted from (a) region (1) and (b) region (2) in Fig. 6 with energy dispersive X-ray analysis. In region (1), both Ni and Cu were observed, while X-ray intensity by Ni was smaller than that by Cu in region (2). Figure S9 shows the EDX peak intensity ratio for Ni K$_\alpha$ and Cu K$_\alpha$ at (1) and (2). The intensity ratio was almost constant in both (1) and (2) for specimens with 0.5 ≤ x ≤ 0.9, thereby showing an agreement with the existence of the miscibility gap.

3.3 Trial for preparation of Sm$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ and Eu$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$

Figure 7 shows the XRD patterns of (a) Sm$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ and (b) Eu$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$. The single tetragonal T'-phase was obtained for Sm$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ with 0.95 ≤ x ≤ 1.0 and Eu$_2$CuO$_4$; however, only peaks identified as NiO and Sm$_2$O$_3$ or Eu$_2$O$_3$ were observed, except T'-phase. No T-phase generated for all the specimens.

3.4 Variation of crystal structure of Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ on ionic radius of Ln

The difference in the structural variation behavior among La$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, Pr$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, Nd$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, Sm$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, and Eu$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$ described above can be ascribed to the difference in the ionic radius of Ln in Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$. To verify the above hypothesis, preparation of various Ln$_2$Ni$_{1-x}$Cu$_x$O$_{4+\delta}$, Ln of which was a solid solution, was attempted. The examined Ln were La$_{0.4}$Pr$_{0.5}$, Pr$_{0.2}$Nd$_{0.8}$, Nd$_{0.875}$Sm$_{0.125}$, and Nd$_{0.5}$Sm$_{0.5}$; the average
The ionic radius of which were estimated to be 1.1975, 1.1710, 1.1591, and 1.1475 Å, respectively, by using Shannon’s ionic radius.38) The employed coordination number was 9 considering the crystal structure of T-phase. Like discussion in 3.1 and 3.2, variation of $\delta$ by Cu content was assumed to be so small that it scarcely affected crystal structure.

The XRD patterns of LaPrNi$_{1-x}$Cu$_x$O$_{4+\delta}$ are shown in Fig. 8. The diffraction patterns of the specimens with $x = 0.0$ could be successfully indexed as a single phase of a face-centered orthorhombic T-phase. By increasing the Cu content to $x = 0.1$, some two peaks, 311 and 131 for example, changed to a single peak, indicating variation in the crystal structure. The diffraction patterns with $0.1 \leq x \leq 0.8$ could be indexed as a single phase of the body-centered tetragonal T-phase. The diffraction pattern for the specimen with $x = 0.9$ was identified as a mixture of an orthorhombic T-phase and a tetragonal T$^2$-phase, thereby indicating the existence of the miscibility gap. For the specimen with $x = 1.0$, i.e., LaPrCuO$_{4+\delta}$, two types of tetragonal structures were identified: one was T$^2$-phase with $a = 3.985$ Å and $c = 12.38$ Å, and the other was a
tetragonal T*-phase with \( a = 3.991 \, \text{Å} \) and \( c = 12.449 \, \text{Å} \), which contained pyramidal [CuO₅], as also reported by Manthiram et al. and Bringley et al. \( ^{39, 40} \)

The XRD patterns of PrNdNi\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\) are shown in Fig. 9. The diffraction patterns of the specimens with 0.0 ≤ \( x \leq 0.15 \) and 0.2 ≤ \( x \leq 0.4 \) were successfully indexed as a single phase of an orthorhombic and tetragonal T-phase, respectively. The phase transition was also observed for Nd\(_2\)Ni\(_1\)-Cu\(_x\)O\(_{4+\delta}\) between \( x = 0.1 \) and 0.2. \( ^{32} \)

The diffraction patterns of the specimens with 0.5 ≤ \( x \leq 0.9 \) were identified as a mixture of T-phase and T'-phase, thereby indicating the existence of the miscibility gap, which is also observed in Nd\(_2\)Ni\(_1\)-Cu\(_x\)O\(_{4+\delta}\) and Pr\(_2\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\).

Figure 10 shows the XRD patterns of Nd\(_{1.75}\)Sm\(_{0.25}\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\). The diffraction pattern of Nd\(_{1.75}\)Sm\(_{0.25}\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\) was indexed as a single phase of an orthorhombic T-phase. The diffraction patterns of 0.1 ≤ \( x \leq 0.3 \) were indexed as a single phase of the tetragonal T-phase. The diffraction patterns of the specimens with 0.4 ≤ \( x \leq 0.9 \) indicated a mixture of T-phase and T'-phase because of the miscibility gap, which was also clarified in Nd\(_2\)Ni\(_{1-x}\)-Cu\(_x\)O\(_{4+\delta}\). \( ^{32} \)

Figure S10 shows the lattice constants and molar volume of PrNdNi\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\) and Nd\(_{1.75}\)Sm\(_{0.25}\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\). For the \( x \) region, where a single phase (T-phase) was observed, the \( c \)-axis and the molar volume systematically increased with the Cu content, indicating successful partial Cu substitution for the Ni site. For the \( x \) range, where the specimens were composed of mixture of T-phase and T'-phase, every axis and molar volume were almost constant with the Cu content because of the miscibility gap.

Figure 11 shows the XRD patterns of NdSmNi\(_{1-x}\)-Cu\(_x\)O\(_{4+\delta}\) at room temperature. The single phase of T'-phase was obtained for the specimen with 0.9 ≤ \( x \leq 1.0 \); however, the specimens with 0.2 ≤ \( x \leq 0.8 \) were mixture of T'-phase, NdSmO\(_3\), NiO and Nd\(_2\)NiO\(_{4+\delta}\), while NdSmNiO\(_{4+\delta}\) is mixture of NdSmO\(_3\) and NiO. It was concluded that single T-phase could not be obtained if Ln is too small.

3.5 The relationship among crystal structure of Ln\(_2\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\), ionic radius of Ln and tolerance factor

Figure 12(a) shows the variation of obtained phases of Ln\(_2\)Ni\(_{1-x}\)Cu\(_x\)O\(_{4+\delta}\) on Cu content and Shannon’s ionic radius of nine-coordinated Ln. The coordinate number of Ln is 9 in T-phase; thus, nine-coordinated ionic radius was employed. For the specimens with Ln, whose ionic radius was larger than 1.21 Å, the single T-phase was obtained irrespective of Cu content as shown above line (1) in Fig. 12(a). For the specimens in which ionic radius of Ln was between 1.21 Å, line (1), and 1.15 Å, line (2), the miscibility gap composed of T-phase and T'-phase was observed. With the decreasing ionic radius of Ln, the range of Cu content that the miscibility gap was observed increased while that where single T-phase was obtained decreased. The single T-phase was not obtained below line (2), where ionic radius of Ln was below 1.15 Å.

The T-phase is composed of alternate stacking of rock-salt and perovskite layers; thus, stability in the perovskite structure should be necessary for the preparation of the crystal structure of T-phase. Assuming hard sphere model, stability of perovskite oxide is frequently evaluated by tolerance factor, \( t \), which is expressed as follows:
\[ t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}, \]  

where \( r_A, r_B, \) and \( r_O \) denote the ionic radius of the A site ion, B site ion, and oxide ion, respectively. The coordinate number of the A site ion, \( Ln, \) is 9 for T-phase; thus, \( r_A \) for nine-coordination was employed in this study. Equation (1) was more than 0.865 (rough estimation). This \( t \) value was higher than 0.85, which was proposed as the T-phase stable region by Poix.41) Between lines (1) and (2) in Fig. 12(b), the miscibility gap composed of T\(_B\)-phase with \( x = 1.0 \) and T-phase with less Cu content was observed, which could be ascribed to the decrease in the stability of T-phase by decreasing \( t \) with increasing Cu content. Further decrease in \( t \) below line (2) makes the preparation of the single T-phase impossible.

In Fig. 12(b), hard sphere model was assumed and the other possible parameters, such as difference in oxygen content among \( Ln_2Ni_{1-x}Cu_xO_{4+\delta} \) and difference in the stabilization energy among \([CuO_6]\) octahedron, \([NiO_6]\) octahedron in T-phase, and \([CuO_2]\) sheet in T\(_B\)-phase were ignored; however, Fig. 12(b) indicated that the crystal structure and obtained phases of \( Ln_2Ni_{1-x}Cu_xO_{4+\delta} \) could be roughly prospected by using the tolerance factor.

### 3.6 Explanation of lattice constant variation and phase separation behavior with increasing Cu content considering Jahn–Teller effect

As depicted in Figs. 4, S1 and S10, molar volume and c-axis of T-phase of every \( Ln_2Ni_{1-x}Cu_xO_{4+\delta} \) increased with increasing Cu content, whereas a-axis and b-axis decreased or unchanged within experimental error. Assuming \( \delta \) is negligibly small, valence of Ni and Cu is 2+. Since electronic configuration of Ni\(^{2+}\) is \( d^8 \), no Jahn–Teller effect...
Cu content, and (b) tolerance factor and Cu content. The results shown in Fig. 12(a) revealed that the single T-phase was obtained if the Cu content in Ln2Ni1−xCuO4+x was so-called T-phase with the K2NiF4 type structure, regardless of the Cu content. The crystal structures of Pr2Ni1−xCuO4+x were T-phase and T'-phase for 0.0 ≤ x ≤ 0.4 and x = 1.0, respectively. A miscibility gap was observed for 0.5 ≤ x ≤ 0.9, whose range was smaller than that of Nd2Ni1−xCuO4+x. For specimens with Ln=Sml and Eu, T-phase could not be prepared. The preparation of Ln2Ni1−xCuO4+δ with various ionic radii of Ln was examined by employing a solid solution as Ln, and dependence of the crystal structure on the size of Ln was clarified. The single T-phase was successfully prepared for Ln with ionic radius larger than 1.21 Å, regardless of the Cu content, while the single T-phase was not obtained for Ln with ionic radius below 1.15 Å. For Ln with ionic radius between 1.15 and 1.21 Å, the observed crystal structure changed from single T-phase to single T'-phase, through the mixture of T-phase and T'-phase along with the increasing Cu content. The range of Cu content, in which the mixture was obtained because of the miscibility gap, increased with the decreasing size of Ln. It was also revealed that the single T-phase was obtained if the tolerance factor was more than 0.865 approximately. If the tolerance factor was smaller than 0.865, preparation of single T-phase was not possible. The mixture of T-phase and T'-phase was obtained because of the miscibility gap by decreasing the tolerance factor slightly below about 0.865. The T-phase was never generated by decreasing the tolerance factor any further. The variation of lattice constants with Cu content and dependence of phase separation behavior on Cu content and kinds of Ln can be explained by extension of [CuO6] octahedron along with c-axis direction due to Jahn–Teller effect.

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Appendix A. Supplementary data Supplementary data associated with this article can be found in the online version.

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works, resulting in high symmetry of [NiO6] octahedron in Ln2NiO4. On the contrary, bond between Cu2+ and apical oxide ion is prospected to be longer than that between Cu2+ and equatorial oxide ion in [CuO6] octahedron because of Jahn–Teller effect of Cu2+ with electronic configuration of d6. This prospect shows agreement with experimentally observed increase of c-axis and decrease (or unchanged) of a- and b-axis with increasing Cu content in Ln2Ni1−xCuO4+x of T-phase. It is also expected that enough c-axis length should be required to stabilize T-phase with high Cu content owing to Jahn–Teller effect of Cu2+. Figure S11 shows the c-axis of Ln2Ni1−xCuO4+x (Ln: La, La0.3Pr0.7, Pr, Pr0.3Nd0.7, Nd, Nd0.875Sm0.125) with 0.0 ≤ x ≤ 0.3 where T-phase was obtained for every specimen. For T-phase of La2Ni1−x−yCuO4+y, c-axis can be long because of large size of La, which is enough for perfect substitution of Cu2+ for Ni site although [CuO6] octahedron is prolonged along c-axis direction due to Jahn–Teller effect. With decreasing ionic radius of Ln, the c-axis systematically decreased. It was prospected that Cu solution limit appeared for T-phase of Ln2Ni1−xCuO4+x other than Ln=La because shorter c-axis due to smaller Ln limited concentration of [CuO6] octahedron with prolonged bond along c-axis direction. For the specimens with Cu content more than solution limit, [CuO6] sheet was generated by removal of apical oxide ion due to short c-axis, resulting in formation of T'-phase as second phase. This prospect agreed with decrease of range of Cu content, where single T-phase was obtained, with decreasing Ln size shown in Fig. 12(a).

4. Conclusion

The dependence of crystal structure of Ln2Ni1−xCuO4+δ on the Cu content at room temperature, along with various types of Ln was investigated. The crystal structure of La2Ni1−xCuO4+δ was so-called T-phase with the K2NiF4 type structure, regardless of the Cu content. The crystal structures of Pr2Ni1−xCuO4+δ were T-phase and T'-phase with ionic radius between 1.15 and 1.21 Å.

Fig. 12. Dependence of the obtained phases and crystal structure of Ln2Ni1−xCuO4+δ in terms of (a) ionic radius of Ln and Cu content, and (b) tolerance factor and Cu content. The results reported by Manthiram et al.39 are overlapped for comparison.
