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Doctoral Dissertation

Studies on Color Tone Control from Yellow to Red in Environmentally Friendly Inorganic Pigments via Adjustment of Crystal Structure Distortion

(優環境型無機顔料の結晶構造歪み調整による
黄色から赤色への色調制御に関する研究)

Yo Shimura

January 2026

Division of Applied Chemistry
Graduate School of Engineering
The University of Osaka

Preface

The study in this thesis has been carried out under direct supervision of Emeritus Professor Dr. Nobuhito Imanaka and Associate Professor Dr. Shinji Tamura at the Division of Applied Chemistry, Graduate School of Engineering, The University of Osaka.

The objective of this thesis is to achieve systematic color control of nontoxic inorganic pigments within the yellow–orange–red spectrum by intentionally distorting the crystal structure of harmless inorganic compounds, and to elucidate the mechanism governing these color changes.

The author hopes that the results and insights gained from this study will contribute to systematizing design guidelines for novel environmentally friendly inorganic pigments and provide some benefits toward the development and practical application of these new materials.

Yo Shimura

Division of Applied Chemistry
Graduate School of Engineering,
The University of Osaka,
2-1 Yamadaoka, Suita,
Osaka 565-0871,
JAPAN

January 2026

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General Introduction

Pigments are opaque powders that are insoluble or only sparingly soluble in water, oils, alcohols, and other organic solvents. Together with dyes, they serve as indispensable coloring materials that enrich various aspects of daily life. Unlike dyes, pigments adhere to material surfaces in particle form through the action of a binder or disperse within media such as resins. The origin of pigments can be traced back to prehistoric times. Evidence from the Chauvet Cave—one of the oldest known cave art sites, dating to approximately 35,000 years ago—indicates that red earth was mined or processed for use as body decoration. Similarly, the Lascaux Cave paintings, created about 20,000 years ago, demonstrate the use of ochre (red/yellow), manganese oxides (brown/black), and calcite (white). In the Altamira Cave paintings, produced around 18,000 years ago, hematite (iron oxide, red) was used prominently.

Around 3000 BCE, synthetic pigments first appeared, particularly in ancient Egypt, where materials such as Egyptian blue ($\text{CaO} \cdot \text{CuO} \cdot 4\text{SiO}_2$) and white lead ($\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) were produced from natural minerals and even exported abroad. From the 5th to the 15th century, pigment diversity increased markedly, featuring materials such as realgar (As_2S_2 , yellow), red lead (Pb_3O_4 , red), ultramarine ($\text{Na}_{(6-8)}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{(2-4)}$, blue), and lake pigments made by insolubilizing dyes. By the 17th century, advances in science and technology dramatically improved pigment manufacturing, resulting in large-scale production. In 1704, “Prussian blue” ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), a deep blue pigment with strong tinting strength, was discovered and became the first modern synthetic pigment. From the 18th to the 19th century, the growth of the chemical industry led to the development of numerous synthetic pigments with vivid colors, including lead chromate (PbCrO_4 , yellow) and cobalt blue ($\text{CoO} \cdot n\text{Al}_2\text{O}_3$, blue). Concurrently, the rise of organic chemistry spurred the development of organic pigments, whose diversity expanded rapidly during the 20th century and continues to grow today [1–3].

Pigments are generally classified into three categories: “coloring pigments,” which impart color

and hiding power; “extender pigments,” which adjust coating hardness and viscosity while increasing paint volume; and “glitter pigments,” which add decorative gloss. Coloring pigments, which directly produce color, are further divided into organic and inorganic types [1]. Their color arises from the selective absorption of visible light; the perceived color corresponds to the complementary color of the absorbed wavelength. Table G1 shows the relationship between light wavelength, color, and its complementary color. For example, preferential absorption in the blue region yields a yellow appearance, whereas absorption in the green region produces a purple-red appearance.

Table G1 The relationship between the absorbed light and complementary color

light	Purple	Blue	Green blue	Blue green	Green	Yellow green	Yellow	Orange	Red	Purple red
wavelength (nm)	380	435	480	490	500	560	580	595	605	750
	λ	λ	λ	λ	λ	λ	λ	λ	λ	λ
	435	480	490	500	560	580	595	605	750	780
complementary color	Yellow green	Yellow	Orange	Red	Purple red	Purple	Blue	Green blue	Blue green	Green

Most organic pigments exhibit color through visible-light absorption originating from π - π^* electronic transitions between the HOMO and LUMO within conjugated molecular systems composed of alternating double bonds and chromophoric substituents. Because this absorption wavelength can be tuned relatively easily by modifying molecular π -conjugation, organic pigments typically show vivid color and a broad range of hues. However, their organic molecular structures are inherently susceptible to degradation via light, heat, and chemicals, limiting their use in applications requiring durability. Even highly stable condensed polycyclic organic pigments—such as perylene and quinacridone types—are prohibitively expensive due to complex synthetic processes [4].

In contrast, inorganic pigments generally exhibit lower chroma but possess superior hiding power, weather resistance, and thermal stability. Consequently, they are widely used not only in paints, inks, and plastics but also in outdoor structures and high-temperature applications such as ceramic glazes

[5, 6]. Indeed, over 90% of pigments currently used worldwide are inorganic [7], underscoring their importance.

Representative inorganic pigments include red lead (Pb_3O_4), cadmium-based pigments ($\text{CdS} \cdot \text{CdSe}$, red ~ orange ~ yellow), lead chromate (PbCrO_4 , yellow), cobalt blue ($\text{CoO} \cdot n\text{Al}_2\text{O}_3$), and cobalt green ($\text{CoO} \cdot \text{ZnO}$), all valued for their vivid coloration and widespread industrial utility [5,8]. However, these materials contain toxic heavy metals such as Pb, Cd, Se, Cr^{6+} , and Co, which pose significant risks to human health and the environment. Their use is therefore restricted by international regulations such as the PRTR Act, the RoHS Directive, and the REACH Regulation [9].

Non-toxic inorganic pigments—such as iron oxides (Fe_2O_3 , red), Prussian blue ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, blue), viridian ($\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, green), and bismuth vanadate (BiVO_4 , yellow)—remain in commercial use today. However, compared with hazardous heavy-metal pigments, these alternatives often lack sufficient chroma, hiding power, and thermal stability. Accordingly, global research efforts are underway to develop safe inorganic pigments with vivid colors, including red [10–21], orange [14–17, 22–27], yellow [16–21, 25–33], blue [34–42], and green [43–46] materials. Despite these efforts, no non-toxic pigment has yet achieved coloristic performance comparable to existing heavy-metal-based pigments. As a result, while optimization of particle morphology, purity, and dispersibility has advanced, the development of entirely new pigment materials has long remained stagnant.

The fundamental mechanism of color development in pigments helps explain why heavy metals often produce strong and vivid coloration in inorganic pigments. Pigment coloration is governed mainly by three parameters: hue, which specifies color type; brightness, which describes color lightness; and chroma, which represents color intensity or vividness. While brightness depends largely on powder characteristics such as particle size, shape, and surface roughness, hue and chroma—critical factors for vividness—are determined predominantly by the electronic structure of the constituent material, including oxidation state and electron configuration [47–49]. Visible-light absorption at specific wavelengths arises from electronic transitions between energy levels within the material. Consequently, inorganic compounds containing electron-rich heavy elements often show strong and

sharp absorption bands in the visible region, leading to vivid coloration. However, the electronic structure of an inorganic compound is influenced not only by its elemental composition but also by its crystal structure. Therefore, even compounds composed solely of harmless elements could, in principle, be engineered to exhibit vivid color by intentionally modifying their crystal structures—particularly metal–oxygen bond lengths and local coordination environments.

Guided by this concept, the present thesis focuses on the relationship between crystal structure and color development in inorganic compounds to design new environmentally friendly inorganic pigments. Particular emphasis is placed on warm-toned pigments (yellow, orange, red), which are both highly visible and in strong industrial demand. By intentionally distorting interatomic distances and local coordination structures around chromophoric units, the electronic states were modulated, enabling systematic tuning of color across the yellow–orange–red spectrum.

Furthermore, pigment coloration is inherently multifactorial, making it difficult to attribute color development to a single cause. Consequently, historically, pigment development has prioritized improving coloration performance, with limited effort toward understanding the underlying mechanisms. While achieving vivid color is essential for industrial application, elucidating the mechanisms governing color formation is equally important for accelerating next-generation materials design. Accordingly, this thesis also aims to clarify the color-forming mechanisms of the developed materials through comprehensive characterization and analysis of factors contributing to improved optical properties and coloration.

The thesis is organized into three chapters.

Chapter 1 focuses on developing a novel environmentally friendly inorganic yellow pigment based on the foolite-type compound SnNb_2O_6 . This material exhibits a relatively narrow bandgap and an electronic structure comparable to commercial yellow pigments such as PbCrO_4 and BiVO_4 . To modulate the bandgap and shift the absorption edge, partial substitution of Nb^{5+} with the smaller and lower-valence cation Ga^{3+} is introduced to generate localized lattice strain. The effects of this structural distortion on the electronic structure, visible-light absorption, and resulting color properties of

$\text{Sn}(\text{Nb}_{1-x}\text{Ga}_x)_2\text{O}_{6-\delta}$ are subsequently examined.

Chapter 2 investigates the development of an enhanced inorganic orange pigment by inducing additional absorption on the longer-wavelength side of the green–yellow region. A small amount of Mn is substituted for the octahedrally coordinated W sites in the yellow-colored triclinic LiCeW_2O_8 solid, which shows strong absorption in the yellow wavelength region. Through detailed analysis of the effects of Mn incorporation on WO_6 octahedral distortion and the resultant changes in the electronic structure, the factors governing the absorption and color characteristics of $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ are elucidated.

Chapter 3 aims to control coloration across yellow, orange, and red hues by tuning visible-light absorption derived from charge-transfer and d–d transitions through targeted distortion of local structural units. The study focuses particularly on the WO_6 chromophore within the highly symmetric perovskite-structured NaWO_3 solid. Localized distortion is introduced by partially substituting Na^+ with the smaller alkali metal Li^+ , and its influence on light absorption and coloration is examined in detail.

Finally, in the field of coloring pigments, color coordinates are quantitatively evaluated using the CIE $L^*a^*b^*$ color space, which represents all perceptible colors (Figure G1). The L^* parameter denotes lightness on an intermediate grayscale, while the a^* (red (+)–green (–)) and b^* (yellow (+)–blue (–)) parameters describe hue. From these values, the chroma parameter C ($C = (a^{*2} + b^{*2})^{1/2}$) and the hue angle H° ($H^\circ = \arctan(|b^* / a^*|)$) can be calculated. In this system, the hue angle ranges from 0° to 360° , with pure red at $H^\circ = 0^\circ$ and pure yellow at $H^\circ = 90^\circ$.

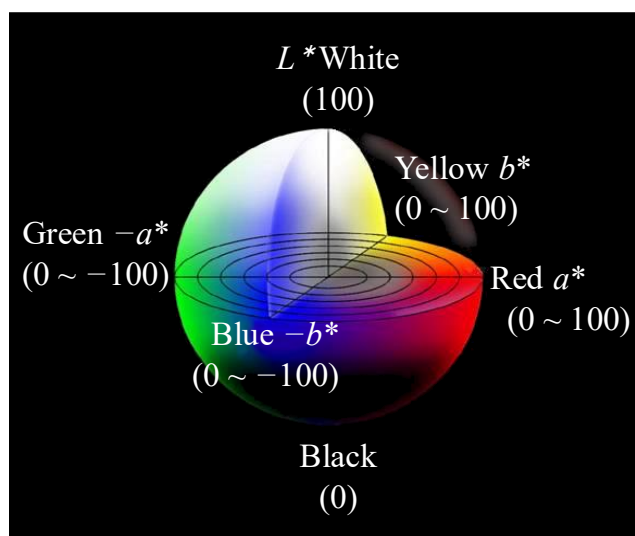


Figure G1 CIE $L^*a^*b^*$ color space.

Chapter 1

Color Tone Control from Greenish Yellow to Pure Yellow in Inorganic Yellow Pigments Focusing on Crystal Lattice Contraction

1.1 Introduction

Among various hues, yellow inorganic pigments—recognized as one of the primary and visually striking warning colors—are widely used in applications such as road signage and traffic markings, giving them particularly high industrial demand. Consequently, developing alternative pigments that provide both safety and vivid coloration is an urgent requirement.

The commercially available inorganic yellow pigments introduced previously, such as lead chromate (PbCrO_4) and bismuth vanadate (BiVO_4), possess relatively narrow bandgap energies of approximately 2.38 and 2.51 eV, respectively [28]. These bandgaps originate from electronic transitions between the valence band, comprising O 2p orbitals hybridized with the s orbitals of typical metals (Pb or Bi) with an s^2d^{10} electron configuration, and the conduction band formed by the d orbitals of transition metals (Cr or V) with a d^0 electron configuration. These transitions absorb light in the blue–green region (< 560 nm), resulting in a yellow appearance. Therefore, selecting a parent crystal exhibiting bandgap absorption at wavelengths < 560 nm—a region corresponding to blue–green light—offers a viable strategy for obtaining vivid yellow pigments composed only of environmentally benign elements.

This chapter investigates foordite-type tin diniobium oxide (SnNb_2O_6) as a base crystal for designing a novel nontoxic yellow pigment. SnNb_2O_6 consists solely of harmless elements and exhibits an electronic structure analogous to PbCrO_4 and BiVO_4 . The compound absorbs light below 530 nm owing to bandgap transitions between hybridized Sn 5s–O 2p orbitals and Nb 4d orbitals [50]. However, its relatively weak absorption in the green region (500–560 nm) produces a slightly greenish-

yellow color.

To address this limitation, attention was directed toward the dependence of bandgap energy on interatomic distances within the crystal lattice. Local structural strain in a crystal—arising from changes in interatomic distances—modifies the overlap between atomic orbitals and thus the degree of orbital hybridization [10, 11, 28]. Such changes influence the bandwidths of the valence and conduction bands. Band broadening typically narrows the bandgap, shifting the absorption edge toward longer wavelengths, i.e., lower energies. Therefore, inducing controlled lattice distortion in SnNb_2O_6 is expected to enhance green-light absorption, thereby yielding a purer yellow hue.

Based on this concept, the SnNb_2O_6 lattice was intentionally distorted by partially substituting Nb^{5+} sites (ionic radius 0.064 nm, CN = 6) [51] with smaller and lower-valent Ga^{3+} ions (0.062 nm, CN = 6) [51]. The resulting changes in bandgap energy and their influence on the optical and colorimetric properties of $\text{Sn}(\text{Nb}_{1-x}\text{Ga}_x)_2\text{O}_{6-\delta}$ were systematically investigated.

1.2 Experimental procedure

$\text{Sn}(\text{Nb}_{1-x}\text{Ga}_x)_2\text{O}_{6-\delta}$ ($0 \leq x \leq 0.10$) powders were synthesized by a conventional solid-state reaction. Stoichiometric amounts of SnO , Nb_2O_5 , and Ga_2O_3 were mixed in an agate mortar, and the homogeneous mixture was calcined at 900 °C for 6 h at a heating rate of 200 °C·h⁻¹ under a flowing 2% H_2 –98% Ar atmosphere.

Phase identification was carried out using X-ray powder diffraction (XRD; SmartLab, Rigaku) with Cu K α radiation (40 kV, 30 mA) over the 2θ range of 10–70° with a step size of 0.02°. UV–visible diffuse reflectance spectra were recorded using a UV–vis spectrophotometer (UV-2600, Shimadzu) with BaSO_4 as the reference. Colorimetric properties were evaluated in the CIE $L^*a^*b^*$ color space using a colorimeter (CR-400, Konica Minolta). Optical bandgap energies were estimated from absorption edges using the Kubelka–Munk function,

$$f(R) = (1 - R)^2 / 2R,$$

followed by Tauc analysis,

$$(h\nu f(R))^2 = A(h\nu - E_g),$$

where R is reflectance, h is Planck's constant, ν is frequency, and A is a proportionality constant [52, 53]. Particle morphology was observed by scanning electron microscopy (SEM; JCM-6000Plus, JEOL), and average particle sizes were determined from measurements of 200 particles in the SEM images.

1.3 Results and discussion

Figure 1.1 shows the XRD patterns of $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.20$). Samples with $x \leq 0.14$ were indexed to the monoclinic SnNb_2O_6 -type phase, whereas the $x = 0.20$ sample exhibited additional peaks corresponding to metallic Sn. Because the ionic radius of Sn^{2+} (0.102 nm, CN = 6 (estimated)) [53, 54] is much larger than that of Ga^{3+} (0.062 nm) [51] and the Sn^{2+} site possesses a lone pair with strong electrostatic repulsion, incorporation of Ga^{3+} into Sn^{2+} sites is energetically unfavorable. Thus, the solubility limit of Ga^{3+} in the Nb^{5+} sites of SnNb_2O_6 is estimated to be around $x = 0.14$.

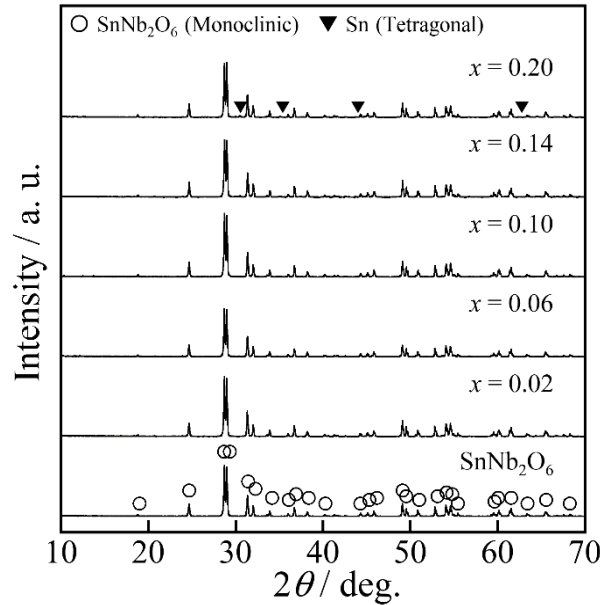


Figure 1.1 XRD patterns of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.20$) samples.

Figure 1.2 presents the UV-vis diffuse reflectance spectra of single-phase $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$). All samples exhibited strong absorption below 530 nm and selectively high reflectance above 530 nm, corresponding to the yellow region (580–595 nm). Absorption in this region arises from bandgap transitions between hybridized Sn 5s–O 2p valence bands and Nb 4d conduction bands [50]. As Ga^{3+} content increased, the absorption edge shifted to longer wavelengths and reflectance in the green region (approximately 500–530 nm) decreased, indicating enhanced green-light absorption. This trend is attributed to lattice distortion induced by Ga^{3+} substitution. Incorporation of smaller Ga^{3+} ions shortens (Nb,Ga)–O bond lengths while concurrently increasing Sn–O distances, widening the valence-band width and reducing the bandgap, thereby red-shifting the absorption edge.

In addition, at wavelengths above 530 nm, which includes the yellow color region (580–595 nm), the reflectance of the single-phase Ga^{3+} -doped sample decreased with increasing Ga^{3+} concentration (x), and the samples with $x = 0.02$ and 0.06 exhibited higher reflectance than those with $x = 0$ at this region. Degree of visible light reflectance in pigments, that is, brightness of the hue, is known to be influenced by powder characteristics such as particle size and particle shape, as mentioned in the general introduction. Therefore, to investigate the effect of morphology on the reflectance spectrum, the prepared samples were confirmed by SEM. Figure 1.3 displays the SEM images of the single-phase $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples, and Table 1.1 lists the average particle size defined by the

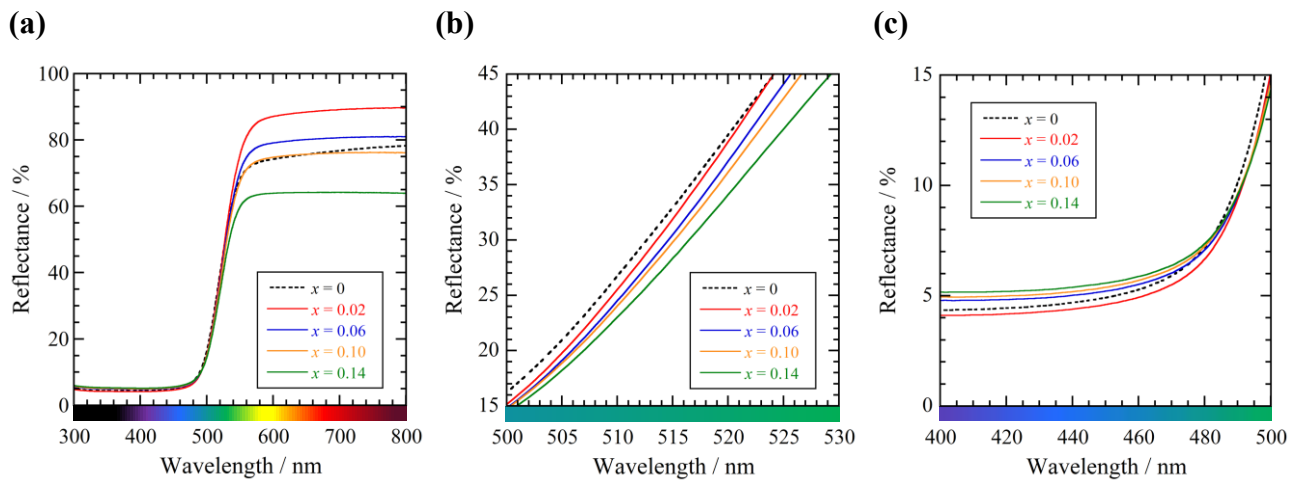


Figure 1.2 (a) UV-vis reflectance spectra and (b) its magnified view in the range from 500 to 530 nm and (c) from 400 to 500 nm for the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples.

major axis of 200 primary particles. SEM images and average particle sizes reveal systematic morphology changes with Ga^{3+} content. Samples with $x \leq 0.06$ exhibited cube-like particles, whereas those with $x \geq 0.10$ showed predominantly rod-like morphologies, with increasing aspect ratio as Ga^{3+} concentration increased. The average particle size decreased slightly at $x = 0.02$ but increased for $x > 0.02$. These morphology changes correlate well with anisotropic lattice contraction.

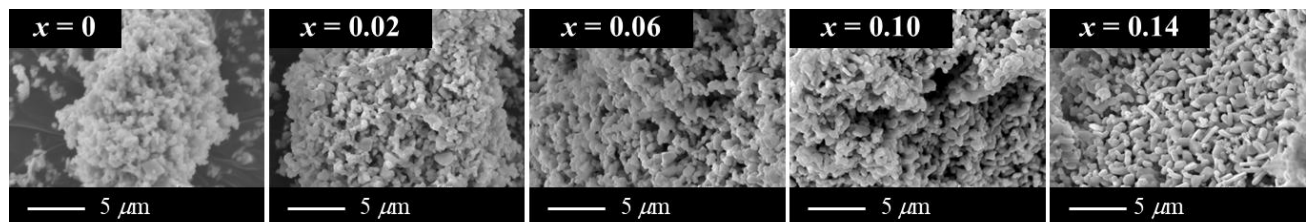


Figure 1.3 SEM images of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples.

Table 1.1 The average particle sizes of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples	
samples	average particle sizes (μm)
SnNb_2O_6	0.98 ± 0.02
$\text{SnNb}_{0.98}\text{Ga}_{0.02}\text{O}_{6-\delta}$	0.92 ± 0.01
$\text{SnNb}_{0.94}\text{Ga}_{0.06}\text{O}_{6-\delta}$	0.94 ± 0.02
$\text{SnNb}_{0.90}\text{Ga}_{0.10}\text{O}_{6-\delta}$	0.99 ± 0.02
$\text{SnNb}_{0.86}\text{Ga}_{0.14}\text{O}_{6-\delta}$	1.19 ± 0.02

Figures 1.4 and 1.5 show the SnNb_2O_6 crystal structure together with a schematic diagram of the SnO_4 unit and the lattice parameters a , b , and c for the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples. While the lattice parameter b decreased almost monotonically with increasing x , distinct discontinuities were observed around $x = 0.06$ for the lattice parameters a and c . These anisotropic changes likely arise from the unique crystal structure of foordite-type SnNb_2O_6 . Highly symmetric crystal systems, such as cubic structures, generally exhibit isotropic lattice parameter variation upon partial elemental substitution; however, lower-symmetry systems frequently undergo anisotropic changes that alter crystal shape. This tendency becomes particularly pronounced in crystals containing distorted polyhedral units. As illustrated in Figure 1.4 (b), the SnNb_2O_6 crystal structure consists of distorted square-pyramidal SnO_4 units oriented along the b -axis. Substitution of smaller Ga^{3+} ions for Nb^{5+}

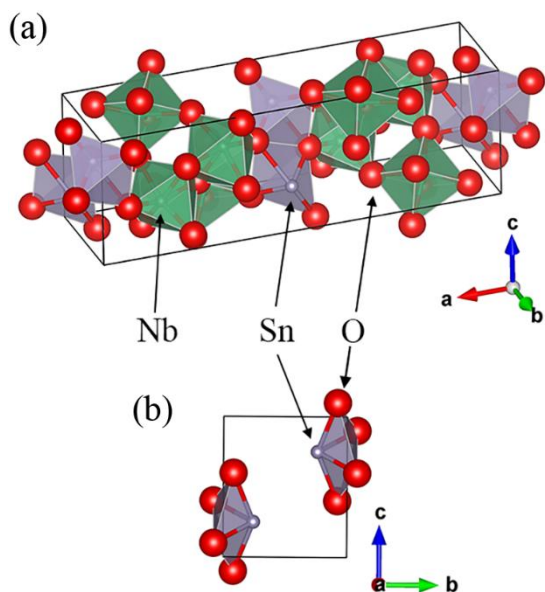


Figure 1.4 (a) Crystal structure of SnNb_2O_6 and (b) schematic diagram of SnO_4 units of the SnNb_2O_6 .

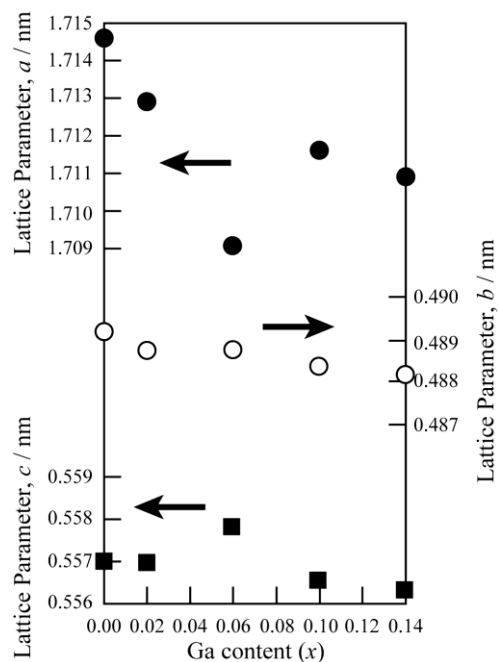


Figure 1.5 Lattice parameters, a (●), b (○), c (■), of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) samples.

shortens the (Nb,Ga)–O distances and leads to overall lattice contraction. Correspondingly, the Sn–Sn separation—directly related to the b lattice constant—likely decreases along the b -axis, where no bridging oxygen atoms are present between Sn sites. However, shortening of the (Nb,Ga)–O bonds can also distort the SnO_4 square pyramid due to repulsion between the non-bonding electron pairs of Sn^{2+} projected along the b -axis. As a result, the structural strain associated with the SnO_4 pyramids reaches a maximum near $x = 0.06$, giving rise to the observed discontinuity in lattice constants. Such anisotropic lattice distortions originating from the SnO_4 units also influence particle morphology.

This interpretation is consistent with the reflectance behavior at wavelengths above 530 nm. Light reflection from the material surface is strongly affected by particle morphology and size; smaller or smoother particles tend to exhibit stronger regular reflection. Therefore, the samples with $x = 0.02$ and 0.06—both having smaller grain sizes and more uniform, isotropic particle shapes—display higher and flatter reflectance above 500 nm compared with the undoped sample. In contrast, the uniform decrease in reflectance for $x = 0.10$ and 0.14 is attributed to increased scattering of regularly reflected light due to the anisotropic growth of primary particles.

Table 1.2 summarizes the color coordinates, chroma, and hue angle of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$) pigments. Partial substitution of Nb^{5+} sites with Ga^{3+} decreased greenness ($-a^*$), consistent with reduced reflectance in the green region caused by lattice distortion. However, the sample with $x = 0.14$ exhibited higher greenness ($-a^*$) than that with $x = 0.10$, despite its lowest reflectance in the 500–530 nm green region. This behavior stems from increased reflectance in the blue to near-green region below 500 nm (Fig. 1.2 (c)). The enhanced reflectance originates from weakened bandgap-transition absorption due to the reduced amounts of O^{2-} and Nb^{5+} —the ions that constitute the valence and conduction bands—as a result of Ga^{3+} substitution and accompanying charge compensation. Furthermore, the samples with $x = 0.02$ and 0.06 showed increased yellowness (b^*), attributed to enhanced reflectance in the yellow region caused by smaller particle size. Among all samples, $\text{SnNb}_{1.98}\text{Ga}_{0.02}\text{O}_{6-\delta}$ exhibited the highest yellowness ($b^* = 90.0$) and a hue angle ($H^\circ = 90.6$) closest to pure yellow. Compared with pristine SnNb_2O_6 ($b^* = 84.9$, $H^\circ = 92.3$), this sample displayed superior yellowness and a hue angle nearer to pure yellow, demonstrating its vivid coloration as an inorganic yellow pigment (Fig. 1.6).

It should be noted that the bandgap values (E_g) remained nearly constant for samples with $x \geq 0.06$, despite the red-shift of the absorption edge in the reflectance spectra (Fig. 1.2 (b)). This is because the optical bandgap determined using the Kubelka–Munk function is influenced not only by the intrinsic electronic structure but also by particle morphology. Consequently, changes in particle morphology masked variations in the true electronic bandgap values.

Table 1.2 The color coordinates and bandgap values of the $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.14$)

samples	L^*	a^*	b^*	C	H°	E_g (eV)
SnNb_2O_6	85.8	−3.4	84.9	84.9	92.3	2.34
$\text{SnNb}_{0.98}\text{Ga}_{0.02}\text{O}_{6-\delta}$	89.0	−0.9	90.0	90.0	90.6	2.33
$\text{SnNb}_{0.94}\text{Ga}_{0.06}\text{O}_{6-\delta}$	87.4	−0.3	88.3	88.3	90.2	2.32
$\text{SnNb}_{0.90}\text{Ga}_{0.10}\text{O}_{6-\delta}$	83.8	0.3	86.5	86.5	89.8	2.32
$\text{SnNb}_{0.86}\text{Ga}_{0.14}\text{O}_{6-\delta}$	82.6	−3.2	79.8	79.9	92.3	2.32



Figure 1.6 Photographs of $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$.

1.4 Conclusion

Novel environmentally friendly inorganic yellow pigments, $\text{SnNb}_{2-x}\text{Ga}_x\text{O}_{6-\delta}$ ($0 \leq x \leq 0.20$), were synthesized by partially substituting Nb^{5+} with smaller and lower-valent Ga^{3+} ions to modulate the bandgap-transition absorption of SnNb_2O_6 , which intrinsically exhibits a greenish-yellow color. Ga^{3+} incorporation caused both (i) a red-shift of the absorption edge through lattice distortion of hybridized Sn 5s–O 2p and Nb 4d bands, and (ii) increased reflectance due to reduced and more uniform particle sizes. As a result, $\text{SnNb}_{1.98}\text{Ga}_{0.02}\text{O}_{6-\delta}$ achieved the most vivid yellow hue, with $a^* = -0.9$, $b^* = 90.0$, and $H^\circ = 90.6$, demonstrating the effectiveness of lattice-strain engineering for color tuning in nontoxic inorganic pigments.

Chapter 2

Color Tone Control from Yellow to Orange in Inorganic Orange Pigments Focusing on Coordination Structure of Chromophore

2.1 Introduction

In Chapter 1, it was shown that lattice strain induced by partially substituting Nb^{5+} sites in SnNb_2O_6 with Ga^{3+} —a cation with a smaller ionic radius and lower valence—caused a red shift in the bandgap-transition absorption and reduced reflectance in the green region. As a result, the intrinsic greenish-yellow coloration of SnNb_2O_6 was transformed into pure yellow, yielding a vividly colored inorganic yellow pigment.

Building on these findings, the present and subsequent chapters aim to develop novel environmentally friendly inorganic orange and red pigments. Among eco-friendly inorganic pigments, research reports have concentrated predominantly on yellow systems, followed by red and then orange, resulting in an evident imbalance across the warm-color spectrum. This disparity arises because the absorption wavelength required for yellow pigments extends up to approximately 560 nm, whereas orange pigments require absorption up to ~595 nm and red pigments up to ~605 nm. As these longer wavelengths are close in energy, distinguishing absorption bands and precisely tuning color becomes more challenging. Therefore, controlling light absorption solely through structure-derived mechanisms—such as bandgap transitions described in Chapter 1—is insufficient for achieving vivid orange or red coloration.

The coloration of inorganic pigments originates not only from the overall electronic structure of the host crystal but also from localized coordination environments known as chromophores, in which oxide ions surround electron-rich central metal ions (typically transition metals). Visible-light absorption by chromophores mainly arises from electronic transitions between the d orbitals of the

central metal. Because the splitting pattern of d orbitals varies drastically depending on the coordination geometry, many transition metal ions exhibit strong coloration only when situated in specific coordination environments. Therefore, achieving a targeted color through chromophore-derived absorption requires attention not only to the chromophoric metal ion but also to its coordination structure.

One widely known chromophore capable of producing orange to red hues is octahedrally coordinated Fe^{3+} , which is used in numerous commercial products such as Bengala (Fe_2O_3 , red) and Bayferrox Orange ($\text{Fe}_2\text{O}_3\text{FeO}(\text{OH})$, orange). In Fe-based pigments, deep orange to red coloration results from charge-transfer (CT) transition absorption near ~ 560 nm and d–d transition absorption near ~ 640 nm [56, 57]. However, the d–d absorption of Fe^{3+} is so intense that even small amounts of Fe^{3+} dopant can result in dark, dull colors. To avoid this limitation, Mn was selected as an alternative chromophore in this study. In octahedral coordination, Mn^{4+} is known to exhibit d–d transition absorption in the 500–560 nm region [58–61]. Several orange and red pigments based on Mn^{4+} chromophores—such as Li_2MnO_3 -derived materials—have been reported [12, 13, 22]. However, many Mn-containing compounds still suffer from dull or near-black coloration due to excessive d–d transitions, making them relatively insensitive to coordination-environment tuning. Consequently, meaningful improvement in color development has been difficult when Mn is incorporated as a host element.

From this perspective, the present study selected a parent crystal containing octahedral sites centered on d^0 transition metals, which inherently lack d–d transitions and therefore act as non-chromophoric structural units. By doping Mn into these octahedral sites, absorption originating from MnO_6 can be intentionally introduced into the yellow-light region at tunable intensities, facilitating the development of bright orange to red hues. Based on this rationale, LiCeW_2O_8 was selected as the parent compound. Although LiCeW_2O_8 exists in multiple polymorphs, its triclinic phase contains octahedral WO_6 units (Fig. 2.1). Furthermore, although not previously reported as a pigment material, triclinic LiCeW_2O_8 is known to exhibit a yellow color [62]. Therefore, doping Mn at the W sites in triclinic

LiCeW_2O_8 is expected to shift the color toward orange without compromising chromatic vividness. This chapter describes the synthesis and characterization of optical and colorimetric properties for $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$). Changes in the electronic states of constituent elements were also investigated to clarify the effects of Mn substitution on the absorption behavior.

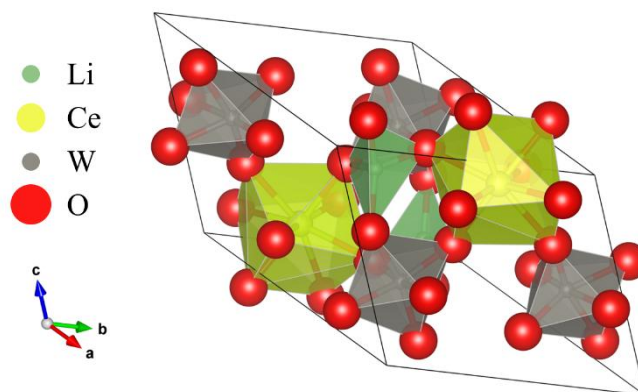


Figure 2.1 Optimal structure of triclinic LiCeW_2O_8 .

2.2 Experimental procedure

The solid solutions of $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$) were synthesized via a conventional solid-state reaction. Stoichiometric amounts of Li_2CO_3 , CeO_2 , WO_3 , and MnO_2 were mixed in an agate mortar, and the homogenized mixture was calcined at $700\text{ }^\circ\text{C}$ for 6 h at a heating rate of $200\text{ }^\circ\text{C}\cdot\text{h}^{-1}$ under a flowing 2% H_2 –98% Ar atmosphere.

Crystal structures were analyzed by X-ray powder diffraction (XRD; SmartLab, Rigaku) using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) in the 2θ range of 10 – 70° with a step size of 0.02° . Structural refinements were performed using RIETAN-FP [63]. UV–vis diffuse reflectance spectra were measured using a UV-2600 spectrophotometer (Shimadzu) with BaSO_4 as the reference. X-ray photoelectron spectroscopy (XPS; KRATOS ULTRA2, Shimadzu) was performed at room temperature using $\text{Al K}\alpha$ radiation (1486.6 eV), with binding energies referenced to the C 1s peak at 284.6 eV. Colorimetric evaluations were conducted using the CIE $L^*a^*b^*$ system with a colorimeter (CR-400, Konica-Minolta).

2.3 Results and discussion

Figure 2.2 shows the XRD patterns of $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$). All samples predominantly exhibited the triclinic LiCeW_2O_8 phase, although minor impurities of Li_2WO_4 and $\text{Ce}_2\text{W}_2\text{O}_9$ were detected, particularly for $x \geq 0.05$.

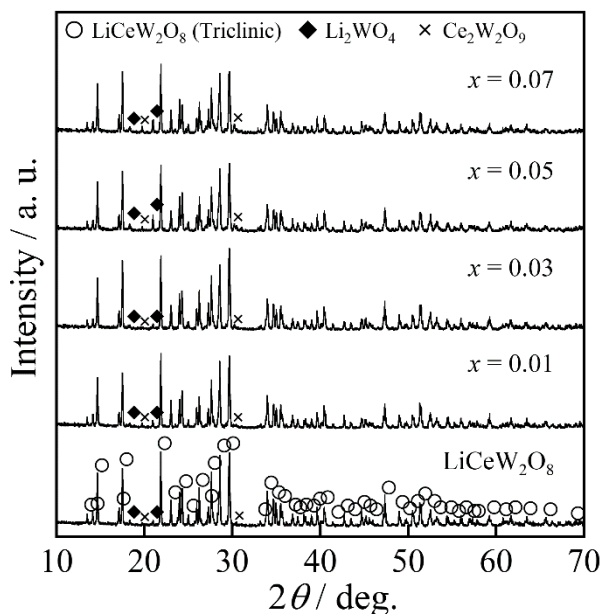


Figure 2.2 XRD patterns of the $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$) samples.

Figure 2.3 displays the UV-vis reflectance spectra of the samples. All compositions showed strong absorption below 520 nm and high reflectance above 520 nm, including the yellow-to-red region ($>$ approximately 580 nm). Absorption below 520 nm arises from the overlap of Ce^{3+} 4f-5d transitions ($<$ around 500 nm) [29] and O-to-W charge-transfer transitions ($<$ around 520 nm) [64]. For pristine LiCeW_2O_8 , reflectance above 600 nm remained near 50%, likely due to d-d transitions of $\text{W}^{(6-\delta)+}$ species occurring around 600 nm [64, 65]. However, Mn substitution decreased absorption near 600 nm while enhancing absorption near 560 nm, corresponding to d-d transitions of octahedrally coordinated $\text{Mn}^{(4-\delta)+}$ [58–61]. Thus, reflectance in the yellow region (near 580 nm) was suppressed, whereas reflectance in the red region ($>$ approximately 600 nm) increased significantly. For $x \geq 0.05$, excessive Mn-induced absorption led to reduced reflectance beyond 560 nm. The most favorable spectral characteristics were observed for $\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$.

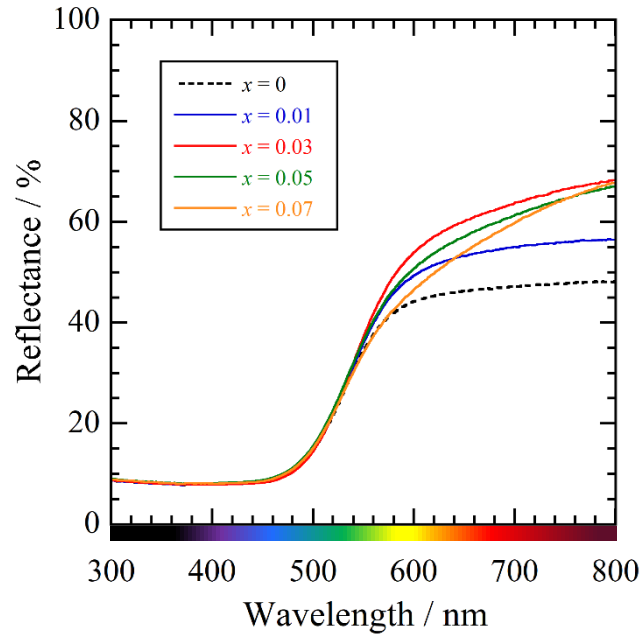


Figure 2.3 UV-vis reflectance spectra for the $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$) samples.

To elucidate the factors governing the changes in d–d absorption intensity from MO_6 units ($\text{M} = \text{W}, \text{Mn}$), XPS analysis was conducted. Figure 2.4 and Table 2.1 show the chemical-state distributions of Ce and W in $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$). In pristine LiCeW_2O_8 , approximately 61% of Ce existed as Ce^{4+} and ca. 62% of W as $\text{W}^{0/4+/5+}$ [62], indicating substantial deviation from ideal Ce^{3+} and

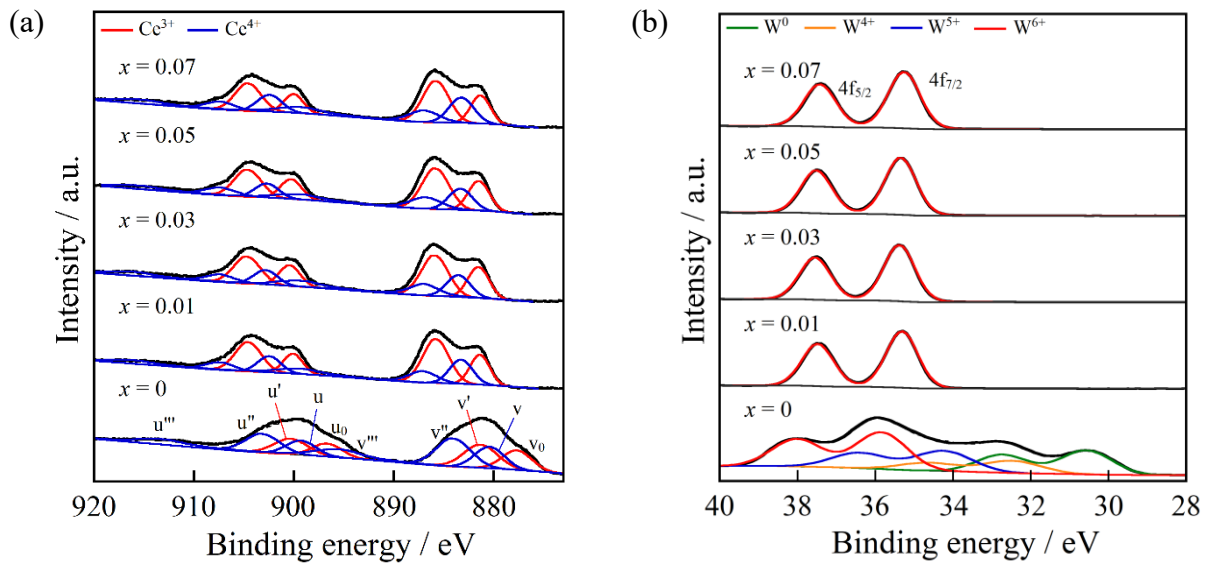


Figure 2.4 XPS spectra of (a) Ce 3d and (b) W 4f core levels for the $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$) samples.

Table 2.1 Proportion of Ce and W species in $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$) samples determined by XPS

samples	Ce Ratio (%)		W Ratio (%)			
	Ce^{3+}	Ce^{4+}	W^0	W^{4+}	W^{5+}	W^{6+}
LiCeW_2O_8	38.8	61.2	25.2	13.4	23.4	38.0
$\text{LiCeW}_{1.99}\text{Mn}_{0.01}\text{O}_{8-\delta}$	58.8	41.2	0	0	0	100
$\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$	57.5	42.5	0	0	0	100
$\text{LiCeW}_{1.95}\text{Mn}_{0.05}\text{O}_{8-\delta}$	59.2	40.8	0	0	0	100
$\text{LiCeW}_{1.93}\text{Mn}_{0.07}\text{O}_{8-\delta}$	54.1	45.9	0	0	0	100

W^{6+} states. These results suggest that electrons were localized within the Ce–O–W framework, generating electron-rich W species. Moreover, the large distortion of WO_6 units in triclinic LiCeW_2O_8 (Fig. 2.5) may relax Laporte-forbidden selection rules, allowing d–d transitions otherwise disallowed. Collectively, these characteristics contribute to the pronounced d–d absorption near 600 nm (in the red region).

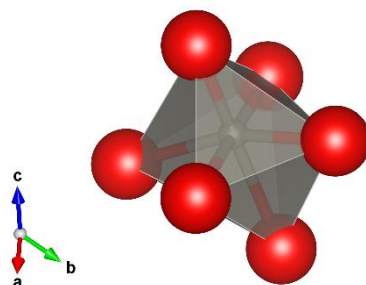


Figure 2.5 Schematic diagram of WO_6 unit of triclinic LiCeW_2O_8 structures.

Mn substitution reduced the proportion of Ce^{4+} to ~41–45% and stabilized all W species as W^{6+} (Table 2.1). Although Mn valence states could not be determined due to the low doping level, Rietveld refinement (Fig. 2.6) provided notable insights regarding oxygen occupancy. Specifically, oxygen sites coordinated to two W (Mn) sites and one Ce site showed reduced occupancy from 0.94 ($x = 0$) to 0.86 ($x = 0.03$). This decrease is attributable to charge compensation processes during substitution. Replacement of W^{6+} with lower-valence $\text{Mn}^{(4-\delta)+}$ reduces the formal valence of adjacent W sites; since

valence states of W and Ce adjust through electron transfer mediated by shared oxygen ligands (Ce^{4+} : 61% $\rightarrow$ 41–45%; W^{6+} : 38% $\rightarrow$ 100%), oxygen sites bridging these cations are considered to become energetically less stable, facilitating oxygen vacancy formation. These findings indicate that the observed decrease in W-related d–d absorption (red region) and increase in Mn-related d–d absorption (yellow region) arise not only from compositional changes but also from altered d–d transition probabilities due to charge redistribution.

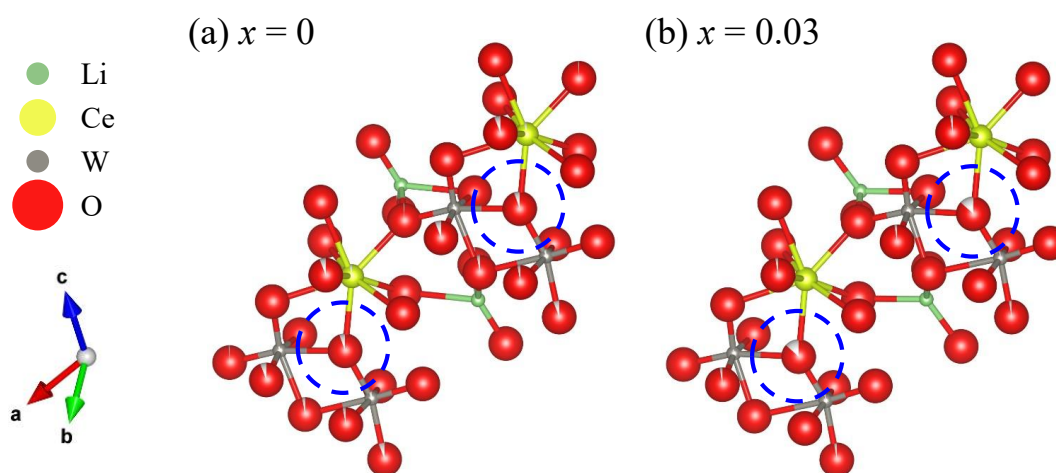


Figure 2.6 Rietveld refinement results for $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ structures (a) $x = 0$ and (b) $x = 0.03$.

Table 2.2 summarizes the colorimetric parameters for $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$). All Mn-doped samples exhibited increased redness (a^*) and decreased hue angle (H°), shifting toward more reddish coloration. This trend reflects enhanced absorption in the yellow region (around 580 nm) and reduced absorption in the red region ($>$ approximately 600 nm) due to modified MO_6 d–d transitions. For $0 \leq x \leq 0.03$, both redness (a^*) and yellowness (b^*) increased, with redness showing a more pronounced enhancement, causing the hue to approach 45° , indicative of orange coloration. For $x > 0.03$, excessive Mn-induced absorption reduced redness, yellowness, and chroma (C), resulting in duller tones. Consequently, $\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$, which exhibited the highest red-region reflectance, simultaneously showed the maximum lightness (L^*), redness, and chroma, yielding a bright orange pigment with a hue angle closest to orange ($H^\circ = 45^\circ$) (Fig. 2.7).

Table 2.2 The color coordinates of the $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$ ($0 \leq x \leq 0.07$)

samples	L^*	a^*	b^*	C	H°
LiCeW_2O_8	66.1	7.1	64.3	64.7	83.7
$\text{LiCeW}_{1.99}\text{Mn}_{0.01}\text{O}_{8-\delta}$	68.5	11.3	68.0	68.9	80.5
$\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$	72.0	14.9	73.7	75.2	78.6
$\text{LiCeW}_{1.95}\text{Mn}_{0.05}\text{O}_{8-\delta}$	69.7	13.3	68.2	69.4	78.9
$\text{LiCeW}_{1.93}\text{Mn}_{0.07}\text{O}_{8-\delta}$	66.6	11.9	64.0	65.1	79.5

**Figure 2.7** Photographs of $\text{LiCeW}_{2-x}\text{Mn}_x\text{O}_{8-\delta}$.

2.4 Conclusion

A novel environmentally friendly inorganic orange pigment was successfully developed by partially substituting octahedral W sites in yellow-colored LiCeW_2O_8 with Mn, thereby introducing Mn-derived d–d transition absorption in the yellow region. Mn doping induced characteristic changes in the electronic structure via substitution at specific coordination sites, adjusting the d–d absorptions of both W and Mn. This modification increased absorption of yellow light while selectively enhancing reflectance in the red region. As a result, $\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$ exhibited the brightest orange color, with color parameters $a^* = 14.9$, $C = 75.2$, and $H^\circ = 78.6$, due to its high reflectance above approximately 600 nm. Compared with octahedral Fe^{3+} chromophores, Mn-doped octahedral units produced sharper absorption in the yellow region and shallower absorption in the red region, demonstrating that MnO_6 is a promising chromophore for achieving bright orange pigments.

Chapter 3

Color Tone Control from Yellow to Orange and Red in Inorganic Pigments Focusing on Local Structural Distortions in the Chromophore

3.1 Introduction

In Chapter 2, orange-to-red coloration was achieved by focusing on chromophores and their coordination environments, combining appropriate chromophoric metal ions with host compounds that provide suitable dopant sites. A small amount of Mn ions—capable of inducing d–d transition absorption in the yellow-light region when adopting octahedral coordination—was introduced into the octahedral WO_6 units of triclinic LiCeW_2O_8 , which exhibits a yellow color. This partial substitution altered the electronic structure of the entire material, modifying the intensity of d–d transition absorption originating from MO_6 units ($\text{M} = \text{W}, \text{Mn}$) and shifting the color from yellow to bright orange.

As discussed in the previous chapter, the absorption regions required for orange and red pigments are extremely close (orange: < 595 nm; red: < 605 nm), necessitating finer control of the absorption range to produce distinct colors. In Chapter 1, coloration was controlled through lattice distortion of the parent crystal, while in Chapter 2 it was tuned by introducing chromophoric metal ions into specific coordination sites within the host lattice. These findings suggest that even finer color tuning may be achieved by intentionally inducing localized distortions within the chromophore units themselves—structural units smaller than the unit cell.

Such an approach has been widely explored in the development of blue–green inorganic pigments. Numerous studies have reported that local strain in the coordination environment of chromophores effectively modulates absorption characteristics and resulting colors in blue–green systems [34–39, 42, 45, 46]. In contrast, for yellow–red pigments, relatively little attention has been paid to the relationship between the local chromophore structure and color variation, and the applicability of similar concepts

has not been sufficiently discussed. Demonstrating such a correlation for yellow–red pigments would therefore provide valuable insights for future pigment design.

This chapter describes the investigation of color control based on local structural distortion using NaWO_3 as the parent compound. This complex oxide, commonly referred to as a “tungsten bronze” in electrochromic materials research, can be represented as Na_xWO_3 ($0 \leq x \leq 1$), where the Na content varies continuously [66, 67]. Na_xWO_3 exhibits visible-light absorption associated with electronic transitions between W^5 and W^{6+} species and with localized lattice distortion induced by excited electrons [66]. Its color changes systematically from blue ($x = 0.2\text{--}0.4$) to violet ($x \approx 0.6$), red ($x = 0.7$), orange ($x = 0.8$), and yellow ($x = 0.8\text{--}1.0$) depending on Na content [67]. Thus, Na_xWO_3 provides an ideal platform for investigating color variations across the yellow–red spectrum.

Furthermore, when $x \geq 0.4$, Na_xWO_3 adopts a highly symmetric cubic perovskite-type structure [66], which facilitates clearer observation of optical and color changes induced by intentional lattice distortion. Such distortion is expected to strongly affect the electron-rich WO_6 octahedra, which act as chromophores (Fig. 3.1). To introduce controlled strain into the NaWO_3 lattice and modify the coordination environment of the WO_6 units, $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) was synthesized by partially substituting Na^+ sites (0.139 nm, CN = 12 [51]) with smaller Li^+ ions (0.116 nm, CN = 12 (estimated) [54, 55]). The optical and colorimetric properties of these materials were analyzed in detail. This

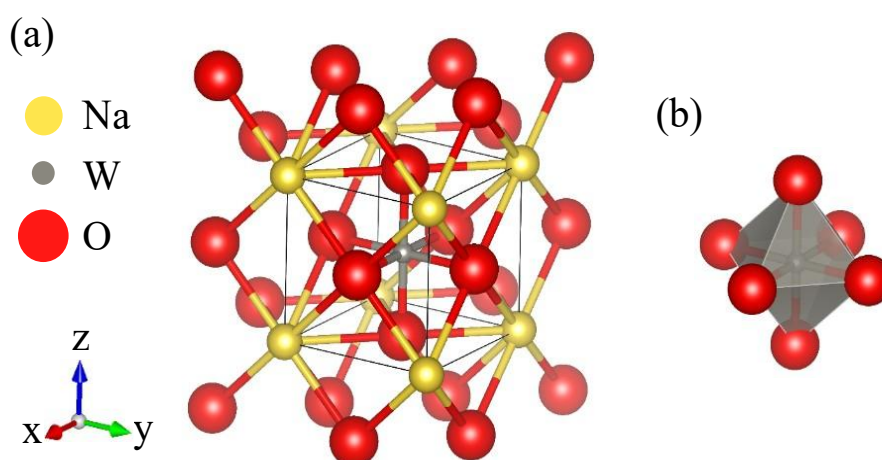


Figure 3.1 (a) Crystal structure of NaWO_3 and (b) schematic diagram of WO_6 units in the NaWO_3 .

chapter comprehensively investigates how localized structural distortions induced by Li substitution in Na_xWO_3 influence light absorption and coloration, with particular emphasis on elucidating the potential of structural control for tuning yellow–orange–red inorganic pigments.

3.2 Experimental Procedure

$\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) samples were synthesized by a conventional solid-state reaction. Stoichiometric amounts of Na_2CO_3 ($0.90 - x$ equivalents), NaH_2PO_4 (0.10 equivalents), Li_2CO_3 , and $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ were thoroughly mixed in an agate mortar. The mixture was placed on a platinum plate and calcined at 650°C for 6 h at a heating rate of $100^\circ\text{C} \cdot \text{h}^{-1}$ under a flowing 2% H_2 –98% Ar atmosphere.

Crystal structures were characterized by powder X-ray diffraction (XRD; SmartLab, Rigaku) using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 30 mA) over the 2θ range of 10 – 70° with a step size of 0.02° . Structural parameters were refined using the Rietveld method with RIETAN-FP software [63]. UV–vis diffuse reflectance spectra were recorded using a UV-2600 spectrophotometer (Shimadzu) with BaSO_4 as the reference. Optical bandgap energies were estimated from absorption edges using the Kubelka–Munk function,

$$f(R) = (1 - R)^2 / 2R$$

and Tauc plot,

$$(h\nu f(R))^2 = A(h\nu - E_g),$$

where R is reflectance, $f(R)$ is absorption ratio, h is Planck constant, ν is frequency, and A is proportionality constant [52, 53]. Colorimetric properties were evaluated in the CIE $L^*a^*b^*$ color space using a colorimeter (CR-400, Konica Minolta).

3.3 Results and Discussion

Figure 3.2 shows the XRD patterns of the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$). Samples with $x \leq 0.15$ retained a single phase of cubic NaWO_3 without detectable impurities, whereas the $x = 0.20$ sample

contained a small amount of Na_2WO_4 , indicating that the solubility limit of Li in the NaWO_3 lattice is approximately $x = 0.15$.

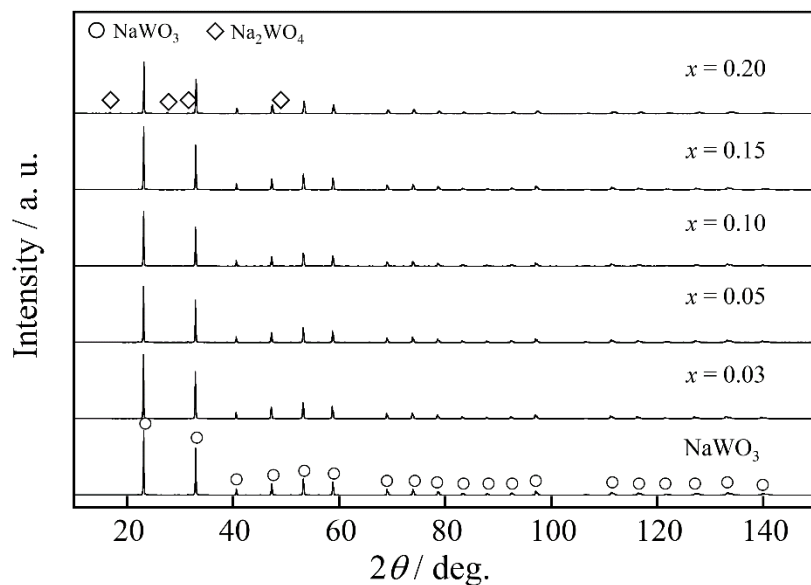


Figure 3.2 XRD patterns of the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) samples.

Figure 3.3 presents the UV-vis reflectance spectra. All samples exhibited strong absorption below 520 nm and weaker absorption centered around 600 nm, resulting in selective reflection in the yellow-red region (> 580 nm). The short-wavelength absorption originates from $\text{O} \rightarrow \text{W}$ charge-transfer

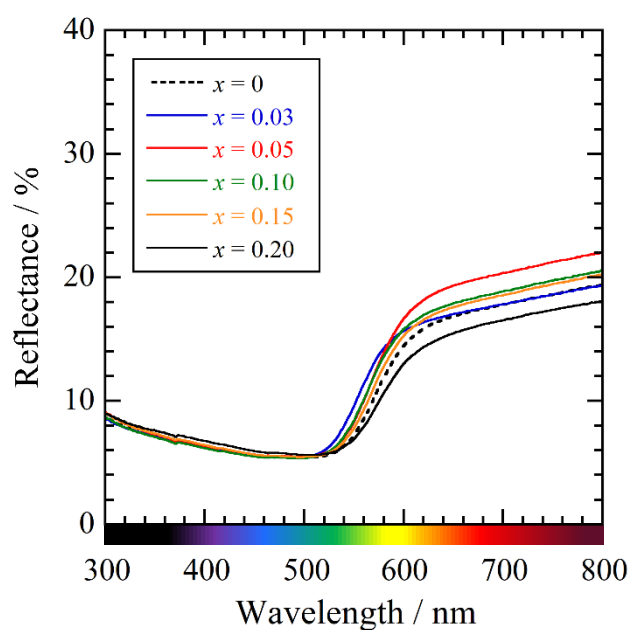


Figure 3.3 UV-vis reflectance spectra for the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) samples.

transitions [64], while the longer-wavelength absorption near 600 nm is attributed to d–d transitions of $W^{(6-\delta)+}$ species [64, 65]. The absorption behavior varied systematically with Li content. At $x = 0.03$, the charge-transfer absorption edge shifted toward shorter wavelengths, increasing reflectance in the green region (500–560 nm). For $x > 0.03$, the absorption edge shifted toward longer wavelengths. In contrast, the d–d transition absorption around 600 nm showed little change at $x = 0.03$ relative to $NaWO_3$, decreased between $x = 0.03$ and 0.05—leading to enhanced reflectance in the red region—and then increased again for $x > 0.05$, causing reflectance to decrease.

To clarify the origin of these changes, Rietveld refinements were conducted (Tables 3.1–3.3), and optical bandgap energies were estimated from Kubelka–Munk analysis (Table 3.1). Figures 3.4 and 3.5 show the lattice constant a and O–W–O bond angles of the WO_6 octahedra. Although substitution of smaller Li^+ ions for Na^+ would be expected to monotonically decrease the lattice constant, the lattice parameter initially increased from $x = 0$ to 0.03, then gradually decreased for $x > 0.03$, and finally decreased significantly at $x = 0.20$ due to phase separation.

Table 3.1 Lattice parameters and bandgap energy of the $Na_{1-x}Li_xWO_3$ ($0 \leq x \leq 0.20$)

samples	a (nm)	α (deg.)	β (deg.)	γ (deg.)	V (nm ³)	E_g (eV)
$NaWO_3$	0.38462 (0)	90.00 (0)	89.99 (0)	89.99 (0)	0.05689 (0)	2.14
$Na_{0.97}Li_{0.03}WO_3$	0.38508 (0)	90.00 (0)	90.00 (0)	89.99 (0)	0.05710 (0)	2.22
$Na_{0.95}Li_{0.05}WO_3$	0.38484 (0)	90.00 (0)	90.00 (0)	90.00 (0)	0.05699 (0)	2.17
$Na_{0.90}Li_{0.10}WO_3$	0.38477 (8)	90.00 (1)	89.99 (0)	90.00 (0)	0.05696 (2)	2.16
$Na_{0.85}Li_{0.15}WO_3$	0.38475 (7)	90.01 (0)	89.99 (0)	89.99 (0)	0.05695 (2)	2.13
$Na_{0.80}Li_{0.20}WO_3$	0.38409 (2)	89.99 (1)	89.99 (0)	89.99 (0)	0.05666 (0)	2.08

Table 3.2 Site occupancy of Na, Li, Na, W, and O for the $Na_{1-x}Li_xWO_3$ ($0 \leq x \leq 0.20$)

samples	Na site		W site		O
	Na	Li	W	Li	
$NaWO_3$	0.762 (0)	-	0.995 (6)	-	1.000 (6)
$Na_{0.97}Li_{0.03}WO_3$	0.739 (6)	0.022 (-)	0.925 (5)	0.007 (-)	0.962 (6)
$Na_{0.95}Li_{0.05}WO_3$	0.724 (6)	0.036 (-)	0.936 (6)	0.013 (-)	0.897 (6)
$Na_{0.90}Li_{0.10}WO_3$	0.686 (6)	0.068 (-)	0.919 (5)	0.031 (-)	0.909 (6)
$Na_{0.85}Li_{0.15}WO_3$	0.648 (6)	0.097 (-)	0.924 (5)	0.052 (-)	0.922 (6)
$Na_{0.80}Li_{0.20}WO_3$	0.609 (6)	0.122 (-)	0.954 (5)	0.078 (-)	0.959 (6)

Table 3.3 O–W–O angles in the x–y, y–z, and z–x planes of the WO₆ unit in the Na_{1–x}Li_xWO₃ ($0 \leq x \leq 0.20$)

samples	O–W–O(x-y flat) (deg.)	O–W–O(y-z flat) (deg.)	O–W–O(z-x flat) (deg.)
NaWO ₃	89.9983 (0)	90.0043 (0)	89.9939 (0)
Na _{0.97} Li _{0.03} WO ₃	89.9953 (0)	90.0031 (0)	90.0002 (0)
Na _{0.95} Li _{0.05} WO ₃	90.0006 (0)	90.0022 (0)	90.0008 (0)
Na _{0.90} Li _{0.10} WO ₃	90.0008 (0)	90.0077 (0)	89.9977 (0)
Na _{0.85} Li _{0.15} WO ₃	89.9971 (0)	90.0164 (0)	89.9923 (0)
Na _{0.80} Li _{0.20} WO ₃	89.9944 (0)	89.9965 (0)	89.9964 (0)

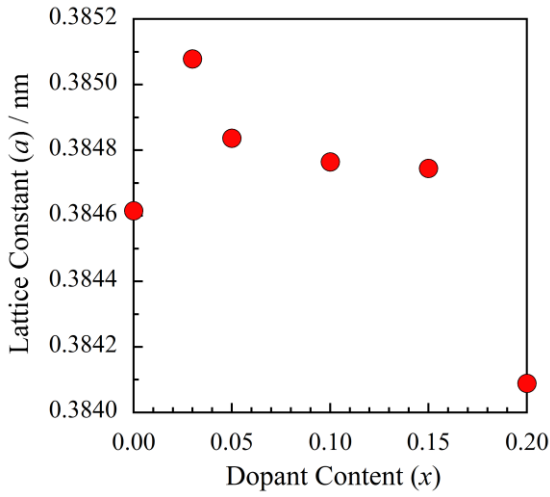


Figure 3.4 Lattice constant (*a*) of the NaWO₃ phase in Na_{1–x}Li_xWO₃ ($0 \leq x \leq 0.20$) samples.

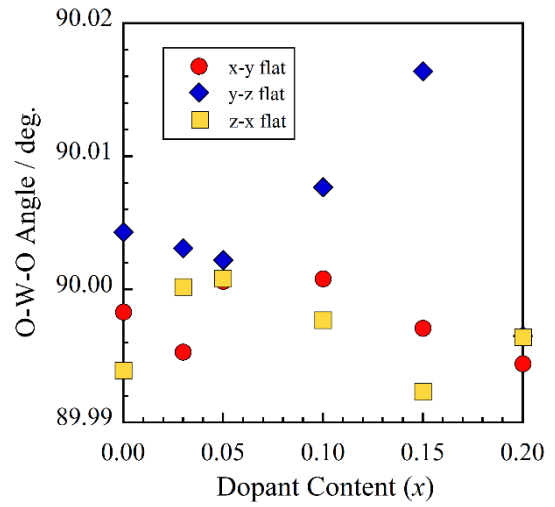


Figure 3.5 O–W–O angles in the x–y, y–z, and z–x planes of the WO₆ unit in the NaWO₃ phase of Na_{1–x}Li_xWO₃ ($0 \leq x \leq 0.20$) samples.

Site-occupancy analysis revealed that Li⁺ substituted not only Na⁺ sites but also W^{δ+} sites (W⁵⁺, 0.062 nm, CN = 6 [51]) (Table 3.2). Given the similar ionic radii of Li⁺ (0.076 nm, CN = 6 [51]) and W⁵⁺, compared to Na⁺, such substitution is reasonable, though it requires charge compensation through oxygen-vacancy formation. The lattice expansion observed at $x = 0.03$ is therefore attributed to structural relaxation accompanying substitution at W sites. At higher x , increased substitution at Na sites led to overall lattice contraction. These lattice changes correlated well with variations in the apparent bandgap energy (Table 3.1). As the lattice expands/contracts as described above, the O–W distance should also lengthen/shorten. Consequently, the blue shift of the CT transition absorption

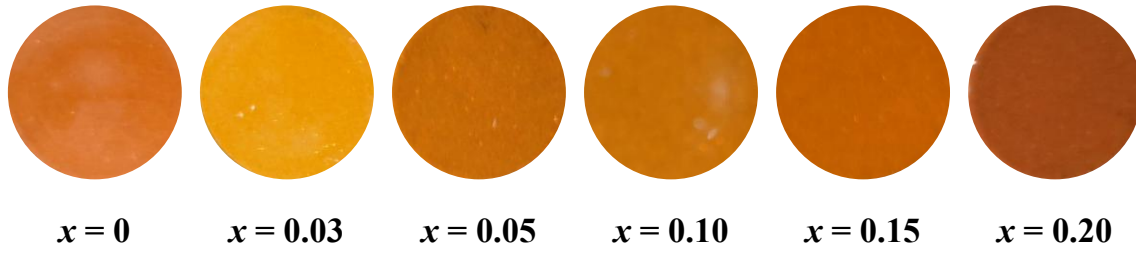
observed between $x = 0$ and 0.03, followed by a red shift at $x > 0.03$, is suggested to be based on changes in absorption energy accompanying variations in the O–W distance.

The intensity of d–d transition absorption near 600 nm was strongly influenced by the local symmetry of the WO_6 chromophores. O–W–O bond angles (Figures 3.5, Table 3.3) deviated from 90° even at $x = 0$, reflecting inherent local distortion due to excited electrons in NaWO_3 [66]. However, the introduction of Li^+ altered this angular dispersion. At $x = 0.05$, the bond angles converged near 90° , indicating maximal octahedral symmetry. Beyond $x > 0.05$, dispersion increased again, showing greater angular distortion at $x = 0.15$, and converging once more at $x = 0.20$ (mixed phase). These changes imply that Li^+ substitution affects the local structural symmetry of the chromophore, thereby modulating the intensity of the d–d transition. For highly symmetric octahedra, d–d transitions are symmetry-forbidden, hence absorption should be weakened. Therefore, the $x = 0.05$ sample of the WO_6 unit with the highest symmetry exhibited the lowest intensity of d–d transition absorption and showed the highest reflectance at wavelengths above 600 nm (the red region). Conversely, in more distorted octahedral structures (e.g., $x = 0.15$), the d–d absorption was enhanced because of the Laporte rule being relaxed. Although the reduction in distortion at $x = 0.20$ may be attributed to structural relaxation of the NaWO_3 lattice due to the formation of Na_2WO_4 , the reflectance in the red region reached its minimum. This is considered to result from absorption originating from impurity.

Table 3.4 summarizes the colorimetric parameters, and photographs of the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) are shown in Fig. 3.6. From $x = 0$ to 0.03, redness (a^*) decreased and hue angle (H°) increased toward 90° , reflecting a shift toward yellow caused by enhanced green reflectance due to an increase in bandgap energy accompanying the expansion of the crystal lattice. The $x = 0.05$ sample exhibited the highest chroma (C) with improved redness, producing a bright reddish-orange color. For $x > 0.05$, both a^* and b^* decreased and H° toward 0° , yielding darker red tones. These trends demonstrate that Li substitution induces both lattice-size changes and localized chromophore distortion, enabling continuous color tuning from yellow to red.

Table 3.4 Color coordinates of the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$)

samples	L^*	a^*	b^*	C	H°
NaWO_3	28.6	24.1	40.6	47.2	59.3
$\text{Na}_{0.97}\text{Li}_{0.03}\text{WO}_3$	32.0	15.4	42.3	45.0	70.0
$\text{Na}_{0.95}\text{Li}_{0.05}\text{WO}_3$	32.0	23.6	45.3	51.1	62.5
$\text{Na}_{0.90}\text{Li}_{0.10}\text{WO}_3$	32.1	20.2	41.3	46.0	63.9
$\text{Na}_{0.85}\text{Li}_{0.15}\text{WO}_3$	29.7	21.7	37.2	43.0	59.8

**Figure 3.6** Photographs of the $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ ($0 \leq x \leq 0.20$) pigments.

3.4 Conclusion

This study demonstrates that Li^+ substitution in NaWO_3 enables precise control of both lattice size and local structural strain within WO_6 chromophores, thereby tuning light absorption and visible color. Unit-cell expansion and contraction shifted the $\text{O} \rightarrow \text{W}$ charge-transfer absorption at shorter wavelengths, while localized distortion of the WO_6 octahedra modulated the intensity of longer-wavelength $\text{W}^{(6-\delta)+}$ d-d transitions. As a result, the color of $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ was continuously tuned from yellow to red. These findings reveal that, even for yellow–red pigments, color control can be achieved not only by adjusting lattice dimensions but also by engineering local structural strain around chromophores.

Summary

This thesis focused on the relationship between crystal lattice distortion in inorganic compounds and color development in environmentally friendly inorganic pigments, with the aim of controlling color tones from yellow to red. By partially substituting cation sites in parent crystals with different metal ions, the size of the crystal lattice and the coordination environment around chromophore sites were intentionally modified. The results revealed that controlled changes in interatomic distances, valence states of constituent elements, and bond angles around chromophores—introduced through metal substitution—induced variations in visible-light absorption associated with bandgap transitions, charge-transfer transitions, and d–d transitions. Consequently, systematic tuning of color tones from yellow to orange and red was successfully achieved.

The results and findings obtained through this study are summarized as follows:

Chapter 1

SnNb_2O_6 exhibits a greenish-yellow color due to bandgap-transition absorption. To control the yellow hue of SnNb_2O_6 , lattice distortion was introduced by partially substituting Nb^{5+} sites with Ga^{3+} ions of smaller ionic radius and lower valence. Increasing the Ga^{3+} content caused a red shift of the bandgap absorption edge, resulting in reduced reflectance in the green region and a corresponding decrease in greenness. In addition, Ga^{3+} substitution influenced particle size and morphology, which correlated with reflectance in the yellow region. Among the prepared samples, $\text{SnNb}_{1.98}\text{Ga}_{0.02}\text{O}_{6-\delta}$, characterized by the smallest particle size and a large number of isotropically grown particles, exhibited both suppressed green-light reflectance and the highest reflectance in the yellow region. As a result, this composition achieved the most vivid yellow coloration, with the highest yellowness ($b^* = 90.0$) and a hue angle ($H^\circ = 90.6$) closest to pure yellow.

Chapter 2

To achieve orange or red coloration, the fact that Mn ions adopting an octahedral coordination state generate d-d transition absorption in the yellow region was highlighted. The color adjustment from yellow to orange was investigated by partially substituting Mn for the W sites in the yellow triclinic LiCeW_2O_8 containing an octahedral WO_6 . The inherent distortion of the WO_6 units in the parent compound and electronic-state changes induced by partial substitution of W sites with lower-valent Mn ions significantly modified the d-d transition behavior. As a result, Mn-derived d-d transition absorption in the yellow region was enhanced, while W-derived d-d transition absorption in the red region was suppressed. Consequently, Mn-doped samples showed suppressed reflectance in the yellow region and enhanced reflectance in the red region. In particular, $\text{LiCeW}_{1.97}\text{Mn}_{0.03}\text{O}_{8-\delta}$ exhibited the highest chroma ($C = 75.2$) and a hue angle closest to orange ($H^\circ = 78.6$), representing a clear shift toward orange compared with the parent compound ($C = 64.7$, $H^\circ = 83.7$).

Chapter 3

Partial substitution of Na^+ sites by smaller Li^+ ions in perovskite-type NaWO_3 induced lattice distortion of the WO_6 chromophore units and enabled finer color tuning. Variation of the Li^+ content induced expansion and contraction of the NaWO_3 lattice, leading to shifts in bandgap-transition absorption, as well as changes in the local symmetry of WO_6 units, which altered the intensity of d-d transition absorption. These effects resulted in systematic changes in reflectance in the green and red regions, respectively. Consequently, continuous color tuning of $\text{Na}_{1-x}\text{Li}_x\text{WO}_3$ from yellow to red was achieved by controlling local structural strain through Li^+ substitution.

Furthermore, this study clarified fundamental relationships between visible-light absorption mechanisms and structural distortion in inorganic pigments. Changes in absorption associated with bandgap and charge-transfer transitions in the shorter-wavelength region (blue to green) originate primarily from expansion or contraction of the host crystal lattice at the unit-cell level. In contrast,

changes in absorption arising from d–d transitions in the longer-wavelength region (yellow to red) are governed by distortions in local structural units, particularly the coordination environment around chromophores. These findings suggest that efficient color control in inorganic pigments can be achieved by targeting lattice dimensions to modify blue–green absorption, while tuning local chromophore distortion is more effective for controlling yellow–red absorption. Overall, this work demonstrates that strain engineering within crystal structures provides a versatile and effective strategy for color control in environmentally friendly inorganic pigments composed solely of harmless elements, offering valuable guidelines for the design of inorganic pigments across a wide range of the visible spectrum.

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List of Publications

1. Novel Environmentally Friendly Inorganic Yellow Pigments Based on SnNb_2O_6

Yo Shimura, Nobuhito Imanaka*, and Shinji Tamura*

Journal of the Japan Society of Colour Material, **2024**, 97 (10), 324–328.

2. Novel Environmentally Friendly Inorganic Orange Pigments Based on Na_xWO_3

Yo Shimura and Shinji Tamura*

Chemistry Letters, **2025**, 54 (9), upaf175.

3. Effect of Mn Doping into the Octahedral WO_6 Unit on the Yellow-Orange Coloration of Triclinic LiCeW_2O_8

Yo Shimura and Shinji Tamura*

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