



Article New Insights into the Coloration Mechanism in Spessartines and the Impact of Munsell Neutral Grey Backgrounds

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Abstract: In this study about spessartines,13 spessartine samples with proper conditions are used for FTIR spectrum and UV-Vis spectrum tests to find the gemological characteristics and coloration mechanism. In the UV-Vis spectrum, spessartines' special color has a relationship with the absorption bands at about 460 nm and 480 nm. Based on the CIE 1976 L*a*b* colour system, we come to the conclusion that both color coordinates a* and b* control the value of chroma C*, and color coordinate b* mostly controls the hue angle h°. We also explore how the different chromogenic ions FeO_{tot} and MnO and their ratio FeO_{tot}/MnO influence spessartines' color, finding that the color of spessartine samples is influenced by both Mn and Fe. By analyzing the FTIR spectrum, we discovered that as the content of Mn decreases, and the A, C and D peaks move to the position of a longer wave, the color of spessartine samples also changes significantly. By using the standard light source D65, we find that N9.5 Neutral Grey Background is the best background to grade the color of spessartines.

Keywords: spessartine; gemology; CIE 1976 L*a*b* colour system; infrared spectrum; UV-visible spectrophotometer; background



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1. Introduction

Garnets are the birthstone of January, the symbol of both love and loyalty, and are named for their beautiful color and special shape. Garnets are an island silicate and a member of the cubical system. The chemical formula is $A_3B_2(SiO_4)_3$; divalent cations such as Fe²⁺, Mg²⁺, Mn²⁺ and Ca²⁺ occupy position A, and trivalent cations such as Cr³⁺, Fe³⁺ and Al occupy position B [1,2]. The coordination number of divalent cations on the A site is 8, forming an AO₈ cube. The coordination number of trivalent cations on the B site is 6, forming a BO₆ octahedron [3]. The coordination number of Si is 4, forming a SiO₄ tetrahedron. Garnets are a complete isomorphous series; if two ions are in a similar position, then they can easily take the place of each other. Aluminum garnet is produced in crystalline schist by regional metamorphism, or produced by magmatic crystallization as the original mineral of the rock mass.

The main chemical composition of spessartine is $Mn_3Al_2(SiO_4)_3$, in which Mn^{2+} is usually replaced by Fe^{2+} or Mg^{2+} , and Al^{3+} is often replaced by Fe^{3+} [4]. As one of the important and popular varieties of the garnet group of minerals, it is also called 'Finda stone' for its color is close to Finda soda. Their high transparence and special color make spessartines have a very high research and business value. Spessartine occurs in pegmatite and some metamorphic rocks. It was first discovered in the Spessart area of Bavaria, and Namibia [5,6], Nigeria [7], California, Brazil [8], Madagascar, Pakistan and Zambia are the world's most prolific producers. In China, we can also find beautiful spessartine in the Fujian, Guangdong and Xinjiang Altai regions.

There are transition metal elements in garnet, and the main theory of its color formation is crystal field theory. Fe²⁺ and Mn²⁺ are the main color-causing ions in purple pyrope– almandines, for Mg²⁺ is insignificant for the color of the samples [9]. As an island silicate

mineral, peridot's beautiful color is also caused by Fe^{2+} . However, it is worth noting that the almandine–skiagite's brownish yellow color is caused by the charge transfer between element ions [10]. Spessartine's color is vivid orange. There are many research studies on the color causes and spectrum about spessartines; we find that the reason why spessartines appear a beautiful orange is not only the Mn^{2+} d-d electron transition [11,12] but also the valence charge transfer transition between Fe^{2+} and Fe^{3+} [13,14]. They obviously absorb in the area of the blue-purple region, which makes the spessartines appear a bright color.

These days, the research on the color of gemstones has been playing an increasingly significant role in the field of gemological study. The CIE 1976 L*a*b* uniform color space converts the X, Y and Z tristimulus values into lightness L* and color coordinates a* and b*; color coordinates a* [15], and b* determine the chromaticity C* and h° of gemstones [16,17]. The creation of the CIE 1976 L*a*b* is conducive to the quantification of gemstones and plays an important role in many gemstone studies. Qiu et al. examined the causes of the color change in pyrope–spessartine garnets and discussed the color of garnet samples that different kinds of light source cause [18]. Yang et al. found the new coloration mechanism of violet-red pyrope–almandine [19]. Lv et al. analyzed how gemstones' composition affects their color parameters, finding the genesis of the body color of opal [20]. Studies also involve Xiuyan jade [21], tourmaline [22], alexandrite [23–25], diamond [26], tsavorite [27,28], garnet [29–31], amber [32], chrysoberyl [33], opal [34], etc.

The objective environment, especially the background brightness, is always able to influence the color of gemstones, and a reasonable selection of non-colored backgrounds is crucial for the accuracy of gemstone grading. Based on the CIE 1976 L*a*b* uniform color space, Ma et al. analyzed the color appearance of tsavorite using 27 Munsell neutral gray backgrounds, found the most proper background to classify tsavorite, and studied the effect of non-colored backgrounds on tsavorite's special green color [28]. Tang et al. found that the objective environment, which both involves neutral backgrounds and different light sources, has an obvious effect on the color of peridots [35]. Based on the CIE 1976 L*a*b*, Jiang et al. discovered the relationship between a background of neutral grey in Munsell and the color of green chrysoprase [36].

As one of the most promising colored gemstones on the market, spessartine is becoming increasingly popular. According to the CIE 1976 L*a*b*, the relationship between chroma C*, the h° and colorate coordinates a* and b* was analyzed. The chemical composition was analyzed according to ED-XRF, then we quantitatively analyzed the impact of the elements FeO_{tot} and MnO and the ratio FeO_{tot}/MnO on color parameters L*, h°. By analyzing the UV-visible spectrum of spessartines, we find the color mechanism of the samples. It is worth noting that this article is the first to studied the relationship between the peaks' position in the infrared spectrum and the color parameters of spessartines. With the increase in MnO content, the A, C and D peaks in the infrared spectrum shifted from the region of high frequency to low frequency, the color parameters L* and h° both increased, and the spessartines' color also changed from dark orange-red to bright orange. What is more, we compared the color of spessartines on 16 neutral backgrounds in order to find out the best background to classify the spessartine samples, and analyzed the influence of background on a spessartine's color.

2. Materials and Methods

2.1. Sample Description

In this study of a quantitative analysis of the color data of spessartines, we selected 13 spessartines as the research objects, which met the requirements of colorimetry experiments and the requirements of instruments in the laboratory. The 13 beautiful orange spessartine experimental samples had various shapes but were uniform in size with the carat weight of 1~3 carats. There were no visible inclusions or defects in the spessartine samples. The color contribution was relatively even, as the color between different spessartine samples gradually transitioned from orange to orange-red.

2.2. FTIR Spectroscopy

The vibration energy levels of the complex anion group, lattice (molecule) and coordination group inside the gemstone underwent transition after being irradiated by infrared light, selectively absorbing the wavelengths which corresponded to the vibrational frequency and generating energy-level transitions. The instrument type in the laboratory used to measure the spessartines' data was a Bruker Tensor 27 Fourier infrared spectrometer, and the test of spessartine samples was carried out on the fifth floor of the gemological laboratory, China University of Geosciences (Beijing). The settings of the instrument were: the power supply was 85–265 V; the power frequency was 47–65 Hz; the range was 400–4000 cm⁻¹; the resolution was 4 cm⁻¹; the scanning run time was 32 s per scan; the grating setting was 6 mm; the scanning speed was 10 Hz; the temperature was 18–35 °C; the humidity was<70%. The fingerprint of the sample was obtained by reflection method in the 400–1500 cm⁻¹ band, and the direct transmission method was used in the 1500–4000 cm⁻¹ band.

2.3. UV-Vis Spectroscopy

The valence electrons of atoms, molecules and ions or the electrons on the molecular orbitals in the gem underwent a transition between the electron energy levels after being subjected to electromagnetic radiation, resulting in an ultraviolet-visible absorption spectrum.UV-Vis absorption spectroscopy is divided into transmission and reflection methods. The test instrument of spessartine samples was a UV-3600 UV-visible spectrophotometer. The test position was the fifth floor of gem laboratory, China University of Geosciences (Beijing). The test conditions of spessartines were: the wave range was 200–900 nm for spessartines; the slit width was 2 nm for spessartines; the sampling interval was 0.5 s for spessartines; high speed. The measurement method was the reflection method.

2.4. Backgrounds

There are different kinds of lightness classifications in Munsell neutral grey backgrounds which range from 0 to 100. Spessartine's color is related to the brightness of backgrounds. Spessartines with different color parameters can also be influenced by the brightness of background to different extents.

This experiment used typical lighting box and a CIE standard illumination D65, evenly selecting 16 Munsell neutral grey color chips with different brightness levels, including N = 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 as the non-colored experimental backgrounds for this experiment.

3. Results and Discussion

3.1. Color Quantization

Color-measuring instruments are more delicate and more proper to quantify the beautiful color of spessartine samples than the naked eye. The CIE 1976 L*a*b* uniform color space owns accuracy and wide applicability, making it a widely recommended standard for color characterization. A D65 standard light source is the typical light of the sun in the northern hemisphere; therefore, it is always considered for international color assessments. According to CIE 1976 L*a*b*, we used the portable Aicolor X-Rite SP62 to take down three color parameters with a D65 light source. With the data we researched before, we also changed the L*, a* and b* of the spessartines into the chroma C* and h° of the spessartine samples. The brightness L* represents the brightness of the gem color. As the L* value changes from $L^* = 0$ to $L^* = 100$, the color changes from dark black to bright white. When the brightness value of spessartines becomes higher, the spessartines become brighter. There are many kinds of color with different intensity of gemstones, and we can use the chroma C^{*} to show this. As the C^{*} value changes from $C^* = 0$ to $C^* = 100$, the color changes from light to intense. Gemstones are usually more beautiful and vivid when the chroma C* value is bigger. The higher the chroma value, the more vivid the gemstone. The chromaticity coordinates a* and b* describe the changes between different colors, which range from -120 to +120. The results showed that $L^* \in [34.6, 55.1]$, $C^* \in [6.2, 44.6]$ and $h^{\circ} \in [22.5, 55.2]$.

To find out the relationship between color parameters, correlation analysis was used to measure the relationship and analyze the strength or weakness. The Pearson correlation coefficient is a statistical measure, which is always tested to reflect how much two values are correlated to each other on behalf of a correlation coefficient with values between -1 and +1. As the value of $|\mathbf{r}|$ becomes bigger, the correlation of spessartines becomes stronger. Assuming $|\mathbf{r}| > 0.6$, then the values of spessartines are highly correlated. As shown in Table 1, the correlation analysis results between the color values of spessartine were measured: there is an obvious correlation between chroma C*, hue angle h° and color coordinates a* and b*.

Table 1. Under the light source D65, the relationship between spessartine color parameters. Bivariate correlation between them was obvious when ** at level 0.01 (double tail).

Color Parameters	a*	b*	C*	h°
a*	1.000	0.897 **	0.958 **	0.878 **
b*	-	1.000	0.986 **	0.998 **
C*	-	-	1.000	0.976 **
h°	-	-	-	1.000

According to Pearson's correlation analysis, color coordinates a* and b* fit to the chroma C*. The relationship between C*, a* and b* is:

$$C^* = 7.44 + 1.07b^* (R^2 = 0.97)$$

$$C^* = -6.36 + 1.74a^* (R^2 = 0.91)$$

As shown in Figure 1a, the colored areas show the prediction band of spessartine samples. By analyzing the test results, we figured out that the color coordinates a* and b* are notably positively correlated to the chroma value C* ($R^2 = 0.97$, $R^2 = 0.91$, respectively). The value of the spessartines' chroma value C* becomes bigger as the color coordinates a* and b* increase. Therefore, the C* value of the spessartines is determined by both color coordinate a* and b* values.

Based on the Pearson correlation analysis, the h° of the 13 spessartines is fitted to the value b*. And as shown in Figure 1, the fitting equation is: $h^{\circ} = 19.26 + 0.96b^{*}$ ($R^{2} = 0.97$). By observing the color parameter relationship of the spessartines, the determination coefficient (R^{2}) of the spessartine samples in Figure 1b is 0.97, showing us that the color coordinate b* of the spessartine samples is highly positively related to the h° of the spessartines. The correlation between the color coordinate a* of the spessartine samples and the h° of the spessartines is smaller than that between b* and h° ; therefore, the color coordinate b* mostly manages the h° of spessartines.

3.2. UV-VIS Spectrum Analysis of Spessartine

The valence electrons of atoms, molecules and ions or the electrons on the molecular orbitals in the gem underwent a transition between the electron energy levels after being subjected to electromagnetic radiation, resulting in an uv-vis absorption spectra. However, two gemstones with the same color under the same light source may appear to have very different UV-visible spectral characteristics, because the gemstones selectively absorb the different-wavelength incident light. In gemology, the composition of gem samples can be qualitatively and quantitatively analyzed by the extent of absorption and the coverage of wavelength, so as to find the color-causing ions of gems and explore their coloration. The test method has the advantages of being fast and non-destructive. The thirteen spessartine samples' color was a relatively homogeneous orange; therefore, these spessartine samples were chosen in this paper. The UV-visible absorption spectra in the 400–700 nm of the

spessartines is shown in Figure 2. The spessartines' spectra were tested by the reflection method; different spessartines with different MnO content show different absorptions in Figure 2, which enables us to offer an analyzation of how the color of spessartine is affected by the chromogenic ion.



Figure 1. (a) Fitting analysis between a^* , b^* and C^* under D65 light source; (b) Relationship between h° and b^* .



Figure 2. UV-Vis spectrum of the spessartine.

As is shown in Figure 2, the UV-visible absorption spectrum in the 400–700 nm range of spessartines appears different. The spessartine UV-visible absorption spectrum shows that there are five obvious absorption bands. The narrow absorption peaks of Mn^{2+} are mainly around 408 nm, 460 nm and 480 nm, which is caused by the d-d electron transition of Mn^{2+} , and the reason why the spessartine samples appear a beautiful orange color is

the blue-region absorption [37]. The absorption peak of Fe^{2+} is mainly around 530 nm and 570 nm, which is due to the d-d electron transition of Fe^{2+} . Comparing C10, which has a higher content of Mn^{2+} , with C9, which has a lower content of Mn^{2+} , the former has more intense absorption at 460 nm and 480 nm in the blue region; therefore, the color of the former spessartine sample appears more orange. This result shows an obvious relationship between UV-visible absorption spectra and chemical composition. It can be seen that the area of 460 nm and 480 nm peaks increases as the content of Mn^{2+} increases, and there is also an obvious correlation with the hue angle. The absorption band of Mn^{2+} at 460 nm and 480 nm in the UV-visible absorption spectra mainly causes the beautiful orange color of spessartines, and when the absorption area of Mn^{2+} becomes larger, the color of the spessartine samples changes from orange-red to light orange.

3.3. Relationship between Fe, Mn and Color

ED-XRF is a quick method (without destruction) to detect most of the elements in spessartines. X-rays are a kind of high-energy electromagnetic radiation; when an X-ray irradiates the surface of the gemstone sample, the inner electrons of the elements contained in the sample are excited to a higher energy level or even outside the atom. At this time, the outer electrons fall into the inner layer to fill the vacant electron potential, which leads to a decrease in the overall energy of the atom, and the generated energy produces fluorescence irradiation. The atomic number of different atoms and the structure of the electron layer are different. Different atoms have characteristic X-rays; the wavelength and intensity are related to the type and content of the FeOtot and MnO, respectively. As the atomic number Z increases, the wavelength λ of X-ray fluorescence will gradually approach the short-wave direction. Therefore, by analyzing the wavelength and intensity of characteristic X-rays produced by different elements in the samples, the elemental composition and content in the samples can be qualitatively or quantitatively analyzed. In this experiment about spessartine samples, an EDX-7000 energy dispersive X-ray fluorescence spectrometer (SHIMADZU, Kyoto, Japan) was used to test the micro-area chemical components of spessartine samples. The test position was the fifth floor of the gemological lab, China University of Geosciences (Beijing). Because the spessartine samples contain the element Mg, the test atmosphere needed to be vacuumed before each test. The voltage was 15 kv or 50 kv when the measurement element was Na-Sc or Al-U; the size of the collimator was set to 3 mm regarding the size of spessartines; the test results of the spessartines are shown as oxides; the measure time of the spessartines was 100 s. Based on the CIE 1976 L*a*b* uniform color space, we tested the lightness L* and color coordinates a* and b* of 13 spessartine samples by using an X-Rite SP62 spectrophotometer. The C* and hue h° of the spessartine samples were figured out according to the formula. By sorting out the data, we found the range of percentage by weight [wt%] of the oxides in the 13 spessartine samples was w(MnO) = 28.28-36.59, $w(Al_2O_3) = 21.78-25.47$, $w(Fe_2O_3) = 0.80-4.05$, w(CaO) = 0.13-0.53. Among the detected elements, as is learned from the previous research, the beautiful orange color of spessartine samples is caused by the elements Mn and Fe. Therefore, we analyzed the relationship between FeOtot, MnO and FeOtot/MnO and the color parameters of the 13 spessartines according to the bivariate correlation analysis.

Energy dispersive X-ray fluorescence spectroscopy (EDXRF) is a rapid and nondestructive method for the detection of most elements in samples. By observing the wavelength and intensity emitted after atomic excitation, the content and type of elements can be obtained. It is worth noting that ED-XRF has a very wide range of elemental concentration analysis and is very important for the qualitative and quantitative analysis of spessartine. Based on the results of XRF, we discuss the relationship between the ratio and content of transition metal elements FeO_{tot}, FeO_{tot}/MnO, MnO and color parameter h° and L* of 13 spessartine samples by bivariate correlation analysis (Table 2). When $|\mathbf{r}| \ge 0.8$, it means that the correlation we discussed before is high.

Ratio and Content		L*	h°
FeO _{tot} /MnO	r	-0.963 **	-0.959 **
	sig	0.000	0.000
FeO _{tot}	r	-0.935 **	-0.942 **
	sig	0.000	0.000
MnO	r	0.874	0.819
	sig	0.000	0.000

Table 2. Bivariate correlation analysis between FeO_{tot}, MnO and FeO_{tot}/MnO and color parameters h° and L*; the correlation of spessartine between them was obvious when ** at level 0.01 (double tail).

As is shown in Figure 3, the ratio of transition metal elements FeO_{tot}/MnO is negatively correlated to color parameter h° and L*. When FeO_{tot}/MnO increases, the L* of the spessartine samples shows a significant decreasing trend (r = -0.963 **). The hue angle h° also decreases when FeO_{tot}/MnO increases (r = -0.959 **), and the color of the samples appears from light to dark orange. W (FeO_{tot}) is negatively correlated to color parameter h° (r = -0.942 **); as the Fe content increases, the h° decreases linearly, and the hue changes into orange-red from orange, as orange spessartine has the lowest Fe content. Fe content is also significantly negatively correlated to L* (r = -0.935 **); light spessartine has the lowest Fe content. What is more, as Mn content increases, the L* of the spessartine samples shows a significant increasing trend, as the spessartine samples are becoming light. The hue angle h° also increases when the Mn content increases, and the samples' color changes from red to orange.



Figure 3. Relationship between FeO_{tot} / MnO, FeO_{tot} , MnO and color parameters h° and L*.

As we discuss the change in the colour of the spessartine samples, we also find that the presence of the Ti^{4+} – Fe^{2+} pairs is also very important. In previous studies on the causes of diaspore–sapphire color, they found that the blue colour is related to the Ti^{4+} – Fe^{2+} closed pair [38,39]. In the spessartine samples, Ti(IV) can easily replace 2 Mn(II) in the neosilicate crystal structure, which will also lead to the beautiful and bright color of the spessartine samples.

In conclusion, the content and ratio of transition metal elements FeO_{tot} and MnO has a significant effect on the color parameters h^o and L^{*}, and spessartines with high FeO_{tot} content and low MnO content appear with a dark orange color and low lightness.

3.4. Relationship between IR Spectrum and the Chemical Composition

Vibration energy levels of the complex anion group, lattice (molecule) and coordination group inside the gemstone undergo transition after being irradiated by infrared light, absorbing the corresponding infrared light and generating in the infrared spectrum. Infrared spectroscopy can help us find out the types of functional groups and their effects. Spessartines' end-member proportions are also able to be inferred according to the functional group activity. Infrared spectroscopy has the advantages of being fast, non-destructive and accurate.

In the infrared spectrum of the spessartine samples, we detected the absorption peak of the structural water. Their peak shape and peak position are almost the same, but the peak intensity changed slightly. The results show that the sample had strong absorption peaks at 3644 cm⁻¹, 3627 cm⁻¹ and 3587 cm⁻¹, and absorption peaks at 3535 cm⁻¹, 3517 cm⁻¹ and 3486 cm⁻¹ in the low frequency region. These absorption peaks were caused by the stretching vibration of OH⁻, and there was no absorption peak caused by molecular water.

The mid-infrared region is particularly important. Figure 4 shows the infrared spectrum of the spessartine sample. The measurement results show that the peak locations of spessartine were: A: $974 \pm 4 \text{ cm}^{-1}$, C: $891 \pm 2 \text{ cm}^{-1}$, D: $867 \pm 4 \text{ cm}^{-1}$, E: $628 \pm 3 \text{ cm}^{-1}$, F: $570 \pm 2 \text{ cm}^{-1}$, G: $518 \pm 4 \text{ cm}^{-1}$, H: $480 \pm 2 \text{ cm}^{-1}$, I: $447 \pm 3 \text{ cm}^{-1}$. Peak B is considered to be merged with peak A. The absorption bands above 500 cm^{-1} were produced by the vibrations of the $[SiO_4]^{4-}$ group, and the absorption below 500 cm⁻¹ was produced by the lattice vibrations of trivalent ions or divalent ions. Among these absorption bands, Peaks A, C and D in the 800–1000 cm⁻¹ range have a relationship with the antisymmetric bending vibrations of the [SiO₄] tetrahedron, which are resulted from the triple-degeneracy splitting of v3. The G and H peaks in the 500–700 cm⁻¹ range have a relationship with the antisymmetric bending vibrations of the [SiO₄] tetrahedron, which are due to the splitting of the v2 double degeneracy or the splitting of the v4 triplet degenerate [40]. The vibration of trivalent ions in the octahedral lattice of $[BO_6]$ causes the two absorption bands H and I below 500 cm⁻¹, and the J–K absorption peaks are caused by the vibration of divalent ions. Because the volume of $[BO_6]$ is higher than $[SiO_4]$, the B-O band is weaker than the Si-O band, making the absorption in the area of the low-frequency region.

The vibration energy levels of the complex anion group, lattice (molecule) and coordination group inside the gemstone underwent transition after being irradiated by infrared light, selectively absorbing the wavelengths which correspond to the vibrational frequency and generating energy-level transitions. Mn²⁺ has a larger radius than other divalent ions and the vibrational frequency is smaller; therefore, with the increase in MnO content, the band frequency in the infrared spectrum shifted from the region of high frequency to low frequency. With the increase in MnO content from 28.27% to 36.59%, peak A moved from 977 nm to 972 nm. The D-peak also moved from 869 nm to 864 nm. Therefore, the content of MnO can be roughly compared by the peak A value of different spessartine samples.

As was discussed before, Mn content positively relates to the color parameters h° (r = 0.819 **) and L* (r = 0.874 **). When the content of Mn increases, the color parameter L* of the spessartine samples shows a significant increasing trend, as the spessartine samples are becoming light. The hue angle h° also increases when the Mn content increases, and the samples' color changes from red to orange. Therefore, with the increase in MnO content from 28.27% to 36.59%, color parameters h° and L* increased, and peak A moved from 977 nm to 972 nm and the D-peak also moved from 869 nm to 864 nm. By analyzing the peaks' position, we can not only compare the content of Mn, but can also compare the color parameters of different spessartines roughly and indicate the color of spessartines.



Figure 4. FTIR spectra of the spessartine.

3.5. Effects of the Brightness of Backgrounds on Spessartines' Special Color

The specially made color card from the brightness N0.5–N9.5, increased by a quarter of the spacing, was divided into 37 gray levels. In total, 16 kinds of non-color neutral color card were used as the background of the experiment, finding the law of the influence of the brightness of backgrounds on spessartines' special color. The Munsell non-color background was the selected Munsell brightness color card, which did not have color rendering. The study about the influence of Neutral Grey Backgrounds on spessartines' beautiful color was carried out using a solitary light source. The standard light source D65 (6504 K) is meant to represent the typical sunlight in the northern hemisphere; the colors of its distribution are very uniform and it is used as the standard light source for international color assessment. Therefore, a D65 light source was selected as the experimental light source, and 16 kinds of non-color neutral color card were used as the background of the experiment, finding the relations between the brightness of the backgrounds and the beautiful orange color of the spessartine samples.

Based on the CIE 1976 L*a*b* uniform color space, under a 6504 K fluorescent lamp and 16 backgrounds with the range level of N0.5 to N9.5, the color parameters L* (Figure 5a) and C* (Figure 5b) of 13 spessartine samples were tested three times. It can be found that the values of lightness L* and chroma C* change enormously under different Neutral Grey Backgrounds. Lightness L* increases as the Neutral Grey Backgrounds become brighter, and the difference of Lightness L* becomes more obvious. The value of chroma C* also increases gradually as the Neutral Grey Backgrounds' brightness increases, and the difference of chroma C* becomes easier to detect. As is discussed, we find that the values of lightness L* and chroma C* both change more obviously when the Neutral Grey Backgrounds become brighter, and the values also increase gradually with the increase in brightness of the backgrounds. Therefore, on a brighter Neutral Grey Background, spessartines are easier to distinguish by the naked eye.



Figure 5. Changes of chroma C^* (**a**) and lightness L^* (**b**) under 16 backgrounds. Chroma C^* and lightness L^* of 13 spessartine samples are shown in the boxes.

The range level of Neutral Grey Backgrounds is N0.5 to N9.5, and the color of spessartines corresponds to the lightness of the backgrounds. The spessartines with different lightness L* and chroma C* can also be affected by the Neutral Grey Backgrounds in different ways. As Figure 6 shows, we chose three spessartines, C11, C4 and C8. C11 has the highest color parameter C*, and background changes make its chroma C* the easiest to produce. As shown in Figure 6a, $|\Delta C^*| \max = 41.32$. C8 has the lowest lightness L* and the change in its lightness L* is the smallest, as shown in Figure 6b, $|\Delta L^*| \min = 8.64$.



Figure 6. (a) Chroma C* change in three samples with different color under different backgrounds.(b) lightness L* change in three samples with different color under different backgrounds.

As is discussed, the value of the spessartine's lightness L* and chroma C* change as the Neutral Grey Background becomes brighter. It can also be found that the change in lightness L* and chroma C* become more obvious as the Neutral Grey Background changes to higher range level. All in all, a bright background would be proper if we want to find a background to grade the color of spessartines.

4. Conclusions

- (1) By discussing the correlation analysis results between the hue angle h° and the chroma C* of spessartine, we find that the color coordinate b* controls the h° of spessartines more than a*, and the chroma C* is controlled by both the variation in the color coordinate b* and the color coordinate a*.
- (2) The UV-Vis spectrum shows that the absorption band of Mn²⁺ at 460 nm and 480 nm causes the special color of the samples; when the area of 460 nm and 480 nm absorption increased, the color of the 13 spessartine samples changed from orange-red to orange. The infrared spectra shows that, with the increase in MnO content, the A, C and D peaks in the infrared spectrum shifted from the region of high frequency to low frequency. By analyzing the peaks' position, we can not only compare the content of Mn, but can also compare color parameters of different spessartines roughly and indicate the color of the spessartines.
- (3) Based on the results of ED-XRF, we find that transition metal elements FeO_{tot} and MnO and the ratio of transition metal elements FeO_{tot}/MnO have a significant effect on the color parameters h° and L*. Spessartines with high FeO_{tot} content and low MnO content appear with a dark orange color and low lightness.
- (4) With the change in backgrounds, the lightness L* and chroma C* of spessartines are both affected obviously. Under the standard light source D65, by comparing three samples with different color parameters, we find that the range of lightness L* and chroma C* widens as the Neutral Grey Background becomes brighter, and the higher the values are, the larger the variations shown. N9.5 Neutral Grey Background is the best background for color grading.

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