SPECTROSCOPIC ANALYSIS OF DENTAL GLASS-CERAMICS

BY

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ABSTRACT

Over the years there have been significant improvements in the field of restorative dentistry, and yet the process of shade selection remains primitive. A number of materials have been developed for the restoration and replacement of teeth, but none of them have demonstrated efficiency in restoring the tooth to its natural color. The demand for a more esthetic dental restoration is increasing in the recent years. The usual method of shade matching using shade guides is subjective and hence is insufficient to meet this demand. To reduce the subjectivity of color matching, derivation of a simple figure of merit is imperative and to achieve this, colorimetric data of dental glass-ceramics should be deduced.

The main objective of this study was to spectroscopically evaluate glass-ceramic samples proposed for use in commercially available shade guides. A spectrophotometer was used to measure diffuse reflectance, specular reflectance and diffuse transmittance of all the samples. A fluorimeter was used to examine the fluorescence of the samples. Results from the glass-ceramic samples were compared to the results obtained from conducting similar experiments on natural teeth. Effects of heat, hydration, and UV exposure were also quantified. To obtain the crystal phases and the crystal morphology, XRD and TEM analysis of the samples were performed. A DSC analysis was also performed on the samples to obtain their temperature of crystallization.

The spectra show the similarity in the curves obtained for the samples and natural teeth. A figure of merit developed based on the equations obtained for the curves and the ABBE number dispersion factor was inconsistent and hence the ΔE values obtained were studied and evaluated. This figure of merit did not include the fluorescence data as fluorescence could be reproduced by incorporating rare earth ions into the composition of the glass-ceramics. The figure of merit developed would reduce the subjectivity involved in the shade selection and communication process.
I INTRODUCTION

Color is one of the most difficult words to define. The Merriam-Webster dictionary defines color as “a phenomenon of light (as red, brown, pink, or gray) or visual perception that enables one to differentiate otherwise identical objects.”1 The Oxford dictionary defines color as “the quality or attribute in virtue of which objects present different appearances to the eye, when considered with regard only to the kind of light reflected from their surfaces.”2 Though it sounds complicated, the definition cannot get any simpler. The great physicist Tyndall described in his book The Notes on Light that “color is due to the extinction of certain constituents of white light within the body, the remaining constituents which return to the eye imparting to the body its color.”

Esthetics is a branch of philosophy concerned with the essence and perception of beauty and ugliness.3 Though the German philosopher Baumgarten coined the term esthetics in 1753, the concept of beauty has been pursued for centuries. As early as 2000 B.C., facial masks of ideal shapes and proportions were popular in ancient Egypt. Shapes and proportions are not the only parameters in esthetics however; there are also other factors, such as colors, line forms, sounds, at times even emotions.4 Esthetics is a psychological and a physiological interpretation of the perceived object. With the latest improvements in the fields of medicine and dentistry, the esthetic perceptions and expectations of people have increased.

Bioesthetics is a branch of esthetics that deals with dental, dento-facial and facial esthetics.5 Dentistry plays a major role in improving the esthetic appearance of people. Dental restorations are changing dramatically to meet the expectations of the people and as a result there are more esthetic tooth colored restorations than the conventional amalgam restorations. In a survey conducted by Albino et al. in 1984, more than 42% of the patients concurred that “appearance” had a strong influence on their decision to obtain the treatment, while only 19% answered to functional problems and a mere 14% answered pain as their main reason to procure the treatment.4
One of the most common dental treatments is to restore decayed teeth or to replace missing teeth with fixed or removable prostheses. There are a number of tooth-colored restorative materials such as acrylcs, porcelains, glass-ceramics, composites, etc. Glass-ceramics, due to their favorable optical and mechanical properties are very popular among dentists. These are the only group of esthetic materials that, on their own, can withstand mechanical strengths up to 500 MPa. Matching the color of these esthetic restorative materials with that of the adjacent teeth is important to reestablish the esthetic look.

The process of shade matching the shade of the restoration to that of the adjacent teeth is challenging, demanding, and frustrating to the dentist and subsequently, fabrication of the crowns and bridges, to the ceramist. Replacement or restoration of anterior teeth, in particular, with a crown or a bridge is difficult, as it demands a higher level of estheticity. Even with tremendous improvements in restorative dentistry, shade matching still remains primitive. Dentists, even today, match the shade of the restorative material with that of the adjacent tooth using a traditional method. This method is called the “winking method” wherein the dentist holds a commercially available tooth shade guide adjacent to the other teeth in the mouth closes one eye and selects the best possible shade that can be used to restore the tooth.
I.1 Factors Affecting Shade Selection

The shade matching process is subjective and a number of factors influence this process. These factors can be classified into.\textsuperscript{7-10}

Figure I.1. Classification of factors affecting shade selection.

I.1.1 Physical Factors

I.1.1.1 Illuminant

Color rendition is a phenomenon that explains that the quality of the illuminant affects the color perception of an object. Standardizing the light source is important to achieve a repeatable and a reliable shade assessment. The American Dental Association recommends the following.\textsuperscript{8}

Color temperature of 5500° K
Color rendition index (CRI) of 90+
Intensity of 200-300 foot candles, 30 inches from the floor
Natural sunlight is a standard to which all the light sources are compared. A color temperature of 5500° K is considered standard as it approximates the natural standard daylight. Standard daylight in the USA is that light available in Washington, D.C., during the months of June between the hours of 12:00 and 1:00 P.M., with a slightly overcast sky. Determining the Kelvin temperature of the light source used is important, as higher Kelvin temperatures render a yellowish hue, while lower Kelvin temperatures render an orange hue to the selected shades. Cook and Vryonis in their study of the dental color-matching lamps found many lamps deficient in one or more regions of the UV and the visible spectrum. They also concluded in their study that the manufacturers should ensure that the reflectance spectra of ceramics to have the same reflectance spectra as that of enamel and dentine to avoid the phenomenon of metamerism. Phillips, in his book *Science of Dental Materials* advocates the use of dental color-matching lamps, which have a sufficient amount of UV-component in order to simulate the natural fluorescence of the teeth.

I.1.1.2 Metamerism

Metamerism is a phenomenon in which the color of an object looks different under different lighting conditions. There are two forms of metamerism - object metamerism and observer metamerism. Object metamerism is a comparison of two objects that have the same color under a given illuminant and appear differently under a different illuminant. For any two objects to match under a given illuminant, their spectral reflectance curves should be identical. To reduce the effect of this phenomenon, shade matching should be done under multiple illuminants. Observer metamerism refers to the illuminant that remains constant with different observers. It is dependent on the physiological sensitivities of cones in the eyes. It is manifested when the patient and the clinician perceive the restoration a good match while other people disagree. To minimize this factor a third person should also be involved during the shade determination process.
I.1.2 Physiological Factors

I.1.2.1 Brunessence

Brunessence is the natural browning of the cornea that occurs with age.\textsuperscript{9} It acts as a filter and changes the appearance of colors. Hence, the age of the dentist also forms an important factor in shade determination.

I.1.2.2 Hue Bias

Difference in tolerance to one color over another is known as hue bias. It is an occupational predicament usually affecting the clinicians and laboratory technicians. Studies have shown that dentists and dental technicians are more tolerant to yellow than to red and hence display a red hue bias.\textsuperscript{7} This further advocates the necessity to involve a third person during shade selection and also active participation from the patient.

I.1.3 Psychological Factors

I.1.3.1 Apperception

Perception is the psychological process of vision. Apperception is how the mind interprets what the eye perceives.\textsuperscript{9} Optical illusions exemplify the perception and apperception phenomena. Shade selection is a combination of perception and apperception, and hence involves a thought process. Teaching dentists about this phenomenon could minimize the influence of this factor on the shade selection. Many studies have advocated incorporating this concept into the dental school syllabi.\textsuperscript{8,15,16}

I.1.3.2 Adaptation

Sensory adaptation is defined as a phenomenon of reduced sensitivity of the eye due to a prolonged or a perpetual stimulus. Chromatic adaptation is the phenomenon of color constancy. These two forms of adaptation influence the dentist, and hence the
shade selection process should be done quickly (60 milliseconds – 5 seconds), before the eye loses its sensitivity and distinguishing between shades becomes more difficult. This time period is referred to as the chromatic assessment period. Since the human eye can differentiate more than 5 million colors when they are placed side by side, it gets more difficult to select the most accurate shade and very easy to distinguish even the smallest difference between the selected shade and the shade of the adjacent tooth.

I.1.4 Clinical Factors

I.1.4.1 Oscillation

Oscillation is the phenomenon of quivering or swaying or wandering, usually associated with mental processes. Attention span, interest, optic fatigue and a myriad of other personal factors determine oscillation. Shifts in attention lead to a lesser alert dentist and consequently the shade selection process is affected. A morning appointment to evaluate the shade usually minimizes the effect of this factor.

I.1.4.2 Mitering

Also known as vectoring, mitering is a process of viewing colors under different viewing angles. The angle of reflectance affects the perceived color, as the colors become diffuse as the angle increases. As the surface anatomy of the teeth affects mitering, teeth should be viewed directly and at different angles during the shade evaluation process to minimize the effect of this factor.

I.1.4.3 Environment

The ambience of the dental clinic, under which the color evaluation process is done, influences the final shade selected. The walls of the dental office should be colored neutrally, avoiding bright colors, especially reds or yellows. Bright environment makes the shade appear duller and hence a proper environment is required for an accurate
evaluation of the shade. A neutral grey card in the background during shade evaluation process helps to obtain a more accurate shade.\textsuperscript{9,19-21}

I.1.4.4 Miscellaneous

A photographic investigation study by Roberts has revealed that the color matching process is not dependent on the skin color, hair color, or gender but certainly on the age group of the patients'.\textsuperscript{22} Other factors that affect proper shade determination includes patients clothing, the drape used on the patient and the color of the patient’s lipstick.\textsuperscript{19} A complete knowledge of the age changes that occur in the teeth, inter-arch differences in teeth color, and the color differences between individual teeth is essential to obtain a proper shade of the tooth. Miscommunication of the shade from the dentist to the technician also forms an important factor in obtaining a good color match.\textsuperscript{18,23-26} The ceramist, who actually fabricates the crown, is not in a position to visualize the patient and has to depend solely on the directions given to him by the dentist. This factor could be eliminated if the dentist chooses the shade in presence of the ceramist.
I.2 Anatomical Considerations

To obtain a good shade match between the teeth and the restorations, a good understanding of the tooth anatomy is essential. To complicate the shade evaluation process, a tooth does not have a uniform shade everywhere. The incisal tips are translucent and the tooth gets darker toward the cervical regions. The teeth in the shade guide simulate the form of the actual tooth, but cannot replicate all the shades exhibited at different regions.²⁷

Dentine is more opaque than enamel and will reflect light. Enamel is crystalline and has tiny prisms or rods cemented together by an inorganic substance. As a result, a light ray is diffused by reflection and refraction to produce a translucent effect and a sensation of depth as the scattered light ray reaches the eye. As the light ray strikes the tooth surface, part of it is reflected and the remainder penetrates the enamel and is diffused. Any light reaching the dentine is either absorbed or reflected, to be again diffused in the enamel. If dentine is not present, as in the incisal tips, the light ray may be absorbed in the oral cavity, and hence this area appears to be more translucent than the cervical area. Besides refraction and reflection, there is also dispersion, which gives color or shade that varies between teeth.

Figure I.2. Variations of shades displayed by the natural teeth.
I.3 Summary

The one factor that cannot be eliminated is the process of actual shade selection by the dentist. The dentist has only a certain number of shades on his/her shade guide and he/she tries to match them to shades of the teeth in the mouth. Covering all the possible ranges of shades exhibited by the natural teeth is not feasible for any commercially available shade,\(^4\,9\,28\,29\) and hence the need to eliminate the shade guide and customizing the shade to individual patient’s requirement is desired. The goal is not to eliminate the dentists’ role, but to facilitate the dentist in determining a better shade.

The main objective of this thesis was to study the spectral data obtained from the glass-ceramic samples received from Ivoclar and conduct similar experiments, for comparison, with extracted natural teeth and a commercially available tooth shade guide (Chromascop, Ivoclar). Diffuse reflectance, diffuse transmittance and specular reflectance curves of the samples, the natural extracted teeth and the shade guides were obtained. Fluorescence measurements were also done on the samples. A simple figure of merit could be generated from these studies, which would represent a particular shade and could be used for communication between the dentist and the ceramist.
II LITERATURE SURVEY

II.1 History of Dental Ceramics

Dental ceramic technology is one of the fastest growing areas of dental material research and development. The past decade has seen the development of shrink-free core materials, castable glass-ceramics, porcelain veneers, acid etched porcelain inlays and onlays. Traditionally these materials have been referred to as dental porcelains. A more acceptable terminology is dental ceramics. However, these two terms are always used interchangeably.

To understand dental ceramics completely, it is necessary to comprehend the differences and nuances of terminology. All porcelains and glass-ceramics are ceramics, but not all ceramics are porcelains or glass-ceramics.

II.2 Evolution of Dental Ceramics

- 21,000 B.C. : Earliest fabricated ceramic artifacts dated
- 5,000 B.C. : Clay pots discovered
- 100 B.C. : Colored, glazed vessels (Han Dynasty)
- 600 A.D. : Translucent porcelain (Tang Dynasty)
- 700 A.D. : Porcelain made in China and fashioned from white china clay (kaolin) and feldspar
- 1500 A.D. : First European porcelain produced (Midici)
- 1723 A.D. : Pierre Fauchard enameled metal denture bases; credited with recognizing potential of porcelain enamels
- 1750 A.D. : Porcelain produced at Sevres, France, and in England by Wedgewood and Derby
- 1788 A.D. : Whiteware first successfully used as a dental material
- 1808 A.D. : Giuseppangelo Fonzi introduced individually formed porcelain
- 1838 A.D. : Elias Wildman formulated more translucent porcelain compared to the old ones resembling other pottery materials
- 1873 A.D. : Beers originated the concept of a porcelain jacket crown
- 1885 A.D. : Logan introduced the Richmond Crown - porcelain fused to platinum post
- 1946 A.D. : Strength of pottery materials markedly increased by replacing quartz with a corresponding amount of calcined alumina
- 1949 A.D. : Dentists’ Supply Co.(NY) invented vacuum-firing of porcelain teeth (dense and translucent)
- 1958 A.D. : Ceramco - the first dental porcelain for veneering
- 1960 A.D. : Porcelain fused to metals
- 1972 A.D. : Dicor – castable glass-ceramics introduced
- 1973 A.D. : Cerestore injection molded core by Sozio and Riley
- 1985 A.D. : Renaissance crown – a platinum bonded crown introduced
- 1988 A.D. : In-Ceram crown – a high strength slip cast crown introduced
- 1989 A.D. : Alceram - replacement for Cerestore
- 1999 A.D. : IPS Empress II – heat pressed and sintered glass-ceramics

### II.3 Glass-Ceramics in Dentistry

Corning Glass Works first developed glass-ceramics in the late 1950s. Though they were envisioned for use in dentistry when Mac-Culloch fabricated a denture in 1968, only in 1985 was a commercially available material for crowns and bridges with a processing method introduced. Glass-ceramics are a type of ceramic consisting of a glassy phase with a huge fraction of crystalline phase. An intermediate material is formed while still in the liquid state and on cooling very stable glass results. Subsequent
heating causes controlled crystallization with the nucleation and growth of internal crystals. This process of generating a partially crystalline material is called ceraming.

The time and temperature of the ceraming heat treatment influences the crystal growth rate and size. The ceraming technique involves heat treatment in two stages as the rates of crystal nucleation and rates of crystal growth are maximized at different temperatures. The first heat treatment is at a temperature to obtain maximum nucleation of crystals and then it is raised to obtain optimum crystal size. Uniform distribution of crystals through the glassy phase is essential to ensure high strength of the glass-ceramic. Ceraming can result in producing the crystalline phase anywhere between 50-100%. The new crystals formed in this way grow directly in the glassy phase and subsequently change the composition of the remaining glass.

**II.4 Classification of Glass Ceramics**

![Classification of Glass Ceramics Diagram](chart)

Figure II.1. Classification of Glass-Ceramics.
II.5 Glass-Ceramic Properties

Properties exhibited by glass-ceramics can be grouped into:6

- Processing Properties
- Thermal Properties
- Chemical Properties
- Biological Properties
- Mechanical Properties
- Optical Properties

II.5.1 Processing Properties

Glass ceramics can be produced by pressing, casting, spin casting, and rolling or by press blowing—all the methods used in the primary shaping of glass. Shrinkage is limited and can be controlled. Porosity is reduced to a minimum or can be eliminated in monolithic glass-ceramics.

II.5.2 Thermal Properties

Glass-ceramics exhibit high-temperature stability. Their expansion can be controlled depending on the temperature and a zero or a negative expansion coefficient of thermal expansion is also achievable.

II.5.3 Chemical Properties

Glass-ceramics can vary from being extremely resorbable to highly stable. Altering the nature of the crystal and adjusting the percentage of glassy phase accordingly can control this property.
II.5.4 Biological Properties

Many glass-ceramics are inert, nontoxic, and biocompatible. These kinds of glass-ceramics are used primarily in developing applications for medicine and, in particular dentistry. Bioactive glass-ceramics have also been devised and used extensively in implantology (e.g. A-W glass-ceramics).

II.5.5 Mechanical Properties

Though glass-ceramics do not exhibit mechanical properties like those exhibited by metal alloys, they do exhibit high flexural strengths up to 500 Mpa. High fracture toughness $K_{IC}$ values of more than 3 Mpa$\cdot$m$^{0.5}$ have been achieved. Occlusal (biting) force ranges from 300-500 Mpa and glass-ceramics are the only esthetic materials, which can withstand them.

II.5.6 Optical Properties

Glass-ceramics are the only materials that exhibit favorable processing properties and mechanical properties and yet are translucent and exhibit good optical properties. Optical properties of glass-ceramics can be further divided into:

- Translucency or Opacity
- Pigmentation
- Fluorescence

High level of translucency and sometimes translucency is due to the glassy phase present in the glass-ceramics. Depending on the type of crystal microstructure glass-ceramics can be produced that are completely opaque. Glass-ceramics can be produced in any desired color by adding pigmentation ions during their processing. Fluorescence, in glass-ceramics is achieved by incorporating rare earth ions into the batch.
All these favorable properties have made glass-ceramics a material of choice among dentists for the restoration and replacement of missing teeth with crowns and bridges.

**II.6 Lithium Silicate Glass-Ceramics**

The samples that were analyzed in this thesis are lithium silicate glass-ceramics based on IPS Empress II system (Ivoclar). Hence it becomes imperative to have a basic understanding of lithium silicate glass-ceramics. They belong to a subgroup of silicates called phyllosilicates and have a Si:O ratio of 2:5. Lithium silicate glass-ceramics have 70 % volume Lithium disilicate (Li₂Si₂O₅) as their primary crystalline phase. The structure of orthorhombic Li₂Si₂O₅ involves corrugated sheets of (Si₂O₅)²⁻ on the (010) plane. The microstructure consists of randomly oriented, interlocking needle like crystals. These can deflect the cracks thus increasing the flexural strength substantially. The compressive strength of lithium disilicates are in the range of 350-450 Mpa and it’s the highest of all the other glass-ceramics among phyllosilicates, almost three times that of leucite glass-ceramic and twice as much of fluoromica glass-ceramics.
II.7 Colorimetry

Sight is the most important of all senses in the human body. As there is no sight without light, it becomes obvious that sight and light are complementary. Visible light is a form of electromagnetic radiation that can be detected by the human eye. The eye is sensitive to wavelength’s from approximately 400 nm (blue region) – 700 nm (red region). Sir Isaac Newton describe light as colorless unless it interacted with an object and was the first to demonstrate that white light from the Sun consists of individual components of different colors (color spectrum): violet, indigo, blue, green, yellow, orange and red. Cognition of color involves multiple processes: stimulation, sensation and perception. Color is an integral aspect of the visual experience and one of the most complex processes that occur in the brain. Color exploration is multidisciplinary and involves physics, chemistry, physiology and psychology.

“Coloring is the sunshine of art, that clothes poverty in smiles, and renders the prospect of bareness itself agreeable, while it heightens the interest and doubles the charm of beauty.”

As this thesis mainly involves evolving a method to convert a shade or a color into an electronic value, it becomes extremely important to understand the attributes affecting the shade evaluation and also the most commonly used terminology and standards.

For an object to be visible, it should either emit light or reflect or partially transmit light. The latter is of interest in dentistry and the factors affecting the visual evaluation of an object can be classified into two categories: color attributes and geometric attributes. Color attributes deal with the description of the perceived color of the object, while geometric attributes deal with the description of its spatial attributes such as gloss, haze, translucency, etc.
II.7.1 Color Attributes

II.7.1.1 Evolution of color difference scales

Figure II.2. Family tree of color scales.
Expressing the perceived color as an electronic value forms the major part of the shade evaluation and matching process. To obtain a better shade match, a complete understanding of the most commonly used color scales, “The Munsell Color System” and the “CIE Color Space,” is required.

II.7.1.2 The Munsell Color System

Albert Henry Munsell, an American artist, in his 1905 book *A Color Notation* described the dimensions of color, and they are still used as a standard in colorimetry. Munsell described color in three dimensions: hue, value and chroma.12,31

![Image of Munsell Color System](image)

Figure II.3. Three dimensions of color as arranged by Munsell. (From Ref. 12)

Hue, as defined by Munsell, is “the quality by which we distinguish one color family from another.”32 There are five principal colors: red, yellow, green, blue and purple. There are five intermediate colors: yellow-red, green-yellow, blue-green, purple-blue and red-purple. All these colors are arranged in a wheel measured off in 100 compass points. Each primary and intermediate color has ten degrees around the compass, identified by its place on the compass. The notation used usually goes with the color it describes, for example: R for red, Y for yellow, YR for yellow-red, etc.
Value is the second dimension described by Munsell. He defined value as “the quality by which we distinguish a light color from a dark one.” It relates to the grey level of the color and ranges from black to white. The notation used is N and ranges from 0-10 N, from pitch black to bright white. The value scale is perceptual and not based on mathematical values or calculations but based on how the differences in relative light are perceived. The more white in a hue, the higher the value; the more grey, the lower the value or duller the color).

Chroma is the third dimension and most commonly confused with value. Munsell describes it as “the quality which distinguishes a strong color from a weak one; the departure of a color sensation from that of white or grey; the intensity of a distinctive hue; color intensity.” Chroma describes the amount of hue in a color and the levels of chroma are arranged perpendicular to the value axis and are not uniform for every hue at every value. The amount of chroma is described after the hue and value designation. The units are arbitrary as the scale starts at zero and there is no absolute end to the scale. The chroma scale for normal reflecting materials extends beyond 20 in some cases. Fluorescent materials can have chromas as high as 30. In simple terms, a dark yellow color has a higher chroma and a light yellow color has a low chroma.
A number of studies have measured the color index of teeth using Munsell color system. Some of the most significant studies are shown in the following table:

Table I. Studies Measuring Color Index of Teeth using Munsell System

<table>
<thead>
<tr>
<th>Number of Teeth</th>
<th>Hue</th>
<th>Value</th>
<th>Chroma</th>
</tr>
</thead>
<tbody>
<tr>
<td>6000</td>
<td>6 YR – 9.3 Y</td>
<td>4/ - 8/</td>
<td>/0 - /7</td>
</tr>
<tr>
<td>81</td>
<td>9.5 YR – 3 Y</td>
<td>6/ - 7.5/</td>
<td>/1.5 - /4.5</td>
</tr>
<tr>
<td>33</td>
<td>7.5 YR – 2.7 Y</td>
<td>5.8/ - 8.5/</td>
<td>/1.5 - /5.6</td>
</tr>
<tr>
<td>268</td>
<td>8.9 YR – 3.3 Y</td>
<td>5.8/ - 8/</td>
<td>/0.8 - /3.4</td>
</tr>
<tr>
<td>100</td>
<td>8.2 YR – 2.9 Y</td>
<td>6.1/ - 8.4/</td>
<td>/2 - /4.3</td>
</tr>
<tr>
<td>95</td>
<td>7.3 YR – 3.5 Y</td>
<td>5.4/ - 8.2/</td>
<td>/0.7 - /4</td>
</tr>
</tbody>
</table>

II.7.1.3 CIE Color Space

CIE (Commission Internationale de l’Eclairage) in 1976 introduced CIE L*a*b* space to describe all the colors in a uniformly distributed space. CIE L*a*b* was derived by doing a nonlinear transformation from CIE XYZ color space. Hence, CIE XYZ color space should be described in order to understand CIE L*a*b* color space.

In 1931, the CIE introduced CIE XYZ space and over the years it has continuously refined this model. The CIE system is based on the description of color as the luminance vector Y and two other vectors X and Z. These three vectors are called XYZ tristimulus values and theoretically they can describe any color visible and invisible to the human eyes. This system was developed after analysis of spectral response data obtained from experiments conducted on human observers.

The CIE experiments utilized a 2-degree standard observer, as it simulates the fovea vision of human eyes, which is limited to 2-degree angle of vision. Two different
types of color mixing are possible: additive and subtractive. Additive (light) color mixing is a process where two or more colored lights are combined by shining them on the same surface. Mixtures obtained by this method usually appear lighter than the two individual colors used because the luminous energy from each light adds up to the final color. All tristimulus color specifications are a result of quantification of the three primaries used by the observer to match the unknown color stimulus. All the CIE standard experiments used additive color mixing during the color evaluations. Subtractive (light) color mixing is a process where two or more lights are combined in such a way that each of them decreases the luminosity of the other. Subtractive mixtures usually appear darker than the two individual colors used, due to the absorption of light by each of the individual colors used. These experiments have lights of single wavelengths in the blue, green, and red regions of the color spectrum used as primaries. All the CIE $L^*a^*b^*$ values are obtained by subtractive color mixing.

The CIE XYZ color space is useful as it helps us to convert any spectral curve into their numbers called tristimulus values, $X$, $Y$, and $Z$ and also help us to identify the color in terms of mixture of primary lights. The $X$, $Y$, and $Z$ values for two objects are similar if they visually appear the same. The $X$, $Y$, and $Z$ values are limited in that they poorly correlate with arrangement of visual attributes such as hue, saturation, depth, vividness, etc., excluding lightness which can be described by the component $Y$.

Hence CIE proposed chromaticity coordinates, also referred to as trichromatic coefficients: $x$, $y$, and $z$, which are defined as:

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z} \quad (1)$$

Because $x + y + z = 1$, only two new variables remain independent. Given the luminance value $Y$ and coordinates in the chromaticity map, we can retrieve the $X$ and $Z$ components of any color using the following equations:
\[ X = \left( \frac{x}{y} \right) Y \]

\[ Y = Y \]

\[ Z = \left[ \frac{(1-x-y)}{y} \right] Y \]  

The CIE chromaticity diagram as shown in the figure below is constructed using only the x and y values.

Figure II.4. The Normal CIE Diagram (Adapted From Ref. 39)

There are two major drawbacks associated with CIE XYZ color space and its chromaticity map. Firstly, from the perceptual perspective, the CIE space has a non-uniform distribution and secondly the color differences cannot be determined as simple
gradations in XYZ space, i.e., the distance between two points on the CIE diagram does not tell anything about the perceived color difference.

In 1976 CIE devised two new color spaces based on the CIE XYZ; one was intended for use with self-luminous colors and the other for surface colors. The CIE L∗a∗b∗ color space was the latter color space and was derived from non-linear transformations of the CIE XYZ space. The objective of this transformation is a color-space to aid the numerical classification of color differences. The transformations from which the CIE L∗a∗b∗ was derived from CIE XYZ space are given as follows:\textsuperscript{4,38,40}

\begin{align*}
L &= 116\left(\frac{Y}{Y_0}\right)^{1/3} - 16 \quad (3) \\
a &= 500\left[\left(\frac{X}{X_0}\right)^{1/3} - \left(\frac{Y}{Y_0}\right)^{1/3}\right] \quad (4) \\
b &= 200\left[\left(\frac{Y}{Y_0}\right)^{1/3} - \left(\frac{Z}{Z_0}\right)^{1/3}\right] \quad (5)
\end{align*}

Where $X_0$, $Y_0$, and $Z_0$ are the $X$, $Y$, $Z$ values obtained for the standard and $X$, $Y$, $Z$ are the values obtained for the sample. It is an opponent color system based on the 1942 system of Richard Hunter, called L, a, b system. In the mid-1960s, scientific studies revealed that the retinal stimuli are translated into distinctions between light and dark, red and green, and blue and yellow. This was the main basis for the opponent color system, which is also referred to as the color opposition system. The $a^*$ and $b^*$ color axes are considered opponent hues because a single stimulus cannot elicit these colors. The major difference in the CIE XYZ and the CIE L∗a∗b∗ is that the latter uses a subtractive system while the former used an additive system to match colors.\textsuperscript{17}
The following diagrams represent a three dimensional representation of the three components of CIE L*a*b*:

Figure II.5. The three dimensions of CIE L*a*b* color space.

- **L*** - Luminosity – vertical axis
- **a*** - Red / green axis – horizontal axis
- **b*** - Yellow / blue axis – horizontal axis

The vertical axis represents lightness (indicated as L*) and it ranges from 0 for black to 100 for white. The horizontal axes a* and b* are composed of colors, red-green and yellow-blue respectively. A positive a* value indicates amounts of red color and a negative a* value indicates amounts of green. Similarly a positive b* value indicates yellow and a negative b* value indicates blue. For both a* and the b* axes, a value of zero indicates a shade of neutral grey.40
L*a*b* color space represents color relative to a reference white point, so it can measure colors under various illuminations. The primary advantage of using L*a*b* space is that a perceived difference between any two colors is proportional to geometric distance in the color space. Any hue can be expressed as a combination of two unique hues. The a* and b* values are related to the amount of each hue present in the color [ref b]. As L*a*b* space is a three-dimensional coordinate system, the distance between two colors can be expressed as the Euclidean distance. The color solid vector is E, after the German word for *Empfindung*, meaning sensation, and represents the total color difference from the ideal black.\(^4\) The degree of color difference (\(\Delta E\)) is calculated by the equation:\(^4,17,41\)

\[
\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}
\]  
(6)

Similarly if only a difference in the chromaticity component is desired, the following equation can be used:

\[
\Delta C = [(\Delta a)^2 + (\Delta b)^2]^{1/2}
\]  
(7)

Where \(\Delta L\) is the lightness difference; \(\Delta a\) is the green-red coordinate difference; \(\Delta b\) is the yellow-blue coordinate color difference and \(\Delta C\) the saturation difference.

Because the L*a*b* system successfully separates luminance from colors, it is widely used in the industry for shade matching, colorimetry, gemstone evaluation and other applications where closeness of color must be quantified.
II.7.2 Geometric Attributes

As previously described, geometric or spatial attributes describe the gloss, haze, translucency etc., of the object perceived. Light is a form of energy and hence when it interacts with matter, a number of processes can occur, including reflection, transmission, absorption, fluorescence, phosphorescence, and photochemical reaction. When visible light is directed on an object, it is either transmitted through an object’s surface, reflected from the object’s surface, or absorbed by the object to impart its color. The absorbance, transmittance and reflectance from an object can be well characterized. The transmitted and the reflected light can be either diffuse or specular (regular). Hence all objects can be characterized as follows:

![Classification of visible spectroscopic methods for objects.](image)

II.7.2.1 Reflectance Spectroscopy
Reflection is a phenomenon in which an object redirects the light directed towards its surface on the same side as that of the illuminant. As described above, the light can be either diffusely reflected or specularly reflected.

II.7.2.1.1 Diffuse Reflection

Diffuse reflection is a phenomenon in which there is uniform reflection of light with no directional dependence on the viewer. It originates from a combination of internal scattering of light (light which is absorbed and then re-emitted) and external scattering from the rough surface of the object. All nonmetallic opaque objects have diffuse reflection as their dominant reflection property.

Figure II.7. Figure displaying specular reflection and diffuse reflection phenomena.

II.7.2.1.2 Specular or Regular Reflection

Specular reflection is a phenomenon in which the incident light is reflected through an object’s surface without diffusion. This is also referred to as regular
reflection or direct reflection. A mirror is a perfect example of a specularly reflecting object. Polished metallic surfaces also reflect light specularly.

II.7.2.2 Transmission Spectroscopy

Transmission is a phenomenon in which an object redirects the light directed towards its surface on the opposite side as that of the illuminant after its passage through the object. As described in the figure, light can either be diffusely transmitted or specularly transmitted.

![Diagram of specular and diffuse transmission](image)

Figure II.8. Figure displaying specular transmission and diffuse transmission phenomena.

II.7.2.2.1 Diffuse Transmission

Diffuse transmission is a process by which incident light, while being transmitted through an object, is redirected or scattered over a range of different angles. This process is very similar to the internal scattering in diffuse reflectance, the only difference being
that the light is transmitted to the opposing surface and not redirected back towards the illuminant. Any translucent material could be classified into this category.

II.7.2.2 Specular Transmission

Specular transmission is a phenomenon in which the incident light while being transmitted through an object does not diffuse, similar to diffuse transmission, differing only in that the light transmitted does not scatter within the object before it leaves the opposite surface. All transparent objects could be classified into this category. A perfect example of a specularly transmitting object would be an empty glass beaker.

II.7.2.3 Absorption

Absorption is a phenomenon in which the incident light scatters and diffuses inside an object and finally gets absorbed. By measuring the transmittance and reflectance values of an object, the amount of light absorbed by the object could be easily calculated. Selective absorption is the process of absorbing only certain wavelengths of light and is the primary source of imparting the color to an object. If all the color wavelengths are absorbed, the object will appear black.

II.7.3 Fluorescence Spectroscopy

Fluorescence is a phenomenon of emission of light of a visible color from a substance under stimulation or excitation by light or other forms of electromagnetic radiation. This phenomenon is different from the phosphorescence phenomenon where the light continues to be emitted even after the excitation from the other radiation is ceased. The distribution of wavelength-dependent intensity that causes fluorescence is known as the fluorescence excitation spectrum, and the distribution of wavelength-dependent intensity of emitted energy is known as the fluorescence emission spectrum.
When an object is exposed to a high-energy electromagnetic radiation, its atoms absorb the energy as its electrons realize an excited state. When these electrons fall back to a lower energy state, they emit photons having adequate energy. These emitted photons are usually of a higher wavelength than the excited one and hence fluorescence occurs. A tooth is naturally fluorescent and hence it becomes imperative to reproduce this fluorescence. In one study by Monsenego et al. they found that the fluorescence of samples of the shade guides are not homogeneous and many a shades fluoresce more in the green region. They also advocated that the cementing medium used affects the fluorescence of the prostheses.\textsuperscript{42} In another study, they revealed that unacceptable levels of fluorescences in the shade guides is responsible for the choice of improper ceramic shade.\textsuperscript{43}

\section*{II.8 Spectrophotometer}

A spectrophotometer is an instrument used to measure the reflection, absorption or transmission of light from objects by wavelength, and thus spectral curves describe color. The human eye can be considered a crude reflectance spectrophotometer, where our brain processes the wavelength-dependent scattering of visible light photons to produce the image and give information about the image. However, a modern spectrophotometer can reveal finer details over a broader wavelength. Over the years reflectance spectrophotometry has been used in various studies related to ceramic color matching procedures. The effects of surface texture on the three dimensions of color have been described by Obregon et al.\textsuperscript{44,45} Jorgenson et al evaluated the stability of color after numerous firings and also the effect of thickness of porcelain on the color produced.\textsuperscript{46}

\section*{II.9 Shade Matching in Dentistry}

Shade matching of dental porcelains to the adjacent teeth in the mouth is many times a challenging and a frustrating step for the dentist and ceramist while a
disappointing one to the patient. Clark identified this problem of shade matching, in his article “An analysis of tooth color” as early as 1931. He also discussed that a numerical record of the color analyzed simplifies the problem. He analyzed the teeth from about 1000 patients over a period of 8 years and discussed his analysis in terms of color stimulus and all the color attributes that affect shade selection. He described the tooth color system completely and identified, classified, and compounded porcelain formulations for teeth. He also explained the importance of spectral measurements as invaluable tools in the process of shade determination. Clark’s efforts were not recognized contemporaneously and even today many of his writings go unheeded.

Since then a number of studies have been conducted in this field but still the shade evaluation process is primitive and has not kept up with other advances in restorative dentistry. Commercially available shade guides are used to evaluate the shade of the tooth. Studies have proven that the commercially available shade guides are inadequate, not logically arranged and do not cover the entire color range of natural teeth. A number of studies were also conducted to evolve a new order of arrangement of shades on the shade guide and to develop custom shades. An advancement in the commercially available shade guides was made when Vita Zahnfabrik Company developed a new shade guide, “Vitapan 3D Master,” based on the three dimensional concept of color. Though this showed an enormous improvement from the previous shade guides, it still displayed disharmony in the shade arrangement. Comparison studies between the commercially available shade guides have been conducted and concluded that there were discrepancies in the shade-matching systems and that none of the systems proved superior than the other.

**II.10 Shade Matching Method**

Shade matching conditions and methods must be standardized to achieve a good match between the selected shade and the adjacent teeth in the mouth. Shade matching should be done in the mornings and at the beginning of the appointment. The shade guide should be held parallel to the tooth that is being matched. Other studies have
shown that masking the cervical part of the shades would improve the shade matching process.19,50,51 Pizzamiglio discussed that a tooth and the shade guide should not be observed for more than 5 seconds and that a blue colored surface could be used to mask the effect of yellow on the eyes.52 Use of multiple illuminants and multiple commercially available shade guides has also been advocated in studies conducted by Seluk and LaLonde.53 Using diagrams or schemes to depict the desired shades of the tooth could minimize communication problems between the dentist and the ceramist.27,54 Photographic evaluation to determine the shades and communicating them has also been studied, and this has been found to be more effective in communicating rather than evaluating the shade.22

II.10.1 Visual and Instrumental Shade Matching Methods

Visual comparison studies have been conducted to determine the color ranges of natural teeth and subsequently have proposed different methods of color matching to minimize the subjectivity.37 Photometric analysis of the tooth shade is also advocated in many studies, and a spectroscopic analysis of the obtained shade and the photograph obtained is proposed.37 A number of studies have proven the accuracy and optical properties of spectrophotometers. Seghi et al. showed that the instruments with which they performed the experiments displayed only short-term repeatability and corroborated these findings from other similar studies.55,56 The degree of accuracy of the obtained color measurements varied depending on the instrument used and the type of material surface used. The spectrophotometer could be used to detect color differences between samples rather than evaluating the color of a sample. This is due to a number of factors causing errors during evaluation of the color of the sample and fewer number of errors during the measurement of color difference.56-58

O’Brien’s studies first advocated the use of an integrating sphere in the spectrophotometer and proved their potency to measure the spectra of the teeth. Several other studies using a spectrophotometer recognized that the color of the tooth is not uniform and two or more measurements on each tooth were required.37 Yap et al.
compared the difference between visual and computerized color evaluation methods and found discrepancies between them. They proposed a need to incorporate of correction factors into the software used, to eliminate the limitation.  

Van der Burgt et al. in their study, compared the efficiency of a fiber-optics colorimeter with that of a standard spectrophotometer and concluded that the fiber-optics colorimeter, though promising, needed some technical improvement.  

Goodkind et al. compared the Chromascan (an instrument which aides the dentist to select shade) and spectrophotometric color measurements of 100 extracted natural teeth and concluded that the Chromascan values correspond to the spectrophotometric measurements. O’Brien et al. reported the chromascan to be more sensitive to the orange pigment and less sensitive to the yellow in porcelains than human observers. 

Goldstein et al. evaluated the repeatability of a modified, Sumita SLS-100 LSE (Sumita Optical Glass Manufacturing Company, Tokyo, Japan) intraoral colorimeter. They concluded that the colorimeter was ineffective in producing repeatable results, unreliable as it needed to be calibrated before each use, and sensitive to the changes in the fiber-optic cord, ambient light, and the room temperature.  

Paul et al. compared visual and spectrophotometric methods of shade analysis. A reflectance spectrophotometer was used with a D\textsubscript{65} (6500° K) illuminant. They concluded that the results from the spectrophotometer are comparable to those of the results obtained from the visual method only in the middle third region of the tooth and that measurements obtained from other parts of the teeth showed disparity. However, a study by Horn et al. compared the visual and spectrophotometric methods and concluded that the spectrophotometric results were superior to the results obtained by visual methods. They used a SP78 sphere spectrophotometer and twenty extracted natural teeth in their study. Okubo et al. also evaluated the visual and instrumental shade matching methods and concluded that, although the instrumental shade matching method was found to be better than the visual method, it was not statistically significant.  

Macentee
and Lakowski instrumentally measured the vital and extracted human teeth, compared their results with the results obtained from similar experiments conducted by other investigators, and concluded that there was a lack of overall agreement for loci of vital and extracted human teeth. They also attributed the instrumental variations as the main reason for the non-corroborative result.66

A team of Japanese investigators developed a new computer color matching system, examined the characteristics of the absorption, and scattering coefficients of dental porcelains using a spectrophotometer (CAS-ID1). After modifying this spectrophotometer, they presented their results obtained and suggested its use in color prescription and evaluation.67-69
III EXPERIMENTAL PROCEDURES

Twelve glass-ceramic samples proposed for use in dental restorative procedures were obtained from Ivoclar. Each glass-ceramic sample was a small flat rectangle about 20 mm long and 6 mm wide. These samples were then washed with water, stored, and labeled appropriately. While the specific composition of these samples is proprietary, the glass-ceramic samples are lithium silicate glasses with traces of other oxides shown in the table below:

Table II. Trace Element Compositions of the Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CeO₂</th>
<th>MnO₂</th>
<th>La₂O₃</th>
<th>V₂O₅</th>
<th>Tb₄O₇</th>
<th>Er₂O₃</th>
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</thead>
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</table>
III.1 X-Ray Diffraction

One sample, VP2184, was analyzed using X-Ray diffraction (XRD). XRD data was obtained with a Cu-K$_\alpha$ radiation using Siemens D500; 40 kV of accelerating potential, 30 mA current. A 2-theta angle scanning range was set for 10°-70°, with a step size of 0.04° and a dwell time of 10.0 sec. The main purpose of this analysis was to determine the crystalline phases present in the sample. The spectra peaks obtained were analyzed using the computer program JADE.

III.2 TEM Analysis

Sample VP2215 was ground into a fine powder, suspended in acetone, and then sonicated for 30 minutes in a water bath. The suspension was pipetted onto a carbon-coated copper grid, allowed to dry, and used as a sample for TEM analysis. A JEOL JEM2000 FX analytical transmission electron microscope was used to analyze the sample. TEM analysis was performed on the sample to analyze its crystal morphology.

III.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris DSC to determine the crystallization temperature. Initially, a baseline curve was obtained with empty platinum pans in both the sample and the reference compartments. Sample VP2117 was crushed and twenty to twenty-five milligrams were then placed in the sample compartment platinum pan, and the instrument was run with a starting temperature of 200°C and a heating rate of 10°C/min up to 725°C. The instrument kept the sample and the reference temperatures the same throughout the program while recording the energy difference in the independent supplies of the sample and reference against the program temperature. A Corrected heat flow sample curve was obtained after subtracting the baseline curve from the sample curve.
III.4 UV-Vis Spectrophotometry

III.4.1 Standardization of the Spectrophotometers

Three different spectrophotometers, Perkin-Elmer Lambda-9, Beckman DU70, and ColorEye 7000A (CE 7000A) were used in obtaining the reflectance and transmittance spectra of all the samples. An erbium glass sample was used to standardize all the equipment used, since the spectrum for erbium is well characterized. Averages of three runs of the glass sample, obtained from all the spectrophotometers, were stacked and plotted against the wavelength for ease of comparison. The standards used for all the spectrophotometers and the spectrophotometric measurements are displayed in the following table:

Table III. Spectrophotometers and Standards Used

<table>
<thead>
<tr>
<th>Spectrophotometers</th>
<th>Standards</th>
<th>Reflectance Measurements</th>
<th>Transmittance Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perkin-Elmer</td>
<td>MgF&lt;sub&gt;2&lt;/sub&gt; Mirror</td>
<td>Specular</td>
<td></td>
</tr>
<tr>
<td>Lambda-900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beckman DU70</td>
<td>Spectralon White</td>
<td>Total Diffuse</td>
<td>Diffuse</td>
</tr>
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<td></td>
<td></td>
<td>Specular</td>
<td></td>
</tr>
<tr>
<td>CE 7000A</td>
<td>Greatag – Macbeth XA1162</td>
<td>Total Diffuse</td>
<td></td>
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</tbody>
</table>
III.4.2 General Outline of the Experimental Procedure

Figure III.1. Outline of the experimental procedure.

III.4.3 Reflectance and Transmittance Spectrophotometry

A Beckman DU70 Spectrophotometer was used to measure the diffuse reflectance, specular reflectance and diffuse transmittance of the samples. An integration sphere was installed into the spectrophotometer to facilitate the measurement and a spectralon white was used as a standard background for all the runs. The CE 7000A spectrophotometer was only used to measure the total and the diffuse reflectance of the samples. Since the objective of this study was color matching only the visible region of light was considered for all the spectrophotometer experiments except fluorescence.
III.4.3.1 Diffuse Reflectance

A sample carrier was custom devised to measure diffuse and the specular reflectance. A ledge, with the dimensions of the samples was drilled in the center surface of a circular piece of aluminum metal with a diameter of 1 inch and a thickness of approximately 0.2 inches. The sample carrier was painted with a matte white paint.

![Sample carrier](image)

Figure III.2. Sample carrier used to elicit reflection spectra.

A zero degree offset sample holder was used to measure the diffuse reflectance of the samples. Samples were secured in the sample carrier using sticky tabs and the reflectance spectra in the visible region (400nm-700nm) were obtained at 600nm/min. Since the noise level was too high, a higher scan rate of 1200nm/min was selected. Each sample was run six times with reflectance measured at different points on the sample. An average of the six runs was then plotted against wavelength for all the samples. The standard deviation obtained was then depicted as Y-axis error bars along the obtained curve at every 50 nm intervals. A trend line was matched for all the curves individually and equations for all the samples were obtained.

III.4.3.2 Specular Reflectance

In the Beckman DU70 Spectrophotometer, an eight degree offset sample holder was used instead of a zero degree offset sample holder to measure the total reflectance of the samples. Sticky tabs were used to secure the samples in the sample carrier and the
spectra in the visible range were obtained at 1200nm/min. Each sample was again run six times and the average of diffuse reflectance values of each sample was subtracted from the values obtained. An average of the six residuals were then plotted to obtain the specular reflectance curves.

Specular Reflectance = Average [Total reflectance (8° offset) – Average diffuse reflectance (0° offset)]

The more advanced CE 7000A spectrophotometer measured the diffuse reflectance and total reflectance values requiring only a 0° offset sample holder. Specular reflectance values were calculated as before by subtracting the diffuse reflectance values from the total reflectance values obtained. Again, the standard deviations obtained were depicted as Y-axis error bars along the curve obtained, for every sample, at every 50nm intervals. A trendline was matched and an equation was obtained for every sample.

III.4.3.3 Diffuse Transmittance

Diffuse Transmittance of the samples was measured using only the BeckmanDU70 Spectrophotometer. A different sample carrier was designed to measure diffuse transmittance. A rectangular hole rather than a ledge was drilled on a circular aluminum disc with the same 1 inch diameter and 0.2 inch thick dimensions. This was also painted matte white.

Figure III.3. Sample carrier used to elicit transmission spectra.
Two sample holders were used to measure the diffuse transmittance. A sample holder at the front end of the integration sphere was used to place the sample carrier. Another sample holder at the rear end of the sphere carried the spectralon standard during all the experimental runs. Transmittance spectra of the entire set of samples were obtained at 1200nm/min, and the whole process was repeated five times for each sample. The average transmittance was plotted against wavelength with the standard deviation plotted at every 50nm interval along the obtained curve. A trendline was matched and an equation was obtained for every sample.

**III.5 Heat Treatment**

Sample VP2215 was selected to elucidate the effect of heat upon the samples. The sample was divided in half – one-half was used as a reference, the other half used for the study. An electric furnace was heated to 530°C (maximum temperature of crystallization obtained after DSC analysis) and the sample was place in the furnace. Reflectance of the sample was measured at regular intervals using a Perkin-Elmer UV-Vis at a rate of 1800nm/min and with a mirror as the standard. An average of three runs was plotted against the wavelength.

**III.6 UV Exposure**

Sample VP2216 was used to study the effect of UV light on the samples. A 20mW UV lamp was used for this purpose, one-half of the sample was exposed to the light for a period of 45 minutes, and the percentage reflectance was measured after the exposure. A mirror was used as a standard background run, and reflectance values of both the halves of the sample were measured at a rate of 1800nm/min using a Perkin-Elmer UV-Vis. The values obtained were plotted against wavelength and a graph was generated.
III.7 Experiments on Natural Teeth

Extracted natural teeth were obtained from the patients of a local dentist. They were washed, cleaned, and stored in vials containing water to retain the teeth in a hydrated state. They were labeled as Y-can, Y-cen, R-lat, W-cen, LL-cen, and W-can. Three teeth were selected to study the effect of hydration on the specular reflectance of a tooth. Reflectance values in the 200-800nm range, of three teeth (R-lat, W-cen & Y-cen) were measured over a period of 30 minutes, 70 minutes, & 7 days using a Perkin-Elmer UV-Vis at a rate of 1800nm/min, using a mirror as the standard background run. The tooth samples were undisturbed during the entire length of the experiment. The values for all the teeth were then plotted against wavelength, and the curves obtained were stacked for the ease of interpreting the results.

Total reflectance and the diffuse reflectance values of the hydrated natural teeth were also measured using the CE 7000A spectrophotometer. These were used for comparison with the values obtained for Chromascop shade guide teeth and the glass-ceramic samples.

In order to study the effect of surface texture on the reflectance values, a natural tooth, Y-can, was selected. Reflectance values in the 200-800 nm range were obtained on the labial surface of the tooth. The tooth was then roughened using a 200-gauge polishing paper and reflectance was measured again. A Perkin-Elmer UV-Vis was used and the values were obtained at a rate of 1800nm/min using a mirror as the background run. The obtained values were plotted against wavelength and stacked to visualize the effect.
**III.8 Fluorescence Spectroscopy**

Fluorescence spectroscopy was performed on all the glass-ceramic samples using a SPEX Fluorolog Double Grating Spectrophotometer. Both emission and excitation data were collected using a 1.0 nm increment and a 0.2 second integration time. Emission slit widths were set at 2 mm and excitation slit widths at 1 mm for all the experiments. Initially an emission spectrum was obtained at 292 nm excitation and peaks were obtained. Excitation spectra were obtained at those specific wavelengths to determine the location of any absorption peaks. Once the location of peaks was obtained from excitation spectra, emission spectra were measured using those wavelengths as excitation energy. Emission and excitation spectra of all the samples were then stacked to facilitate comparison.

**III.9 Munsell Notation and CIE L*a*b* Values Determination**

The samples were run in a research laboratory facility at Oneida Dinnerware, Buffalo. A CE 7000A spectrophotometer was used for this purpose. The reflectance values of a commercially available tooth shade guide, Chromascop (Ivoclar) were determined and compared to the values obtained from the natural teeth and the samples. The experiments were conducted in the visible region of the spectrum at a rate of 2400nm/min with a Greatag – Macbeth XA1162 as the standard background run. The sample carrier that was previously used for reflectance measurements was also used for these runs. Each sample was run four times and an average was obtained. Diffuse reflectance with and without the specular component included was also determined from these experiments.
IV RESULTS AND DISCUSSION

IV.1 UV-Visible Spectroscopy

IV.1.1 Standardization of the Spectrophotometers

An erbium glass with a known, well-characterized spectrum was used to standardize the spectrophotometers. From Figure IV.1 we can deduce that the spectra peaks for the erbium glass sample were identical indicating no wavelength shift in the spectrophotometers used for all the experiments. The spectrum obtained from the Perkin-Elmer Lambda 900 Spectrophotometer also displayed no shift in wavelength.

Figure IV.1. Erbium glass spectra obtained from the spectrophotometers used, indicates no wavelength shift.
Figure IV.2. Erbium glass spectra obtained from the Perkin-Elmer Lambda 900 Spectrophotometer.
IV.1.2 Photographic Evaluation of the Samples and the Standard

Figure IV.3. Photograph showing the variations in shades of the glass-ceramic samples in comparison with the spectralon white standard.

The Figure IV.2 shows the variations in color of the glass-ceramic samples to that of the spectralon white standard. The sample VP2215 shows maximum variation in the color, while sample VP2213 the minimum. The translucency levels of the samples can also be visualized from the photograph. The reflectance – transmittance spectra of the glass-ceramic samples as seen in Figures IV.4 – IV.23 corroborate these findings.
IV.1.3 Results of the UV-Visible Spectroscopy of the Glass-Ceramic Samples

Ten of the twelve glass-ceramic samples were used for the UV-Visible spectroscopy experiments. Of the remaining two samples, one was utilized for TEM analysis and the other to evaluate the effect of heat on the samples. Diffuse reflectance and transmittance spectra as measured by Beckman spectrophotometer, specular reflectance spectra as measured by both Beckman spectrophotometer and the CE 7000A spectrophotometer, and the total and diffuse reflectance spectra as measured using a CE 7000A spectrophotometer for each sample are shown in Figures IV.4 – IV.33.

The first of the three graphs, for each sample, shows diffuse reflectance and the diffuse transmittance spectra and has wavelength (in nanometers) along the X-axis, percent reflectance on the primary Y-axis, and percent transmittance along the secondary Y-axis. Each sample was run six times at different points on the sample surface and the average obtained was plotted. Standard deviations at every 50 nm interval were calculated and depicted as Y-axis error bars. Trend lines were matched for each curve obtained and a polynomial equation was selected.

The total reflectance of the samples was measured from both the spectrophotometers, specular reflectance values were calculated by subtracting the diffuse reflectance values from the total reflectance values, and spectra obtained from these values are shown in the second of the three graphs, where the values obtained from the ColorEye 7000A spectrophotometer are depicted on the primary Y-axis and the values obtained from the Beckman spectrophotometer on the secondary Y-axis, while wavelength was plotted along the X-axis. The low values for specular reflectance for all the samples can be attributed to the fact that the samples were not polished to their final form. Specular reflectance is only secondary for the process of shade evaluation as it denotes only the amount of gloss or luster while the diffuse reflectance – transmittance values from the primary attributes for the expression of color in an object. The difference in the shapes and values of the curves for specular reflectance as measured by the CE 7000A and the Beckman spectrophotometer is ascribed to the fact that different standards
were used for each instrument. In Beckman spectrophotometer, a spectralon white standard with a matte finish was used and hence the specular reflectance values calculated are higher than the values obtained from calculating the same from the values obtained in CE 7000A spectrophotometer, as the Greatag-Macbeth standard used had a glossy finish. The low R-square values reflect the difficulties associated with the measurement of the specular reflectance, because the point at which it is measured greatly contributes to the variation and hence a large standard deviation is observed.

The diffuse and the total reflectance spectra for each sample as measured by the CE 7000A spectrophotometer are plotted in the third graph. Each sample was run four times and the average plotted with wavelength along the X-axis. Again the standard deviations were calculated at every 50 nm interval and depicted as Y-axis error bars. The diffuse reflectance spectra obtained differed greatly from the spectra obtained from the Beckman spectrophotometer, though the basic shape of the curve remained the same. This again is attributed to the difference in standards used for measurements in each instrument. The smoother curve obtained for all measurements in CE 7000A can be attributed to the higher scan rate involved and the difference in the mode of measurement. Though specular reflectance for all the samples were also measured using a Perking Elmer Lambda 900 spectrophotometer, the results were inconsistent as the samples were weakly specular and the instrument was highly sensitive. For these experiments, a mirror was used as a standard and as compared to a mirror the specular reflectance of the samples was negligible. Hence the results obtained from these measurements were not considered.

Figure IV.4 depicts the diffuse reflectance and diffuse transmittance of the glass-ceramic sample VP2076. The diffuse reflectance spectra show that the sample is more reflective in the longer wavelengths and its highest diffuse reflectance value is at 580 nm, the yellow region of the spectrum. Hence it can be concluded that the sample has a yellow hue. The transmittance spectrum reveals that the transmittance increases with wavelength and is highest in the range of 650-700 nm which again is in the yellow – red
region of the spectrum. It can also be deduced that the sample is translucent as seen from the high transmittance values.

Figure IV.5 depicts the specular reflectance spectra obtained from both the Beckman and CE 7000A spectrophotometer. This reveals that the sample has minimal specular reflectance as noted from the low values.

Figure IV.6 depicts the total and diffuse reflectance spectra as measured by a CE 7000A spectrophotometer. As explained above, the difference in the curves obtained using a Beckman spectrophotometer and the CE 7000A can be attributed to the different standards used and method of measurement in each case. The results are the same however, in that the sample is more reflective in the longer wavelengths 550 – 600 nm range which corroborates the findings from the measurement using Beckman spectrophotometer as depicted in Figure IV.4.

Figure IV.4. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2076.
Figure IV.5. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2076.

Figure IV.6. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2076.
Figures IV.7 – IV.9 depict the diffuse reflectance, diffuse transmittance and specular reflectance of the glass-ceramic sample VP2114. Figure IV.7 displays the diffuse reflectance spectrum and it can be seen that the sample is more reflective in the shorter wavelength region. Its highest diffuse reflectance value is in the 450 – 500 nm which is in the violet-blue region. The diffuse and total reflectance spectra from the Figure IV.9 also corroborate these findings. The transmittance spectrum from the Figure IV.7 reveals that the transmittance increases with wavelength and is highest again in the 650 – 700 nm range which is in the yellow – red region of the spectrum. From the specular reflectance spectra in Figure IV.8 it can be noted that the sample is slightly specularly reflective similar to the sample VP2076.

![Graph of UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2114.](image)

Figure IV.7. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2114.
Figure IV.8. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2114.

Figure IV.9. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2114.
Figure IV.10 shows the diffuse reflectance and the transmittance spectra for the sample VP2115. The sample spectra are very similar to that seen for the sample VP2114 and hence it can be deduced that sample VP2115 is spectroscopically similar to sample VP2114 and this can be visually confirmed in the Figure IV.3. Figure IV.12 also confirms the spectroscopic similarities exhibited by the samples. The diffuse transmittance spectra again reveal high transmittance values in the longer wavelength regions. The highest diffuse reflectance value can be seen in the 450 – 500 nm range and the highest transmittance spectra in the 650 – 700 nm range. The sample is more reflective than the sample VP2114 as seen by the larger values of transmittance. Figure IV.11 displays the low specular reflectance exhibited by the sample.
Figure IV.11. UV-Visible specular reflectance spectra of the glass-ceramic sample VP2115.

Figure IV.12. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2115.
Figure IV.13 shows the diffuse reflectance and transmittance spectra for the sample VP2116. From the diffuse reflectance spectra in both Figures IV.13 and IV.15, it can be deduced that the sample has a high diffuse reflectance value in the range of 500-550 nm. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits high a level of translucency. Figure IV.14 displays the low specular reflectance of the sample as noted from the low values.

![Graph showing UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2116.](image_url)

Figure IV.13. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2116.
Figure IV.14. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2116.

Figure IV.15. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2116.
Figure IV.16 shows the diffuse reflectance and transmittance spectra for the sample VP2117. From the diffuse reflectance spectra, in both Figures IV.16 and IV.18, it can be deduced that the sample has a high diffuse reflectance value in the 550 – 600 nm range which is in the yellow region of the spectrum. Hence it can be concluded that the sample has a yellow hue. This is visually confirmed from the Figure IV.3. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits a high level of translucency. Figure IV.17 displays the low specular reflectance of the sample as noted from the low values.

Figure IV.16. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2117.
Figure IV.17. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2117.

Figure IV.18. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2117.
Figure IV.19 shows the diffuse reflectance and transmittance spectra for the sample VP2118. From the diffuse reflectance spectra, in both Figures IV.19 and IV.21, it can be deduced that the sample has a high diffuse reflectance value in the 550 – 600 nm range which is in the yellow region of the spectrum. Hence it can be concluded that the sample has a yellow hue. This is visually confirmed from Figure IV.3. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values it can also be deduced that the sample exhibits high level of translucency. Figure IV.20 displays the low specular reflectance of the sample as noted from the low values.

Figure IV.19. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2118.
Figure IV.20. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2118.

Figure IV.21. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2118.
Figure IV.22 shows the diffuse reflectance and transmittance spectra for the sample VP2141. From the diffuse reflectance spectra, in both Figures IV.22 and IV.24, it can be deduced that the sample has a high diffuse reflectance values in the 600 – 650 nm range which is in the yellow – red region of the spectrum. Hence it can be concluded that the sample has a yellow hue stronger than those of the previous samples. This is visually confirmed from the Figure IV.3. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits a lower level of translucency as compared to the previously mentioned samples. Figure IV.23 displays the low specular reflectance of the sample as noted from the low values.

![Figure IV.22. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2141.](image-url)
Figure IV.23. UV-Visible specular reflectance spectrum for the glass-ceramic sample VP2141.

Figure IV.24. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2141.
Figure IV.25 shows the diffuse reflectance and transmittance spectra for the sample VP2184. From the diffuse reflectance spectra, in both Figures IV.25 and IV.27, it can be deduced that the sample has a high diffuse reflectance values in the 600 – 650 nm range which is in the yellow – red region of the spectrum. Hence it can be concluded that the sample has a strong yellowish-red hue. This is visually confirmed from the Figure IV.3. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits more opacity as compared to the other samples described. Figure IV.26 displays the low specular reflectance of the sample as noted from the low values.

Figure IV.25. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2184.
Figure IV.26. UV-Visible specular reflectance spectrum for the glass-ceramic sample VP2184.

Figure IV.27. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2184.
Figure IV.28 shows the diffuse reflectance and transmittance spectra for the sample VP2213. From the diffuse reflectance spectra, in both Figures IV.28 and IV.30, it can be deduced that the sample has a high diffuse reflectance value in the of 450 – 500 nm range which is in the blue region of the spectrum. Hence it can be concluded that the sample has a bluish hue. This is visually confirmed from the Figure IV.3. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits more opacity as compared to the other samples described. Figure IV.29 displays the low specular reflectance of the sample as noted from the low values.

![Graph](image-url)

Figure IV.28. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2213.
Figure IV.29. UV-Visible specular reflectance spectra for the glass-ceramic sample VP2213.

Figure IV.30. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2213.
Figure IV.31 shows diffuse reflectance and transmittance spectra for the sample VP2214. From the diffuse reflectance spectra, in both Figures IV.31 and IV.33, it can also be deduced that the sample has a high diffuse reflectance value in the 600 – 650 nm range which is in the yellow-red of the spectrum. Hence it can be concluded that the sample has a yellow-red or orange hue. This is visually confirmed from the Figure IV.3. In Figure IV.31 a region 575 nm – 650 nm was not included in the graph in order to facilitate derivation of a better fit for the trendline. This part of the spectrum reflects the presence of a peak (trough) for a rare-earth element erbium which is present in the sample. Figure IV.33 displays the erbium peaks and it can also be noted that the erbium peaks appear to be shifted when a comparison is made between the Figures IV.31 and IV.33. The diffuse transmittance values increase with wavelength and are highest in the 650 – 700 nm range. From the transmittance values, it can also be deduced that the sample exhibits more opacity as compared to the other samples described. Figure IV.32 displays the low specular reflectance of the sample as noted from the low values.

Figure IV.31. UV-Visible diffuse reflectance and transmittance spectra for the glass-ceramic sample VP2214.
Figure IV.32. UV-Visible specular reflectance spectrum for the glass-ceramic sample VP2214.

Figure IV.33. Total and diffuse UV-Visible reflectance spectra for glass-ceramic sample VP2214.
IV.1.4 UV-Visible Spectroscopy of Chromascop Shade Guide Teeth

Diffuse reflectance and total reflectance of a commercially available tooth shade guide, Chromascop, was measured using a CE 7000A spectrophotometer. The Chromascop shade guide is composed of 20 shades, chromatically arranged in five groups: group 100 - white, group 200 - yellow, group 300 - light-brown, group 400 - gray, and group 500 - dark-brown. Within these groups, samples are arranged according to the increasing saturation and the more saturated the samples are, the higher are their numbers. Each group consists of four samples, marked by a number representing the sum of the group number and numbers 10, 20, 30 or 40 (for example 110, 120, 130, and 140).

Figures IV.34 – IV.43 illustrate the diffuse and total reflectance spectra of the various groups of teeth present in the shade guide. Each shade guide tooth was run three times and the average obtained was plotted against the wavelength along the X-axis. The position of the shade guide tooth was not changed during the three measurements, and the measurements were made in the middle third on the labial surface of the tooth. The standard deviation values obtained were very low (about 0.08 – 0.10) and hence were not plotted. Figures IV.34 – IV.43 reveal that the shapes of the curves for the diffuse reflectance and the total reflectance spectra of all the samples in the same group are similar but there is a discernible difference between the shapes of the curves between the groups.

Though each tooth in the shade guide represents a different color, the differences in the spectra of different sets of shade guide teeth are trivial, indicating the visual perspicacity of the eye.
Figure IV.34. Diffuse reflectance spectra of series 1 of the Chromascop shade guide.

Figure IV.35. Total reflectance spectra of series 1 of the Chromascop shade guide.
Figure IV.36. Diffuse reflectance spectra of series 2 of the Chromascop shade guide.

Figure IV.37. Total reflectance spectra of series 2 of the Chromascop shade guide.
Figure IV.38. Diffuse reflectance spectra of series 3 of the Chromascop shade guide.

Figure IV.39. Total reflectance spectra of series 3 of the Chromascop shade guide.
Figure IV.40. Diffuse reflectance spectra of series 4 of the Chromascop shade guide.

Figure IV.41. Total reflectance spectra of series 4 of the Chromascop shade guide.
Figure IV.42. Diffuse reflectance spectra of series 5 of the Chromascop shade guide.

Figure IV.43. Total reflectance spectra of series 5 of the Chromascop shade guide.
IV.1.5 UV-Visible Spectroscopy of Extracted Natural Teeth

Figure IV.44 shows diffuse reflectance spectra of extracted natural teeth. Each tooth sample was run three times and the average plotted against wavelength along the X-axis. Only the middle third region on the labial surface of the teeth was analyzed. As the tooth remained undisturbed during all the runs, the standard deviation obtained was very low and hence not plotted. It can be noted from the graph that the natural teeth spectra obviously reflect more in the longer wavelength, in the yellow region of the spectrum. The commercially available shade guide teeth and the glass-ceramic and porcelain samples mimic the natural teeth spectra to obtain a shade closer to that of the natural teeth.

Figure IV.45 is a combined graph displaying the total reflectance spectra obtained for the glass-ceramic sample VP2118, extracted natural tooth R-lat, and Chromascop shade guide tooth 140. Trendlines were matched for all the spectra obtained for natural teeth and polynomial equations were selected. Similarity between the glass-ceramic sample and the natural tooth spectra is apparent. The difference in the shape of the curve obtained for the shade guide tooth however could be attributed to its specular component, as the shade guide teeth are polished and have a high gloss as compared to the extracted natural tooth or the glass-ceramic sample.
Figure IV.44. Total reflectance spectra of the natural teeth.

Figure IV.45. Comparison of the total reflectance spectra of Chromascop shade 140, extracted natural tooth rlat, and glass-ceramic sample VP2118.
IV.2 Fluorescence Spectroscopy Results of the Glass-Ceramic Samples

The fluorescence spectra for the glass-ceramic samples are shown in Figures IV.46 and IV.47. Figure IV.46 shows the emission spectra and Figure IV.47 the excitation spectra for the glass-ceramic samples. The emission spectra for all the samples were collected at an excitation wavelength of 292 nm and excitation peaks were recorded at an emission of 539 nm.

Figure IV.46 reveals major emission peaks at 539 nm, 547 nm, and minor emission peaks at 484 nm, 492 nm and 620 nm for all the glass-ceramic samples. Emission peaks can also be observed in some samples at 415 nm. The emission peaks at 539 nm and 547 nm indicate that the samples fluoresce in the yellow region of the visible spectrum. The emission peaks at 415 nm, 484 nm, and 492 nm denote that the samples also fluoresce in the blue region of the spectrum and this is seen in the samples possessing a bluish hue.

Figure IV.47 shows excitation peaks at 350 nm, 374 nm, and 481 nm obtained at 539 nm emission wavelength. The peaks indicate the wavelengths at which incident light is absorbed in the sample.

Terbium, a rare earth element when present in soda-glasses exhibits fluorescence peaks at 552 nm, 543 nm, 497 nm, 488 nm, 459 nm, 444 nm, 437 nm, 415 nm, and 380 nm, though the peaks may shift depending on the type of glass or glass-ceramic. Hence, the fluorescent peaks seen could be attributed to the presence of Terbium in all the samples. Hence by altering the amount of Terbium or by incorporating a different rare earth element into the samples, a desired level of fluorescence similar to those exhibited by natural teeth could be attained.
Figure IV.46. UV-Visible fluorescence emission spectra of all the glass-ceramic samples at 292 nm excitation wavelength.

Figure IV.47. UV-Visible fluorescence excitation spectra of all the glass-ceramic samples at 539 nm.
IV.3 Results from the XRD, TEM, and DSC Analysis of the Glass-Ceramic Samples

Glass-ceramic samples were received from Ivoclar and as their composition was proprietary, the samples were subjected to X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), and Differential Scanning Calorimetry (DSC).

IV.3.1 Results of XRD Analysis of the Sample

Figure IV.48 shows the XRD pattern obtained for the glass-ceramic sample VP2184. The XRD pattern matches well with the PDF #49-0803 indicating that the glass-ceramic is probably analogous to a Lithium Silicon Oxide crystalline phase.

![XRD pattern for the glass-ceramic sample VP2184.](VP2184.MDI)

Figure IV.48. XRD pattern for the glass-ceramic sample VP2184.
IV.3.2 Results of TEM Analysis

A bright field TEM image of the glass-ceramic sample is shown in the Figure IV.48. Figure IV.49 shows the selected area diffraction pattern of Figure IV.48. From both the Figures it can be deduced that the glass-ceramic is polycrystalline.

Figure IV.49. Bright field TEM image of the glass-ceramic sample VP2216 taken at 120 kV and a magnification of 25X.
Figure IV.50. Diffraction pattern taken at 80.0cm camera length and 120 kV, of the sample reveals rings of spots suggesting that the sample is polycrystalline.
IV.3.3 Results of the DSC Analysis

DSC analysis was performed on a sample VP2115 to determine the crystallization temperature. Figure IV.50 shows the DSC thermogram for the glass-ceramic sample. Approximate crystallization temperature is also marked at 400 – 525 °C.

![DSC thermogram for the sample VP2115 using a 10 °C/min heating rate. Range of the approximate crystallization temperature (T_c) is provided.](image)

Figure IV.51. DSC thermogram for the sample VP2115 using a 10 °C/min heating rate. Range of the approximate crystallization temperature (T_c) is provided.
IV.4 Results of the experiments on natural teeth

IV.4.1 Effect of Hydration on Specular Reflectance of Natural Teeth

Figures IV.52 and IV.53 show the effect of hydration over a period of time on the specular reflectance of the tooth R-lat and W-cen using a Perkin – Elmer Lambda 900 spectrophotometer. It can be seen that the specular reflectance increases as the tooth changes from a completely hydrated state to a dry state. The teeth remained undisturbed during the entire period and an average of three runs was plotted. Trendlines were matched and a polynomial equation was selected for all the spectra.

Figure IV.52. Effect of hydration over time on the specular reflectance of tooth R-lat.
Figure IV.53. Effect of hydration over a period of time on the specular reflectance of the extracted natural tooth W-cen.
IV.4.2 Effect of Surface Roughness on the Specular Reflectance of Natural Teeth

Figure IV.54 shows the effect of surface roughness on the specular reflectance of extracted natural tooth Y-can. Perkin – Elmer Lambda 900 spectrophotometer was used for these experiments. Specular reflectance of the tooth was measured on the middle third of the labial surface. The tooth was then roughened and specular reflectance values were obtained again. The specular reflectance of the tooth increases with roughness as seen from the spectra. Though the specular reflectance should decrease as the tooth becomes rougher and loses its gloss, the results do not demonstrate this. The extracted natural teeth are feebly specularly reflective and hence the results obtained are inconsistent and were disregarded.

![Graph showing the effect of surface texture on the specular reflectance values.](image)

Figure IV.54. Graph showing the effect of surface texture on the specular reflectance values.
**IV.5 Effect of Heat and UV-light on the glass-ceramic samples**

Effects of heat and UV-light on the specular reflectance of the glass-ceramic samples were studied using the Perkin – Elmer Lambda 900 spectrophotometer. Figures IV.55 and IV.56 show the graphs displaying the effect of heat and UV-light on the glass-ceramic samples respectively. It can be noted in Figure IV.55 that heating the samples to their crystallization temperature increases the specular reflectance of the glass-ceramics, the results were inconclusive and more experiments need to be done to confirm the findings. However, this does indicate that by manipulating the time and temperature of crystallization, the actual appearance of the glass-ceramics could be modified.

![Graph showing the effect of heat on the glass-ceramic sample VP2115.](image)

**Figure IV.55.** UV-Visible specular reflectance spectra showing the effect of heat on the glass-ceramic sample VP2115.
Figure IV.56 illustrates the effect of UV light exposure on the glass-ceramic sample VP2215. Though there is an indication that exposing the sample to the UV light increases its specular reflectance, the results are unconvincing. Further experiments using a higher strength UV lamp should be performed, and the results obtained analyzed. However, this indicates the ability to modify the appearance of the glass-ceramics by exposing them to UV light. Hence, masking the samples and exposing a desired region to the UV light would help in obtaining a choice of shades similar to the different shades exhibited by the various regions of a single tooth.

![UV-Visible specular reflectance spectra](image.png)

Figure IV.56. UV-Visible specular reflectance spectra showing the effect of UV exposure on the glass-ceramic sample VP2215.
IV.6 Munsell and CIE L*a*b* values of the samples

Munsell and the CIE L*a*b* values for glass-ceramic samples, natural teeth and the shade guide teeth from Chromascop were determined using a CE 7000A spectrophotometer in Oneida Dinnerware research facility in Buffalo. Tables 4 – 6 express the color of the glass-ceramic samples, extracted natural teeth and Chromascop shade guide teeth respectively in both the Munsell and the CIE L*a*b* nomenclature systems. An average of four runs was obtained for all the samples, natural teeth and shade guide teeth and is shown the table. ∆L* is the difference in the luminosity values, ∆a* the difference in values along the red – green axis, and ∆b* the difference in values along the yellow – blue axis from the values obtained for the Greatag – Macbeth XA1162 standard. ∆E* is the total color difference from that of the standard.

It can be seen from Table 4 that some of the values obtained for Munsell notation for extracted natural teeth do not correlate well with the values obtained from previous studies as represented in Table 1. This can be attributed to the fact that the values here were obtained from experiments on natural teeth while the values construed in Table 1 were conducted on people or simply, unextracted natural teeth.
Table IV. Munsell and CIE L*a*b* Notations of Glass-ceramic Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Munsell Notation C/2°</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>∆L*</th>
<th>∆a*</th>
<th>∆b*</th>
<th>∆E*</th>
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<td>-</td>
<td>-</td>
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<td>13.71</td>
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Table V. Munsell and CIE L*a*b* Notations of Extracted Natural Teeth

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<th>∆a*</th>
<th>∆b*</th>
<th>∆E*</th>
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## Table VI. Munsell and CIE L*a*b* Notations of Chromascop Teeth

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</table>
IV.7 **Generation of a Figure of Merit**

The main goal of this thesis was to study the UV-visible spectroscopy results of the glass-ceramic samples and derivation of a figure of merit that could be used for communicating between the dentist and the ceramist. Color is mainly observed due to the diffuse reflectance nature of the glass-ceramic samples, while specular reflectance levels indicate the levels of gloss or shininess and diffuse transmittance values indicate its translucency or opacity. Hence, a figure of merit is derived based on the total reflectance values obtained for all the glass-ceramic samples. For comparison, figures of merit for the natural teeth and the shade-guide teeth were also derived.

Dispersion, the degree to which a material shows color, is the difference in the refractive index of a material at the B and G Fraunhofer wavelengths of 686.7 nm and 430.8 nm. The Abbe Number, named after Ernst Abbe, a German physicist, also referred sometimes to as a *V – number* or *constringence* of a material is a measure of its dispersion.

The Abbe number $V$ of a material is defined as:

$$V = (n_d - 1) / (n_F - n_C)$$  \hspace{1cm} (8)

Where $n_d$, $n_F$ and $n_C$ are the refractive indices of the material at the wavelengths of the Fraunhofer d-, F- and C- spectral lines 587.6 nm, 486.1 nm and 656.3 nm respectively. The Abbe number calculation usually involves three wavelengths, two from the ends and one from the center of the visible spectrum. On the same principle, three wavelengths at 450 nm, 700 nm, and 580 nm were considered to calculate the figure of merit (FOM). The constant obtained, after the calculations for the glass-ceramic samples, shade-guide teeth, and the natural teeth are presented in the following table.
### Table VII. Figure of Merit

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It can be seen from the FOM values depicted in the table above that the values are incongruent. The FOM for some of the samples were similar though there was a significant difference in the actual shades when perceived visually, giving an indication that the figure of merit based on the Abbe number principle would not relate well with the visual perception of the human eye. Hence, this method of deriving a FOM was disregarded.

Tables 4, 5, and 6 illustrate the $\Delta E$ values of the glass-ceramic samples, shade-guide teeth and extracted natural teeth, obtained from the CE 7000A spectrophotometer. As explained before, $\Delta E$ values signify the total color difference from that of the standard used. The $\Delta E$ values of samples that visually appear similar correlate well and these values can be used for shade comparison and eventually shade determination. As the values obtained were in reference to a white standard, a huge number is obtained for $\Delta E$. As the $\Delta E$ values increase, the perceptible shade difference also increases. The total color difference $\Delta E$ can be divided into:

- Lightness difference, $\Delta L$,
- Red – green coordinate difference, $\Delta a$,
- Yellow – blue coordinate difference, $\Delta b$,
- Saturation difference, $\Delta C$ and
- Hue difference, $\Delta H$

If the $\Delta E$ values of any two objects match, along with their $\Delta C$ and $\Delta H$ values, the objects must appear similar. A $\Delta E$ value lesser than one usually indicates that the shades of the two objects compared are visually similar. $\Delta E$ values in the range of 1 – 2 are acceptable for visual comparison of shades; as the $\Delta E$ value increases, the visual discrimination of the shade of the objects compared becomes easier. Figure IV.57 illustrates the graphical method of acquiring $a$, $b$, $\Delta C$, and $\Delta H$ parameters which contribute to the final shade difference.
Figure IV.57. Figure showing the color difference calculation using a, b, C and H coordinates.

These values can be calculated using any set of spectroscopic data. Hence, by manipulating the processing procedures, such as heat treatment, incorporation of coloring ions, etc., during the manufacture of glass-ceramics the required $\Delta C$, $\Delta H$, and consequently $\Delta E$ values could be attained and the shade required obtained.

Hence $\Delta E$ values can be considered as FOM and could be used in the development of custom shades of glass-ceramics.
V CONCLUSIONS

In this study, glass-ceramic samples obtained from Ivoclar were spectroscopically analyzed and consequently figure of merit (FOM) derived to express a shade into a value. Though the exact sample composition was proprietary, the samples were Lithium Silicate glass-ceramics of different shades. Diffuse reflectance, diffuse transmittance and specular reflectance values for the glass-ceramics were obtained and compared to similar experiments done on extracted natural teeth and teeth from a commercially available dental shade-guide, Chromascop (Ivoclar).

Three spectrophotometers were used for all the experiments: Beckman DU70, CE 7000A, and Perkin-Elmer Lambda-900. The results from the Perkin-Elmer Lambda-900 spectrophotometer were incongruous and hence were disregarded. The diffuse reflectance spectra obtained from the glass-ceramic samples indicated that most of the samples were reflective in the longer wavelength region (yellow) and a few of them in the shorter wavelength (blue) regions. Samples were visually evaluated to confirm the results obtained from the spectroscopic measurements. The diffuse transmittance values obtained indicated the levels of translucency in the glass-ceramic samples and this could be confirmed visually.

Fluorescence studies were conducted on the glass-ceramic samples to examine the level of fluorescence exhibited. From the fluorescent spectroscopy measurements, it was deduced that a rare-earth ion, Terbium was incorporated into the glass-ceramics to mimic the fluorescence exhibited by natural teeth. It was also seen that by varying the levels of rare-earth ions, the desired level of fluorescence could be obtained.

The purpose of this thesis was to develop a FOM from the spectroscopic data obtained from the glass-ceramic samples after comparison with similar data obtained
from natural teeth and shade-guide teeth. A FOM based on the Abbe number principle was evaluated using three random wavelengths, two from the ends and one from the center of the visible spectrum. The figure of merit derived did not correlate well when the samples were evaluated visually. This was repeated at different wavelengths and yet the FOM based on Abbe number principle never corroborated well with the visual findings.

CIE L*a*b* values were obtained from CE 7000A spectrophotometer and the total color difference (ΔE) was calculated. The ΔE values corroborated well with the visual findings and these could be used to communicate a shade in the form of a number.
VI SUGGESTIONS FOR FUTURE WORK

Further research would include the spectroscopic analysis of the glass-ceramics using individual dental shade-guide teeth as standard runs rather than the standard calibration tile or a Spectralon standard and comparing the $\Delta E$ values obtained during each run. Similar experiments could also be performed on natural teeth of volunteers using a hand-held spectrophotometer. This would give us the actual deviation in the shade of the glass-ceramics from the shade of the shade-guide tooth.

More experiments to study the effect of heat and UV-light on the glass-ceramic samples should be performed and the total color difference observed after these experiments be quantified. The data obtained from these results could also help in confirming the efficacy of the $\Delta E$ values in expression of the shade. Once the efficacy of $\Delta E$ values in expression of the shade is determined, a hand-held spectrophotometer could be customized for dental use.
References


