

Production and Characterization of Colored Feldspathic Enamel for Dental Application

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In this work we synthesized pigments capable of developing dental shades when mixed with dental porcelain and fired at appropriate temperatures. TiO₂-xCeO₂ pigments (x = 2, 6, 10, 13 and 18 mol%) were synthesized by the Pechini method. Characterization by thermal analysis revealed the stability of the material at temperatures up to 1200 °C. X-ray diffraction showed stable crystalline phases (rutile to TiO₂ and cerianite to CeO₂) for all pigments studied. Color of pigments was characterized by colorimetric coordinates according to the CIELAB method and reflectance measurements in the visible region. Through colorimetric analysis it was possible to verify the potential use of these pigments in dental ceramics.

Keywords: polymeric precursor method, CIElab, ceramic pigments, dental application

1. Introduction

Ceramics have been used commercially as synthetic tooth filling materials and in dental prosthesis. In conventional dental ceramics, such as dental porcelain, a ceramic pigment or a combination of several pigments is incorporated into the composition. Pigments' crystals remain sufficiently intact during the firing process to impart the desired color in the finished product¹.

In order to produce acceptable colors for use in dental ceramics, pigments which produce yellow to yellow-red shades in the crystallized product are needed. There is no single transition metal or rare earth metal ion which yields a clear yellow effect, except those that are restricted, such as uranium. However, methods for combining certain pairs of colorant ions have been described, such as the combination of Ce and Ti oxides that can produce yellow colors in glazes and glasses^{2,3}.

Property studies on Ce and Ti oxide systems are promising for various reasons. They can be applied to surfaces which need yellow pigments, including application in dental ceramics, due to the fact that titanium-based and rare-earth pigments present low toxicity, high thermal and chemical resistance⁴ and to the fact that they have already been mentioned in biomedicine⁵. Cerium oxide (CeO₂) is already used in dentistry to simulate the fluorescence of tooth enamel¹ and titanium dioxide (TiO₂) to supply opacity^{6,7}.

Several methods have been used to prepare Ce and Ti oxides, mainly the conventional ceramic method. However, several studies have demonstrated that the polymeric precursor method (Pechini Method) can provide powders with improved qualities. In this method certain metal-ion chelates forming carboxylic acids are used. Those metal chelates are polyesterified when heated in polyhydroxy alcohols, giving rise to a resin in which ions are immobilized and the desired oxides are obtained after heat treatment. This method for forming homogeneous powders provides small particle sizes, high purity, low cost and relatively low processing temperature^{8,9}.

Taking into consideration what has been aforementioned, this work presents the results from characterization of TiO₂-xCeO₂ yellow pigments obtained through the Pechini method, including an insight to their potential application in dental ceramics coloration.

2. Experimental Procedure

2.1. Synthesis of TiO₂-xCeO₂ pigments

TiO₂-xCeO₂ pigments (x = 2, 6, 10 mol%) were synthesized through the polymeric precursor method⁹. The molar ratio between the citric acid and the metal cation was 3:1, while the citric acid/ethylene-glycol was 1:2.

Alcohol solution (40%) of titanium (IV) isopropoxide (C₁₂H₂₈O₄Ti, 97%, Aldrich) was slowly added to a 1 molar

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aqueous solution of citric acid ($C_6H_8O_7$, 99.5% - Vetec) heated to 70 °C. Next, 0.1 molar aqueous Cerium nitrate hexahydrate solution ($Ce(NO_3)_3 \cdot 6H_2O$, 99%, Sigma) was added varying the amount as desired percentage. Then, ethylene glycol was added ($C_2H_6O_2$, 99.5% - Vetec). The temperature was raised to 90 °C, where the system remained for 10 hours. The resins obtained were heat treated at 500 °C for 4 hours and calcined in air at 1000 °C for 2 hours. In both heat treatments the heating rate was 10 °C/min.

2.2. Preparation of frits and glazes

For dental ceramics preparation enamel layers composed primarily of frits (feldspar based) and pigments are used. So, Feldspar from the Borborema-Seridó region (northeast of Brazil) was used to prepare the frit. Borax ($Na_2B_4O_7 \cdot 10H_2O$, 99.5-105%, Vetec) and carboxymethylcellulose (CMC, Synth) were analytical grades.

Frits were obtained through the melting of borax (20%) and feldspars (80%) at temperatures of the order of 1100 °C and quenched in water.

For glaze preparation, the proportions 1 and 2wt% of pigments to a mass of frit were used (named $RTiO_2-xCeO_2$, 1% and $RTiO_2-xCeO_2$, 2% in the text). 0.5mL of CMC solution at 0.01% was used as organic binder, the mixture was homogenized and applied with a brush on the alumina substrates (supplied by Saint Gobain, 3.5 × 3.5 cm). The ceramic tiles were dried at 100 °C for 20 min and fired at 900 °C for 30 min.

2.3. Characterization techniques

Thermal analyses (TG/DTA) were carried out in a SHIMADZU TA-50WSI (thermogravimetric analysis) and a DTA-50 (differential thermal analysis) at a 10 °C/min heating rate up to 1200 °C in air.

Crystallographic structure of the resultant powders were determined by X-ray diffraction using a *Bruker-AXS D5005 diffractometer*, $Co K\alpha$ radiation (35kV/40mA); 2θ range from 5° to 80°. The chemical composition was analyzed by X-ray fluorescence, in an S4 Bruker equipment.

$L^*a^*b^*$ color parameters and diffuse reflectance of fired pigments and ceramic tiles were measured by a Color Touch

colorimeter, using D65 illumination in an angle of 2° and also a Vita Easyshade spectrophotometer.

3. Results and Discussion

3.1. Glaze characterization

The chemical composition for the feldspar used in the preparation of the frit is provided in Table 1. Its chemical analysis has evidenced that this mineral presents the requested characteristics to be applied as a glaze, given that its impurities content (iron and other colorant oxides) is low⁵. In addition, frits based on feldspar composition are common to obtain ceramic glazes for dental use.

X-ray diffraction has indicated that this feldspar is a mixture of albite (sodic feldspar - $NaAlSi_3O_8$) and orthoclase (potassic feldspar - $KAlSi_3O_8$), Figure 1a, present almost in the same proportion as it can be verified in Table 1 (concentration of Na_2O and K_2O). In agreement with the phase diagram under these conditions, feldspar presents a

Table 1. Chemical Composition of the feldspar used in the preparation of the frit.

Substances	weight %	Substances	weight %
SiO_2	66.0	K_2O	5.5
Al_2O_3	20.0	Rb_2O	0.07
CaO	0.26	NiO	0.11
Na_2O	5.9	Ashes	1.3
P_2O_5	0.34	-	-

Table 2. Concentrations of Ce in TiO_2-xCeO_2 .

Concentrations of Ce (mol%)			
Nominal (as designed)	Experimental (as analyzed)	Nominal (as designed)	Experimental (as analyzed)
0	0	10.0	10.2
2.0	2.0	14.0	13.0
6.0	6.2	20.0	17.0

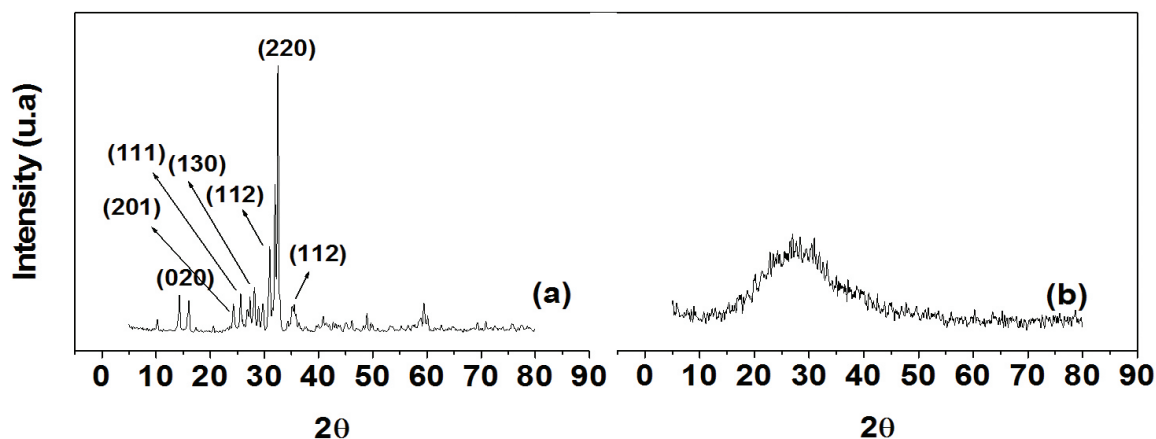


Figure 1. X-ray diffraction patterns for (a) feldspar and (b) frit.

melting temperature of the order of 1200 °C. However, it was possible to apply an even lower temperature (1100 °C) due to the borax incorporation into the composition¹⁰.

The X-ray diffraction pattern, Figure 1b, shows that the frit obtained is entirely amorphous, with a halo centered around $2\theta = 27^\circ$ characteristic of glassy materials, without any crystalline phases remaining from the original feldspar¹¹.

3.2. Pigments characterization

3.2.1. Chemical composition, thermal analysis and crystalline phases

The compositional homogeneity of the synthesized product achieved with the use of the Pechini method could be confirmed through the results of the chemical analysis of the pigments. The obtained data, summarized in Table 2, give good evidence of the agreement between the theoretical and experimental values.

Figure 2 shows the TG and DTA curves for the polymeric resin precursor of the $\text{TiO}_2\text{-}0.1\text{CeO}_2$ pigment. In the TG curve profile four mass loss regions are seen: the first, between 30 and 200 °C, with 20.64 wt% loss, was related to the elimination of water physically adsorbed and the alcohol utilized as a solvent; the second and third regions (50 wt% loss), from 200 to 380 °C, were attributed to organic matter combustion; and the fourth one, about 11.9 wt% loss,

between 380 and 520 °C, was associated with the elimination of chemically combined water and residual organic matter.

The events observed in the analysis of mass loss could be confirmed through the constructional details of the DTA profile, Figure 2b, where endothermic peaks were found in the 200-500 °C region - related to the combustion of organic matter (243 and 311 °C). The exothermic peaks at 543 and 724 °C were associated with the formation of TiO_2 in amorphous state and to the phase change to rutile, respectively, as confirmed by the x-ray diffraction analysis.

$\text{TiO}_2\text{-}x\text{CeO}_2$ pigments in powder form were studied through XRD for the samples fired at 500 °C (precursor powder) and further calcined at 1.000 °C (calcined powder), as shown in Figure 3.

The XRD pattern for pure titanium dioxide showed that the powder fired at 500 °C is still amorphous, and only after calcination at 1.000 °C it became entirely crystalline in the rutile phase.

The analysis of XRD patterns for TiO_2 samples containing additions of cerium oxide, Figure 4, as well as the peaks corresponding to the rutile phase, point out two peaks corresponding to the cerianite phase, for samples containing 6 mol% or more of cerium oxide, its intensity growing with the increase in the cerium oxide content, disclosing the dual-phase nature of the synthesized product ($\text{TiO}_2 + \text{CeO}_2$). This result was expected since some authors had already suggested that cerium oxides were not capable of forming solid solutions with TiO_2 , as usually only mixture of oxides were obtained¹².

3.2.2. Colorimetric characterization

Colors are usually characterized using the CIElab system, which provides three color parameters, named L^* , a^* and b^* . Index L^* corresponds to brightness variation, in a scale from 0 (black) to 100 (white); a^* represents color variation from green (-60) to red (+60); and b^* color variation from blue (-60) to yellow (+60)¹³.

The colorimetric results for $\text{TiO}_2\text{-}x\text{CeO}_2$ pigments are shown in Table 3, where the negative values of a^* indicate predominance of the green color over red while the high values of b^* correspond to the yellow color, which is the real aspect of the samples. Through the obtained values, the effect of the cerium oxide was verified in the development of the yellow color, because the introduction of only 2 mol% of

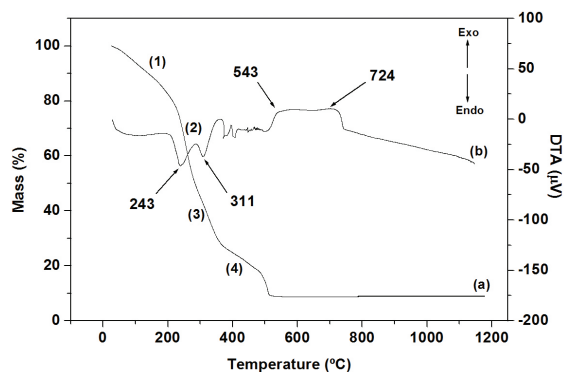


Figure 2. Curves of (a) TG and (b) DTA of the precursor resin of $\text{TiO}_2\text{-}0.1\text{CeO}_2$.

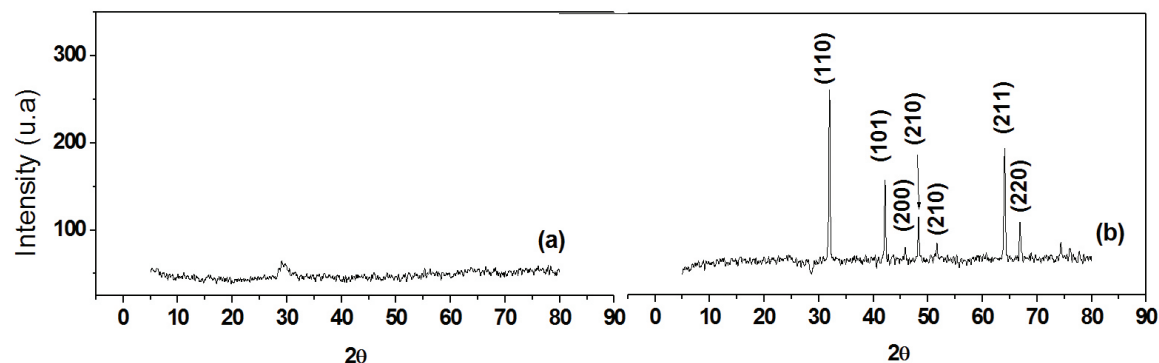


Figure 3. X-ray diffraction patterns for TiO_2 calcined: (a) 500 °C and (b) 1.000 °C.

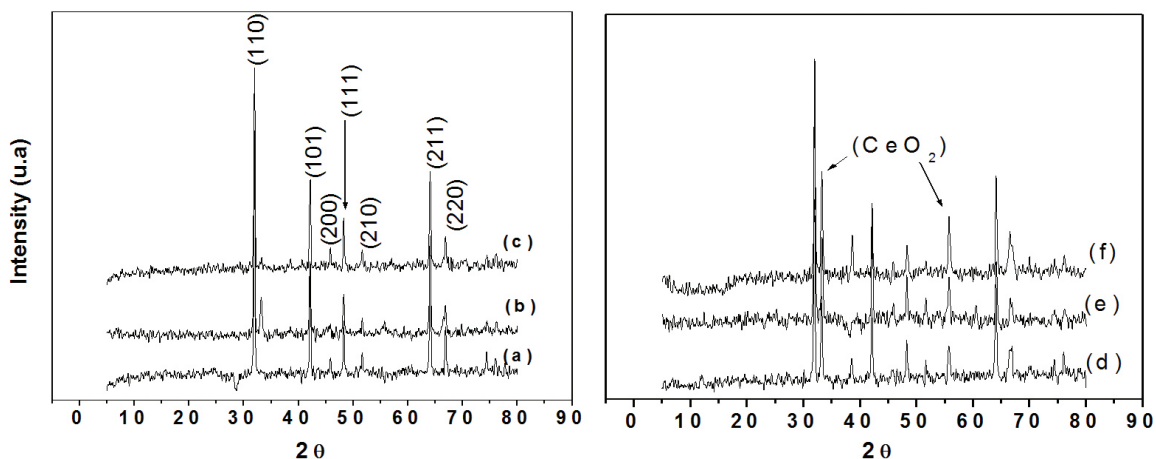


Figure 4. X-ray diffraction patterns (a) TiO_2 , (b) $\text{TiO}_2\text{-}0.02\text{CeO}_2$, (c) $\text{TiO}_2\text{-}0.06\text{CeO}_2$, (d) $\text{TiO}_2\text{-}0.10\text{CeO}_2$, (e) $\text{TiO}_2\text{-}0.13\text{CeO}_2$ and (f) $\text{TiO}_2\text{-}0.17\text{CeO}_2$.

Table 3. Colorimetric parameters of $\text{TiO}_2\text{-}x\text{CeO}_2$ pigments.

Pigments	L^*	a^*	b^*	Pigments	L^*	a^*	b^*
TiO_2	94.04	-0.71	6.80	$\text{TiO}_2\text{-}0.10\text{CeO}_2$	89.59	-3.68	29.47
$\text{TiO}_2\text{-}0.02\text{CeO}_2$	86.51	-3.06	31.48	$\text{TiO}_2\text{-}0.13\text{CeO}_2$	90.05	-3.63	31.13
$\text{TiO}_2\text{-}0.06\text{CeO}_2$	89.93	-3.95	30.17	$\text{TiO}_2\text{-}0.17\text{CeO}_2$	87.42	-3.88	33.97

this oxide produced an increase of the value of b^* from 6.80 in pure titanium dioxide to 31.48 in the mixture of oxides.

It was also observed that an increase of the cerium oxide concentration did not produce a significant change of color coordinates. This might be due to the fact that the $\text{TiO}_2\text{-}x\text{CeO}_2$ pigment containing 6 mol% ceria reached its saturation limit.

XRD results did not indicate any sharp evidence of cerium oxide in the titanium dioxide network, i.e., no solid solution was obtained, only the mixture of oxides. However, the reflectance curve, Figure 5, indicated that there was some interaction between these oxides giving rise to the observed yellow color⁴, since the absorption band of pure cerium oxide centered at about 560 nm moves to approximately 460 nm in the mixture of oxides, pointing out the occurrence of an interaction that could be of the type charge transfer from titanium cation to the cerium cation.

The yellow color has already been observed in thin films of the cerium-titanium mixed oxide^{5,10}. Titanium dioxide clearly represents the whitest color¹¹ and CeO_2 itself does not produce any color in glass¹⁴, so the yellow color is clearly the result of a complex interaction between the electronic structures of both oxides, whose interactions are modified with the light wave.

3.2.3. Potential application of the pigments

The potential application of the pigments was evaluated by comparing the colorimeters data from ceramic glazes containing these synthesized pigments to those from ceramic glaze used for dental restorations (VITA products). Four commercial references were used, see Table 4.

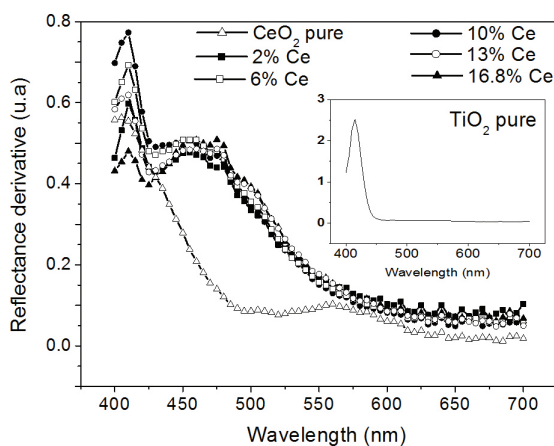


Figure 5. First derivative reflectance curve for $\text{TiO}_2\text{-}x\text{CeO}_2$ pigment. Insert: First derivative reflectance curve for pure TiO_2 .

Table 5 provides the values for L^* , a^* and b^* of the glazes containing 1 and 2wt% of $\text{TiO}_2\text{-}x\text{CeO}_2$ and the values obtained from commercial references. It was verified that samples made up with titanium-cerium pigments provided similar values to those from commercial dentins. Indeed, the values $a^* = -0.85$ and $b^* = 6.72$ for the experimental $\text{RTiO}_2\text{-}0.06\text{CeO}_2$ 1% sample are comparable to the values $a^* = -0.84$ and $b^* = 6.93$ of reference 3 (commercial sample).

The increase in pigment concentration produced only an increase in the value of b^* , leading the experimental samples to closer values to those provided by reference 1 (commercial sample).

The CIELab method can also be used for evaluation of the instrumental tolerance (ΔE^*) or the range of clinically acceptable color difference between the prosthesis and the natural tooth color of a patient¹⁵. This analysis is accomplished by applying Equation 1, presented below:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Taking into account the criteria of $\Delta E^* > 3.6$ as the acceptable level of color difference^{15,16} above mentioned, Table 6 evidences that many of the experimental samples fit the requirements needed for approval as potential coating material in dental prosthesis application.

The Vita Easy-shade dental spectrophotometer, capable of scanning a small area on the surface of a dental restoration material, was used in order to classify the colors of the samples of the present study according to Vita shade scales: Vita 3D-Master (VI) and Vita Classic (CL), as well as to get CIEL*a*b* parameters. Five measures in each square alumina plate were accomplished with this equipment (at each of the four corners and the fifth at the center of the square plate, whose values gave an average value for each sample).

Table 7 presents some of the results obtained through Vita Easy-shade. All of the experimental porcelain glazes

Table 4. Description of the commercial references used.

Ref. of dentins	Trademark	Ref. of dentins	Trademark
Reference 1	2M3 base dentin	Reference 3	3M2 dentin
Reference 2	3M2 dentin Vita	Reference 4	Base Dentin 3R2.5

Table 5. Colorimetric parameters for frit-pigment glaze and commercial glaze.

Pigments	L*	a*	b*	Pigments	L*	a*	b*
RTiO ₂ -0.02CeO ₂ ,1%	91.12	-0.94	7.36	RTiO ₂ -0.10CeO ₂ ,2%	90.65	-1.08	9.67
RTiO ₂ -0.06CeO ₂ ,1%	91.24	-0.85	6.72	RTiO ₂ -0.13CeO ₂ ,2%	90.48	-0.95	8.21
RTiO ₂ -0.10CeO ₂ ,1%	90.73	-0.92	8.25	RTiO ₂ -0.17CeO ₂ ,2%	90.06	-1.15	10.33
RTiO ₂ -0.13CeO ₂ ,1%	91.19	-0.83	7.05	Reference 1	91.18	-1.21	11.38
RTiO ₂ -0.17CeO ₂ ,1%	90.73	-0.91	7.80	Reference 2	92.61	-0.82	6.12
RTiO ₂ -0.02CeO ₂ ,2%	89.98	-1.17	11.58	Reference 3	92.38	-0.84	6.93
RTiO ₂ -0.06CeO ₂ ,2%	90.33	-1.13	10.01	Reference 4	91.36	-0.82	9.38

Table 6. Color difference (ΔE^*) between commercial glaze and experimental glaze.

Glazes	ΔE^* / Ref 1	ΔE^* / Ref 2	ΔE^* / Ref 3	ΔE^* / Ref 4
RTiO ₂ -0.06CeO ₂ ,1%	4.67	1.50	1.16	2.67
RTiO ₂ -0.10CeO ₂ ,1%	3.18	2.84	2.11	1.30
RTiO ₂ -0.13CeO ₂ ,1%	4.35	1.70	1.20	2.34
RTiO ₂ -0.17CeO ₂ ,1%	3.62	2.52	1.87	1.70
RTiO ₂ -0.06CeO ₂ ,2%	1.61	4.52	3.71	1.25
RTiO ₂ -0.10CeO ₂ ,2%	1.79	4.06	3.25	0.81
RTiO ₂ -0.13CeO ₂ ,2%	3.26	2.99	2.29	1.47
RTiO ₂ -0.17CeO ₂ ,2%	1.54	4.93	4.13	1.64

Table 7. Dental shade classification and CIEL*a*b* parameters for commercial glazes and experimental glazes.

Glazes	CL*	VI**	Color Touch colorimeter			Vita Easy Shade spectrophotometer		
			L*	a*	b*	L*	a*	b*
RTiO ₂ -0.02CeO ₂ ,1%	A1	1m2	91.12	-0.94	7.36	88.68	-0.34	18.30
RTiO ₂ -0.06CeO ₂ ,1%	A1	1.5m1.5	91.24	-0.85	6.72	86.48	-0.50	17.80
RTiO ₂ -0.10CeO ₂ ,1%	A1	1.5m1	90.73	-0.92	8.25	86.52	-2.48	14.62
RTiO ₂ -0.13CeO ₂ ,1%	A1	1m1.5	91.19	-0.83	7.05	88.30	-0.34	17.60
RTiO ₂ -0.17CeO ₂ ,1%	A1	1m1.5	90.73	-0.91	7.80	87.24	-0.22	16.18
Reference 1	A2	2m3	91.18	-1.21	11.38	81.58	0.40	22.70
Reference 2	A1	1m1.5	92.61	-0.82	6.12	90.26	-0.30	14.94
Reference 3	A1	1.5m1	92.38	-0.84	6.93	88.56	-0.16	15.40
Reference 4	A1	1m1.5	91.36	-0.82	9.38	88.60	0.38	20.60

*Vita Classic, **Vita 3D-Master.

studied could match one range of dental colors, their CIEL*a*b* parameters fit those previously determined by the Color Touch colorimeter. Moreover, some samples could be classified in the range of shades belonging to other commercial references.

An additional comment is necessary: for each sample analysed, the CIEL*a*b* parameters obtained through the Vita Easy Shade spectrophotometer were slightly different from those obtained through the Color Touch colorimeter. This difference can be easily explained given that the Color Touch colorimeter requires the use of large scanning areas (at least 3 cm × 3 cm), giving an average result, without discriminating eventual short-range deviation in color. On the other hand, the Easy Shade spectrophotometer scans very small areas (e.g., 4 mm × 4 mm) and, therefore, it reads in a much more discriminating way. Also color shades present sensitivity in relation to processing techniques and conditions and techniques for measuring color shades (as scanning angle, pressure, light intensity and wave-length). Dental laboratories use methods somewhat different from those used in this work. Even under these natural difficulties, the present work has evidenced that TiO₂-xCeO₂ pigments have potential application in the coloration of porcelain dentins.

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4. Conclusions

Pigments of titanium and cerium oxides, with good crystallinity and thermal stability, were synthesized by using the Pechini method with citrate precursor.

The yellow color of the mixed TiO₂-CeO₂ pigments generated in this study were classified in the CIEL*a*b* scale through the Color Touch colorimeter and the Vita Easy Shade spectrophotometer that enabled the classification of the colors in two Vita Color Scales.

It was possible to demonstrate the potential application of the studied pigments through the preparation of coating on alumina substrates, whose color results matched the adequate ΔE* value for clinically acceptable dental prosthesis materials.

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