



UNIVERSITAT JAUME I

Escola Superior de Tecnologia i Ciències Experimentals
Grau en Química

**Synthesis and characterization of
ceramic pigments based on karroite,
geikielite and qandilite structures
co-doped with Co^{2+} and Al^{3+}**

Final Degree Work

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1. Abstract

This investigation is focused on the analysis of the effect of Al co-doping on the reactivity, formation, color properties and performance as ceramic pigments of cobalt-doped karroite (MgTi_2O_5), geikielite (MgTiO_3) and qandilite (MgTi_2O_4) solid solutions.

With this aim, different solid solutions ($\text{Mg}_{0,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$, ($\text{Mg}_{0,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$ and ($\text{Mg}_{1,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_4$) were prepared with $x=0,1$ and $x=0,2$ through the use of citrates-gel MOD method. The homogenous raw xerogels were first charred at $500\text{ }^\circ\text{C}/1\text{h}$ and then fired directly at 1000 and $1200\text{ }^\circ\text{C}$. The fired pigments were characterized by means of X-ray diffraction (XRD), optical spectroscopy (UV-vis-NIR) and CIE-L*a*b* colorimetry (also with samples enameled in different glazes).

XRD confirmed the total formation of karroite solid solutions of ($\text{Mg}_{0,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$) at $1200\text{ }^\circ\text{C}$ and the presence of secondary phase rutile at $1000\text{ }^\circ\text{C}$. On the other hand, regarding to geikielite, the solid solutions ($\text{Mg}_{0,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$) did not form completely on account of the formation of MgAl_2O_4 spinel. The large amount of Al^{3+} favors the formation of Mg spinel, geikielite is form accompanied by two secondary phases karroite and MgAl_2O_4 spinel.

Finally, qandilite solid solutions ($\text{Mg}_{1,8-x}\text{Co}_x\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_4$) also formed successfully, although accompanied by minor amounts of secondary phases, geikielite in greater proportion and MgAl_2O_4 spinel. In this case, the samples were subsequently fired at $1400\text{ }^\circ\text{C}$, leading to a higher amount of qandilite phase, with only small amounts of residual geikielite.

The optical properties and performance as ceramic pigments were evaluated by UV-vis-NIR spectroscopy and CIE-L*a*b* color measurements applying them in different industrial double-firing transparent glazes (glaze A and B). The pigments exhibit slight greater stability using the glaze with high temperature ($1050\text{ }^\circ\text{C}$, high Ca and Zn content and free of Pb), these present a greenish-blue color. The blue color is associated with Co^{2+} in tetrahedral environments.

2. Introduction

A ceramic pigment is an inorganic structure containing chromophore ions (transition or lanthanide ions)¹, and it is responsible of the color of ceramic wares by remaining stabilized and insoluble (forming a heterogeneous mixture) within the ceramic body or glaze in which it is dispersed. This is the main difference with ceramic dyes or colorants which produce the color by the solubility of chromophore ions in the ceramic matrix.

Nowadays, the recent research tendencies in the field of ceramic pigments are based on the search of new crystalline host lattices, the utilization of new chromophores and/or the employment of new synthesis routes². The main objective of these new investigations is improve the existing pigments and develop new pigments that get better the following properties³:

- Good technological performance: high intensity or color saturation, easy dispersion, high chemical and thermal stability at high temperatures (1050-1200 °C) and in different ceramic glazes and glassy coatings, etc.
- Less economic cost, to obtain higher profitability or mark-up
- No toxic or less toxic, environmental-friendly and ecological

To be a good ceramic pigment it must satisfy certain basic requirements⁴:

- Thermostable, at high temperatures it is stable
- Insoluble in glass matrix, it must keep his entity structural in the firing producing uniform color in the matrix
- No modify matrix properties, the pigment must be a material with good physical properties that do not modify the characteristics of resistance to abrasion, cracking and weathering, as well as attack by acids and bases of the matrix

Many investigations have been reported concerning Co-based pigments, in which Co^{2+} ions are incorporated mainly in octahedral or in tetrahedral coordination sites of the mixed-oxide host lattices. In general terms, d-d transitions of Co^{2+} in tetrahedral environments give rise to more intense blue colors with a stronger optical density. In contrast, Co^{2+} ions allocated in octahedral sites normally produce less intense colours, with a shift to pink or violet hues. Nevertheless, the color pallet of Co pigments also includes green violet, brown or even black pigments⁵.

Different titanate-based structures doped with transition metals have been postulated as new or emergent families of ceramic pigments. A good example is the case of titanium pseudobrookites (M_2TiO_5 or MTi_2O_5), ilmenites (MTiO_3) or spinels (M_2TiO_4).

Titanium pseudobrookites AB_2O_5 (i.e. FeTi_2O_5 , MgTi_2O_5 , Fe_2TiO_5 , Al_2TiO_5 , Cr_2TiO_5 ...) ⁶ are isostructural phases with orthorhombic symmetry (Cmcm spatial group) and an extraordinary structure flexibility to accommodate many distinct metals (with +2, +3 or +4 oxidation states) in their two different and distorted octahedral cationic sites, M1 or A (4c) and M2 or B (8f)⁷.

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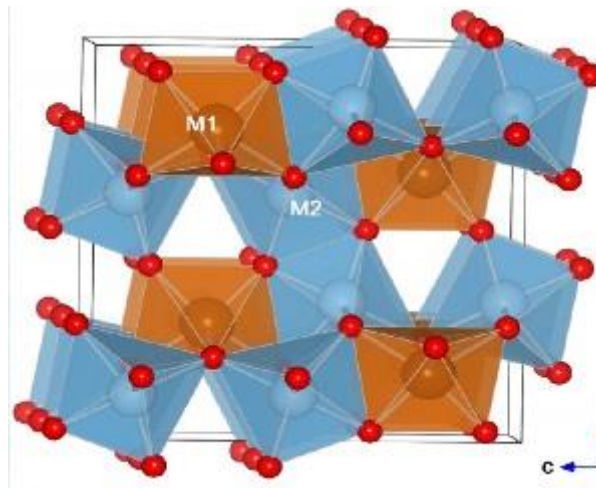


Figure 1: Crystal structure of MgTi_2O_5 (Cmcm space group). Source: Reference 10 of Suzuki

In this structure, the strongly distorted octahedra share edges to form trioctahedral units, which are linked into infinite double chains along the axis c ⁶. (Fig. 1)

In general, depending on the presence of divalent or trivalent metals in the formula, pseudobrookites may be formulated as $\text{M}^{3+}_2\text{Ti}^{4+}\text{O}_5$ (with $\text{M}^{3+} = \text{Fe, Al, Ga, Ti} \dots$) in which Ti is M1 (4c) positions or $\text{M}^{2+}\text{Ti}^{4+}_2\text{O}_5$ (with $\text{M}^{2+} = \text{Mg, Fe, Co, Ti} \dots$) in which Ti occupies mainly M2 (8f) positions, the less distorted in this case⁸. However, this ideal ordered occupation is uncommon due to the existence of an important cationic disorder between both positions (M1 and M2), resulting in a number of solid solutions with general formula $\text{M}^{3+}_{2(1-x)}\text{M}^{2+}\text{Ti}_{1+x}\text{O}_5$ or $[\text{M}^{3+}, \text{M}^{2+}, \text{Ti}]^{\text{M1}}[\text{Ti}, \text{M}^{2+}, \text{M}^{3+}]^{\text{M2}}_2\text{O}_5$ ⁹. This disorder has been studied by many authors, analyzing its dependence with several factors such as temperature of preparation, composition or pressure. The cationic disorder and its related configurational entropy enables the stabilization of pseudobrookites phase at high temperatures and these phases can be quenched in some cases at low temperatures¹⁰. In the case of Mg-Ti pseudobrookite, also denominated karroite, different degrees of cationic disorder have been reported. Some investigations have been reported about karroite co-doped with different chromophore ions. For example, the coloring performance has been investigated combining X-ray powder diffraction with UV-vis-NIR spectroscopy on karroite doped with V, Cr, Mn, Fe, Co or Ni (M) according to the formula $\text{Mg}_{1-x}\text{Ti}_{2-x}\text{M}_x\text{O}_5$ with $x=0.02$ and 0.05 ¹, and solid solutions of Ni in MgTi_2O_5 pseudobrookite have been investigated to develop new yellowish ceramic pigments or dyes⁷.

On the other hand, other Mg-titanates structures have been investigated as possible ceramic pigments, like ilmenite (MgTiO_3 geikielite) and spinel (Mg_2TiO_4 qandilite). In the MgO-TiO₂ phase diagram it may be appreciated the existence of these three Mg-titanates. (Fig. 2)

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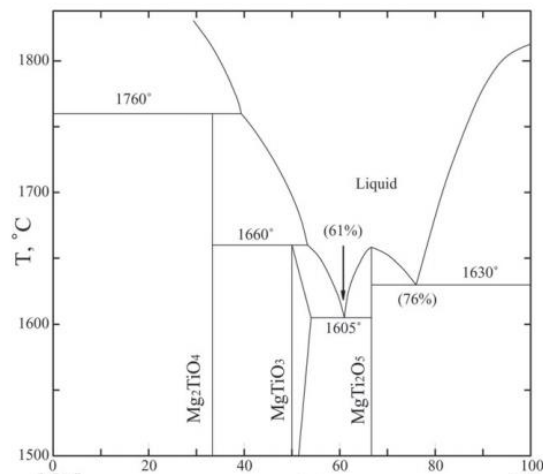


Figure 2: MgO-TiO₂ phase diagram

Karroite (pseudobrookite): $\text{MgO}(\text{s}) + 2\text{TiO}_2(\text{s}) \rightarrow \text{MgTi}_2\text{O}_5(\text{s})$ ($\text{MgO}:\text{TiO}_2 = 1:2$)

Geikielite (ilmenite): $\text{MgO}(\text{s}) + \text{TiO}_2(\text{s}) \rightarrow \text{MgTiO}_3(\text{s})$ ($\text{MgO}:\text{TiO}_2 = 1:1$)

Qandilite (inverse spinel): $2\text{MgO}(\text{s}) + \text{TiO}_2(\text{s}) \rightarrow \text{Mg}_2\text{TiO}_4(\text{s})$ ($\text{MgO}:\text{TiO}_2 = 2:1$)

The ilmenite-type structure $\text{A}^{2+}\text{Ti}^{4+}\text{O}_3$ (rhombohedral R-3 spatial group) is an ordered derivative of the archetype corundum structure, with hexagonally close-packed oxygen layers and cations occupying two-third of the available octahedral interstices. In MgTiO_3 ilmenite (geikielite) layers of MgO_6 and TiO_6 octahedral alternate in an ordered fashion along the hexagonal c direction¹¹.

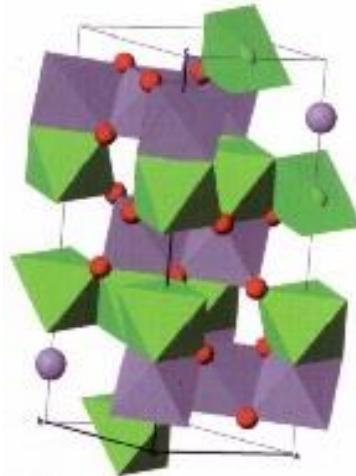


Figure 3: Crystal structure of MgTiO₃ (R-3 space group)

$\text{M}^{2+}\text{Ti}^{4+}\text{O}_3$ titanates with ilmenite structure ($\text{M}=\text{Mg}^{2+}$ or transition divalent metals such as Co, Fe, Mn, Ni, Cu and Zn) have been profusely investigated as functional material showing a wide variety of electrical, magnetic, optical, gas-sensing and even catalytic properties¹².

However, there are only a few investigations reporting the use of ilmenites as ceramic pigments. For instance, we can mention two reports on green pigments based on CoTiO_3 ^{13,14} and also a previous investigation reporting on the bluish color of $(\text{Co},\text{Mg})\text{TiO}_3$ ilmenites¹⁵, although its stability and color performance in ceramic glazes was not analyzed.

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Finally, the spinel-type crystal structure (AB_2O_4 , space group symmetry Fd-3m) represents one of the archetype structures based on a cubic close packing of ions, in which A and B cations occupy one-half and one-eighth of the available octahedral and tetrahedral sites, respectively¹⁶. The oxidation states of A and B cations can be +2 and +3 (2-3 spinels) and +4 and +2 (4-2 spinels).

Two extreme distributions of spinels (normal and inverse) may be found, considering the allocation of A and B cations among the available tetrahedral and octahedral sites. In “normal spinels”, cations A and B occupy the tetrahedral and octahedral sites ($[\text{A}]^{\text{tet}}[\text{B}]^{\text{oct}}\text{O}_4$). Nevertheless, in “inverse spinel” the B cations are equally partitioned among tetrahedral and octahedral sites ($[\text{B}]^{\text{tet}}[\text{AB}]^{\text{oct}}\text{O}_4$), the A cations occupying exclusively the octahedral sites¹⁷.

The inversion or disordering degree occurring in spinels is very sensitive to temperature and composition.

According to octahedral site preference energy (OSPE) considerations, Cr^{3+} ions occupy only octahedral sites and also the high affinity of Ni^{2+} and Cu^{2+} ions for octahedral sites forming inverse spinels, whereas Mg^{2+} , Fe^{2+} , Mn^{2+} or Co^{2+} exhibit preference for tetrahedral sites¹⁸. Nevertheless, OSPE arguments fail to explain for instance the preference of Al^{3+} for octahedral site.

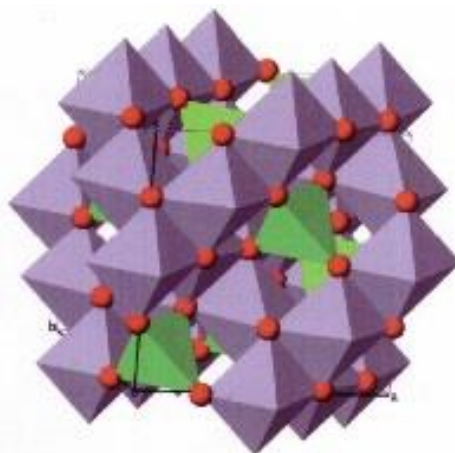


Figure 4: Crystal structure of Mg_2TiO_4 (Fd-3m space group)

Mg_2TiO_4 qandilite is a completely inverse spinel ($[\text{Mg}]^{\text{tet}}[\text{MgTi}]^{\text{oct}}\text{O}_4$), with Mg^{2+} ions being equally partitioned between both octahedral and tetrahedral sites¹⁹.

There are some preliminary studies reporting on the structural and thermal characterization of inverse spinel $\text{Zn}_{2-x}\text{Co}_x\text{TiO}_4$ solid solutions²⁰. On the other hand, the stability of Mg_2TiO_4 qandilite doped with Mn^{2+} , Co^{2+} and Fe^{2+} ion (only 1% molar) has also been reported by M.R.S. Silva et al²¹.

Related to reports on Mg_2TiO_4 spinels employed as ceramic pigments, Co_2TiO_4 spinel is already included within the CPMA (Classification and chemical descriptions of the complex inorganic color pigments) classification as a green pigment, which is exceptionally suited for use in systems requiring infrared reflectance. On the other hand, C. Soraia et al have investigated the effects of Co, Ni and Mn doping ($x=0-0.4$) on the thermal processing, formation and crystallinity of $\text{Zn}_{2-x}\text{M}_x\text{TiO}_4$ pigments²².

Finally, also recently Mario Llusar et al have reported about the green to blue color modulation in Co-doped Mg titanates with karroite, geikielite and qandilite lattices²³.

3. Objectives

The main objective of this study is to investigate the influence of Al^{3+} co-doping (40% molar) replacing both Mg^{2+} and Ti^{4+} ions in solid solutions of karroite (MgTi_2O_5), geikielite (MgTiO_3) and qandilites (Mg_2TiO_4) already doped with Co^{2+} (10 and 20% molar) on different aspects like:

- the reactivity of the precursor solid solutions synthesized by metalorganic decomposition or MOD method (explain in section 4.1.)
- the evolution of crystalline phases (formation and stability of solid solutions) at distinct temperatures.
- the cell parameters of the formed solid solutions
- the coloration (CIE-L*a*b* parameters) of the pigments and
- the thermo-chemical stability and coloring performance of the obtained solid solutions enameled within different double-firing glazes

As a previous an important remark in a preliminary study on the MgTi_2O_5 - Al_2TiO_5 system ($\text{Mg}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{O}_5$ solid solutions prepared by the ceramic route), the karroite solid solution was stabilized already at 1200 °C/3h for $x=0.2$ with only a very small proportion of residual rutile (TiO_2), and the whole range of solid solubility (from $x=0$ to $x=1$) was accomplished after firing at 1400 °C. Moreover, XRD characterization confirmed a strong decrease in karroite cell parameters already for $x=0.2$ (40% mol), as a result of the smaller ionic radius of Al^{3+} ions with respect to Mg^{2+} and Ti^{4+} in six-fold coordination (Al^{3+} (53.5 pm), Mg^{2+} (72 pm) and Ti^{4+} (60.5pm)). This important contraction of the karroite unit cell accomplished with Al^{3+} doping involves necessarily an important shortening of M^{2+} -O and Ti^{4+} -O distances within the karroite lattice, and therefore the crystalline field intensity exerted onto Co^{2+} ions in Co^{2+} -doped karroite could be also modified a great deal giving rise to an important color shift. Therefore, doping with Al^{3+} ions could result in important or at least interesting modification of the color hue of Co^{2+} -doped karroite and also of related Co^{2+} -doped Mg titanates (geikielite and qandilite).

Taking into a count this previous study, we chose this amount of Al^{3+} co-doping (40%mol) for Co^{2+} -doped karroite, and investigated the effect of Al^{3+} on the above-mentioned issues. Similarly, we decided also to use the same amount of Al^{3+} co-doping in the other related Mg titanates structures (geikielite ilmenite and qandilite spinel), even though preliminary studies on Al^{3+} solid solubility were not performed in these systems.

Once obtain the pigments are characterized by different techniques: X-ray diffraction (XRD), UV-VIS-spectroscopy, CIE-L*a*b* color measurements and introducing the pigments into different industrial glazes to evaluate the color and stability.

This Co^{2+} -doped magnesium titanates are studied because, in some pigmenting structures, the addition of co-dopants can modify the stability, reactivity and the optical properties of these pigments.

4. Experimental procedure

4.1- Samples preparation by citrates-gel MOD route

The metalorganic decomposition or MOD method is based on chelation by addition of polycarboxylic acid to a dissolution of soluble salts. The combined chelation of different cations of the composition allows obtaining a material with high chemical homogeneity. With this route is prevented the slow cationic diffusion of ceramic route. Oxalic and citric acid may be used as chelating agent, in different molar ratios (normally a mole of polycarboxylic acid is used per total moles of cations in the composition). In this investigation we used citric acid to form the precursors.

Therefore, instead of the ceramic route we used a more homogeneous and reactive citrate gel route (MOD) to prepare the solid solutions. To this respect, the decomposition or combustion of citrate-based co-precipitates or polymeric xerogels leads to the formation at lower temperatures of more homogeneous and reactive multicomponent powders (mixed oxides), often with nanostructured morphologies which are highly demanded to fulfill the requirements of modern inkjet application of ceramic tiles^{7,24}.

To make the experimental procedure of MOD method the following steps were carried out.

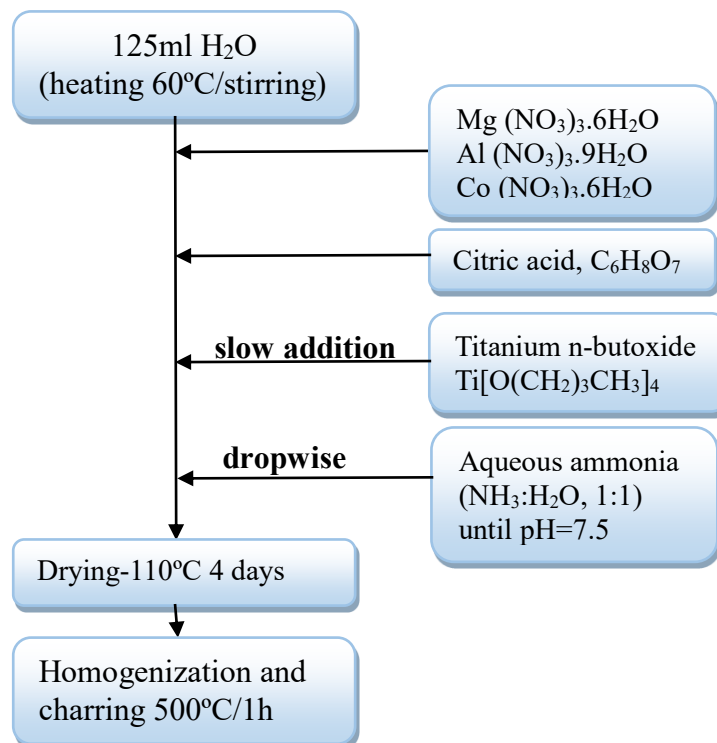


Figure 5: MOD method diagram

In this investigation different karroite, geikielite and qandilite solid solutions doped with Co^{2+} (10 and 20% mol; in replacement of Mg^{2+} ions) and co-doped with Al^{3+} (40 %mol; in replacement of Mg^{2+} and Ti^{4+}) were prepared by metal-organic decomposition route (MOD): $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{1.8}\text{O}_5$ karroite, $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_3$ geikielite and $((\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4)$ qandilite with $x=0.1$ and 0.2 in all cases).

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To make easier reading compression, Table 1 shows the nomenclature employed for samples:

Samples	Nomenclature
$(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$	KAR
$(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$	GEI
$(\text{Mg}_{1,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_4$	QAN

Table 1: Nomenclature employed for MOD samples

In order to prepare these compositions, the required amounts of the precursors were calculated in order to obtain 6 g of pigment. The precursors used for the synthesis of the samples were: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Panreac), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, Aldrich), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98-102%, Panreac), $\text{C}_6\text{H}_8\text{O}_7$ (99.5%-100.5%, Panreac) and $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ (97%, Aldrich). Citric acid, was used as a quelating agent. The molar amount of citric acid used was 1 mole of citric per total moles of cation in each system, that is 3 moles of citric per mole of karrooite and qandilite and 2 moles of acid per mole of geikielite.

To carry out the synthesis (see the employed experimental procedure in the diagram of Fig. 5) the suitable amount of nitrates was solved in 125ml of distilled water in continuous stirring at 65 °C. Afterward, citric acid was added and titanium n-butoxide was slowly added. Finally, aqueous ammonia (30%) was added dropwise until a pH value of 7.5. The temperature was kept constant at around 65 °C.

When titanium n-butoxide is added we can observe that appear a white precipitation and with aqueous ammonia (pH value more acid) this precipitation was redissolved.

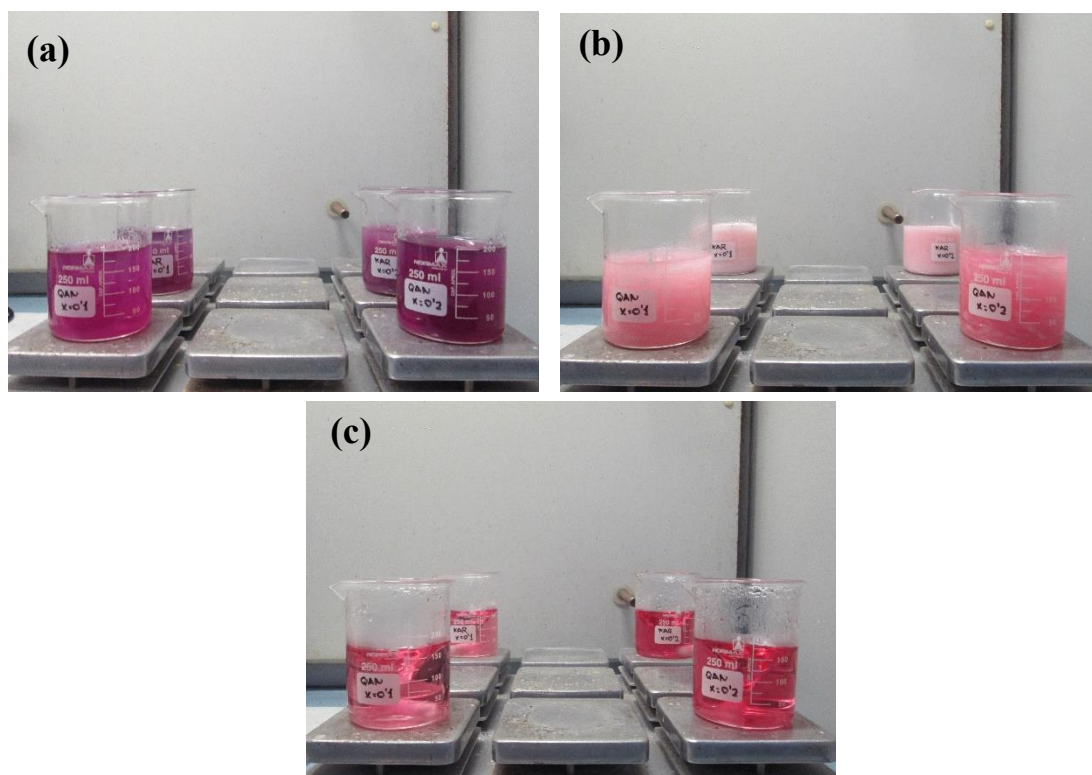


Figure 6: Qandilite and karroite synthesis, (a) Aqueous solution of nitrates, acetate and citric acid. (b) After adding titanium n-butoxide. (c) After adding $\text{NH}_3:\text{H}_2\text{O}$ (1:1) until pH=7.5.

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After one-day drying at 110 °C in the oven, a homogeneous purple gel (still wet) was obtained in all cases (see for instance KAR and QAN samples in Fig.7), and these gels evolved to a dark brownish xerogels after additional drying for 3 more days, due to the partial dehydration or decomposition reactions of the citrate gel.

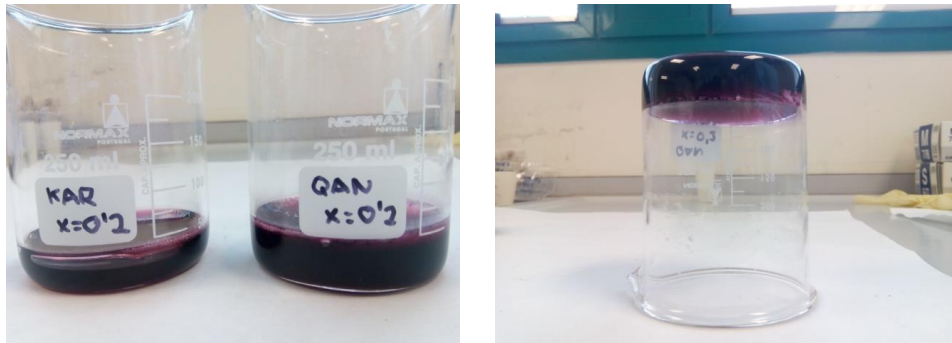


Figure 7: After a day in the oven xerogel is formed. Images of karroite and qandilite $x=0.2$

Finally, the resulting dark xerogels were charred at 500 °C during 1 hour to obtain a fine powders to almost complete all the decomposition reactions, and the resulting fine powders (after homogenization in mortar with pestle) were separated in three parts: one portion perform the XRD characterization at 500 °C, and the other portions were directly fired in an electrical furnace under air atmosphere using $\text{SiO}_2\text{-Al}_2\text{O}_3$ crucibles at 1000 °C and 1200 °C with a heating rate of 5 °C/min and with a soaking time of 3h at 1000/1200 °C).



Figure 8: once realized charring at 500 °C

We can see in the photo the samples that were charred at 500 °C present a black/brown color. Whereas in the samples calcined at 1000 °C and 1200 °C we observed that appear coloration.

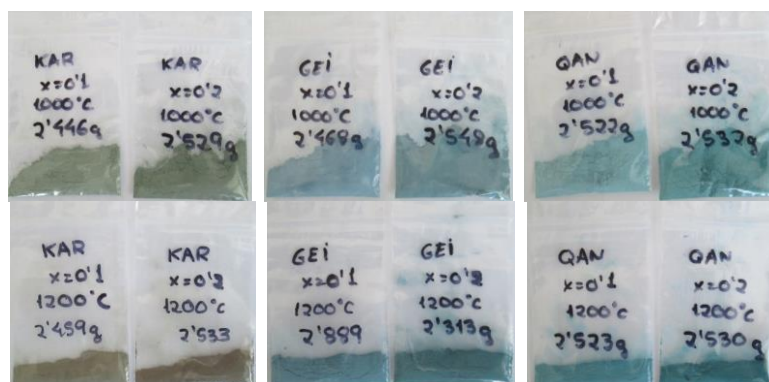


Figure 9: samples calcined at 1000 °C/3h and 1200 °C/3h

The next step once the samples have been calcined is to characterize them with different techniques

4.2-Characterization techniques

4.2.1-X-ray diffraction

X-ray diffraction (XRD) is the more frequent technique used to study of crystalline solids and the more important in the solid state chemistry. This technique is used to study the steps of the reactions, transition phases, thermal expansion, cell parameters, crystalline structures... It is a useful method to obtain information about structure, composition and polycrystalline state of the materials.

This technique consists in the interaction of an X-ray beam, of a certain wavelength with a crystalline solid. The X-ray diffraction is based on the diffraction phenomenon that occurs when an X-ray beam strikes a crystalline sample. The phenomenon of diffraction can be described by Bragg's law, which predicts the direction in which constructive interference occurs between beams of X-rays scattered coherently by a crystal^{25,28}.

The diffraction data of each calcined sample was performed in a Siemens D-500 powder diffractometer provided with a copper cathode. Measurements were made at 2θ intervals from 10 to 70°. The speed of the goniometer for semiquantitative analysis was 0.05° 2θ /s and the collection time of counts per step was 2 s (time constant).

4.2.2-Measurement of cell parameters: evolution with Co/Al-doping

The cell parameters of selected $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{1.8}\text{O}_5$ (karroite) and $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ (qandilite) fired pigments were measured to see the effect of Co^{2+} and Al^{3+} co-doping.

In this study we determined the values of cell parameters and volume for Al co-doped karroite and qandilite samples ($x=0.1$ and $x=0.2$) at 1200 and 1400 °C, respectively. These values were compared with those measured for related compositions without Al co-doping (with $x=0.2$, and at 1200 °C in both karroite and qandilite).

These values of cell parameters and volume of the selected fired pigments were determined using the WinXPow software (version 1.06). In the case of qandilite fired powders at 1400 °C it was not possible to obtain a satisfactory refinement using XRD from 10 to 70° 2θ , with steps of 0.05° 2θ and a counting time of 2 s per step. To determine the cell parameters of qandilite, the speed of the goniometer for analysis was 0.02° 2θ and the collection time of counts per step was 6-8 s.

4.2.3-Samples enameling

In order to analyze the thermo-chemical stability and coloring performance either as ceramic pigments or as ceramic dyes, all the fired compositions (also xerogels charred at 500 °C) were 5 wt-% enameled in a different double-firing transparent glazes. Glaze A has low Ca and Zn content and is free of Pb and glaze B of the SiO_2 – CaO - ZnO system has a high Ca and Zn content. These glazes were fired at different fast-firing schemes, glaze A up to 980 °C and glaze B up to 1050 °C (see these schemes in Fig. 10)

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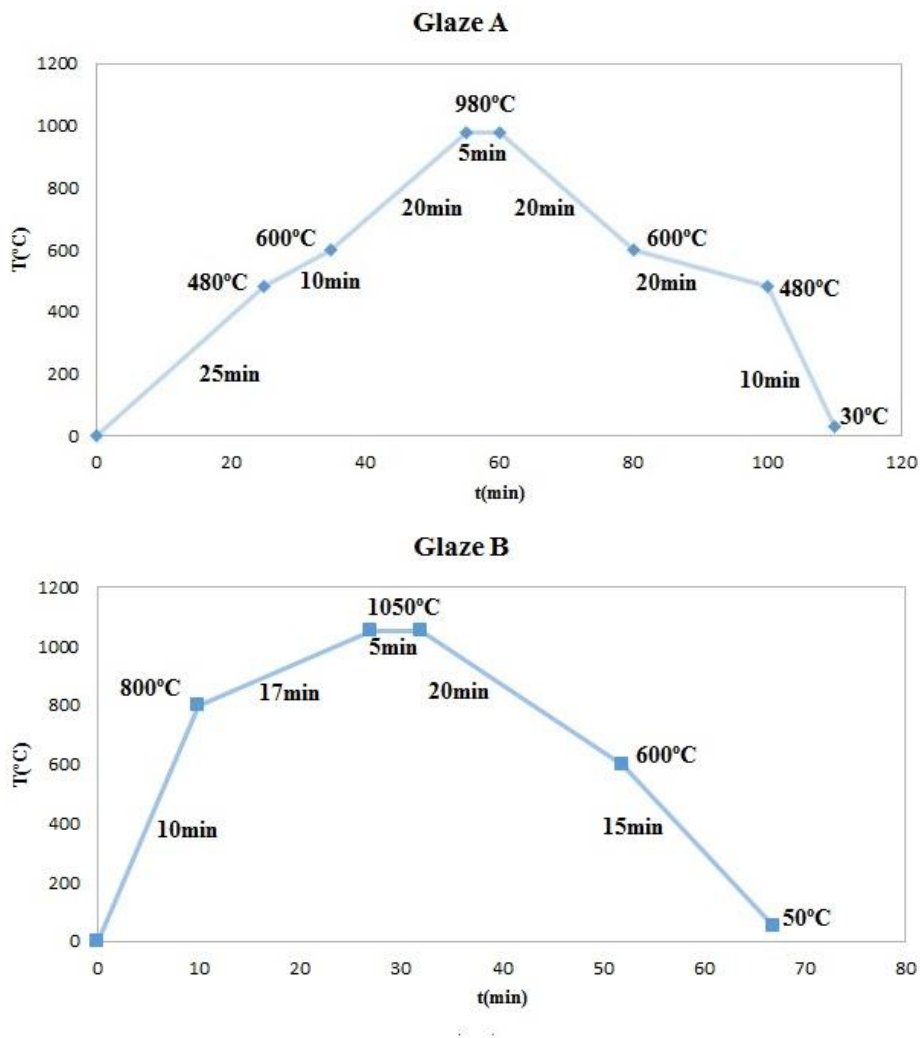


Figure 10: enameling temperature cycle

To realize the enameling of different pigments, 0,5 gr of fired powder is blended together with 10 gr of pertinent glaze and approximately 9 ml of distilled water and homogenized in a ball mill during ten minutes.

4.2.4- Optical properties: UV-vis-NIR spectroscopy and color (CIE-L*a*b*)

The optical properties of fired powders and enameled samples were characterized by ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy and evaluated colorimetrically determining CIE-L*a*b* parameters with a Jasco V670 spectrophotometer.

In order to understand the color of the obtained pigments, we must to know that the light absorption in the visible region (700 to 400 nm) and near ultraviolet (400 to 200 nm) of the electromagnetic spectrum results in electronic transitions, which can be collected in the form of spectra with appropriate instrumentation.

The color of the pigments is produced by d-d electronic transitions.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

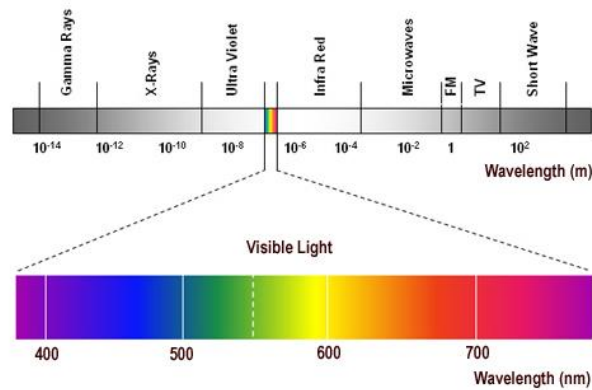


Figure 11: Visible spectrum

The color was expressed in the CIE- $L^*a^*b^*$ color coordinates, CIE refers to the Commission Internationale de l'Eclairage (International Commission on Illumination). In the CIE (L^* , a^* , b^*) color space, abbreviated CIELAB, the lightness coefficient, L^* , ranges from black = 0 to white = 100. On the other hand, the a^* and b^* parameters have no specific numerical limits. Positive a^* is red and negative a^* is green, positive b^* is yellow and negative b^* is blue. The color at the grid origin ($a^* = 0$, $b^* = 0$) is achromatic (gray).

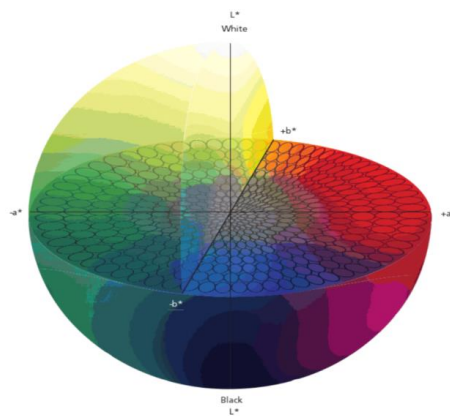


Figure 12: Chromaticity coordinates CIE- $L^*a^*b^*$

5. Results and Discussion

5.1- Evolution of crystalline phases (XRD) and color with firing temperature and $\text{Co}^{2+}/\text{Al}^{3+}$ doping.

This section consists in XRD analysis of crystalline phases of the pigments obtained by MOD method. Next, XRD patterns present the stability and evolution of the different pigments KAR($(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$), GEI ($(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$) and QAN ($(\text{Mg}_{1,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_4$) at different firing temperatures (500, 1000 and 1200 °C; and also 1400 °C for QAN samples).

At 500 °C the XRD patterns clearly show (Fig. 13) all the charred compositions still remained amorphous, without crystallization of any crystalline phase.

The color aspect of the obtained 500 °C charred powders (all dark brown colors) is shown in Fig. 14.

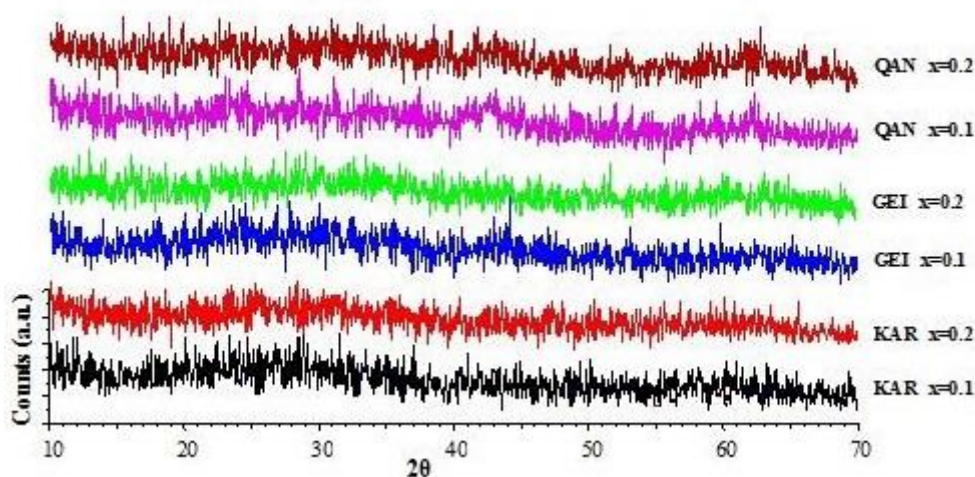


Figure 13: XRD patterns of compounds fired at 500 °C

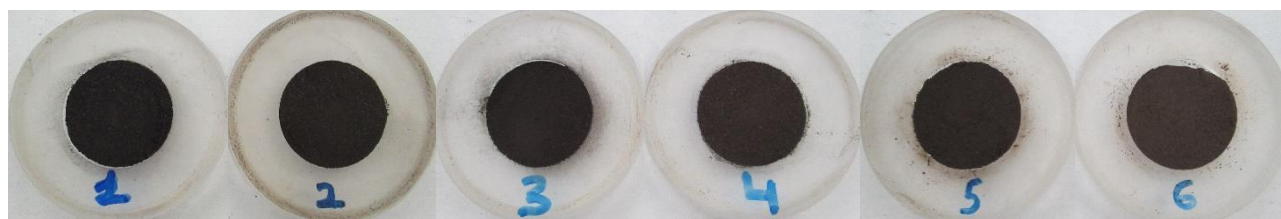


Figure 14: Pictures of powders fired at 500 °C

Number	Samples	Composition
1	KAR	x=0.1
2	KAR	x=0.2
3	GEI	x=0.1
4	GEI	x=0.2
5	QAN	x=0.1
6	QAN	x=0.2

Table. 2: Description of the powders calcined

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

XRD patterns of the pigments calcined at 1000 °C and 1200 °C are analyzed to know the different phases formed. The pigments powders calcined at 1000 °C and 1200 °C are shown below to have the visual aspect of their coloration. Also, the respective colorimetric parameters(CIE-L*a*b*) are shown in the next image. The powders calcined at 1000 °C and 1200 °C continue with the same numeration that the powders at 500 °C (Table 2).

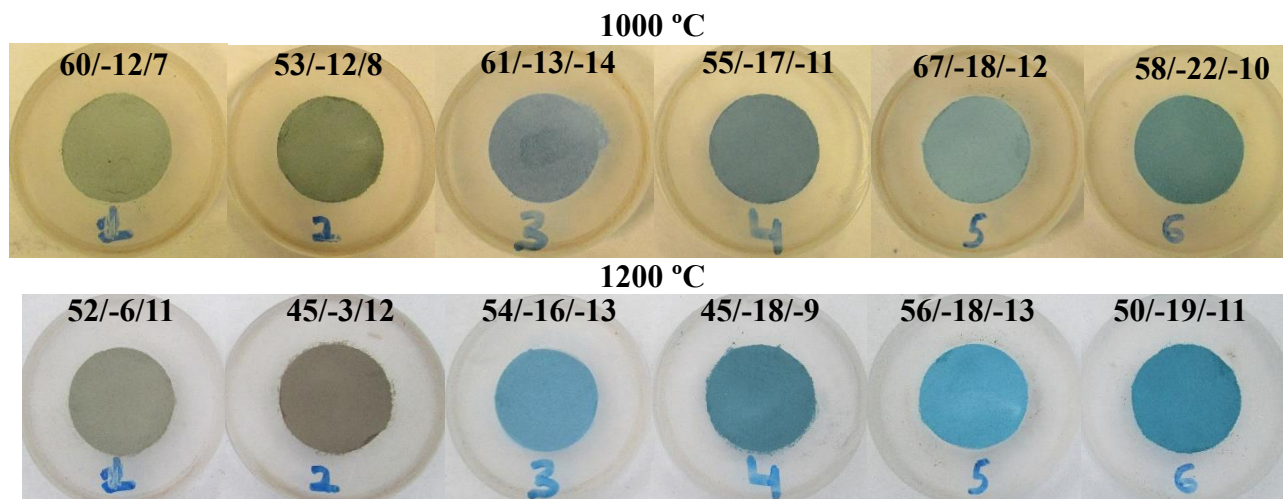
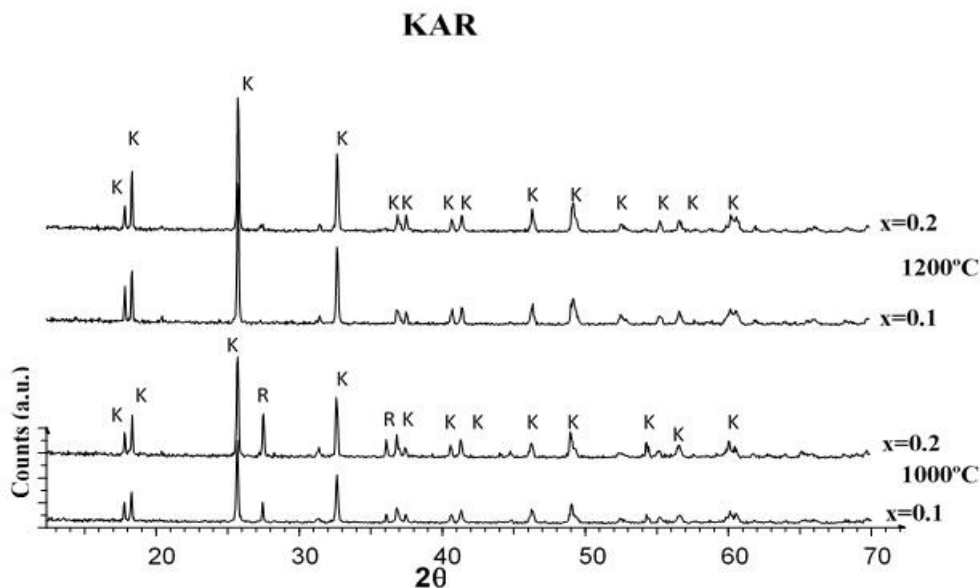


Figure 15: Pictures of powders fired at 1000 °C and 1200 °C

Karroite is thermodynamically unstable due its positive enthalpy of formation. Consequently, it decomposes at low temperature in an assemblage of binary oxides or a mixture of ilmenite MgTiO_3 and rutile TiO_2 . However, its structure is stabilized by the configurational entropy of formation due to partially disordered cation distributions on both M1 and M2 octahedral sites²⁶. By increasing the firing temperature, this cationic disorder increases due to entrance of the larger Mg^{2+} ions in the smaller M2 sites (the larger Mg^{2+} prefers to enter the larger M1 sites)²⁷.



Crystalline phases: K= karroite(MgTi_2O_5) and R=rutile (TiO_2)

Figure 16: XRD patterns of $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{1.8}\text{O}_5$ powders fired at 1000 °C/3h and 1200 °C/3h

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

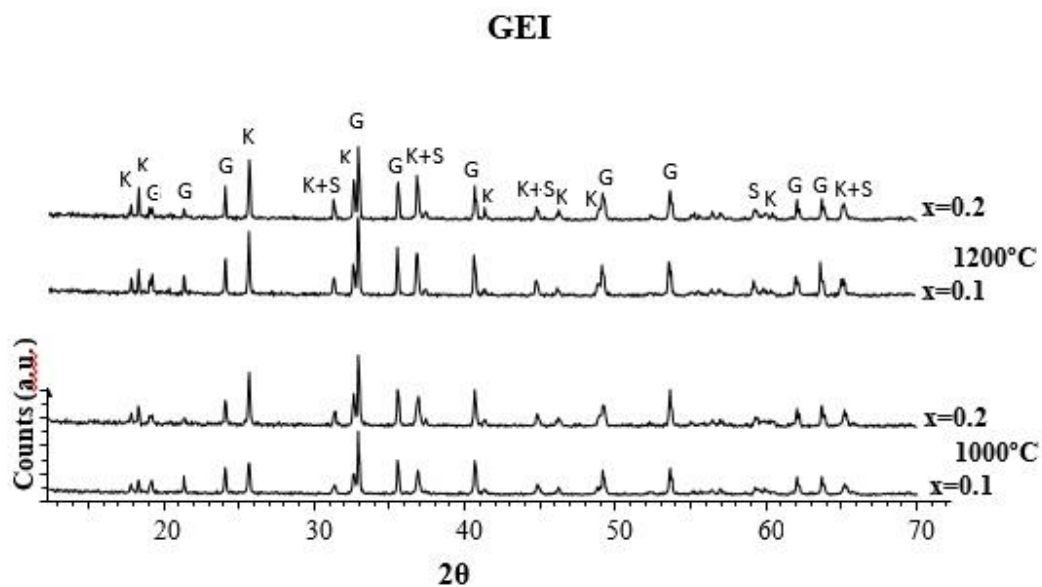
As it may appreciate in Fig. 16 and explained previously, at 1200 °C the karroite is formed as single phase in both compositions. In contrast, a residual phase of rutile (TiO_2) appears at 1000 °C, which can be result of karroite decomposition or oxide precursors that have not fully reacted. It can be appreciated that the difference between both compositions is less at 1200 °C; at 1000 °C the difference in the intensity of peaks is higher, mainly in the rutile phase.

On the other hand, in the case of geikielite (MgTiO_3) the distribution of Mg and Ti over the two octahedral sites is found to be completely ordered. According to calorimetric evidence indicating no enthalpy difference quenched from 1400 °C and quenched from 800 °C, it has been suggested that the ordered distribution in MgTiO_3 is retained at high temperature².

In this case geikielite does not appears as the major phase, we can observe secondary phases like karroite (MgTi_2O_5) and spinel of Al (MgAl_2O_4). The formation of this MgAl_2O_4 spinel phase may be easily understood, due to the strong amount of Al^{3+} formulated in these compositions (40% mol) and the thermodynamic stability of this phase; in addition, the decrease of the $\text{Mg}^{2+}/\text{Ti}^{4+}$ ratio (<1) due to the formation of MgAl_2O_4 spinel can explain the coexistence of MgTi_2O_5 karroite (with lower Mg to Ti ratio) with MgTiO_3 geikielite.

Remarkably, the increase of firing temperature and Co-doping (from $x=0.1$ to $x=0.2$) has not influence in the evolution of crystalline phases, and similar amount of geikielite, karroite and spinel phases are present in all cases, being geikielite the major phase.

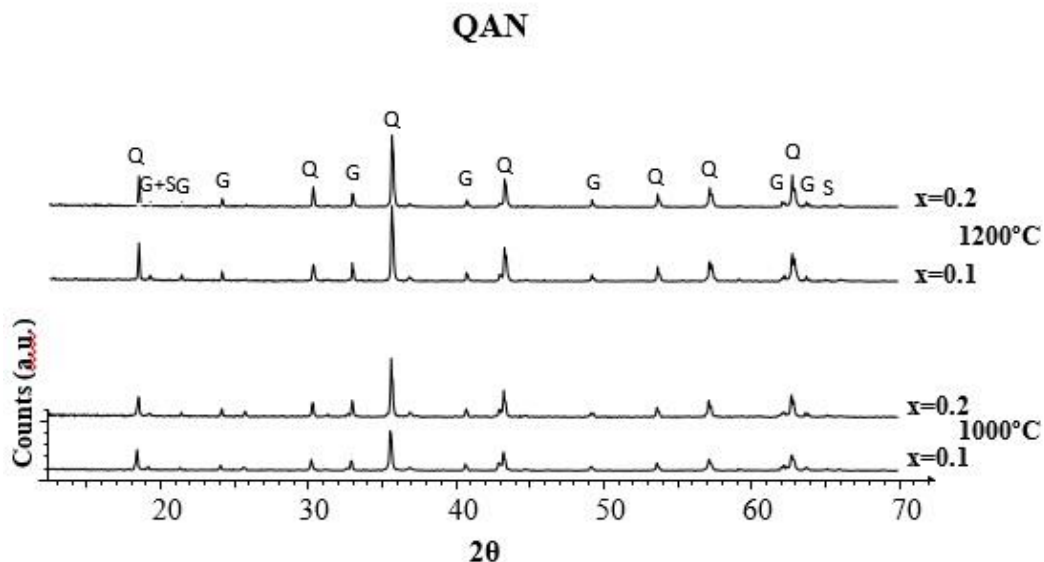
Owing to the high stability of the formed MgAl_2O_4 secondary phase, and its advanced crystallization, the geikielite compositions were not subsequently calcined at 1400 °C, since these secondary phases would be presumably present also at this higher temperature.



Crystalline phases: G= geikielite (MgTiO_3), K= karroite(MgTi_2O_5) and S= spinel (MgAl_2O_4)
Figure 17: XRD patterns of $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_3$ powders fired at 1000 °C/3h and 1200 °C/3h

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

Mg_2TiO_4 qandilite is one of the three intermediate magnesium titanates of MgO-TiO_2 system, along with MgTiO_3 geikielite and Mg_2TiO_5 karroite. Both Mg_2TiO_5 karroite and Mg_2TiO_4 qandilite are stabilized at high temperatures because of the configurational entropy arising from cation disorder. Qandilite is stabilized at high temperatures by configurational entropy arising from cation disorder. Below 1200-1300 °C a mixture of MgTiO_3 geikielite and MgO periclase is thermodynamically more stable (it is necessary to calcine at temperatures equal or higher to 1300 °C to stabilize Mg_2TiO_4 qandilite). Interestingly, with Co^{2+} and Al^{3+} co-doping the qandilite spinel is already stabilized as the major phase at 1000 °C, although accompanied with a small amount of geikielite and of MgAl_2O_4 spinel (almost negligible). This is consequence of Al^{3+} that stabilized the spinel formation.



Crystalline phases: Q= qandilite(Mg_2TiO_4), G= geikielite (MgTiO_3) and S= spinel (MgAl_2O_4)
Figure 18: XRD patterns of $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ powders fired at 1000 °C/3h and 1200 °C/3h

Since the Mg_2TiO_4 qandilite was not stabilized as single phase at 1200 °C, being still accompanied by residual MgTiO_3 geikielite and MgAl_2O_4 spinel phases, and in order to improve determination of the color of Mg_2TiO_4 qandilite co-doped with Al^{3+} and Co^{2+} , we decided to make a subsequent calcination at 1400 °C of the powders previously fired at 1200 °C, to see the possible stabilization of qandilite as single phase, and the color evolution. (Fig.19)

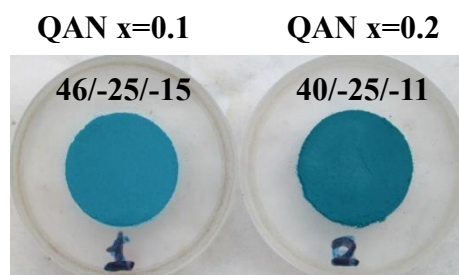
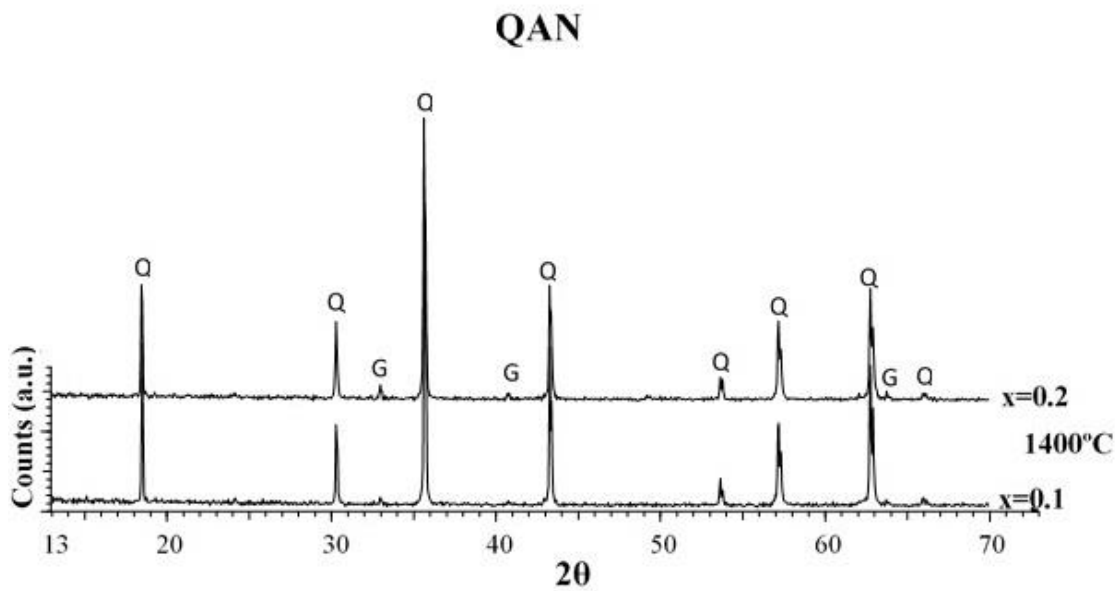


Figure 19: Pictures of powders subsequently calcined at 1400 °C

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}



Crystalline phases: Q= qandilite(Mg_2TiO_4) and G= geikielite (MgTiO_3)
Figure 20: XRD patterns of $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ powders recalcined at 1400 °C/3h

As it can be observed in Fig. 20 at 1400 °C Mg_2TiO_4 qandilite is formed in greater amount than at 1200 °C, it coexists with geikielite still but in lesser amount. It is appreciated that increasing the composition ($x=0.2$) increases the geikielite phase slightly.

Below, the intensity of phases of all XRD patterns are described in Table 3

Composition/firing	1000 °C/3h	1200 °C/3h	1400 °C/3h
KAR $x=0.1$	K(vs),R(m)	K(vs)	-
KAR $x=0.2$	K(vs),R(s)	K(vs)	-
GEI $x=0.1$	G(w),Q(s),S(vw)	G(w),Q(s),S(vw)	-
GEI $x=0.2$	G(w),Q(s),S(vw)	G(w),Q(s),S(vw)	-
QAN $x=0.1$	Q(s),G(w),S(vw)	Q(s),G(w),S(vw)	Q(vs),G(vw)
QAN $x=0.2$	Q(s),G(w),S(vw)	Q(s),G(w),S(vw)	Q(vs),G(vw)

Table 3: Evolution of crystalline phases

Crystalline phases: K= karroite(MgTi_2O_5), G= geikielite (MgTiO_3), S= spinel (MgAl_2O_4), Q= qandilite(Mg_2TiO_4) and R=rutile (TiO_2)

Peaks intensity: vs (very strong), s (strong), m (medium), w (weak) and vw (very weak)

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

To see the difference between compounds, temperatures and compositions, color parameters (CIE- $L^*a^*b^*$) have been obtained and represented in the next table:

Firing Samples	Composition	1000 °C/3h $L^*a^*b^*$	1200 °C/3h $L^*a^*b^*$	1400 °C/3h $L^*a^*b^*$
KAR	$x=0.1$	60/-12/7	52/-6/11	-
KAR	$x=0.2$	53/-12/8	45/-3/12	-
GEI	$x=0.1$	61/-13/-14	54/-16/-13	-
GEI	$x=0.2$	55/-17/-11	45/-18/-9	-
QAN	$x=0.1$	67/-18/-12	56/-18/-13	46/-25/-15
QAN	$x=0.2$	58/-22/-10	50/-19/-11	40/-25/-11

Table 4: Color parameters (CIE- $L^*a^*b^*$) of powders fired

As we can observe all the compounds with Co composition $x=0.1$ present less intensity (greater parameter L^*) and at a greater temperature the intensity increase.

Karroite present an “olive-green” color with a yellowish shade or hue (positive b^*), being less green (less negative a^*) and more yellowish (more positive b^*) and thus becoming a brownish green at 1200 °C.

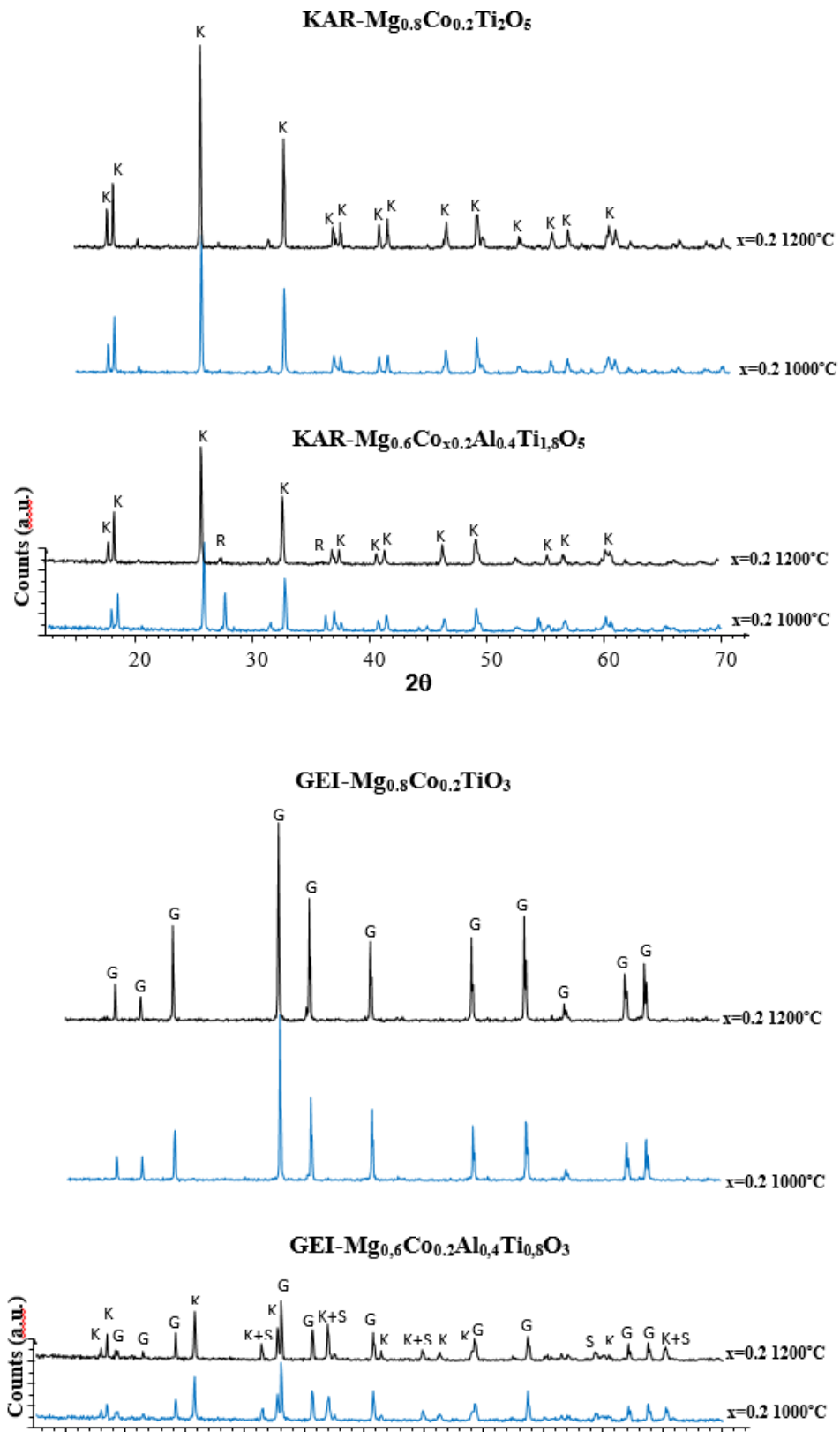
On the other hand, the greenish blue coloration of geikielite is more green (more negative a^*) and less blue (less negative b^*) at increase the temperature from 1000 °C at 1200 °C and the Co-doped.

Finally, qandilite present similar greenish blue coloration that geikielite at 1000 and 1200 °C. It can be observed an increased in the intensity (less L^*) and in the green contribution (more negative a^*) at 1400 °C, that occurs when qandilite spinel appears almost as a unique phase.

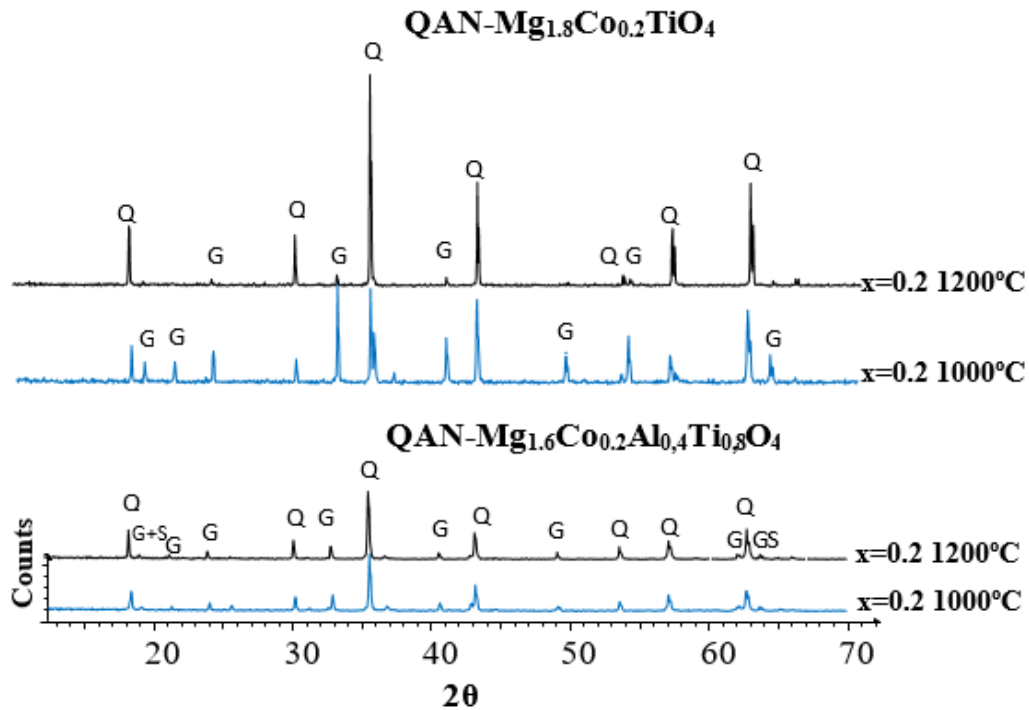
The crystalline phases of compositions with Al co-doped and without Al co-doped (previous studies) are compared in order to determinate the effect of Al co-doping in reactivity. The compounds present a Co-doping $x=0.2$ and are calcined at 1000 °C and 1200 °C. Following, the XRD patterns of karroite, geikielite and qandilite with and without Al co-doped are shown in Fig.21.

In the case of karroite without Al co-doping we can appreciate only karroite(K) as unique phase at both temperatures 1000 and 1200 °C, whereas when karroite is Al co-doped appear rutile(R) as a secondary phase at both temperatures but significantly at 1000 °C. Thus, Al co-doping makes difficult to obtain karroite as a unique phase free of rutile residual, mainly at temperatures under 1000 °C. (Fig. 21)

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}



Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}



Crystalline phases: K= karroite(MgTi_2O_5), G= geikielite (MgTiO_3), Q= qandilite(Mg_2TiO_4), R=rutile (TiO_2) and S= spinel (MgAl_2O_4)

Figure 21: XRD patterns of karroite, geikielite and qandilite powders fired at 1000 °C/3h and 1200 °C/3h which Co composition is $x=0.2$ with and without Al co-doped

The different reactivity and the evolution of crystalline phases of geikielite with and without Al co-doping is more significant than in the case of karroite. As we can appreciate, in the samples without Al^{3+} ions the geikielite phase appears as a unique phase in both temperatures, it is consequence that geikielite is completely crystallized. While, the solid solution of geikielite has not been formed as unique phase in the samples Al co-doped, since there are important proportions of secondary phases of karroite(K) and also MgAl_2O_4 spinel(S), possibly also introducing Co^{2+} ions.

As it may be appreciated, in Co-doped qandilite without Al^{3+} co-doping, the qandilite phase still coexists with geikielite in very similar amounts after firing at 1000 °C, while at 1200 °C (at lower temperature than in the case of undoped Mg_2TiO_4 , the qandilite spinel forms as almost single phase with only a very small amount or residual geikielite. In contrast, in the case of Al^{3+} co-doped samples, the qandilite appears to become stabilized at much lower temperatures, observing the formation of the qandilite spinel as the major phase already at 1000 °C, with only a small amount of geikielite as residual phase (and still smaller amount of MgAl_2O_4).

Therefore, it appears that Al^{3+} co-doping has a beneficial effect on the stabilization of qandilite solid solution at lower temperatures (1000 °C). Also remarkably, the relative quantity of qandilite and geikielite phases remain almost unaffected with the increase of firing temperature and also with the Co-doping.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

On the other hand, Co-doped pigments with and without Al co-doped (previous studies) are compared in order to determinate the effect of Al co-doping in coloration. The pigments Co-doped ($x=0.2$) calcined at 1000 °C and 1200 °C are shown next. (Fig.22)

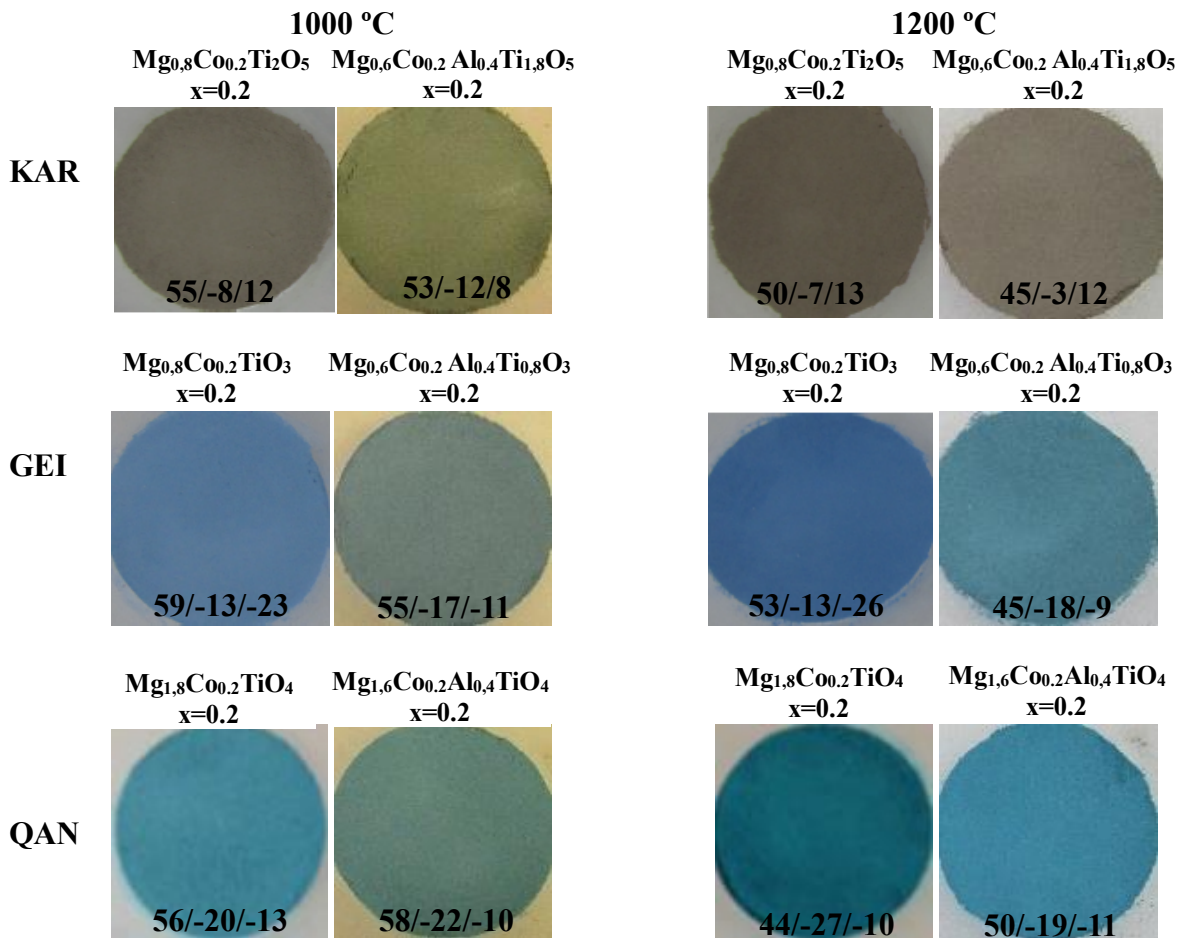


Figure 22: Pictures of powders co-doped with or without Al calcined at 1200 °C

As it may be appreciated, there are a slight difference between the color parameters (CIE- $L^*a^*b^*$). We can observe that with the presence of Al co-doped pigment powders developed greater greenish-blue coloration (a^* value less negative) except in the case of qandilite at 1200 °C. On the other hand, b^* parameter (blue contribution) decrease with Al co-doped and the intensity (L^* value) increased with Al co-doped except in the case of qandilite.

5.2- Cell parameters measurement in karroite and qandilite solid solution

The variation of the unit cell edge length and volume in karroite and qandilite likely arises as a combination of two factors^{1,19}:

- The difference ionic size of doping ions, Co^{2+} (58 pm tetrahedral coordinated and 74.5 pm octahedral coordinated), Al^{3+} (39 pm tetrahedral coordinated and 53.5 pm octahedral coordinated), Mg^{+2} (57 pm tetrahedral coordinated and 72 pm octahedral coordinated) and Ti^{4+} (42 pm tetrahedral coordinated and 60.5 pm octahedral coordinated).
- The order-disorder process among the two non-equivalent octahedral sites (M1 and M2) in the case of karroite and among the tetrahedral and octahedral sites of fully inverse spinel in the case of qandilite.

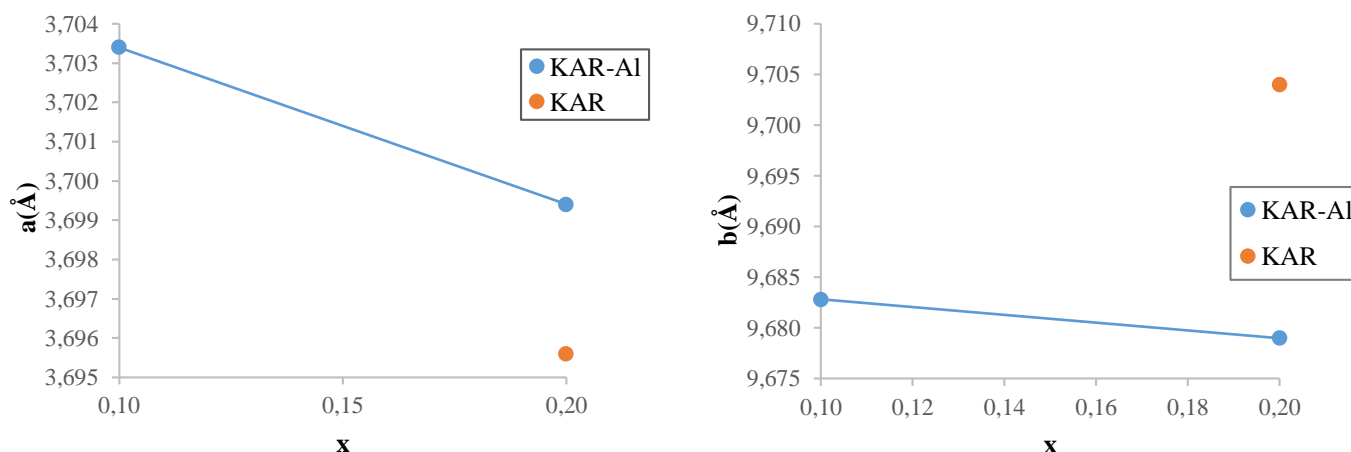
On the other hand, it is clear that a smaller ion replacing a larger one will bring about a volume contraction, and in this respect, the increase of Co-doping is expected to produce a slight increase of the volume, because of the larger ionic size of Co^{+2} with respect to Mg^{+2} ions.

With the help to previous studies we are going to compare karroite and qandilite pigments doped with or without Al^{3+} in the same composition.

In the next table, the measurements of cell parameters obtain of karroite are shown:

Samples x	a(Å)	b(Å)	c(Å)	V(Å ³)
KAR x=0.1	3.7034(7)	9.6828(13)	9.9537(16)	356.94(8)
KAR x=0.2	3.6994(13)	9.679(4)	9.999(10)	358(3)
KAR x=0.2 without Al	3.6956(13)	9.704(8)	10.013(4)	359.09(17)

Table 5: Evolution of cell parameters and volume in $(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$ and $\text{Mg}_{0,8}\text{Co}_{0,2}\text{Ti}_2\text{O}_5$ fired at 1200 °C



Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

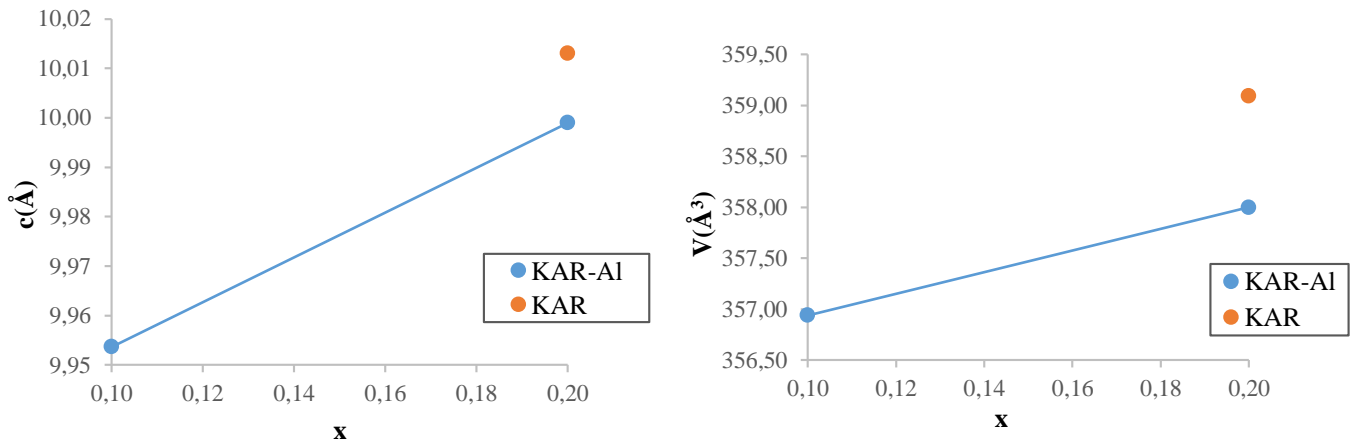


Figure 23: Cell parameters and volume of compositions $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{1.8}\text{O}_5$ and $(\text{Mg}_{0.8-x}\text{Co}_x)\text{Ti}_{1.8}\text{O}_5$ fired at $1200\text{ }^\circ\text{C}$

In the next table, the measurements of cell parameters obtain of qandilite are shown:

Samples x	a(Å)	V(Å ³)
QAN x=0.1 at $1400\text{ }^\circ\text{C}$	8.3423(10)	580.58(12)
QAN x=0.2 at $1400\text{ }^\circ\text{C}$	8.3625(16)	584.81(19)
QAN x=0.2 without Al at $1200\text{ }^\circ\text{C}$	8.437(3)	600.60(3)

Table 6: Evolution of cell parameters and volume in $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ and $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Ti}_{0.8}\text{O}_4$ fired at $1400\text{ }^\circ\text{C}$ and $1200\text{ }^\circ\text{C}$ respectively

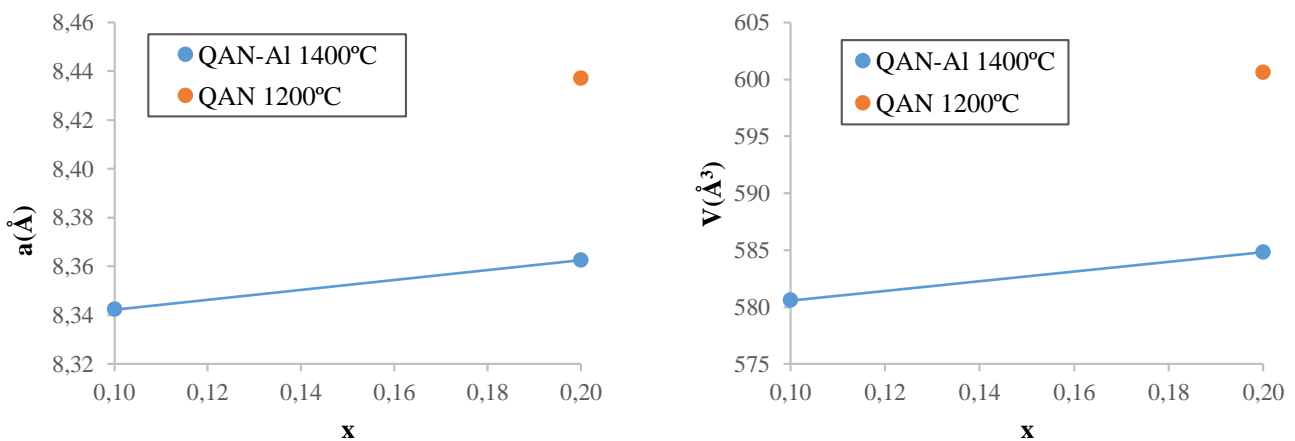


Figure 24: Cell parameters and volume of compositions $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ and $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Ti}_{0.8}\text{O}_4$ fired at $1400\text{ }^\circ\text{C}$ and $1200\text{ }^\circ\text{C}$ respectively

As expected, the change observed in cell parameters with Co-doping (increase of x) is not isotropic, since there are distinct variables (different ionic ratio and a feasible variation in cationic disorder) that can concern to the variation of cell parameters and in the grade of distortion of coordination environment, previously mentioned.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

In effect, we can observe a slight decrease in a and b parameters with the increase of Co-doping, whereas we can observe an appreciable increase of c parameter. As result, a noteworthy increase of cell volume occurs, this fact is expected with the larger ionic ratio of Co^{2+} with respect to Mg^{2+} ions.

Concerning the Al co-doping ($x=0.2$), it may be appreciated an anisotropic variation in the cell parameters, this variation denotes that Al co-doping affects to the distortion of M1 and M2 environments of karroite, appreciating an increase of “a” parameter and a decrease of b and c parameters with Al-doping. All these variations produce a decrease of cell volume, that corresponding with the lesser ionic ratio of Al^{3+} with respect to Mg^{2+} .

In the case of the compositions of qandilite, we appreciated as the increase of Co-doping produce an increase in the edge and in the volume of cubic cell, whereas these parameters decrease with Al co-doped, as expected by the greater ionic ratio of Co^{2+} ions, and by the lesser ionic ratio of Al^{3+} ions, respectively.

5.3-Optical properties (UV-vis-NIR spectra) and coloring performance in ceramic glazes

5.3.1-Optical properties of powders

Co^{2+} is a d^7 ion with a ground state ${}^4\text{T}_{1g}({}^4\text{F})$ associated to the unique electron configuration $(t_{2g})^6(e_g)^1$. According to Tanabe-Sugano diagram in an octahedral environment Co^{2+} presents three spin-allowed transitions²⁹ (Fig. 24):

- $v_1: {}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F}) \approx 1350 \text{ nm}$ (near infrared)
- $v_2: {}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F}) \approx 800 \text{ nm}$ (near infrared)
- $v_3: {}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P}) \approx 580 \text{ nm}$ (green)

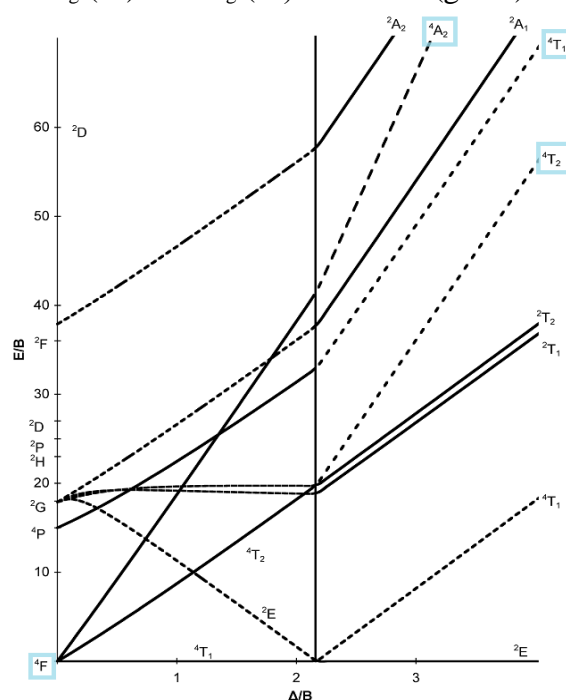


Figure 25: Tanabe-Sugano diagram Co^{2+} (d^7)

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

The absorption band responsible for the color is which belong to the spin-allowed transition (ν_3), this transition appear at yellow region. The others transitions (ν_1 and ν_2) are into the near infrared region and are not responsible for the obtained colorations.

Another feature band of titanates correspond with an intense absorption in the UV-region, around 250-300 nm, due to the charge transfer transition of $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$. A similar charge transfer between $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ may also appear in the UV, these bands do not affect the color.

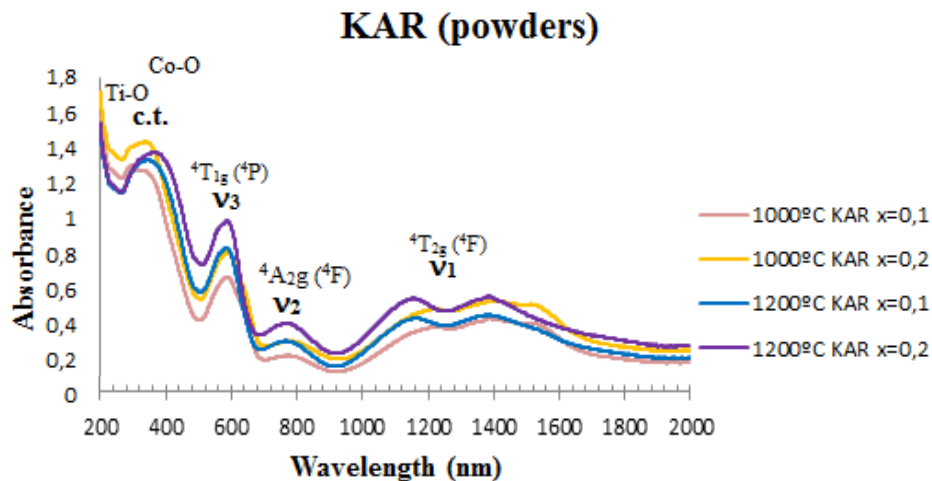


Figure 26: UV-vis-NIR absorption of $(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$ powders fired at 1000 °C/3h and 1200 °C/3h

As it may be appreciated in the UV-vis spectra of 1000 °C and 1200 °C fired pigments (Fig. 26), three bands can be distinguished. These bands are characteristic of Co^{2+} with octahedral environment, as explained previously. We can observe a split band in the near infrared region (1100-1600 nm), this band belong to ν_1 transition and the splitting of this band can be caused by the occupation of ions in different positions (M1 and M2) of the structure which have different Co-O distances. Others bands represented belong to ν_2 transition and ν_3 transition and appear around 800 nm and 550 nm, respectively. Finally, the charge transference band appear in the near UV (300 nm approximately) and correspond to $\text{Ti}^{4+}-\text{O}^{2-}$ and $\text{Co}^{2+}-\text{O}^{2-}$.

We can observe slight differences in the spectra owing to that at 1200 °C only there are phase karroite and at 1000 °C geikielite and rutile appear as secondary phases. For this reason, we can observe a slight blue shift for ν_1 and ν_2 and a minor splitting of band of ν_1 cause of the appearance of geikielite. Geikielite present a unique band without splitting.

Also we can see a difference in the charge transference band, at 1000 °C the intensity of this band increased due to the presence of rutile and geikielite as a secondary phases.

The ν_3 transition is the responsible of the coloration, as we can observe in the Table 4 of the CIE- $L^*a^*b^*$ parameters the increased of Co-doping increase the luminosity (lesser L^* parameter, more intense and saturated color) and at 1000 °C the pigments powders have a higher green shade (greater negative a^* and less b^*) that pigments powders at 1200 °C.

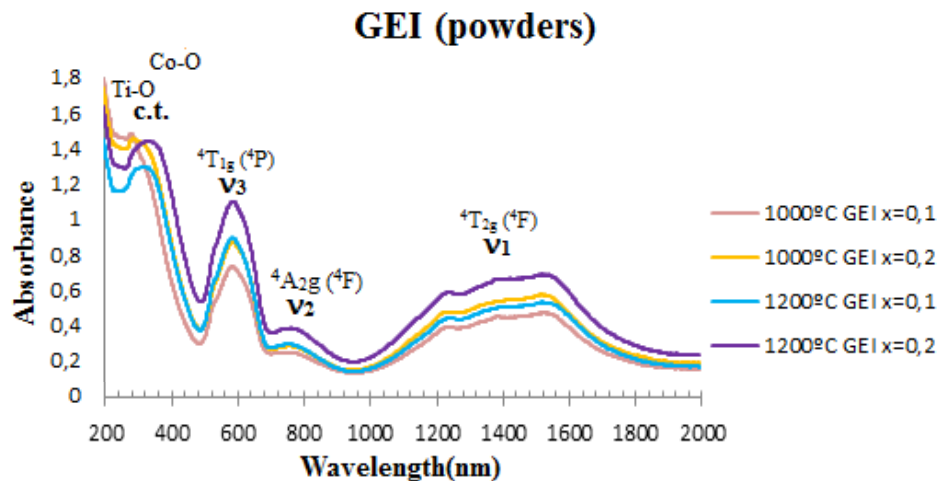


Figure 27: UV-vis-NIR absorption of $(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$ powders fired at 1000 °C/3h and 1200 °C/3h

As previously mentioned, Co^{2+} in octahedral environment presents three spin-allowed transitions v_1 , v_2 and v_3 and the charge transfer band. In the case of geikielite Co^{2+} ions are only occupying one type of the two alternating octahedral sites of geikielite structure, for this reason in the UV-vis spectra the band belonging to v_1 transition not must appear split. But in this case the geikielite is not formed completely at any temperature and there are karroite and Mg spinel (MgAl_2O_4) in important proportion as a secondary phases. As consequence of presence of karroite the UV-vis spectra of geikielite is similar to spectra of karroite. We can observe that the band of v_1 is split as in the case of karroite, but in the case of geikielite the maximums of the split band not appear so distinguished because the maximum corresponding to transition v_1 karroite. Another difference remains in the transition v_3 of geikielite that is slightly more intense and narrow.

In general, the UV-vis spectra of geikielite is similar to spectra of karroite at both temperatures and compositions, because are present almost in the same proportion the distinct phases.

With respect the CIE-L*a*b* parameters represented in the Table 4, it may be observed that the intensity decreased with the temperature and composition (lesser L*). Regarding to a* and b* parameters we can observed that with temperature and composition, a* decreased (more negative, green contribution) and b* increased (less negative, blue contribution). For this reason, as we can see in the Fig. 14, at 1000 °C and composition $x=0,1$ the fired pigments present more blue shade and at 1200 °C and composition $x=0,2$ presents a greenish blue shade.

On the other hand, geikielite compositions present a negative parameter b* (bluish color) unlike to karroite, which exhibited a positive b* value (yellowish hue). As consequence of positive parameter geikielite has a blue coloration.

As we can observe below (Fig. 28) there are slight differences between UV-vis-NIR spectra of powders fired Al co-doped and the powders fired without Al co-doped. The UV-vis spectra without Al belong to preliminary studies. The Co composition is $x=0,2$ in the two systems, karroite and geikielite at 1000 °C and 1200 °C.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

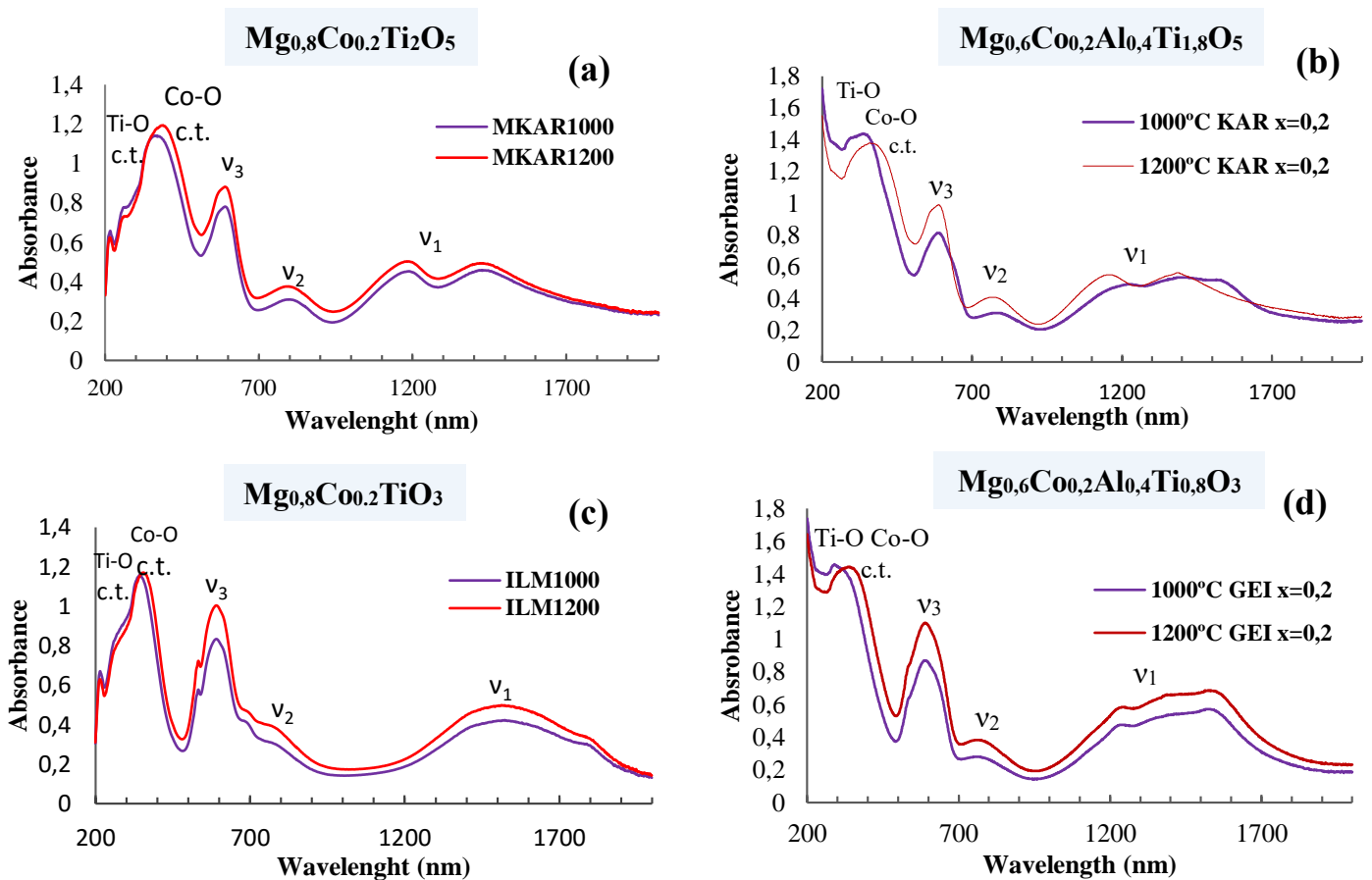


Figure 28: (a),(c) UV-vis-NIR absorption of $\text{Mg}_{0,8}\text{Co}_{0,2}\text{Ti}_2\text{O}_5$ and $\text{Mg}_{0,8}\text{Co}_{0,2}\text{TiO}_3$ powders fired at 1000 °C/3h and 1200 °C/3h
 (b),(d) UV-vis-NIR absorption of $(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{1,8}\text{O}_5$ and $(\text{Mg}_{0,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_3$ powders fired at 1000 °C/3h and 1200 °C/3h

As the Fig. 28 shows, a slight enhanced absorption appear in the UV-vis-NIR spectra of karroite Al co-doped. Also, we can observe a difference in the bands of regions of Co-O and Ti-O charge transfer and specially a lower split of the band belongs to v_1 transition. This band present a less splitting on account of that Al^{3+} ions delayed the effective formation of karroite, and the occupation of Co^{2+} ions in different positions (M1 and M2) not correspond with effective formation of karroite. On the other hand, also a slight enhanced absorption appears in the UV-vis-NIR spectra of geikielite Al co-doped, but only in the bands of regions of Co-O and Ti-O charge transfer. We can observe a difference in the band belong to v_1 transition, Al co-doped not favor the formation of geikielite. As we can see in the XRD pattern corresponding to geikielite (Fig. 17), karroite and Mg spinel (MgAl_2O_4) appear in important proportion as a secondary phases. As consequence of presence of karroite we can observed that the band of v_1 is split slightly as in the case of karroite. Al co-doped prevent the complete formation of geikielite.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

Co environment can change in the case of inverse spinel qandilite. Mg^{2+} ions are equally partitioned between both octahedral and tetrahedral sites of the fully inverse spinel. For this reason, Co^{2+} doping can replace octahedral Mg sites or tetrahedral Mg sites.

Co^{2+} in the d^3 Tanabe-Sugano diagram (Fig. 29), which is used according to the $d^{10-n} (d^7)$ rule in the case of tetrahedral environment, presents three spin allowed transitions from its ground state ${}^4\text{A}_{2g} ({}^4\text{F})$ associated to the unique electron configuration $(eg)^3$ in a tetrahedral environment.

$$v_1: {}^4\text{A}_{2g} ({}^4\text{F}) \rightarrow {}^4\text{T}_{2g} ({}^4\text{F}) \approx 1600 \text{ nm (near infrared)}$$

$$v_2: {}^4\text{A}_{2g} ({}^4\text{F}) \rightarrow {}^4\text{T}_{1g} ({}^4\text{F}) \approx 1400 \text{ nm (near infrared)}$$

$$v_3: {}^4\text{A}_{2g} ({}^4\text{F}) \rightarrow {}^4\text{T}_{1g} ({}^4\text{P}) \approx 540\text{-}600\text{-}650 \text{ nm (multiple band in visible region)}$$

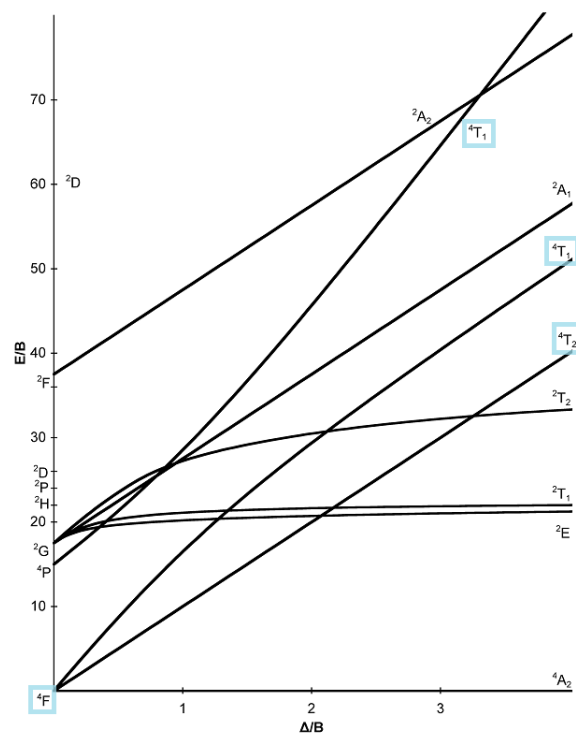


Figure 29: Tanabe-Sugano diagram Co^{2+} in tetrahedral environment (equivalent to d^3 octahedral)

Bands 1 and 2 “fall” into the near infrared region (NIR) and they are not responsible for the color, while the other spin-allowed transition (v_3) appear usually around 540-650 nm (extending almost up to 700 nm) in the blue-red region.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

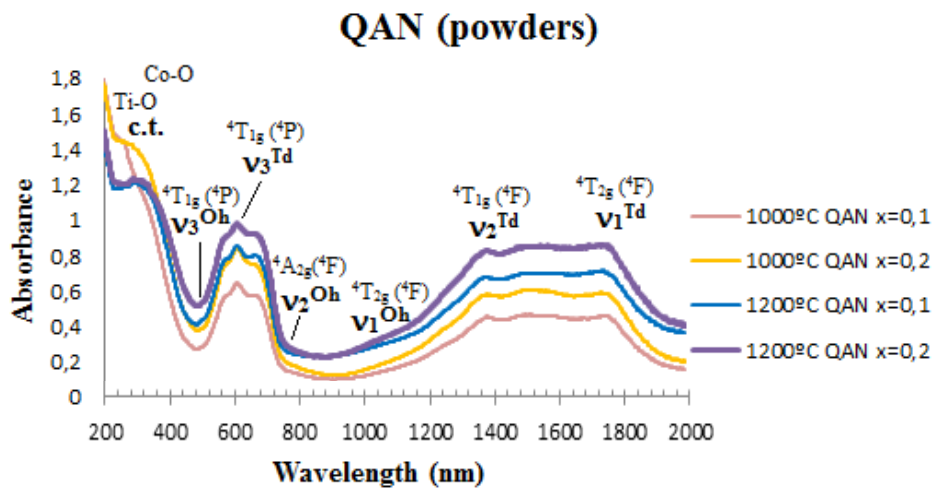


Figure 30: UV-vis-NIR absorption of $(\text{Mg}_{1,8-x}\text{Co}_x)\text{Al}_{0,4}\text{Ti}_{0,8}\text{O}_4$ powders fired at 1000 °C/3h and 1200 °C/3h

In qandilite composition Co^{2+} ions are mainly occupying the tetrahedral sites of qandilite spinel (and also of the accompanying MgAl_2O_4 spinel phase), occupying in a minor proportion the octahedral sites. As we can see in the UV-vis spectra there are bands characteristics of both sites.

Co^{2+} ions are present in the spinels, qandilite and MgAl_2O_4 , mainly in tetrahedral sites but in minor proportion in octahedral sites. For this reason, we can see transitions pertinent to tetrahedral environment, at around 600 nm appear v_3^{Td} transition that is responsible of the color. In near infrared appear the characteristics bands of spinels that belong to transitions v_1^{Td} (1600 nm) and v_2^{Td} (1400 nm), these transitions are the responsible to argument that Co^{2+} in tetrahedral environment predominate front to octahedral environment.

The minor shoulders observed in the spectra at around 1100 (v_1), 800 (v_2) and 500 nm (v_3) may be attributed to octahedral transitions of Co^{2+} , which are due to the minor fraction of Co^{2+} occupying the octahedral sites of the spinels, and also to Co^{2+} ions accommodated in the octahedral sites of the geikielite phase, which it is also present as residual phase along with the spinels (qandilite and MgAl_2O_4). (Fig.30)

Regarding the measured CIE color parameters ($L^*a^*b^*$) (Table 4), it may be observed that qandilite present a higher green shade (greater negative a^* and lesser negative b^*) than geikielite.

Taking into a count the temperatures and compositions the intensity (L^* parameter) increased, parameter a^* (green contribution) increased negatively and parameter b^* (blue contribution) increased negatively with the temperature and positively with the composition. As consequence at 1200 °C the powder fired presents major green color scheme.

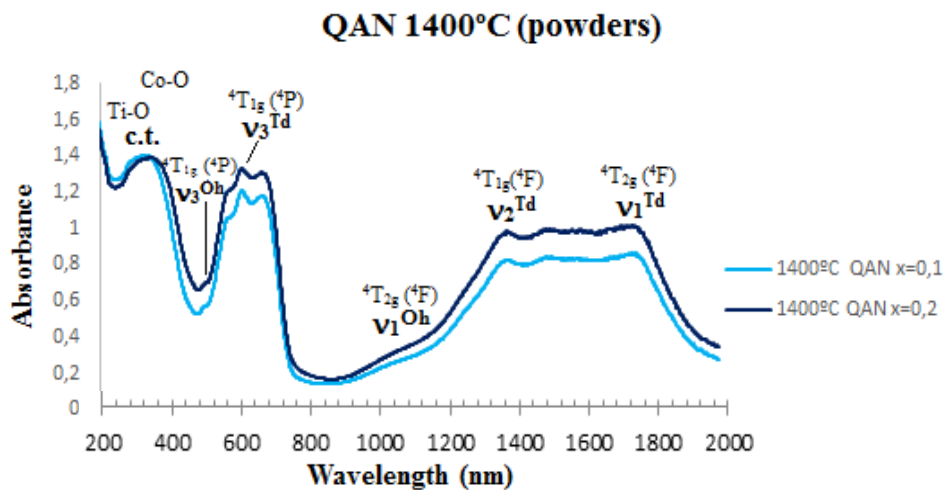


Figure 31: UV-vis-NIR absorption of $(\text{Mg}_{1.8-x}\text{Co}_x)\text{Al}_{0.4}\text{Ti}_{0.8}\text{O}_4$ powders recalcined at 1400 °C/3h

Comparing both spectra, Fig. 30 and 31, we can see that at 1400 °C the octahedral transitions have a lesser intensity that at 1000 °C/1200 °C. The difference more important consist in the disappearance of ν_2^{Oh} at 1400 °C. This happens because as we can see in XRD patterns of qandilite at 1400 °C (Fig. 20) the geikielite phase decreased slightly. Geikielite is the principal structure that favor the Co^{2+} octahedral environment.

Both spectra are similar due to the predominance of the Co^{2+} tetrahedral that is present in the spinels, qandilite and MgAl_2O_4 spinel.

Considering CIE-L*a*b* parameters colorimetric we can observe that at 1400 °C qandilite present a greater greenish-blue hue (a^* and b^* parameters more negative) and a less intensity (less L* parameter).

5.3.2-Optical properties of enameled samples: stability and coloring performance of pigments in different glazes

In order to analyze the stability and optical or coloring properties (pigmenting performance) of fired powders, they were enameled using two double-firing glazes, glaze A and glaze B, at 980 °C and 1050 °C firing temperature respectively.

First it is important to remark that the pigments are not stable enough to withstand the chemical attack within the employed ceramic glazes during enamel firing; this may be more clearly appreciated in the case of karroite samples, since these pigment powers were originally green, and the color of enameled samples become blue.

Considering the information mentioned in 5.1 section, the UV-vis-NIR absorption spectra of fired powders at 500 °C enameled with different glazes are analyzed below. (Fig. 32)

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

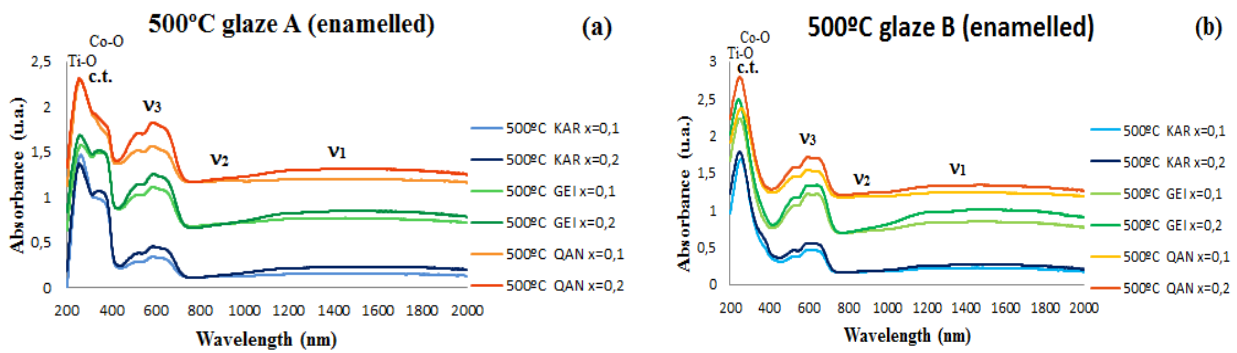


Figure 32: UV-vis-NIR absorption of powders charring at 500 °C enameled with glaze A and B

The coloring performance of cobalt pigments depends very much on their stability, on their chemical reactivity toward the glaze components and also on the coordination of Co^{2+} ions. Normally, tetrahedral coordination is preferred to octahedral and the blue color is attributed to tetrahedral coordination.

In this respect, although ceramic pigments are made from oxide crystals which are thermally stable to glaze firing temperatures and which exhibit a substantially low reactivity with molten glazes reaction with and dissolution of the pigment in the glaze cannot be completely prevented. As a result, the same pigment can produce different colors in different glazes^{29,30,31}.

As it may be appreciated, the bands are plenty broad and little intense and definite, but the characteristic bands of Co^{2+} ions in tetrahedral environment can be distinguished. This fact indicates that Co^{2+} ions in powders calcined at 500 °C (still not crystallized) have been introduced mainly as dissolution of Co into the glassy phase, as happen in most of pigments based on Co^{2+} ^{29,30}.

Fired powders are enameled using the different glazes and the appearance of enameled samples is shown in the next figure.

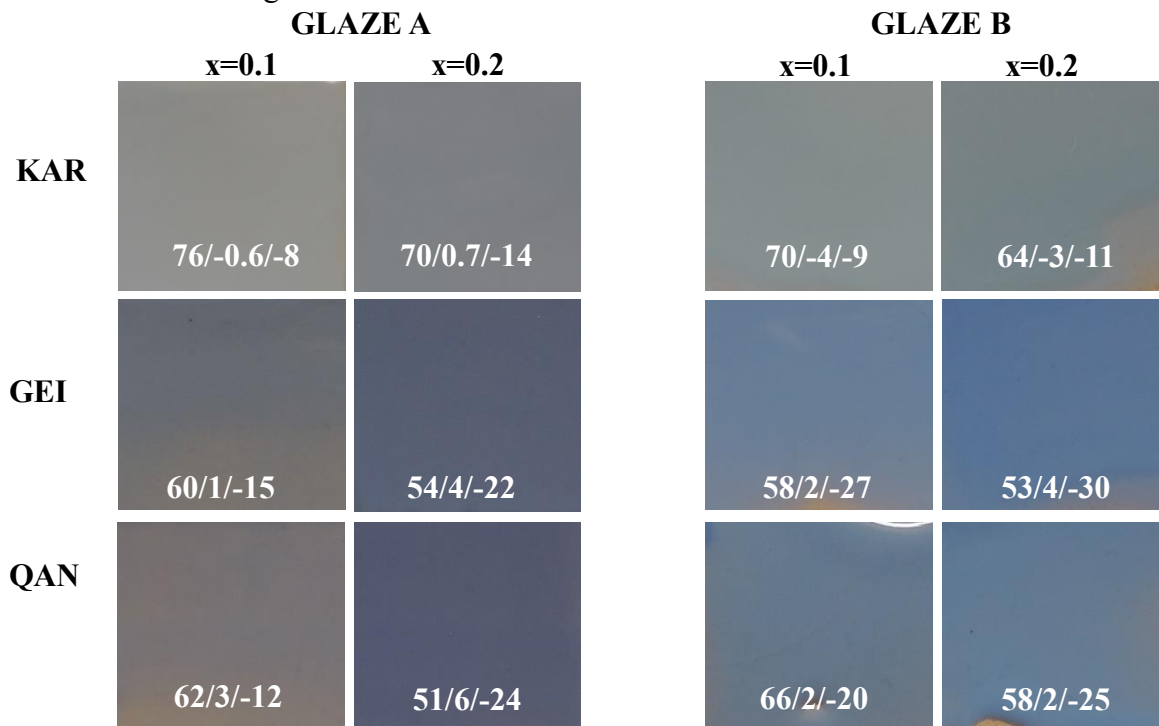


Figure 33: Color aspect of samples enameled at 500 °C with glaze A and B

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

In order to understand the results obtained, Table 7 shows CIE- $L^*a^*b^*$ parameters.

Samples	Composition	Glaze A (980 °C) $L^*/a^*/b^*$	Glaze B (1050 °C) $L^*/a^*/b^*$
KAR	x=0.1	76/-0.6/-8	70/-4/-9
KAR	x=0.2	70/0.7/-14	64/-3/-11
GEI	x=0.1	60/1/-15	58/2/-27
GEI	x=0.2	54/4/-22	53/4/-30
QAN	x=0.1	62/3/-12	66/2/-20
QAN	x=0.2	51/6/-24	58/2/-25

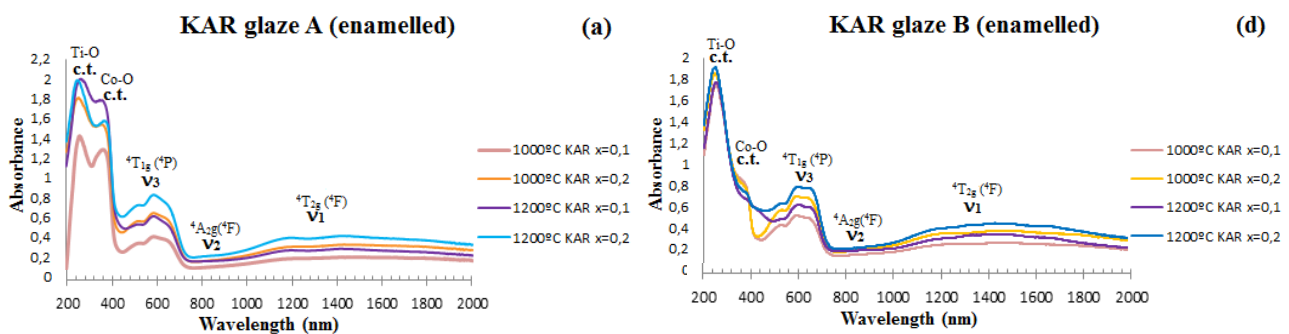
Table 7: Color parameters of pigments charring at 500 °C enameled in glaze A and B

As we can observe in enameled samples and comparing the CIE- $L^*a^*b^*$ parameters, there are a difference between the fired powders enameled with glaze A and B.

According to certain studies¹, karroite pigments have colors ranging from orange to brown (Cr, Fe, Mn, V), to green (Co) and yellow (Ni) that are stable in low-temperature (<1050 °C) ceramic glaze and glassy coatings. In this case, we obtain green colors in glaze B (1050 °C) (more negative a^* value) being more stable pigments in high temperature glazes which had greenish-blue color. The same occurs with the others pigments geikielite and qandilite, they present a less a^* parameter that give to green color.

But must take into a count that at 500 °C the pigments are not formed completely and the samples enameled not represented the real color of the different pigments.

Following, the powders fired at 1000 °C and 1200 °C enameled are analyzed to determinate the stability and optical or coloring properties. The UV-vis-NIR absorption spectra of the different pigments enameled with distinct composition and temperature are represented below (Fig. 34)



Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

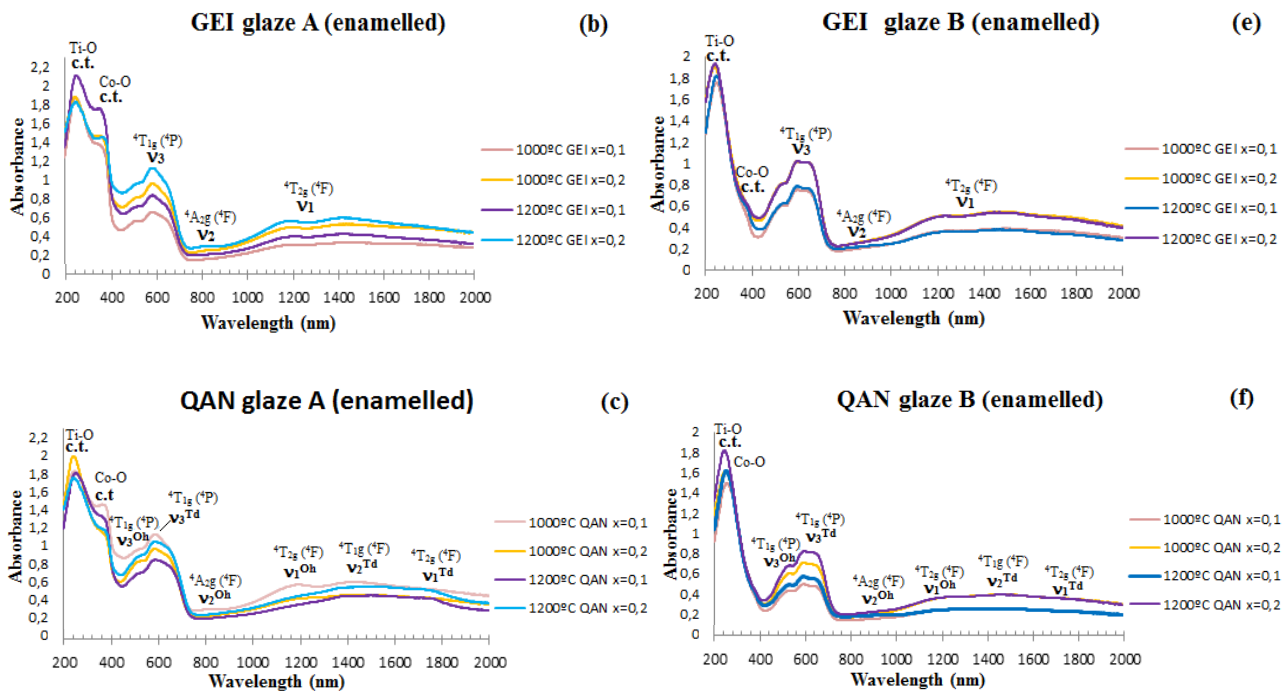


Figure 34: (a),(b),(c) UV-vis-NIR absorption of powders calcined at 1000 °C/1200 °C enameled in glaze A (d),(e),(f) UV-vis-NIR absorption of powders calcined at 1000 °C/1200 °C enameled in glaze B

Regarding to karroite enameled with glaze A, the characteristics bands of Co^{2+} in tetrahedral environment are more intense at higher temperature and composition. A difference in intensity of the charge transference band can be appreciated, appear a double shoulder (250-400 nm). With respect transitions ν_2 and ν_1 , the intensity and the splitting of the band belonging to ν_1 transition decreased in comparison with spectra of powder.

Spectra of karroite enameled with glaze B presents more similarity with spectra of powder (Fig. 26), the principal difference consist of charge transference band (greater double shoulder) and band belonging to ν_1 transition (the split of the band is less distinguished owing to dissolution of Co-pigment in the glaze).

Regarding to enameled samples, the spectra of enameled geikielite samples shows an enhanced and broader intensity in the near UV-region (200-400 nm) using glaze A, this fact is associated to charge transference. Also appear an enhanced and broader intensity in yellow region (around 500-700 nm) using both glazes. On the other hand, the increase of Co-doping at both firing temperatures produced a gradual increase of absorption intensity in both glazes.

As it may be appreciated, the spectra of enameled samples are similar to spectra of powders fired, but the profiles and intensities of the multiple bands are characteristic of tetrahedral Co^{2+} ions, which indicate that an evolution from octahedral to tetrahedral coordination into the glassy phase has occurred by an important dissolution of Co-pigments in the glaze.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

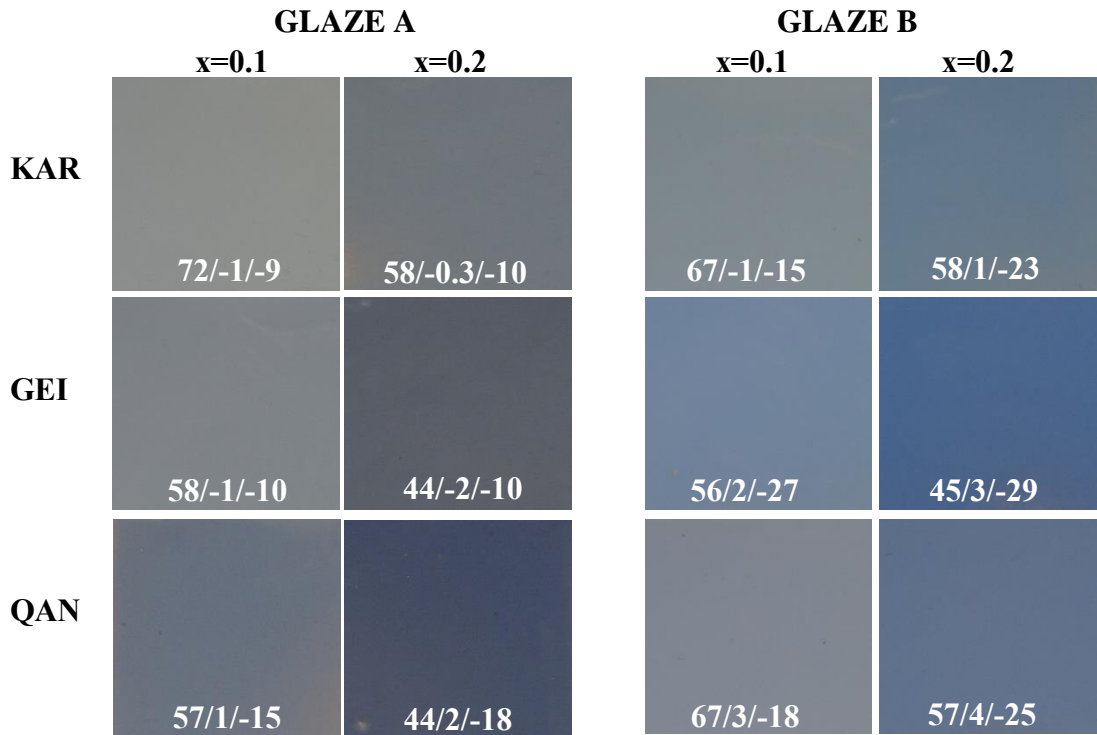
As it has explained previously in UV-vis spectra of qandilite powders (section 5.2.1), Co^{2+} ions can occupy the Mg tetrahedral and octahedral sites and as we can see in the UV-vis spectra there are bands characteristics of both sites. The spectra of enameled qandilite samples show the same characteristics bands that the spectra of powders. However, a substantial difference is observed in the spectra of enameled samples. As it may be appreciated, the absorption intensity of all bands increase using glaze A and a double shoulder appears in charge transference transition.

On the other hand, the increase of Co-doping at both firing temperatures produce a gradual increase of absorption intensity in both glazes.

Comparing the UV-vis-NIR spectra of fired powders with their corresponding UV-vis-NIR spectra of enameled sample, we can appreciate that the samples enameled with glaze B (greater temperature) present a spectra more similar with the spectra of fired powders in karroite and geikielite enameled samples. Whereas we can be appreciated that in the case of qandilite using glaze A (lesser temperature) present a spectra slightly most similar with the spectra of fired powders. Is difficult to confirm in which of both glazes the pigments are more stable since the UV-vis-NIR is similar. This fact can be confirming with CIE-L*a*b* parameters that are represented in Table 8.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

1000 °C



1200 °C

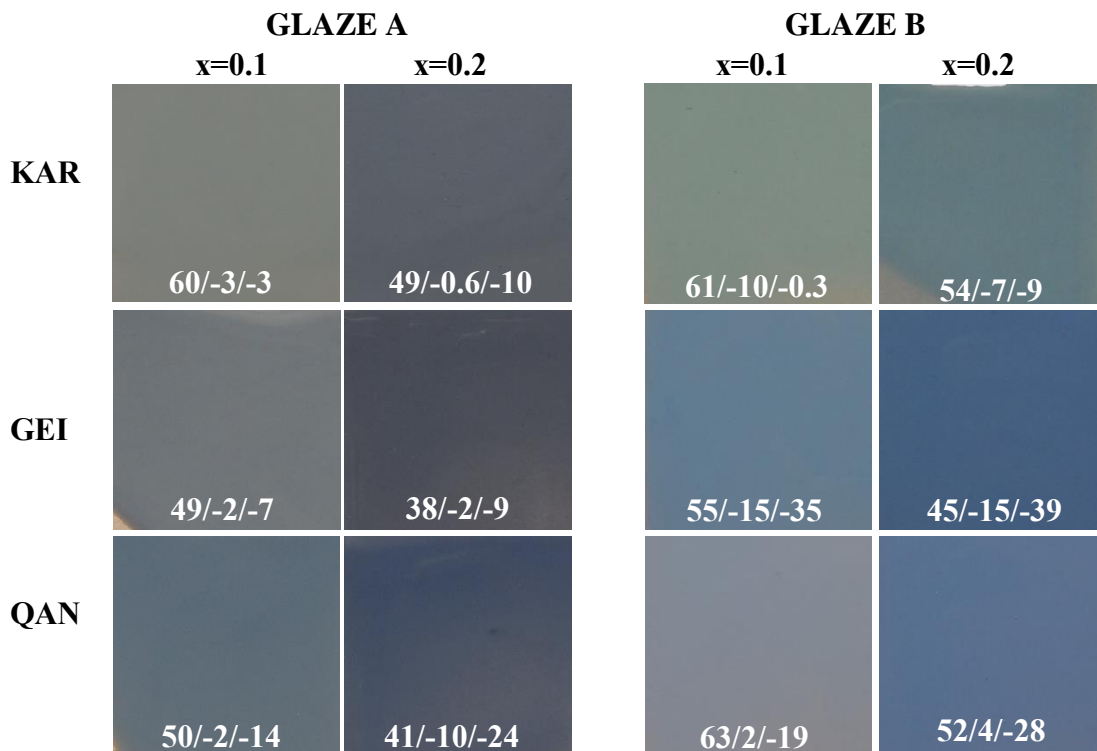


Figure 35: Color aspect of samples enameled at 1000 °C/3h and 1200 °C/3h with glaze A and B

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co²⁺ and Al³⁺

Samples	Composition	1000 °C/3h		1200 °C/3h	
		Glaze A (980 °C) L*/a*/b*	Glaze B (1050 °C) L*/a*/b*	Glaze A (980 °C) L*/a*/b*	Glaze B (1050 °C) L*/a*/b*
KAR	x=0.1	72/-1/ -9	67/-1/ -15	60/-3/ -3	61/-10/ -0.3
KAR	x=0.2	58/-0.3/ -10	58/1/ -23	49/-0.6/ -10	54/-7/ -9
GEI	x=0.1	58/-1/ -10	56/2/ -27	49/-2/ -7	55/-15/ -35
GEI	x=0.2	44/-2/ -10	45/3/ -29	38/-2/ -9	45/-15/ -39
QAN	x=0.1	57/1/ -15	67/3/ -18	50/-2/ -14	63/2/ -19
QAN	x=0.2	44/2/ -18	57/4/ -25	41/-10/ -24	52/4/ -28

Table. 8: Color parameters of pigments firing at 1000 °C/3h and 1200 °C/3h enameled with glaze A and B

Thus, the results obtain in this investigation would be indicated that the pigments are more stable partially within the employed high-temperature ceramic glaze (glaze B) except in the case of qandilite that is slightly more stable within glaze A (less-temperature). It may be confirmed by the measured CIE-L*a*b* color parameters summarized in Table 8. As it may be appreciated, the green hue diminished notably in glazed samples (a* values less negative) with respect to fired powders. The greenish-blue hue increased with the temperature (a*value more negative) and decreased generally with the composition.

As we can observe in the three systems the intensities increased at 1000 °C (less L* value) and normally increased using glaze B. Comparing the intensity between fired powders and their respectively enameled samples we appreciated that the intensity is greater in fired powders.

Also noteworthy, the pale blue colors obtained with the three systems change between them. The most important difference belongs to qandilite that present the best blue coloration (b* value more negative and a* value less negative), this is consequence of Co²⁺ ions in tetrahedral environment and in karroite. In the samples of karroite a slight increase of green hue (greater stability) occurs with glaze B (greater firing temperature and Ca and Zn content), which may indicate a crystallization in situ of a small portion of karroite phase and this resist better in glaze B.

Finally, the UV-vis spectra of enameled samples fired at 1400 °C are shown next.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

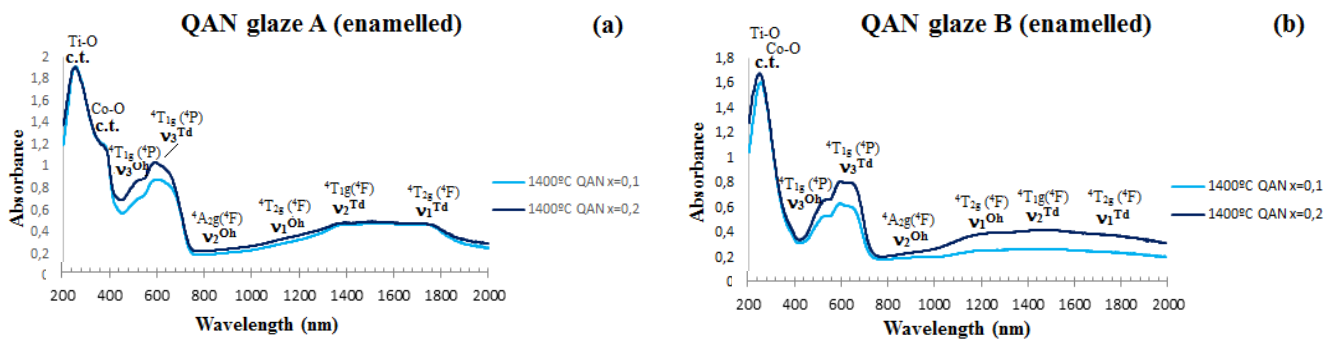


Figure 36: (a),(b) UV-vis-NIR absorption of powders calcined at 1400 °C/3h enamelled in glaze A and B

Comparing UV-vis spectra of enamelled samples calcined at 1200 °C and at 1400 °C, Fig. 34 and 36, we can see that the corresponding spectra are very similar. This happens because as we previously mentioned (Section 5.2.1), the predominance of the Co^{2+} tetrahedral produced these characteristics bands. The phases that present Co^{2+} in tetrahedral environment are qandilite and MgAl_2O_4 spinel that be present at 1200 °C.

Next, the color aspect of qandilites enamelled at 1400 °C with glaze A and B are shown in images and in a table.

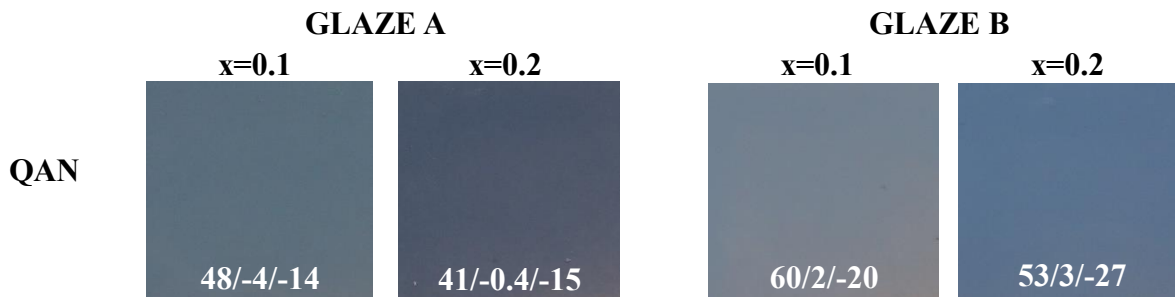


Figure 37: Color aspect of qandilites enamelled at 1400 °C with glaze A and B

Samples	Composition	Glaze A (980 °C) $L^*/a^*/b^*$	Glaze B (1050 °C) $L^*/a^*/b^*$
QAN	x=0.1	48/-4/-14	60/2/-20
QAN	x=0.2	41/-0.4/-15	53/3/-27

Table. 9: Color parameters of pigments firing at 1400 °C/3h enamelled in glaze A and B

Finally, enamelled sample of qandilite present similar values at 1200 °C and at 1400 °C. Noteworthy, in enamelled samples at 1400 °C there are a slight increase of green tonality by the increase (more negative) of a value and a decrease of b value using glaze A. This fact is consequence of the decreased of geikielite as a secondary phase at 1400 °C and the decreased of Co^{2+} in tetrahedral environment. But the CIE- $L^*a^*b^*$ parameters remain almost constant within glaze B.

Synthesis and characterization of ceramic pigments based on karroite, geikielite and qandilite structures co-doped with Co^{2+} and Al^{3+}

On the other hand, the color characterization of enameled sample of karroite and geikielite at 1000 °C and 1200 °C with Co composition $x=0.2$ are compared with their respective enameled pigments without Al co-doped, that were obtained in previous studies. This fact is carried out to determinate the consequence to use Al as co-doped in coloration. The glaze used to compare the samples is glaze B since is slightly more stable in this study.

Next, the enameled samples are shown:

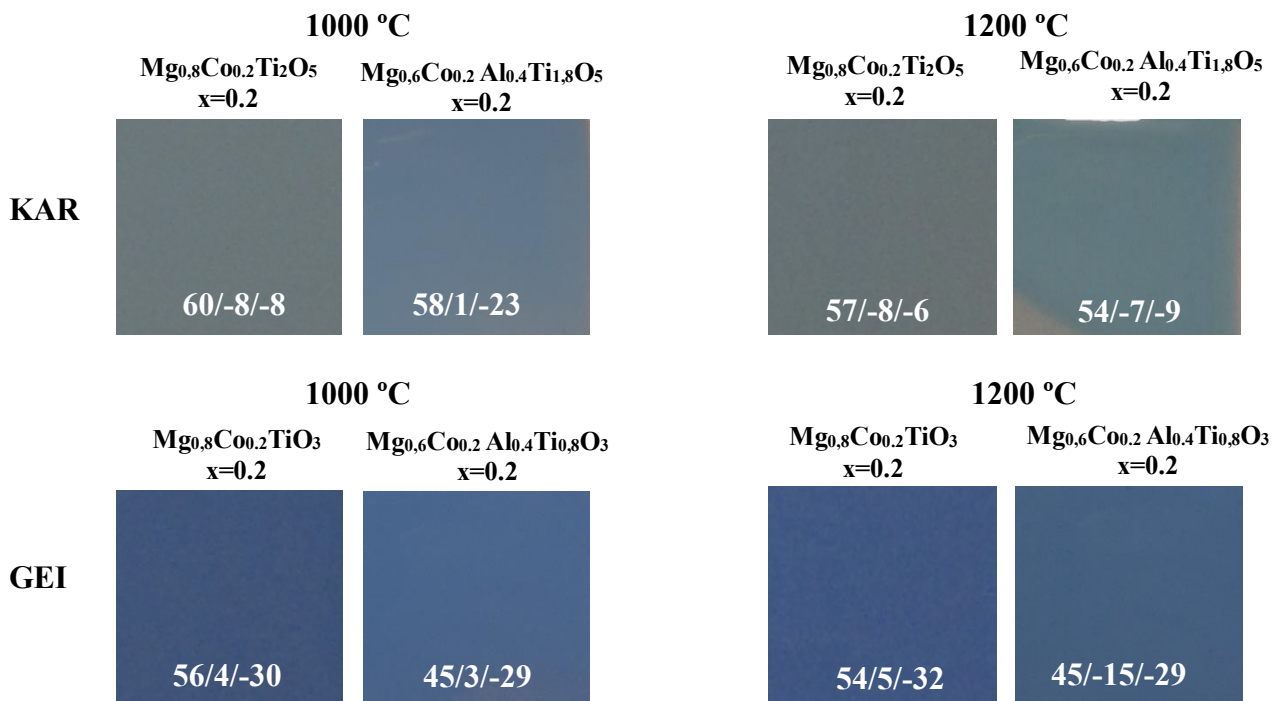


Figure 37: Color aspect of samples enameled at 1000 °C and 1200 °C with and without Al co-doped

As it may be appreciated, there are a difference between the color parameters (CIE- $L^*a^*b^*$). We can observe that with the presence of Al co-doped karroite enameled pigments developed lesser greenish-blue coloration (a^* value less negative and b^* value more negative) and in the case of geikielite developed more greenish-blue coloration.

On the other hand, the intensity of the colors increase (lower L^*) with Al co-doped. The samples without Al co-doped presents a greater blue hue owing to b^* parameter is more negative (greater blue contribution).

6. Conclusions

In this investigation we analyzed the development of new ceramic pigments based on three Co-doped Mg-titanates (Co-pseudobrookite, Co-ilmenite and Co-spinel) co-doping with Al, synthesized by metalorganic decomposition method (MOD). These pigments have been studied in order to observe its influence on the stability against decomposition, the possible modification of optical properties and also their pigmenting performance within ceramic glazes. The following main conclusions may be drawn from this investigation:

1. According to XRD results:

1.1. In the case of karroite solid solutions, karroite crystalline phase is effective at 1200 °C with both compositions. Whereas at 1000 °C a residual phase appears, rutile TiO_2 , can be result of karroite decomposition or oxide precursors that have not fully. This amount of rutile increase with Co-doping.

1.2. In geikielite solid solutions, the formation of crystalline phase of geikilite as a single phase not occurs, we can observe secondary phases like karroite (MgTi_2O_5) and spinel of Al (MgAl_2O_4). The formation of this MgAl_2O_4 spinel phase may be easily understood, due to the strong amount of Al^{3+} formulated in these compositions (40 %mol) and the thermodynamic stability of this phase. The increase of firing temperature and Co-doping (from $x=0.1$ to $x=0.2$) has not influence in the evolution of crystalline phases, and similar amount of geikielite, karroite and spinel phases are present in all cases, being geikielite the major phase.

1.3. Finally, the formation of solid solution qandilite is more effective at greater temperature. At 1000 °C and 1200 °C a mixture of MgTiO_3 geikielite (in greater amount) and a spinel of Al (MgAl_2O_4) is formed. On the other hand, at 1400 °C Mg_2TiO_4 qandilite is formed in greater amount that at 1200 °C, it coexists with geikielite still but in lesser amount. It is appreciated that increasing the composition ($x=0.2$) increases the geikielite phase slightly.

1.4. In summary, co-doping with Al^{3+} ions delay the effective formation of the systems of karroite and geikielite, whereas it appears to have a beneficial effect on the stabilization of qandilite solid solution at lower temperatures (1000 °C). Also remarkably, the relative quantity of qandilite and geikielite phases remain almost unaffected with the increase of firing temperature and also with the Co-doping

2. The measured unit cell parameter of fired compositions shows an anisotropic variation in all the pigments. An increase of cell volume occurs with the increase of Co doping (Co^{+2} (58 pm tetrahedral coordinated and 74.5 pm octahedral coordinated), Mg^{+2} (57 pm tetrahedral coordinated and 72 pm octahedral coordinated), that corresponding with the grater ionic ratio of Co^{2+} with respect to Mg^{2+} .

If we appreciated the effect of Al co-doped in the pigments (Al^{3+} (39 pm tetrahedral coordinated and 53.5 pm octahedral coordinated) is appreciated a decrease of cell volume, that corresponding with the lesser ionic ratio of Al^{3+} respect to Mg^{2+} .

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3. The optical (UV-vis-NIR) spectra of fired pigments were consistent with the accommodation of Co^{2+} on octahedral sites (karroite, geikielite and qandilite) or on tetrahedral sites (qandilite), it depends of the type of structure and the position of Co. Co^{2+} ions in octahedral coordination, presents three spin allowed transitions: ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F}) \approx 1350$ nm, ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F}) \approx 800$ nm and ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P}) \approx 580$ nm. On the other hand, Co^{2+} ions in tetrahedral coordination, presents three spin allowed transitions too. These transitions are: ${}^4\text{A}_{2g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F}) \approx 1600$ nm, ${}^4\text{A}_{2g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{F}) \approx 1400$ nm and ${}^4\text{A}_{2g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P}) \approx 540\text{-}600\text{-}650$ nm.
 - 3.1. A noticeable increase of absorption intensity is observed in the spectra of the three systems with the temperature and composition.
 - 3.2. The stability and optical or coloring properties (pigmenting performance) of fired powders are tested by applying them in two double-firing glazes, glaze A and glaze B, at 980 °C and 1050 °C firing temperature respectively. The results obtain in this investigation indicated that the pigments are slightly most stable partially within the employed high-temperature ceramic glaze (glaze B) except in the case of qandilite. It may be confirmed by the measured CIE- $L^*a^*b^*$ color parameters, a^* parameter more negative that contribute to green coloration. Furthermore, comparing the UV-vis-NIR spectra of fired powders with their corresponding UV-vis-NIR spectra of enameled sample, we can appreciate that the samples enameled with glaze B (high temperature) presents a spectra more similar with the spectra of fired powders usually.
 - 3.3. Al co-doping delayed the effective formation of karroite and geikielite. A slight enhanced absorption appears in the regions of Co-O and Ti-O charge transfer and specially a lower split of the band belongs to ν_1 transition in both pigments. The band belongs to ν_1 transition present a less splitting on account of that Al^{3+} ions delayed the effective formation of karroite, and the occupation of Co^{2+} ions in different positions (M1 and M2) not correspond with effective formation of karroite. On the other hand, Al co-doped prevent the complete formation of geikielite because of the amount of Al^{3+} favor the formation of spinel, geikielite is not formed completely owing to the bad stoichiometry.
4. Concerning color (CIE- $L^*a^*b^*$) parameters, the powders colors are more intense (less L^*) with the temperature and composition. b^* parameter (blue contribution) increased with temperature and with the amount of Co. Whereas, a^* parameter decreased (less negative, green contribution) with temperature and increased slightly with Co-doping.
 - 4.1. The parameters of enameled samples present variations with the powders fired. As it may be appreciated, the green hue diminished notably in glazed samples (a^* values less negative) with respect to fired powders. The greenish-blue hue increased with the temperature (a^* value more negative) and decreased generally with the Co composition.
 - 4.2. The pale blue colors obtained with the three systems change between them. The most important difference remains in the qandilite that present the best blue coloration (b^* value more negative and a^* value less negative), this is consequence of Co^{2+} ions in tetrahedral environment. The more greenish-blue hue belongs to karroite at 1200 °C with composition $x=0.1$.

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- 4.3. Al co-doping show a change in the coloration of powders fired. We can observe that with the presence of Al co-doped, pigment powders developed greater greenish-blue coloration (a^* value less negative) except in the case of qandilite at 1200 °C. On the other hand, b^* parameter (blue contribution) decrease and the intensity (L^* value) increased with Al co-doped.
- 4.4. In enameled pigments the presence of Al co-doped produced an increase of intensity (lower L^* value) and karroite enameled pigments developed lesser greenish-blue coloration (a^* value less negative and b^* value more negative) at difference of geikielite that present more greenish-blue coloration.

To sum up, it is important to optimize the use of cobalt in order to minimize the costs the environmental impact of the manufacturing process. Co is scarce, expensive and is consider as toxic or hazardous, so we have to look for optimum compositions.

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