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Title: CERAMIZATION IN $(Ba_{1-X}M_x)Al_2Si_2O_8$ CELSIAN SOLID SOLUTIONS OF HEAVY METALS AND RECYCLING AS PIGMENTS

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Abstract: Ceramization of several heavy metals such as $M=Cr, Fe, Co$ and Ni in celsian lattice has been studied by sintering up to $1500^\circ C$ of its oxides with $BaCO_3, Al(OH)_3$ and SiO_2 in order to obtain $(Ba_{1-X}M_x)Al_2Si_2O_8$ solid solutions. Cr^{3+} enters in solid solution forming anionic vacancies up to $x=0.5$ (both celsian and hexacelsian coexists), Fe^{3+} and Co^{2+} only up to $x=0.1$ (both celsian and hexacelsian coexists) and melts at higher x values, Ni only forms solid solution at low $x=0.02$ coexisting hexacelsian and celsian, at higher x crystallizes $NiAl_2O_4$ spinel. But using forming glasses mineralizers such as borates increase the reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding 10wt% of glass forming agent at only $1000^\circ C/3h$ of sintering temperature. Powders have been reused as ceramic pigments and leachate test is performed in order to classify the resulting solid solution in order to its landfill disposal (Council Directive 1999/31/EC on the waste landfill).

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Highlights.

- Heavy metals have been immobilized in celsian ($\text{Ba}_{1-x}\text{M}_x$) $\text{Al}_2\text{Si}_2\text{O}_8$ solid solutions.
- Borates have been used as mineralizers obtaining monophasic celsian at 1000°C/3h.
- Solid solutions act as ceramic pigments in ceramic glazes.
- Solid solutions have been evaluated by leachate test for its landfill disposal.

CERAMIZATION IN $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ CELSIAN SOLID SOLUTIONS OF HEAVY METALS AND RECYCLING AS PIGMENTS

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Abstract.

Ceramization of several heavy metals such as $\text{M}=\text{Cr}$, Fe , Co and Ni in celsian lattice has been studied by sintering up to 1500°C of its oxides with BaCO_3 , $\text{Al}(\text{OH})_3$ and SiO_2 in order to obtain $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ solid solutions. Cr^{3+} enters in solid solution forming anionic vacancies up to $x=0.5$ (both celsian and hexacelsian coexists), Fe^{3+} and Co^{2+} only up to $x=0.1$ (both celsian and hexacelsian coexists) and melts at higher x values, Ni only forms solid solution at low $x=0.02$ coexisting hexacelsian and celsian, at higher x crystallizes NiAl_2O_4 spinel. But using forming glasses mineralizers such as borates increase the reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding 10wt% of glass forming agent at only $1000^\circ\text{C}/3\text{h}$ of sintering temperature. Powders have been reused as ceramic pigments and leachate test is performed in order to classify the resulting solid solution in order to its landfill disposal (Council Directive 1999/31/EC on the waste landfill).

Key words: Heavy metals, Solid solution, Celsian, Ceramic pigment.

1. Introduction.

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 g/l, their toxicity depends on several factors including the dose, route of exposure, and chemical species, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals [1]. For an effective immobilization of wastes by sintering (ceramization), ceramic oxide materials such as perovskite (CaTiO_3), zirconolite $\text{CaZrTi}_2\text{O}_7$, hollandite ($\text{Ba}_{1.23}\text{Al}_{2.46}\text{Ti}_{5.54}\text{O}_{16}$), pyrochlore ($\text{Ln}_2\text{Zr}_2\text{O}_7$ and $\text{Ln}_2\text{Ti}_2\text{O}_7$, Ln = rare earth metals), NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$) and sphene (CaTiSiO_5), have gained tremendous interest in the eighties because of their application as the geological medium for the immobilization of radioactive wastes due to the stacking of the metal-oxygen polyhedra in their structure results in the formation of cavities and vacant interlayers capable of accommodating a large number of radioactive cations. [2]. With a similar cation distribution to hollandite $\text{Ba}_{1.23}\text{Al}_{2.46}\text{Ti}_{5.54}\text{O}_{16}$ (monoclinic, point group 2/m, space group I2/m), celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$ (monoclinic, point group 2/m, space group I2/c), is a feldspar, although its symmetry is somewhat different: the order in the Celsian is simple, each tetrahedron AlO_4 is surrounded by four SiO_4 tetrahedra and vice versa, the Ba shows an irregular configuration with 10 neighbours equidistant. This disorder induces a low symmetry and increases the kinetic barrier of nucleation, in fact the Celsian has a metastable polymorph, the Hexacelsian or hexagonal celsian composed of a double alternating sheet of tetrahedra $(\text{AlSi})\text{O}_4$ [3,4]. In this communication the immobilization of several heavy metals such as $\text{M}=\text{Cr}$, Fe , Co , Ni in celsian system has been studied by sintering up to 1500°C of its oxides with BaCO_3 , $\text{Al}(\text{OH})_3$ and SiO_2 in order to obtain $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ solid solutions.

2. Material and methods.

By the solid state conventional method or ceramic method (heat and beat, shake and bake) solid

1 solutions ($\text{Ba}_{1-x}\text{M}_x$) $\text{Al}_2\text{Si}_2\text{O}_8$ $x=0.02, 0.1, 0.5, 1.0$ and $\text{M}=\text{Cr, Fe, Co, Ni}$ into celsian lattice has
2 been studied by sintering up to 1500°C the metal oxides ($\text{Cr}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Co}_3\text{O}_4$ or NiO) with
3 $\text{BaCO}_3, \text{Al}(\text{OH})_3$ and SiO_2 (quartz) as precursors in order to immobilize the metals into the
4 celsian crystal lattice. In the ceramic method the precursors were homogenised in a planetary
5 mill in acetone media. When acetone was evaporated the raw powders were successively fired
6 at $800^\circ\text{C}, 1000^\circ\text{C}, 1200^\circ\text{C}$ and 1500°C with a soaking time of 3 hours and with free cooling to
7 room temperature. The as-prepared powders were homogenized manually with mortar and
8 pestle The resulting powders were 5 wt% glazed into a conventional ceramic glaze of the
9 CaO-ZnO-SiO_2 system for double firing stoneware (1050°C) in order to characterize its
10 pigmenting properties.

11
12 Samples were characterized by the following techniques: a) X-Ray Diffraction (XRD) carried
13 out on a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation, $10-70^\circ 2\theta$ range, scan rate 0.02
14 $^\circ 2\theta/\text{s}$, 4 s per step and 40 kV and 20 mA conditions, b) UV-Vis-NIR spectra of fired powder
15 samples and of 5 wt% glazed samples collected using a Jasco V670 spectrometer through
16 diffuse reflectance technique, c) $L^*a^*b^*$ color parameters of glazed samples measured
17 following the CIE- $L^*a^*b^*$ (Commission International de l'Eclairage) colorimetric method (29)
18 using a X-Rite SP60 spectrometer, with standard lighting D65 and 10° observer. On this
19 method, L^* is a measure of lightness (100=white, 0=black) and a^* and b^* of chroma
20 ($-a^*=\text{green}, +a^*=\text{red}, -b^*=\text{blue}, +b^*=\text{yellow}$), d) Microstructure characterization of powders
21 was carried out by Scanning Electron Microscopy (SEM), using a Leo-440i microscope
22 supplied by LEYCA.

23
24 In the case of cobalt solid solution $x=0,1$, two leachate test were performed: (I) a weight ratio of
25 powder:water=1:5 was stirred a room temperature during 24h simulating the conventional
26 washing procedure of ceramic pigments before its commercialization, and (II) the as dried (a)
27 whased powders with a weight ratio powder:water=1:16 were stirred a room temperature
28 during 24h in order to classify the resulting solid solution for its landfill disposal (Council
29 Directive1999/31/EC on the waste landfill).

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3. Results and discussion.
XRD evolution of crystalline phases for samples ($\text{Ba}_{1-x}\text{M}_x$) $\text{Al}_2\text{Si}_2\text{O}_8$ $\text{M}=\text{Cr, Fe, Co, Ni}$ with
temperature is shown in Table 1. Results indicate that Cr^{3+} enters in solid solution forming
anionic vacancies up to $x=0.5$ (both celsian and hexacelsian coexists), Fe^{3+} and Co^{2+} only up to
 $x=0.1$ (both celsian and hexacelsian coexists) and melts at higher x values, Ni only forms solid
solution at low $x=0.02$ coexisting hexacelsian and celsian, at higher x crystallizes NiAl_2O_4
spinel. In the case of Co the XRD patterns are shown in Figure 1.a. The reactivity of the
powders can be increased using forming glasses mineralizers such as borates (boric acid or
sodium perborate); in the case of Co-celsian solid solution, monophasic monoclinic celsian is
obtained adding 10wt% of glass forming agent at only $1000^\circ\text{C}/3\text{h}$ of sintering temperature as it
can be observed in Figure 1.b.

Powders have been reused as ceramic pigments and leachate test is performed in order to
classify the resulting solid solution in order to its landfill disposal (Council Directive
1999/31/EC on the waste landfill). Table 2 displays the visual colour and CIEL $^*a^*b^*$ colour
parameters of powders and 5wt% glazed tablets into a double firing frit (1050°C). Samples with
 $x=0.02$ and 0.1 don't show colour showing L^* values higher than 80 except Co that show light
blue colour in $x=0.02$ and blue colour $L^*a^*b^*=57.4/1.8/-22.4$ in $x=0.1$. In $x=0.5$ and $x=1$
samples Iron and Cobalt melt, Ni powders show turquoise colour that turns in green colour in
the glaze, finally Cr samples produce green coloured powders and green glazed tablets. Figure

1 2.a displays the UV-Vis-NIR spectra of glazed samples (of powders fired at 1500°C) and SEM
2 micrograph of the $x=0.1$ corresponding powder: Co samples show bands associated to Co(II) in
3 tetrahedral coordination (5), Fe samples show bands associated to Fe(III) in octahedral
4 coordination (6), Cr glazed samples show Cr(III) in octahedral coordination (7) and finally Ni
5 glazed tablets show Ni(II) in octahedral sites (7). Figure 2.b shows the UV-Vis-NIR spectra of
6 M=Co mineralized by progressive addition of acid boric (from 0 to 10 wt%) fired at 1000°C
7 before leachate I and SEM micrographs of 0% and 10% addition of H_3BO_3 . The UV-Vis-NIR
8 absorption increases with the addition of the mineralizer and the feature of SEM images
9 indicates that sintering of powders is similar in 0% and 10% addition of H_3BO_3 .

11 Table 3 shows the obtained results of leachate tests (I) and (II) for $(Ba_{0.9}Co_{0.1})Al_2Si_2O_8$
12 mineralized by progressive addition of acid boric (from 0 to 10 wt%) fired at 1000°C. In order
13 to its landfill disposal the leaching limits of the “COUNCIL DECISION of 19 December 2002
14 establishing criteria and procedures for the acceptance of waste at landfills” (minimum pH=6)
15 and the Spanish “Real Decreto 849/1986 del reglamento del Dominio público Hidráulico” (pH
16 between 5.5-9.5 and boron 10 ppm) has been considered. pH and conductivity were measured
17 with pH-metter and conductimeter (both supplied by Crison) respectively, boron has been
18 measured by azometine optical spectroscopy at 410 nm in a Jasco spectrometer, cobalt was
19 measured by ethyl ether extraction of the blue complex $Co(SCN)_4^{2-}$ by addition of NH_4SCN to
20 the leachates. On leachate II the Microtox™ test based on Photobacter phosphoreum (*Vibrio*
21 *fischeri*) bioluminescence inhibition was performed. The results indicate a decrease on the
22 screening measurement for Microtox™ test which always is lower than 25% (indicating a
23 EC50 higher than 3000) and good inertization of cobalt (always over the detection limit by the
24 $Co(SCN)_4^{2-}$ assay) but the presence of boron increases with mineralizer addition and exceeds
25 the limit of 10 ppm, then although mineralizer increase the reactivity it contravenes
26 environmental criteria.

32 4. Conclusions.

33 Immobilization of several heavy metals such as M=Cr, Fe, Co and Ni in celsian lattice has been
34 reached by sintering up to 1500°C of its oxides with $BaCO_3$, $Al(OH)_3$ and SiO_2 in order to
35 obtain $(Ba_{1-x}M_x)Al_2Si_2O_8$ solid solutions: up to $x=0.5$ for Cr^{3+} , Fe^{3+} and Co^{2+} only up to $x=0.1$
36 and Ni only at $x=0.02$. Using forming glasses mineralizers, such as borates, increase the
37 reactivity and monophasic celsian is obtained in the case of Co-celsian solid solution, adding
38 10wt% of glass forming agent at only 1000°C/3h of sintering temperature. Powders have been
39 reused as ceramic pigments and leachate test has been performed in order to classify the
40 resulting solid solution in order to its landfill disposal. Co produces adequate blue pigmentation
41 shades and both Cr and Ni, green colours in conventional double firing frit (1050°C). The
42 addition of boron mineralizers increase the reactivity but from leachate tests, although a
43 decrease on the screening measurement for Microtox™ test and good inertization of cobalt is
44 detected, boron exceeds the limit of 10 ppm, then the use of boron mineralizer contravenes
45 environmental criteria.

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Figure 1. XRD patterns of samples: a) $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ $\text{M}=\text{Co}$, $x=0,02$ and 0.1 powders fired at 1500°C , b) the composition (a) with additions of boric acid (wt%) fired at 1000°C . CRYSTALLINE PHASES: Q (Quartz SiO_2), U (Unidentified), F (Hexacelsian), M (Celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$).

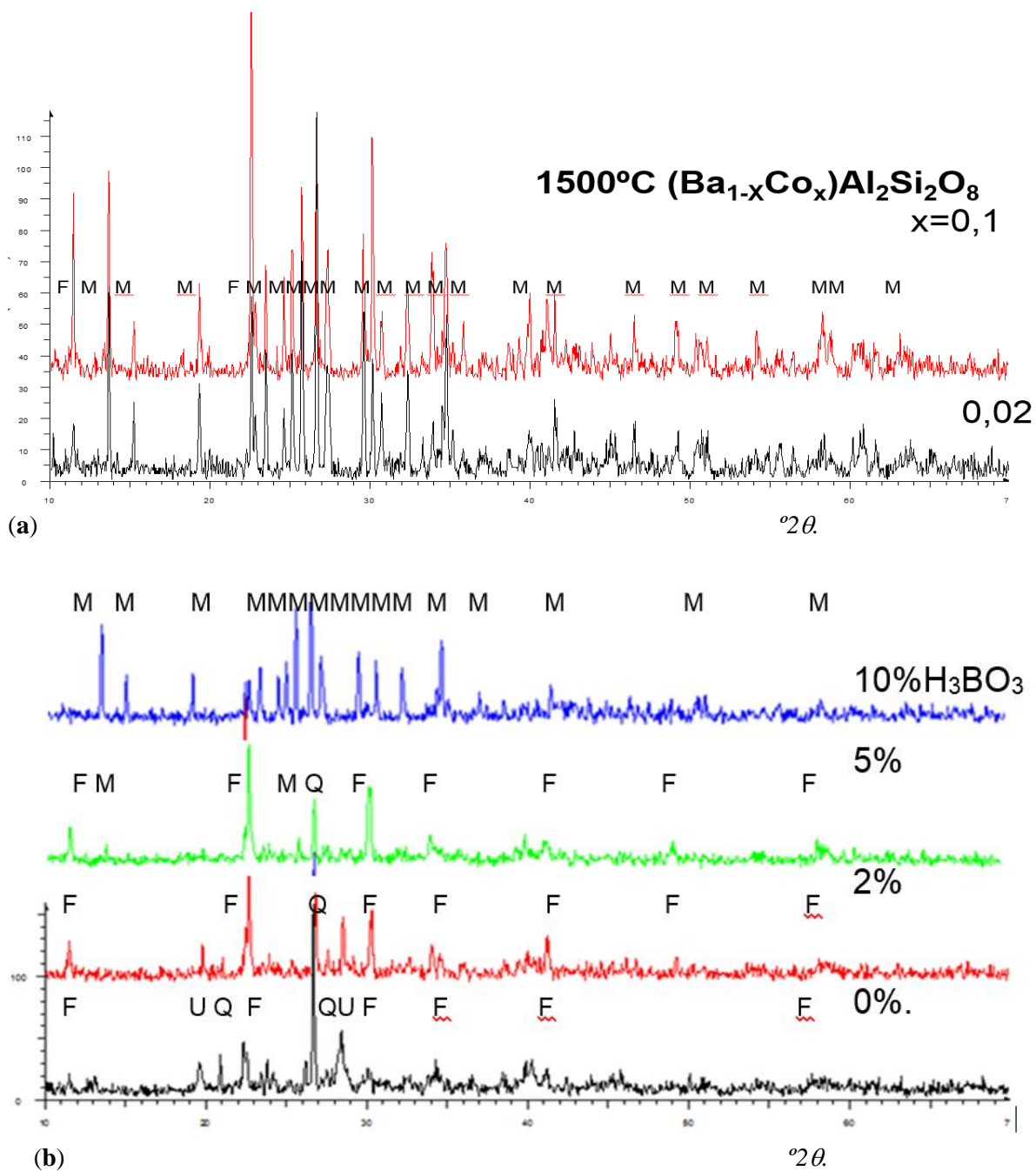


Figure 2. UV-Vis-NIR spectroscopy of glazed samples: a) $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ fired at 1500°C and SEM micrograph of the $x=0,1$ corresponding powder, b) $\text{M}=\text{Co}$ mineralized by progressive addition of boric acid (from 0 to 10 wt%) fired at 1000°C , SEM micrographs of 0% and 10% addition of H_3BO_3 .

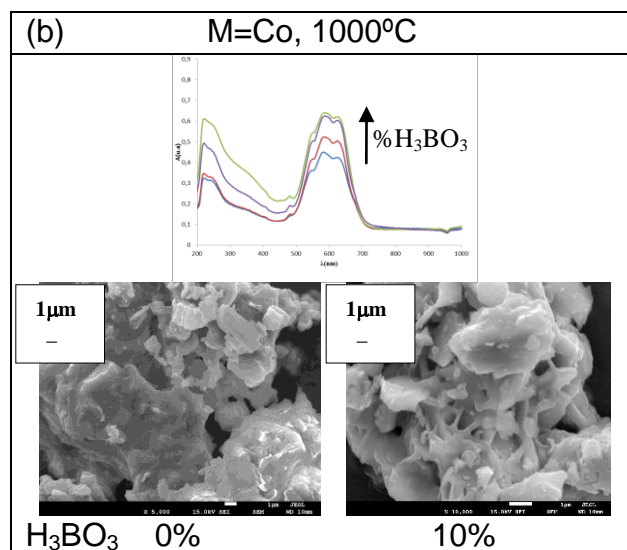
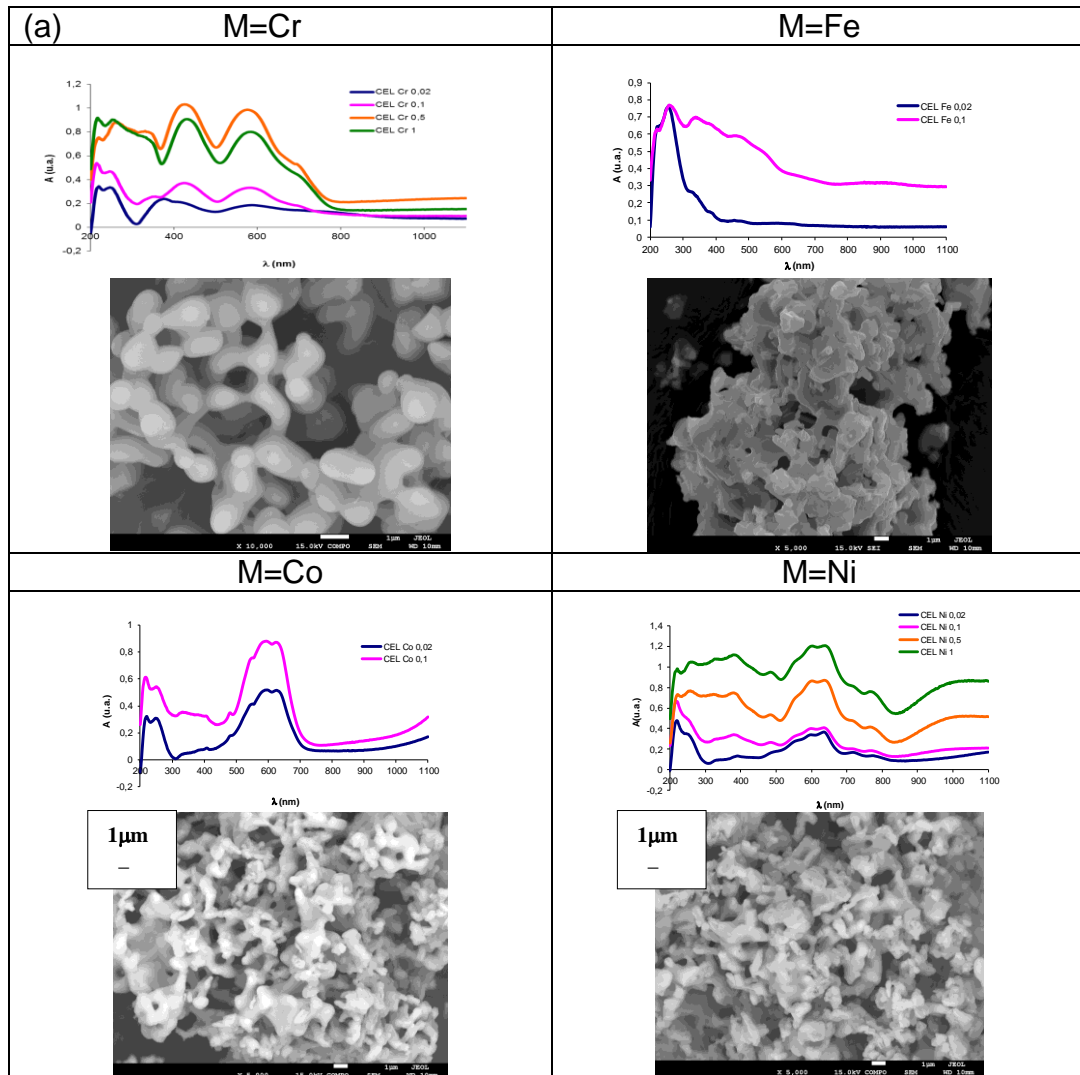


Table 1. XRD evolution of crystalline phases for samples $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ with temperature.

Sample	800°C/3h	1000°C/3h	1200°C/3h	1500°C/3h
$(\text{Ba}_{1-x}\text{Cr}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
x= 0,02	Q,W(s)BA(w)	Q(s) BA(m) H(vw) CF(w)	Q(w) BA(m) CF(s)	F(s)M(m)
x=0,1	Q(s)W(w)BA(m)	Q(s) BA(m) H(w) CF(w)	BA(w) F(s)	F(s)M(m)
x=0.5	Q(s) H(m)	Q(s) H(m) F(w)	Q(m) F (s)	F(m)M(m)
x=1	Q(s) E(m)	Q(s) E(m)	Q(s) E(m)	MU,CR,Q(m) E,U(w)
$(\text{Ba}_{1-x}\text{Fe}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
x= 0,02	Q,W(s)BA(w)	Q(s) BA(m)BS(vw) CF(w)	Q(w) BA(m) F(s)	F(s)M(m)
x=0,1	Q(s)W(m)BA(m)	Q(s)BA(94)BS(vw)CF (m)	Q(vw)BA(m) F(s)	F(w)M(m)
x=0.5	Q(s)BA(m) H(w)	Q(s)BA(m)CF(m)	Q(m) F(s) BA,CR(w)	-
x=1	Q(s) H(m)	Q(s) H(m) U(w)	Q(s) CR,HE,CO(m)	-
$(\text{Ba}_{1-x}\text{Co}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
x= 0,02	Q,W(s) BA(w) BS(vw)	Q(90) BAO(m) F(w)	BA(w) F(s) M(w)	F(m)M(m)
x=0,1	Q(s)W(w)BA(m)	Q,BA(m) F(w)	BA(m) F(s) M(w)	F(s)M(m)
x=0.5	Q(s) W(vw) BA,CO(w)	Q(s) BA,F,M(w) CO(vw)	Q,F(m) M(w) CO(w) CR(vw)	-
x=1	Q(s) CO(m)	Q(s) CO(m)	Q(s) CO(m)	-
$(\text{Ba}_{1-x}\text{Ni}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
x= 0,02	Q,W(s)BA(w) BS(w)	Q(s) BA(m) BS2(vw) F(w)	BA(w) F(s)	F(m)M(m)
x=0,1	Q(s)W,BA(w)	Q,BA(m) BS2(w) F(m)	Q,BA(w) F(s)	F(m)M(m) NA(w)
x=0.5	Q(s) BA,B(m)	Q(s) BA,B(m) F(w)	Q(s) BA,NA(w) F(s)	F,NA(m)
x=1	Q,B(s)	Q,B(s)	Q,NA(s)	NA(s)

CRYSTALLINE PHASES: W (Witherite BaCO_3), Q (Quartz SiO_2), BA (Ba_2AlO_4), BS (Ba_2SiO_4), BS2 ($\text{Ba}_2\text{Si}_3\text{O}_8$), HE ($\alpha\text{-Fe}_2\text{O}_3$), CO (corundum, Al_2O_3), B (Bunsenite NiO), NA (NiAl_2O_4), MU (Mullite $\text{Al}_{2.3}\text{Si}_{0.7}\text{O}_{4.85}$), CR (Cristobalite SiO_2), E ($\alpha\text{-Cr}_2\text{O}_3$), H (Hashemite BaCrO_4), U (Unidentified, F(Hexacelsian), M (Celsian $\text{BaAl}_2\text{Si}_2\text{O}_8$). PEAKS INTENSITY s(strong), m(medium),w(weak),vw(very weak).

Table 2. CIEL*a*b*measurements for powders and 5wt% glazed tiles of $(\text{Ba}_{1-x}\text{M}_x)\text{Al}_2\text{Si}_2\text{O}_8$ samples fired at 1500°C.

Sample	x= 0,02	x=0,1	x=0.5	x=1
$(\text{Ba}_{1-x}\text{Cr}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
powder	88.5/-2.1/2.7 white	81.9/-4.6/4.9 cream	54.3/-4.8/4.4 dark green	62.3/-9.6/8.9 green
glazed	80.3/4.5/11.6 white	74.2/0.8/14.8 cream	49.3/-5.9/8.1 green	46.9/-9.5/9.6 green
$(\text{Ba}_{1-x}\text{Fe}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
powder	89.2/-0.2/3.0 white	71.6/7.0/13.2 pink	melts	melts
glazed	81.6/5.2/10.4 white	79.3/6.8/13.1 light pink	-	-
$(\text{Ba}_{1-x}\text{Co}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
powder	76.2/-2.4/-23.5 Light blue	62.4/-2.2/-29.8 blue	melts	melts
glazed	73.3/0.3/-3.4 light blue	57.4/1.8/-22.4 blue	-	-
$(\text{Ba}_{1-x}\text{Ni}_x)\text{Al}_2\text{Si}_2\text{O}_8$				
powder	84.4/-4.1/-11.8 light blue	80.9/-7.0/-4.0 light blue	63.7/-12.5/-7.4 turquoise	58.4/-11.2/-4.6 green
glazed	79.7/3.8/8.8 white	76.2/4.4/14.2 cream	59.6/-5.0/9.0 green	53.3/-1.2/9.1 dark green

Table 3. Results of leachate test (I) and (II) for $(\text{Ba}_{0,9}\text{Co}_{0,1})\text{Al}_2\text{Si}_2\text{O}_8$ mineralized by progressive addition of boric acid (from 0 to 10 wt%) fired at 1000°C.

% H ₃ BO ₃ addition	TEST	pH	Cond. (μS)	B (ppm)	Co (ppm)	MICROTOX (screening)
0	I	12,82	990	5	ND*	-
	II	8.63	316	3	ND	13,26%
2	I	11,22	3300	48	ND	-
	II	8.67	432	47,9	ND	11,76%
5	I	9,60	1386	55	ND	-
	II	9.06	642	55,2	ND	9,84%
10	I	9,95	2450	56	ND	-
	II	8.69	1043	55,4	ND	0%

(*) ND: Not Detected by $\text{Co}(\text{SCN})_4^{2-}$ test.