SPODUMENE-BASED CERAMIC PIGMENTS

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1. INTRODUCTION

For ceramic pigment development it is necessary to obtain crystalline phases that meet three basic requirements: pigmenting strength, thermostability and insolubility in relation to the glaze. This requires using thermodynamically stable crystalline structures in relation to the glazes and, therefore, insoluble in glasses that devitrify in the glazes. These insoluble phases are made up of glass network modifying metallic ions with high ionic potential such as Ti, Zr, Sn or Al (5.9, 5.0, 5.6, 6 electrons/angstrom as opposed to 15 of boron or 9.8 of silicon), which is why they display a tendency to form MO_n structural units given their relative acidity; Ti crystallizes rutile, anatase and sphene, Zr zirconia and zirconium silicate (zircon), Sn cassiterite and tin sphene, and Al corundum, gahnite, anorthite, gehlenite, spodumene or celsian [1]. Also relatively insoluble are the crystalline phases with Zn (crystallizes willemite) and with calcium (which can devitrify wollastonite, diopside, scheelite or powellite, depending on the conditions). The phases mentioned contain a large part of the classic ceramic pigment structures (zircon, rutile, spinel and corundum encompass 39 pigments of the 51 recognized by the DCMA) [2], and others like spodumene or diopside pyroxene network, which have pigmenting possibilities by doping with chromophore cations of the first transition series [3]. Spodumene ($LiAl(SiO_3)_2$) belongs to the family of pyroxene silicates consisting of long chains of SiO_4^{4-}silicate anions that share corners. Spodumene, as already indicated, is stable in ceramic glazes and devitrifies from glazes rich in Al_2O_3 when LiO is added, which is why it is attempted to colour it with chromophore cations for use as a ceramic pigment.

2. EXPERIMENTAL

Compositions were prepared of $LiAl_{1-x}M_x(SiO_3)$ x=0.05, 0.1, 0.15, 0.2, 0.3, 0.5, 0.75 with M=Fe,Co chromophores, which were studied as ceramic pigments. The samples were prepared by the ceramic route using AlO(OH), Li_2CO_3, Fe_2O_3 and Co_3O_4 as precursors and H_3BO_3 as mineralizer (0.5 mol by formula weight) and calcined at 800 and 1000°C for 2 hours. The powders were studied by X-ray diffraction and when the solid solution was detected by means of this technique, its pigmenting properties were studied by 5% additions to a conventional transparent double-fire glaze and 2% additions to a porcelain tile body. The glazed and fired samples were studied by CIEL*a*b* colorimetry and UV-V spectroscopy.

In the solid solutions with iron, at 800°C, the samples keep quartz without reacting until x=0.75, the presence of hematite therefore showing a reaction catalyzing effect. At 1000°C the quartz disappears at x=0.2. These samples display brown porcelain matrix colorations from 74/7/7 at 800°C/x=0.75 and 73/4/9 at 1000°C/x=0.2. UV-V spectroscopy of the glazed samples (Figure 1) indicates the presence of Fe^{3+} in octahedral coordination. The [measurement of the lattice parameters indicates expansion of the tetragonal network due to the entry of iron, particularly in the c axis (increase from 9.126 to 9.157 Å).

The solid solutions with cobalt do not react completely at 800°C in the studied dopings. At 1000°C the quartz disappears after x=0.1, with spinel Co_3O_4 appearing after x=0.2. UV-V spectroscopy indicates the presence in the glazed samples of Co^{2+} in tetrahedral environment with development of blue colorations of 49/19/-30 in double firing and 73/-5/-3 in porcelain tile.

x	800°C/2h	L*a*b*	1000°C/2h	L*a*b*
0.05	Q (380)E (1120) Pale pink	-	Q (110)E (1710) Brownish pink	P:85/2/11
0.1	Q (290)H (45)E (930) Brownish pink	-	Q (90)E (1850)H (60) Pink brown	P:77/3/11
0.15	Q (230)H (70)E(1150) Brownish pink	B:83/16/11 P:78/5/9	Q(50)E(1650)H(110) Pink brown	P:75/4/9
0.2	Q (350)H (70)E (725) Brownish pink	B:84/6/13 P:78/8/10	E (1875)H (150) Dark brown	P:73/4/9
0.3	Q(260)H(90)E(750) Reddish brown	B:75/9/11 P:76/7/8	Very dark deep red	-
0.5	E(700)Q(110)H(100) Brown	B:71/9/12 P:69/6/7	Very dark deep red	-
0.75	E(1000)H(200)	B:66/8/9 P:74/7/7	Very dark deep red	-

*Table I. X-ray diffraction of the doped powders with iron, colour of the powders and CIEL*a*b* coordinates of the glazed samples in double firing (B) at 5% and porcelain tile at 2% (P). CRYSTALLINE PHASES: Q Quartz ($2\theta=26.7°$), H Hematite Fe_2O_3 ($2\theta=33.2°$), E Spodumene ($2\theta=25.7°$)*

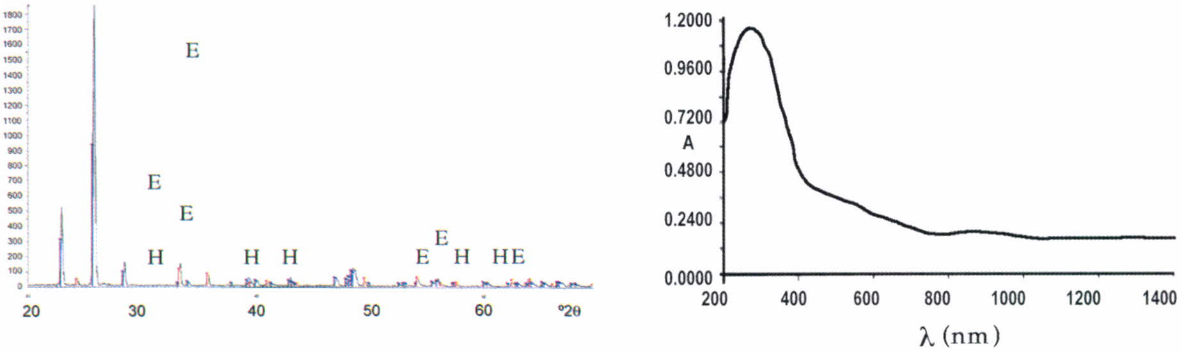

Figure 1. X-ray diffraction and UV-V spectra of the sample with iron x=0.2 at 1000 °C (E=spodumene, H=Hematite)

x	800°C/2h	1000°C/2h	L*a*b*
0.05	Q(400)E(760) Purplish blue	Q (110)E (2250) Violet	P:76/-1/7
0.1	Q (675)E(555) Blue	E (1900) Purple	P:74/-3/2
0.15	Q (440)E(810) Blue	E (1800) Purple	P:75/-5/-3 B:50/19/-31
0.2	Q (375)E(805) Blue	E (1600)C (75) Dark blue	B:49/19/-30 P:73/-5/-3
0.3	Q (320)E(585) Dark blue	Very dark blue	

*Table II. X-ray diffraction of the powders doped with cobalt, colour of the powders and CIEL*a*b* coordinates of the glazed samples in double firing at 5% and porcelain tile at 2%.*
CRYSTALLINE PHASES:
Q (Quartz, 2θ=26.7°), C (Co_3O_4, 2θ=36.9°), E (Spodumene, 2θ=25.7°)

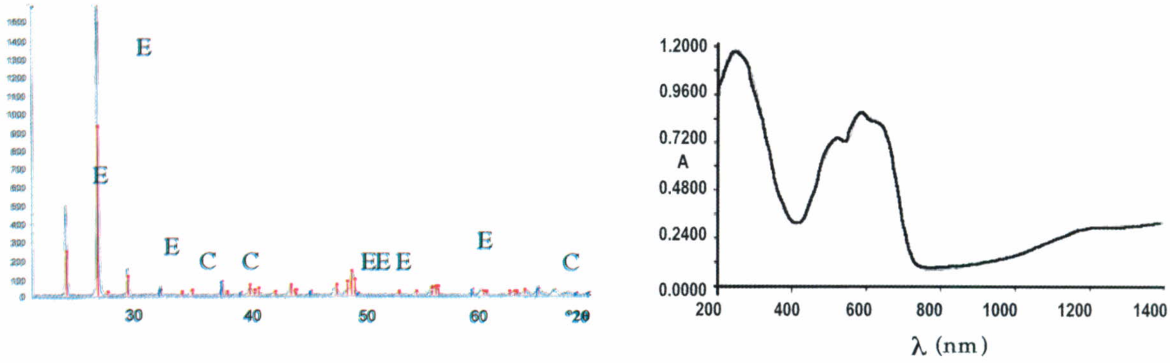

Figure 2. X-ray diffraction and UV-V spectra of the sample with cobalt x=0.2 at 1000°C (E=Spodumene, C=spinel Co_3O_4)

3. CONCLUSIONS

The dopings of spodumene with iron give rise to red brown colorations with Fe^{3+} in octahedral coordination and the dopings with cobalt generate blues with Co^{2+} in tetrahedral coordination, with relatively low iron additions (x=0.2) at 1000°C for both dopants.

4. ACKNOWLEDGEMENTS

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