Experimental report of beamtime HG161

Physico chemical study of dyes and pigments used at the Manufacture Nationale de Sèvres : focus on Thenard's Blue

Context and motivation of the research

When introducing a $Co_{1-x}Al_{2+2x/3}O_4$ ($0 \leq x \leq 1$) spinel or a $CoZr_4(PO_4)_6$ pigments in a porcelain glaze, the pigment reacts with the vitreous matrix and gets partially dissolved, changing the chemistry of the glaze, the crystal phases present and the resulting colour and possibly causing the devitrification of the glaze. This work aims at better understanding the reactions that take place and how to avoid them.

List of the analysed samples with some details on their preparation (powder, cross-section…)

$Co_{1-x}Al_{2+2x/3}O_4$ ($0 \leq x \leq 1$) and $MZr_4(PO_4)_6$ (M = Co, Cu) pigments were prepared and introduced into porcelain glazes (33 wt% of pigment and 67 wt% pf PbO-B_2O_3-SiO_2 glass, fired at 880 °C). Powder samples of the pigments (in 500 µm capillaries) and glazes (in 300 µm capillaries) were analysed at ID22. 13 powder samples were analysed.

Main results obtained

The $Co_{1-x}Al_{2+2x/3}O_4$ pigment has a spinel structure with a tetragonal distortion. $CoAl_2O_4$ was analysed and the structure of γ-Al_2O_3 was solved. It follows the group space $I4_1/amd$ with occupation of Oxygen atoms in 16*h* site and Al atoms in 8*d*, 8*c*, 4*a*, 8*e* and 16*g* sites. $Co_{0.25}Al_{2.5}O_4$ pigment and corresponding glaze were analysed. The pigment consists of two spinel phases, one close to $CoAl_2O_4$ and the other close to γ-Al_2O_3. The structures of both these phases were solved.

Once put in the glaze, the γ-Al_2O_3 reacts with B_2O_3 of the glaze to create $Al_4B_2O_9$ crystals and cause the devitrification of the glaze. Similarly, both $CoZr_4(PO_4)_6$ and $CuZr_4(PO_4)_6$ were analysed, and their structure solved. They are nasicon-type compounds and follow the same structure as $NiZr_4(PO_4)_6$. Once put in the glaze, these pigments react with it to form $ZrSiO_4$ and $PbZr_4(PO_4)_6$. This latter product's structure was also solved.

Eventual communication of results (manuscript in preparation, conference…

This work is part of a PhD project and will be presented in two papers, one about the reactivity of Thénard Blue pigments in a porcelain glaze and another about $MZr_4(PO_4)_6$ (M = Co, Cu) pigments and their stability in a porcelain glaze.