Elaboration and characterization of bismuth containing low temperature glazes belonging to the SiO2-B2O3-Bi2O3-Al2O3 system to replace lead glazes covering Sèvres' porcelain

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Abstract

Some ornamental porcelains from the National Manufacture of Sèvres are currently covered with a colored glaze based on lead borosilicate in which pigment crystallites are incorporated (1). After centuries of improvement that led to these lead borosilicate glazes, they now require a compliance of their compositions in order to follow the evolution of chemical safety standards, including the REACH classification (2). The present study is therefore part of the search for a new lead-free glaze formulation that has similar properties and meets the same quality and aesthetic requirements as lead glazes currently covering a particular kind of porcelain designed at Sèvres.

In this work, we have developed glazes with compositions close to those currently used in which lead oxide (PbO) has been totally replaced by bismuth oxide (Bi2O3). The Bi3+ ion has the same electronic structure as the Pb2+ ion, giving it similar physicochemical properties, while having a lower toxicity, making it a good replacement inside the glazes (3,4). The goal is to create a "greener" composition while trying to maintain the same physicochemical characteristics : a high refractive index guaranteeing brightness, a high hardness and chemical stability, a coefficient of thermal expansion close to that of the substrate, a low crystallization and phase-separation tendency during glaze cooling in the furnace, a density higher than that of the pigments in suspension in order to obtain a satin aspect, as well as melting temperature and viscosity which will enable it to be used in the same temperature range. In this study, the working temperature of our glaze should be around 840◦C to comply with the know-how of the Manufacture.

For this study, six different glasses were elaborated without pigment addition, three of them in the SiO2-B2O3-Bi2O3 system and three in the SiO2-B2O3-Bi2O3-Al2O3 system. In all these compositions B2O3 and Bi2O3 were the only melting agent added to SiO2 and Al2O3 (no alkali oxides were introduced in the mixtures). After grinding the oxides together, the mix was heated at 1000◦C and quickly casted on a metal sheet. Part of the glass was then

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annealed and slowly cooled to mimic Sèvres' process.

The properties of these glasses in the absence of pigment, in particular their behavior as a function of temperature have been studied : fusibility, tendency toward crystallization and phase separation with XRD and SEM-EDX, glass transition temperature with DTA, indirect evaluation of their viscosity with a heating platinum microscope and the density with Archimedes method.

In the SiO2-B2O3-Bi2O3 system, the substitution of PbO by Bi2O3 was optimized to formulate an homogeneous transparent glass. The beneficial effect of the addition of alumina in this system could be observed, in particular on the crystallization tendency of the glass, by avoiding the formation of a bismuth silicate Bi4(SiO4)3. Nevertheless, this addition led to an increase of the viscosity of the glass. By decreasing the amount of Al2O3 added and decreasing the SiO2/B2O3 ratio, a decrease in Tg and viscosity of the glass enabled to obtain a glass composition more adapted to replace the lead-bearing glaze.

References

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