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SPINEL CERAMIC PIGMENTS: A CRYSTAL CHEMICAL APPROACH TO EXPLAIN THEIR TECHNOLOGICAL BEHAVIOR

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Spinel pigments are widely used in the ceramic industry as colorants in glazes and bodies, particularly in porcelain stoneware tiles. The topic of this overview is to outline how a crystal chemical approach, combining chemical and structural parameters, can explain several behaviors of spinel pigments in synthesis and application, thus resulting a useful tool for the industrial practice. The spinel crystal chemistry is described by the general formula AB_2O_4 where A stands for divalent cations (Mg, Fe, Zn, Mn, Ni, Co) and B for trivalent cations (Al, Fe, Cr, Mn). The spinel structure is characterized by an ideal pseudo-cubic close-packed array of oxygen atoms with tetrahedral (T) and octahedral (M) cavities, that is described by the general formula $^{T}(A_{1-i}\ B_i)^{M}(A_iB_{2-i})O_4$ where *i* is the inversion parameter (designing *normal* and *inverse* spinels). The spinel systems are highly flexible from the compositional viewpoint and may exhibit non-stoichiometry, that is oxygen and cation vacancies, as well as disorder in the distribution of A and B cations over the T and M sites. These features depend on the affinity of different cations for the two sites (e.g. Octahedral Site Preference Energy, OSPE) and the thermal history (synthesis) or pigment-glaze interactions (application). A large number of crystal chemical studies have been performed on synthetic materials of well-defined compositions, with the objective to model their physical properties. In the present work, the main colours (black, blue, bluish green, beige and brown) achieved with spinel pigments are considered. For instance, the technological behavior of black-brown pigment spinels (Co-Cr-Fe-Mn-Ni) is strongly connected with their crystal chemistry, reflected by structural parameters, with no effect by grain or crystallite size. In particular, the cation distribution (basically Co^{2+} at T site, Cr^{3+} at M site, while Mn^{2+} and Fe^{3+} are distributed over both sites) is complicated by multiple valences, cation vacancies, and Al incorporation in contact with molten glazes. On the other hand, the blue pigment archetype, i.e. cobalt aluminate, is a largely normal spinel, with a variable degree of inversion affecting its colour strength, depending on thermal cooling and dilution by Zn and Mg. Further examples (beige-brown pigments) are described and discussed.

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