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Pb^{2+} release by lead-ceramic glazes related to the chromophorous ion Cu^{2+}

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A quantitative relationship between lead release and the chemical composition of different lead–ceramic glazes doped by Cu^{2+}, having similar ceramic properties and the same Pb^{2+} release from undoped samples, was established by means of EPR evaluation of the number of C_{2h} (or lower) symmetry sites occupied by Cu^{2+} ions. A parameter was also defined which is a function of the ionic radii and of the ionic molar content of glazes. This parameter is linearly correlated with Pb^{2+} release by acid attack.

1. Introduction

In previous papers, the authors studied the symmetry of the neighbourhood of several chromophorous ions in vitreous matrices [1–3]. In the case of the Cu^{2+} ion, the process of dissolution of CuO micelles versus firing temperature could also be followed by means of electron paramagnetic resonance (EPR) measurements, which enabled us to determine the best conditions for the insertion of this cation. Under these conditions, we observed a dependence of the relative population of the ions in D_{4h} and C_{2h} (or lower) symmetry sites on the $[Na^+]/[K^+]$ ratio. In addition, we observed that the instability of the lattice and the release of Pb^{2+} ions increased with the number of Cu^{2+} ions in C_{2h} or lower symmetry sites.

In order to establish a quantitative relationship between glaze composition and lead release, we compared the properties of the series of glazes FB 1, 2, 3, 4 having an identical composition except for the $[Na^+]/[K^+]$ ratio, with those of a new FC glaze differing both in terms of Pb^{2+} content (which was drastically lower) and in terms of alkaline-earth content. The compositions examined exhibited similar ceramic properties and an almost identical Pb^{2+} release from undoped glazes (of the order of 55 μg dm^{-2}).

2. Experimental details

Controlled-composition frits were prepared by an identical procedure according to a technique previously employed [4]. Compositions of unfired glazes (wt%) are listed in Table I. High-purity reagents were used throughout. For a better understanding of the following discussion, Table II reports the molar content of cations in the different frits. High-purity CuO at various concentrations (between 0.5 and 3.5% wt/wt) was subsequently added to powdered frits.

Measurements of lead release by acid attack were performed on the samples according to a

TABLE I Composition of the examined unfired glazes (errors not exceeding 0.1%) (wt%).

Frits	SiO_2	Pb_3O_4	ZnO	$CaCO_3$	KNO_3	$NaNO_3$	Na_2CO_3	K-feld	H_3BO_3	Kaol.Z.	$MgCO_3$	$BaCO_3$
FB1	30.2	17.2	3.1	10.1	7.6	0	0	0	12.4	19.4	0	0
FB2	30.4	17.3	3.1	10.1	5.1	2.1	0	0	12.4	19.5	0	0
FB3	30.4	17.3	3.1	10.2	2.6	4.3	0	0	12.5	19.6	0	0
FB4	30.6	17.4	3.1	10.2	0	6.5	0	0	12.6	19.6	0	0
FC	29.1	5.4	1.9	2.9	8.5	0	4.1	18.5	17.6	3.1	3.4	5.6

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TABLE II Molar cationic composition of the unfired glazes examined

Ion	FB1	FB2	FB3	FB4	FC
Si^{4+}	0.5937	0.5937	0.5937	0.5937	0.6685
Pb^{2+}	0.0753	0.0753	0.0753	0.0753	0.0237
Zn^{2+}	0.0381	0.0381	0.0381	0.0381	0.0233
B^{3+}	0.2005	0.2005	0.2005	0.2005	0.2846
Al^{3+}	0.2730	0.2730	0.2730	0.2730	0.1276
Mg^{2+}	0	0	0	0	0.0403
Ca^{2+}	0.1010	0.1010	0.1010	0.1010	0.1010
Ba^{2+}	0	0	0	0	0.0284
Na^+	0	0.0251	0.0501	0.0752	0.0774
K^+	0.0752	0.0501	0.0251	0	0.1689

procedure reported elsewhere [5]. EPR measurements on glazes fired at temperatures ranging from 500 to 1100° C were performed in X band with the equipment and techniques described in a previous paper [2].

3. Results and conclusions

The lead release measurements showed that the amount of Pb^{2+} released by acid attack depended on the concentration of the chromophorous ion only at concentrations $\leqslant 1\%$, while it remained constant at higher concentrations. Release values for all samples at a 3% concentration are reported in Table III.

EPR measurements of Cu^{2+} in FC powdered samples were interpreted on the basis of single-ion approximation in crystal field [6, 7]. By the same procedure applied to the study of Cu^{2+} in FB1, 2, 3, 4 and described in detail in a previous paper [2], we succeeded in interpreting the resonance signal as an overlapping of an isotropic signal ($g = 2.16 \pm 0.03$ and $\Delta H = 250 \pm 20$ G) attributable to Cu^{2+} ions in an octahedral trigonally distorted (C_{2h}) or lower symmetry site, and of two axially anisotropic signals, whose spin-Hamiltonian parameters are shown in Table IV, attributable to Cu^{2+} ions in octahedral tetragonally distorted (D_{4h}) sites.

By means of computer-aided numerical methods [2, 8, 9], we were able to determine the percentage of C_{2h} sites (20 ± 3) and of D_{4h} sites (80 ± 4) under conditions of complete cationic insertion, as revealed by the disappearance of the Cu^{2+} signal in CuO (isotropic signal with $g = 2.4$, $\Delta H = 1000$ G). The cationic insertion of Cu^{2+} into FC was already completed at the firing temperature of 800° C. Table III shows the percentage of C_{2h} sites in all the samples examined, these data pointing to a linear dependence of lead release on the percentage of Cu^{2+} ions in sites with C_{2h} or lower symmetry (Fig. 1). The correlation between these variables is very significant because the value of the coefficient of correlation is 0.994.

In the light of the Warren hypotheses [10], also discussed by the authors [11], according to which alkaline and alkaline-earth ions are located in equivalent sites and bonded more or less strongly to silicatic chains, depending on their higher or lower ionic potential, the ions with a bigger ionic radius might exert a destabilizing effect and vice versa. Based on this model, and considering also the role of trivalent cations, we defined the empirical parameter

$$\zeta = \left\{ \sum_i \frac{[M_i^{2+}]}{r_i^{2+}} + \frac{[K^+]}{r_{K^+}} \times \frac{|r_{K^+}[K^+] - r_{Na^+}[Na^+]|}{r_{K^+}[K^+] + r_{Na^+}[Na^+]} \right\} : \sum_j \frac{[M_j^{3+}]}{r_j^{3+}}$$

where Σ_i, Σ_j summations should be extended to all bi- and trivalent cations respectively, and r

TABLE III Lead release m_{Pb} by acid attack and percentage $n(C_{2h})$ of Cu^{2+} in C_{2h} or lower symmetry sites for the various glazes studied

	FB1	FB2	FB3	FB4	FC
m_{Pb} ($\mu g\,dm^{-2}$)	95 ± 10	30 ± 10	24 ± 10	15 ± 10	112 ± 10
$n(C_{2h})$ (%)	17 ± 4	10 ± 2	9 ± 2	7 ± 2	20 ± 3

TABLE IV g-factor, line-width (ΔH) and hyperfine splitting (A) of the two anisotropic components (I) and (II) of the EPR signal of Cu^{2+} in FC

	$g_{\parallel}$	$g_{\perp}$	$\Delta H_{\parallel}$ (G)	$\Delta H_{\perp}$ (G)	$A_{\parallel}$ (G)	$A_{\perp}$ (G)
I	2.325 ± 0.008	2.0805 ± 0.0006	131 ± 10	100 ± 8	120 ± 6	9 ± 0.4
II	2.23 ± 0.01	2.0540 ± 0.0005	290 ± 20	80 ± 5	unresolved	

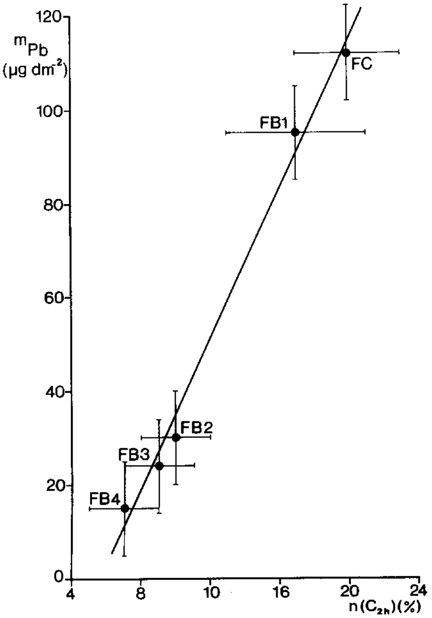

Figure 1 Linear relationship between lead release m_{Pb} and the relative population $n(C_{2h})$ of C_{2h} or lower symmetry sites at a 3% CuO concentration. The line of best-fit, computed by the linear regression analysis, is shown.

represents the ionic radius, according to Spedding and Gschneider [12].

Fig. 2 shows the distribution of the population of C_{2h} sites and Pb^{2+} release as a function of ζ: as it can be seen, in both cases, dependence is significantly linear. A simpler empirical parameter

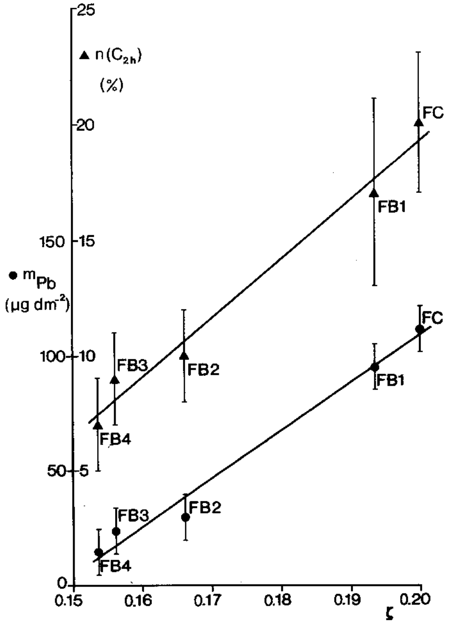

Figure 2 Linear dependence on ζ (see text) of m_{Pb} and $n(C_{2h})$ at a 3% CuO concentration. The lines of best-fit, computed by the method of least squares, are shown.

$$\zeta' = \frac{\sum_i [M_i^{2+}] + [K^+] - [Na^+]}{\sum_j [M_j^{3+}]}$$

which takes more directly into account the $[Na^+]/[B^{3+}]$ ratio [13] is also correlated, though not linearly, with release data.

Although the number of compositions examined was limited by the fact that not all the glazes which could be theoretically formulated exhibit identical ceramic properties, in this work we have been able to show a linear dependence between lead release by acid attack and the relative number of Cu^{2+} chromophorous ions at sites with a C_{2h} or lower symmetry in the vitreous matrix. We have also defined a parameter which enabled us to draw a simple and direct relationship between the composition of the vitreous matrix and the amount of lead released, in terms of molar cationic content and of ionic radii.

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