GARNET-BASED PIGMENTS

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1. INTRODUCTION

At the present time only one garnet-based pigment is used, the victory-green uvarovite garnet $Ca_3Cr_2Si_3O_{12}$, for which has been lost interest in favour of other green colorants with a less toxic load and lower cost, as well as being very versatile, such as the green obtained by mixing the vanadium turquoise in zircon and the praseodymium yellow in zircon, which display certain difficulties in regard to stability in high-temperature glazes. The present study analyses the possibility of obtaining pigments with other garnet systems such as YIG (Yttrium Iron Garnet) $Y_3Fe_5O_{12}$, YAG (Yttrium Aluminium Garnet) $Y_3Al_5O_{12}$, YGAG (Yttrium Gallium Garnet) $Y_3Ga_5O_{12}$ doped with chromium and almandine $Fe_3Al_2Si_3O_{12}$. Garnet has a very stable structure $A_3B_2C_3O_{12}$, in which A is a relatively large divalent or trivalent cation occupying dodecahedral vacancies (IC=8), B is a trivalent cation that occupies octahedral vacancies (IC=6) and C is a tetravalent cation (if A is divalent) or trivalent (when A is trivalent) occupying tetrahedral vacancies in a compact oxide anion network. Chromium can occupy octahedral, tetrahedral or dodecahedral positions stabilising Cr^{3+},Cr^{5+},Cr^{4+} and also Cr(VI) (chromates), which can be eliminated by washing the system[1]; in the case of garnets it is possible to stabilise red or orange Cr^{4+} pigments in dodecahedral or octahedral positions for which co-doping with Ca^{2+} is required to hold the electroneutrality of the lattice.

2. EXPERIMENTAL.

The materials were prepared by the ceramic route (CE) from oxides, as well as by co-precipitation of nitrates (CO) at temperatures of 1200 and 1300ºC. The materials were studied by X-ray diffraction, scanning electron microscopy and colorimetric measurements on samples glazed at 5% in glazes for porcelain tile. Stable brown-orange colorations were obtained in a porcelain tile glaze in the case of YIG and YAG, and greens in the case of YGAG. In the case of almandine, the $FeAlO_3$ perovskite stabilises that produces brown colorations.

SAMPLE	XRD	L*a*b* 3% in porcelain tile
YIG $Ca_{0,4}Cr_{0,4}Fe_{4,2}Y_3O_4$		
CE 1200ºC	YIG(f)$FeYO_3$(m)Y_2O_3(md)	59/6/19
CO 1200ºC	YIG(mf)$FeYO_3$(d)	53/7/18
YAG* $Ca_{0,1}Cr_{0,1}Al_{4,8}Y_3O_4$		
CE 1250ºC	T(mf)$Al_2Y_4O_9$,Y_2O_3 (md)	81/9/9
CO 1250ºC	T(mf)$Al_2Y_4O_9$,Y_2O_3 (md)	73/13/13
YGAG $Ca_{0,6}Cr_{0,6}Ga_{3,8}Y_3O_{12}$		
CE 1200ºC	YGAG(mf)$GaYO_3$	62/3/11
ALMANDINE $Fe_3Al_2Si_3O_{12}$		
CE 1200ºC	Q(mf)$AlFeO_3$(f)	59/8/11
CE 1300ºC	Q(f)$AlFeO_3$(f)C(m)	64/7/10
CO 1200ºC	fuses	

(*) mineralised with 5% Na_2SiF_6, CRYSTALLINE PHASES: T(YAG tetragonal distortion, JCPDS 09-0319), Q(quartz), C(cristobalite) PEAK INTENSITY: mf(very strong) f(strong) d(weak) md(very weak)

Table 1. Results of X-ray diffraction and colorimetric measurements of the samples glazed at 3% by mass of porcelain tile.

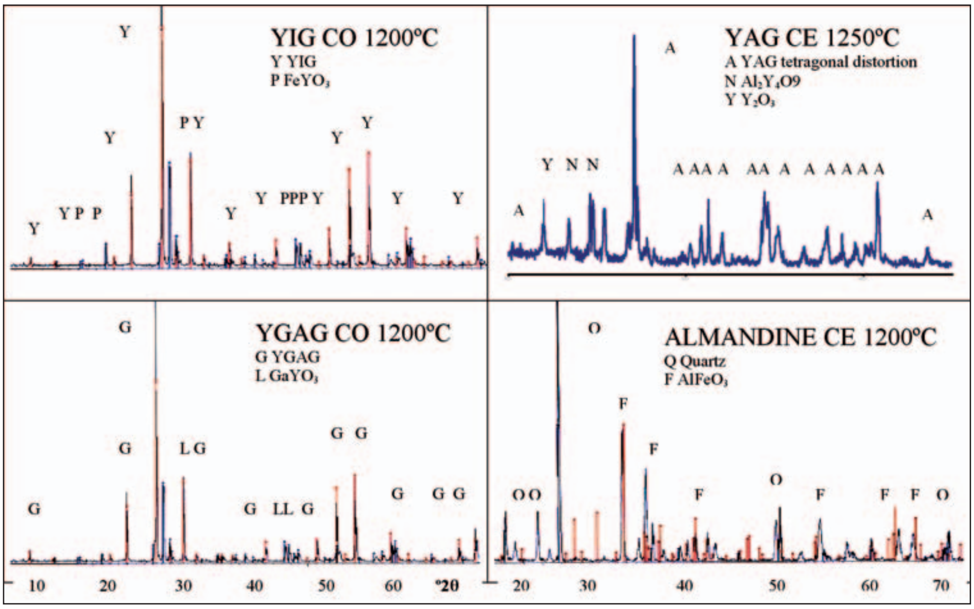

Figure 1. X-ray diffractograms of the samples indicated

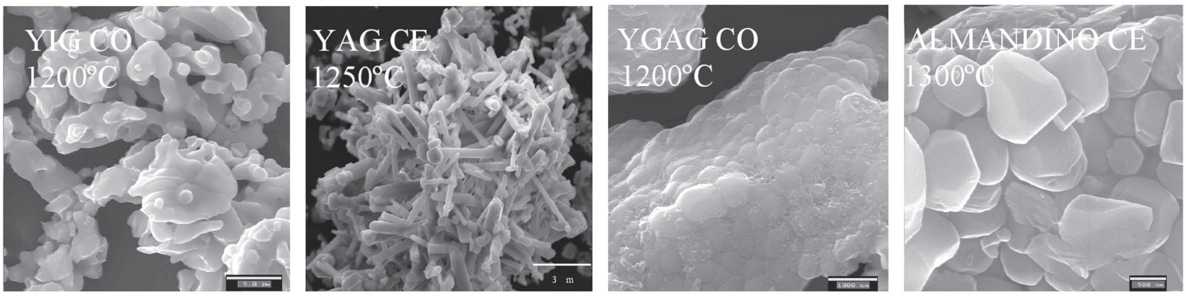

Figure 2. Microstructure of the powders by scanning electron microscopy.

The microstructure of the powders obtained, observed by scanning electron microscopy, indicates the presence of aggregates between 2 and 3 µm consisting of sintered particles in the case of YIG; less sintered and with sizes of about 25 nm in YGAG; the almandine displays coarse particulates of 400-800 nm diameter; and YAG exhibits tetragonal crystallisations 3 µm long by 1 µm wide. The UV-VIS-NIR spectroscopy studies in YAG, YIG and YGAG doped with chromium indicate a powerful band centred at 500 nm and a very wide one at 1200 nm, in addition to the charge transfer of 300 nm that is associated with Cr^{4+} in a very clean dodecahedral environment in YAG, and with the presence of bands associated with Cr^{3+} and Fe^{3+} in YGAG and YIG; in the case of the $AlFeO_3$ perovskite only Fe^{3+} is observed in an octahedral environment.

3. CONCLUSIONS

It is possible to develop stable ceramic pigments in porcelain tile by co-doping with Ca and Cr of garnet structures such as YIG and fundamentally YAG by dodecahedral stabilisation of Cr^{4+} ions; in the case of YGAG Cr^{3+} stabilises preferentially generating greenish brown colorations. In all the cases residual phases appear of $FeYO_3$ perovskites and $GaYO_3$, as well as $Al_2Y_4O_9$ (in YAG). The stabilisation of $AlFeO_3$ perovskite prevents almandine crystallisation in the studied conditions.

4. ACKNOWLEDGEMENTS

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REFERENCES

(1) G. Monrós, “Recenti svilupi nel settore della ricerca sui pigmenti ceramici”, Ceramurgia,5-6(2002)175-181.

(2) Eilers, H., Hömmerich, U., Jacobsen,S. M., Yen, W. M., Hoffman, K. R., Jia, W., Spectroscopy and dynamics of Cr^{4+}:$Y_3Al_5O_{12}$. Physical Review B, 1994, **49** (22), 505-513.