DEVELOPMENT OF CERAMIC MATERIALS USING LASER TECHNOLOGY

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ABSTRACT

The interest in laser technology for processing ceramic materials is growing daily. Laser technology will enable achieving aesthetic improvements in the surface of the materials where it is applied, while also providing improvements in production processes, making it possible to reach high temperatures, and very rapid processing times, thus opening up a new, as yet unexplored, field in chemical knowledge, namely very 'High-Temperature Solid State Chemistry'.

Numerous articles can be found in specialised publications (both scientific and technical) in which laser technology has become pivotal, in technological development as well as in production.

A great variety of lasers are available, many of which are perfectly suited for industrial use, i.e. highly automated and respecting appropriately all the necessary safety standards, for both the workers and reliable operation, almost without any equipment maintenance.

This technology allows obtaining extremely high temperatures, combined with minimum or even zero damage or undesired transformation of the material, as well as obtaining thermodynamically metastable phases, frozen by rapid cooling. These are, among others, some of the most interesting advantages that laser technology can offer in the field of ceramic materials. To date the most widely used variants refer to laser technology in a pulsing regime (for surface ablation processes), continuous laser for surface recrystallisation treatment processes or classic cutting for fusion processes (using high-pressure gas jets).

In view of the potential this technology has to offer for the sector, COLOROBBIA ESPAÑA, S.A., has addressed ceramic pigment synthesis based on the Si-Zr-Fe system.

The study has been conducted using different types of lasers (of medium and high power), in collaboration with the Group for Laser Applications of the Instituto de Ciencia de Materiales of Aragón (CSIC-University of Zaragoza), and with the research group in Solid State Chemistry of University Jaume I of Castellón, specialised in ceramic materials synthesis processes and characterisation.

Finally, all the materials processed have been structurally and microstructurally characterised, and the degree of interest of the results obtained has been evaluated by adding these materials to a ceramic slip for application onto ceramic bodies, subsequently firing the glazed pieces and evaluating the coloration of the finished products.

1. INTRODUCTION

A laser is an electro-optical device that transforms electric power into optical power, in a resonant cavity whose main elements are the pumping mechanism and the active medium. The pumping mechanism is based on the use of laser discharge lamps that emit intense light in a wide zone of the electromagnetic spectrum, and this is focused with mirrors on the centre of the cavity, laser diodes, which emit light in a very narrow spectral range focused on the centre of the cavity, and an electric discharge between two electrodes, uniformly distributed inside the cavity. The first two pumping methods are used in solid state lasers, whereas the third is used in gas lasers. Solid state lasers have an active medium, whose excitation by pumping and subsequent de-excitation produce the laser effect, which is made up of a monocrystal or a glass, the most common being the YAG or yttrium aluminium garnet ($Y_3Al_5 0_{12}$) doped with Nd. The active medium in gas lasers is usually a gas mixture. For example, in the CO_2 laser the active medium consists of a mixture of nitrogen, CO_2 and helium. When the electric discharge takes place in the cavity, the N_2 molecules are excited, which then transfer their excess energy to the CO_2 molecules by means of collisions. These last molecules, when they relax to their fundamental state, emit laser radiation. Helium is found as a diluent in the cavity, to avoid excess CO_2 concentration and to dissipate cavity heat.

CO_2 laser emission takes place typically at 10.6 μm, in the medium IR, corresponding to low energies related to the vibrations and rotations of the atom networks in solids. In this form, this emission interacts practically with any known solid, except with those that are transparent in the IR light (ZnSe, ZnS, Si, Ge, etc.). In contrast, the fundamental emission of a YAG:Nd laser at 1.064 μm, in the near-visible IR light, is transparent to most of the colourless inorganic solids. Only those that display intense dark colours tend to absorb this type of radiation directly by electron interaction. However, the effect of light diffusion makes it possible for many, a priori non-absorbent, materials, to be affected by this radiation when their particle size and related parameters are in an appropriate configuration.

The main parameters that affect materials processing by laser include: (I) the absorption characteristics of the material, (II) laser emission wavelength, (III) focal distance and spot size, (IV) laser power (in continuous mode) or flux (density of energy per unit illuminated area, in pulsing mode), (V) sweep velocity (which affects the previous parameters in section IV).

The laser is a device that is used, nowadays, in a multitude of industrial applications. A great variety of laser machines act in practically every industrial sector, from the metal sector, where it is used mainly for cutting, welding and marking, to the textile sector (cutting, marking), including the polymer sector (cutting, welding and marking), among others. In particular, in the ceramic sector, laser marking and surface treatment systems have been developed, specifically in very concrete applications and materials[1].

The initial idea of the present work focuses on the fusion of powder material to transform this in terms of the features that lasers provide, in particular relating to the high attainable temperatures and the very rapid cooling rates, both unattainable by conventional methods.

Thus, the general objective of the present work is based on the study of the possibilities that laser technology can offer as a new tool for the processing and synthesis of useful pigmenting structures for the ceramic industry.

Within the framework of the experiments performed with different pigmenting structures, the present paper sets out the results corresponding to one of these, in particular relating to the synthesis of pigments based on the Si-Zr-Fe system. Ceramic pigments based on this system are already available in the market, and in this work it is not just attempted to reproduce the existing products by laser treatment, but also to study the advantages or limitations associated with the use of this technology.

2. EXPERIMENTAL DEVELOPMENT

2.1. PRECURSORS

The precursors used in the present project are industrial grade raw materials:

- As zirconium precursors

  Zirconium oxide
  Zirconium silicate

- As silicon precursors

  Quartz
  Zirconium silicate

- As iron precursors

  Iron oxide

Most of the raw materials were tested with different particle sizes, as well as with different degrees of purity, although as already indicated previously all were industrial grade.

2.2. TYPES OF LASERS USED

The lasers used in the present study are:

- Solid state laser : YAG: Nd (yttrium aluminium garnet, doped with neodymium): with 1.064 µm emission in the IR light
- Gas laser: CO_2: with 1.064 µm emission in the IR light

While the latter interacts with almost any known solid, the former is transparent to almost all colourless inorganic solids, and only solids that display an intense dark coloration absorb it well.

2.3. CHARACTERISATION TECHNIQUES USED

X-ray diffraction. (XRD): A Philips model PW1710 diffractometer with copper anode was used. The measurements were performed at an intensity of 30 mA and a voltage of 40 kV, in a range of 2θ from 5 to 80º. Counts collection time per step was 2.5 seconds and goniometer speed was 0.020º 2θ /s.

Scanning electron microscopy (SEM) and microanalysis (EDX): A Philips XL20 scanning electron microscope with backscattered and secondary electron detectors with an energy-dispersive microanalysis EDX model 'compact detector unit' was used.

X-ray fluorescence (XRF): Philips model PW2400 with 3 kW tube and analysis by wavelength scattering, equipped with software for quantitative and semi-quantitative analysis.

Colorimeter: The instrument used has been a Minolta Cr-200 colorimeter with a measurement area of 8 mm in diameter with diffuse illumination by a Xenon lamp and 0º angle of vision (specular component included).

Transmission electron microscopy (TEM): A JEOL 3000F (300 kV of field emission) equipped with an EDX detector was used.

3. RESULTS AND DISCUSSION

3.1. Si-Zr-Fe SYSTEM

The starting point for the experimental part of this work was the laser synthesis of an industrial product widely used in the ceramic sector, the iron-zircon pink pigment[2-7]. It was considered this might be an appropriate compound for the study because of its chromatic tone (close to red, a highly desirable colour in the ceramic sector), and because of its extensive use in production processes. It was used, thus, as a reference for the adjustment of the laser parameters for the synthesis.

The preparation method of this composition for laser treatment was performed by wet milling in a ball mill, followed by drying of the final mixture. A test sweep was thus conducted, varying the laser parameters, without modifying the raw materials mixture, in order to obtain samples in which a product was synthesised that could be 'considered' a ceramic pigment (laser conditions were discarded which yielded a product that could not be milled, that did not have a reddish coloration in the unfired state, etc.).

From these first experiments, data of interest were obtained with respect to the operation of the laser equipment, enabling some reference parameters to be established (lenses, focal distances, powers or sweeping velocities). In addition, it was possible to verify, using a calcination process after the laser treatment at an approximate mean temperature of 900ºC, that the tonality of the resulting samples turns reddish, with the disappearance of the blackish colour that was obtained after laser treatment.

After this, more extensive testing was done on this starting composition, making small changes in its iron content and particle size. In addition, a study was made of whether or not the calcination mentioned previously was needed after the laser treatment.

The compositions and the qualitative results of these tests are detailed in the following table.

SAMPLE	% Fe_2O_3	PARTICLE SIZE Fe_2O_3	POST-CALCINATION 900º C – 2h	SAMPLE COLOUR
2.1A	15	Fine	No	Black
2.1B	15	Fine	Yes	Red
2.2A	15	Coarse	No	Black
2.2B	15	Coarse	Yes	Red
2.3A	30	Coarse	No	Black
2.3B	30	Coarse	Yes	Red

Table 1

With these samples the effects of three variables on the end products were studied. First, between all the A and B samples the changes produced by the calcination process after the laser treatment were observed. Between samples 2.1 and 2.2 the effect can be appreciated of varying the particle size of the iron oxide used as a raw material in obtaining the product. And, finally, the changes are evidenced between samples 2.2 and 2.3, produced by increasing the amount of Fe_2O_3 in the starting mixture.

The samples were added to transparent and opaque glazes for porous single firing. These glazes were applied onto different bodies, which were fired in an industrial roller kiln. The resulting pieces did not have a reddish colour (although the powder samples initially did).

This lack of coloration in the finished pieces can be explained by observing the X-ray diffractograms of the samples:

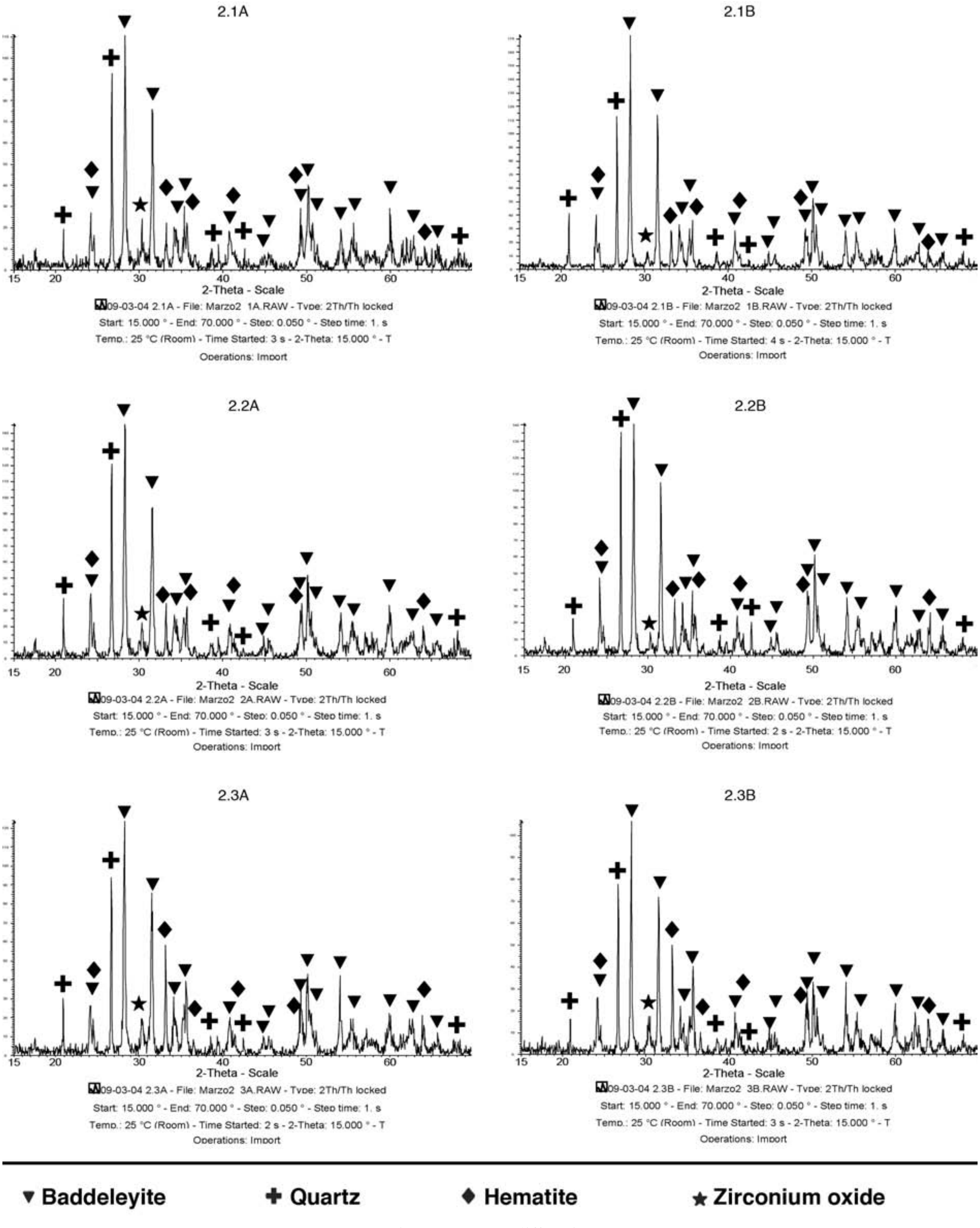

Figure 1. X-ray diffraction

The diffractograms show that no significant changes or differences are to be observed in the products obtained after carrying out the changes mentioned previously:

1 Although the tone of the samples turns red, the post-calcination process causes no change in the crystallinity or in the crystalline composition of the product.

2 No significant changes are observed in the diffractions when iron oxide particle size is varied.

3 No changes are detected either, when the percentage of iron oxide is increased.

As may be observed, the presence of the zircon crystalline phase ($ZrSiO_4$) is not detected in any of the samples. This indicates clearly that, with the laser treatment, the zircon crystalline structure fails to form; this crystalline structure is needed for the formation of the sought-after pigment, since it is the structure in which the iron oxide is encapsulated. In addition, some relatively low intensities can be appreciated, indicating the appearance of glassy phase in the product. These factors could explain the reason for the disappearance of the colour tone in the fired glazed pieces.

The results obtained indicate that zirconium silicate could not form under the tested conditions. This fact prevents the encapsulation of iron oxide in this structure, and also explains why the calcination process causes the material to turn red, since an oxidation process of non-encapsulated and, therefore, free iron oxide is involved. At the same time, the different tested variables (composition, raw materials particle size, process variables) have not enabled obtaining the desired zircon structure and, hence, it has not been possible to evaluate their influence on the obtained product.

3.2. Zr-Fe SYSTEM

The foregoing results led us to search for ways of obtaining the red pigment based on the system ZrO_2-SiO_2-Fe_2O_3 (i.e. using the Fe as a chromophore).

In this case, after a series of preliminary trials, it was decided to study the products obtained by laser processing from zirconium oxide and iron oxide, eliminating silicon oxide from the structure. The objective was to achieve the inclusion of Fe in small zirconia crystals, thus seeking a structurally simpler compound, but one which could yield improvements in the chromatic result and product crystallinity. This was a new system, since it had not been used till then as a ceramic pigment in the industry, nor had it been fabricated with the standard methods for pigment production.

The systematic tests performed on this structure involved adding variable amounts of iron oxide to the zirconia, as set out in the following table.

SAMPLE	Fe_2O_3 CONTENT (% BY WEIGHT)
3.1	2.5
3.2	5.0
3.3	10.0
3.4	15.0
3.5	20.0

Table 2

The treatment followed for all the samples was same as that applied in the previous experiments on the system Fe-Zr-Si. The precursor oxides were mixed in a ball mill and then deposited in crucibles, which were irradiated by laser. After cooling in air, these materials were set in an electric kiln at 900 ºC for 2 hours.

The results obtained in these tests, in regard to the chromatic characteristics of the unfired state, were very positive; in every case coloured solid material were obtained, whose tones varied from pink to deep red. These products were then milled and applied in standard ceramic glazes.

Table 3 details the colorimetric values obtained with these samples when they had been added to an opaque glaze.

SAMPLE	Fe_2O_3 CONTENT (% BY EIGHT)	L	a	b
3.1	2.5	81.2	4.6	13.7
3.2	5.0	76.9	7.6	14.2
3.3	10.0	72.6	10.0	13.1
3.4	15.0	69.0	11.1	13.1
3.5	20.0	68.0	10.5	13.0

Table 3

It was also attempted to obtain the same product by the traditional ceramic method (kiln at high temperature and long soak time). The results obtained by this method evidenced the difficulty of obtaining a product similar to that produced by laser treatment, with infrared radiation.

In addition, a test involving calcination similar to the heat treatment applied to the samples obtained by the laser route (900 ºC, 2 hours) was run on the starting raw materials. The results, as in the case of the traditional ceramic method, did not enable achieving the results obtained by laser treatment.

The microstructural characterisation of these products is set out below, showing the results obtained by X-ray diffraction, X-ray fluorescence spectrometry and scanning electron microscopy, as well as the chromatic coordinates displayed by these materials, when they were added to a glaze, applied onto a body and fired in roller kiln.

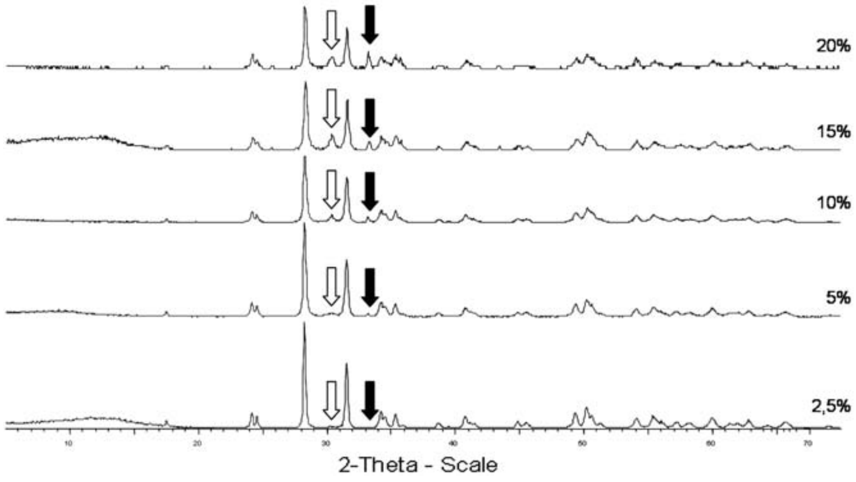

Figure 2. Diffractograms of samples 3.1 to 3.5.

This figure shows that practically all the peaks detected by XRD belong to baddeleyite (monoclinic ZrO_2). However, the diffractograms also display the main peak corresponding to hematite (Fe_2O_3), marked by a black arrow, and another one pertaining to another allotropic form of zirconium oxide (white arrow).

It is obvious that with the increase in the quantity of iron oxide in the mixture, the peak corresponding to hematite increases (corroborated by XRF chemical analysis).

To be noted is that the intensity of the peak corresponding to non-monoclinic zirconium oxide also increases with the quantity of iron.

The morphology of the particles obtained was analysed by SEM, with the aid of backscattered electron detectors, to verify whether the iron was largely located in grain defects, at the boundaries, or was not detectable by this technique, which would suggest the inclusion of iron within the zirconia structure.

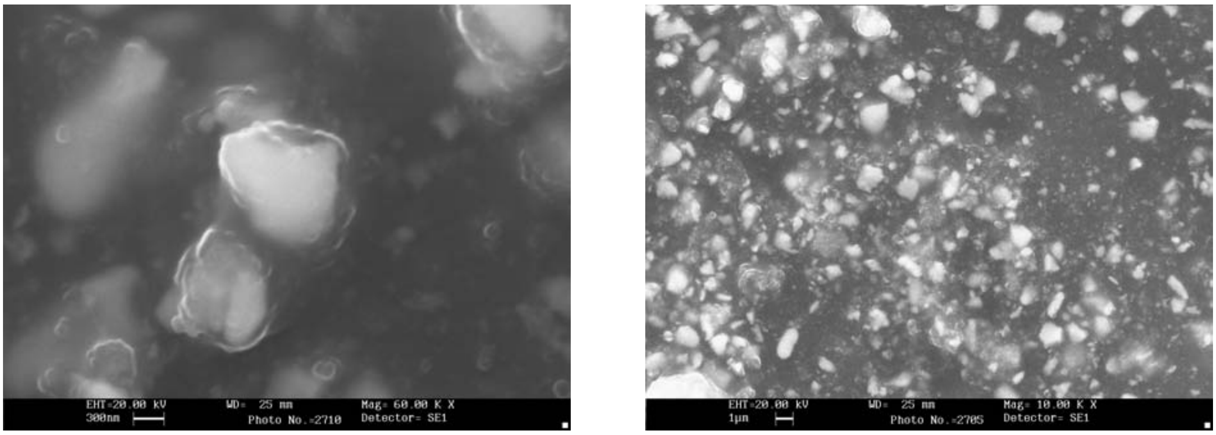

Figure 3. SEM of sample 3.3 (10% Fe) at a magnification of 60,000x and at 10,000x

The particles of the product mainly appear disaggregated, with sizes near micron size. However, they are not spherical particles, which is why it is possible to assume, with relative certainty, that they did not fuse completely during thermal processing by laser.

The SEM with backscattered electron detector, which can show compositional differences between different regions of a sample, did not contribute any further information: the whole sample appeared similar as far as its composition was concerned, without containing groupings or large concentrations of isolated Fe.

Thus, laser technology has enabled obtaining reddish-coloured products, with characteristics to date unattainable by the conventional routes, which can be used as ceramic pigments.

One of the questions yet to be answered was where and how the iron oxide was found in this Zr-Fe system, to allow it to act as a chromophore, and which could not be obtained in the Si-Zr-Fe system.

To answer this question, samples 3.3 and 3.5 were studied by high-resolution electron transmission microscopy (HRETM), which yielded the micrographs shown in Figure 4.

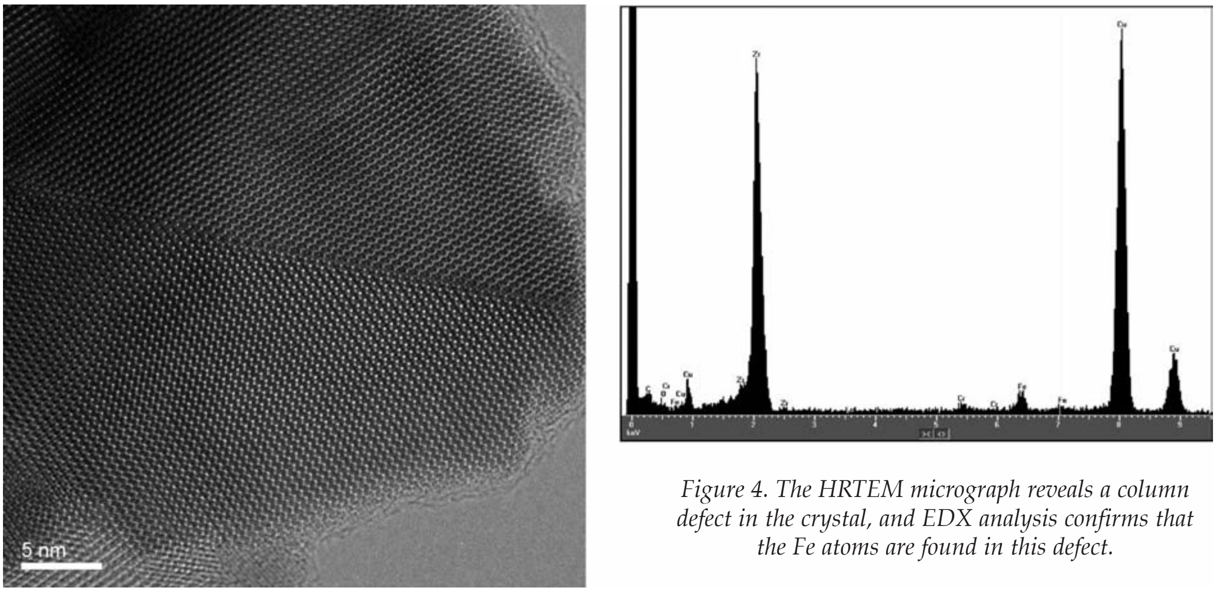

Figure 4. The HRTEM micrograph reveals a column defect in the crystal, and EDX analysis confirms that the Fe atoms are found in this defect.

This technique demonstrates, therefore, that there are iron atoms that enter the crystal defects of the zirconium oxide, incorporating themselves in its structure, which is why visible accumulations cannot be found in the SEM with backscattered electron detectors.

This fact can be compared with the stabilisation produced by the inclusion of yttrium oxide (III) in the zirconia structure, widely studied in the literature[8-12]. This suggests that the Fe atoms might cause and/or be located in the defects of the zirconia crystals.

This would enable explaining two matters: in the first place, the appearance of an allotropic phase of zirconia (cubic, orthorhombic or tetragonal, which is still under study) with the increase in the concentration of iron oxide; secondly, it could explain the chromatic properties of the product and their stability in the tested glassy matrices.

The formation of a mordant pigment could be adopted as a reasonable hypothesis; that is, one in which the chromophore (Fe_2O_3) 'bathes' the surface of the matrix crystalline phase grains (ZrO_2) with a nanometric layer, in a similar to way to what occurs in the vanadium zircon pigment, in which V is located at the surface of the zircon grains.

The question that remains to be solved is why we have been unable to obtain any product in the tests with the Si-Fe-Zr system. An explanation might lie in the fusion process of the materials. The fusion of iron oxide (at a relatively lower temperature than that of the other two precursors) might cause this to solubilise part of the quartz (SiO_2), forming a glass of iron and silica.

Thus, this process would compete with both zircon formation ($ZrSiO_4$) and the inclusion of the iron in zirconia (ZrO_2). Subsequently, in the cooling process, the melt could devitrify a part of the oxide precursors, appearing in the X-ray diffractograms as crystalline species, but with a relatively poor crystallinity in the sample.

Finally, to conclude this study, Figure 5 shows a (colour) image by optical microscopy of sample 3.3. It shows the tonal quality of the crystals obtained.

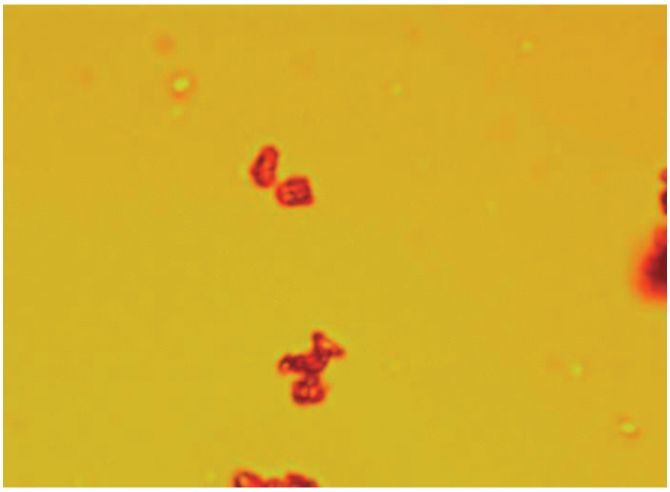

Figure 5. Image obtained by optical microscopy (1000x) of the sample with 10% Fe

4. CONCLUSIONS

A product has been obtained from ZrO_2 and Fe_2O_3 (without mineralisers or fluxing agents) by means of laser technology, which has to date not been obtained by traditional methods, and which can be used as a ceramic pigment.

However, the study also shows the need to improve the preparation processes of the raw materials and precursors, as well as the extension of the residence time in order to obtain a greater yield and better degree of reaction, with a view to obtaining more homogeneous samples.

Some "current" limitations of laser technology for the continuous production of ceramic pigments are evident. However, in spite of this, as this technology evolves substantial improvements may be expected in ceramic materials processing.

For the foregoing reasons, the economic conclusions will need to wait until continuous powder synthesis by the laser treatment technique has developed sufficiently to enable evaluating the costs of the process.

5. ACKNOWLEDGEMENTS

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