# Different Kinds of Solid Solutions in the $V_2O_5$–$ZrSiO_4$–NaF System by Sol–Gel Processes and their Characterization

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## Abstract

*In the $V_2O_5$–$ZrSiO_4$–NaF system, three kinds of substances have been identified by sol–gel methods depending on the $V_2O_5$ amounts in the composition. Their characterization by X-ray diffraction, measurements of unit cell parameters, UV–visible (UV–V) spectroscopy, differential thermal analysis and lab colour parameter determination allow the consideration of three kinds of solid solution in the zircon lattice: (a) $V^{+5},V^{+4}$–$ZrSiO_4$, thermally stable and with a deep green colour; (b) $V^{+4}$–$ZrSiO_4$, thermally stable and blue coloured, made by the sol–gel method and with $V_2O_5$ amounts lower than 0·03 mol per formula weight; and (c) $Na^+,F^-,V^{+4}$–$ZrSiO_4$, a solid solution with a deep blue–turquoise colour, made by addition of NaF to the $V_2O_5$–$ZrO_2$–$SiO_2$ system. Similarly, the green substance is obtained from the bluish substance synthesized at low temperatures (800°C) by both introduction of the $V^{+5}$ ion into the zircon lattice and migration of the $V^{+4}$ ions to the dodecahedral from the tetrahedral sites when the temperature increases.*

*Im System $V_2O_5$–$ZrSiO_4$–NaF wurden drei verschiedene, mittels Sol–Gel–Verfahren hergestellte Substanzen identifiziert. Die Art der gefundenen Substanzen hängt vom Gehalt an $V_2O_5$ in der Zusammensetzung ab. Die Substanzen wurden mit Hilfe von Röntgenbeugung, Messung der Parameter der Einheitszelle, UV–V-Spektroskopie, Differential-Thermoanalyse und Lab-colour-Parameter Bestim-*
*mung charakterisiert. Es handelt sich um drei Arten von Mischkristallen des Zirkoniums: (a) $V^{+5},V^{+4}$–$ZrSiO_4$, thermisch stabil, tief grün gefärbt; (b) mittels Sol–Gel-Verfahren hergestelltes $V^{+4}$–$ZrSiO_4$, thermisch stabil und blau gefärbt, mit einem $V_2O_5$-Gehalt von weniger als 0·03 Mol pro Formeleinheit; (c) $Na^+,F^-,V^{+4}$–$ZrSiO_4$-Mischkristall mit einer tief türkisen Farbe, durch die Zugabe von NaF zum $V_2O_5$–$ZrO_2$–$SiO_2$-System hergestellt. Auf ähnliche Weise konnte die grüne Substanz aus der bläulichen Substanz hergestellt werden, die bei niedrigen Temperaturen (800°C) sowohl durch das Einlagern des $V^{+5}$-Ions in das Zirkoniumgitter als auch durch die Wanderung des $V^{+4}$-Ions von den tetrahedrischen zu den dodecahedralen Gitterplätzen, bei erhöhten Temperaturen, synthetisiert werden.*

*Dans le système $V_2O_5$–$ZrSiO_4$–NaF, trois sortes de substances ont été identifiées par des méthodes sol–gel suivant les quantités de $V_2O_5$ présentes dans la composition. Leur caractérisation par diffraction de rayon X, mesure des paramètres de maille, spectroscopie UV–V, analyse thermique différentielle et par détermination des paramètres de couleur, permet de distinguer trois sortes de solutions solides dans le réseau de zircone: (a) $V^{+5},V^{+4}$–$ZrSiO_4$, stable thermiquement et avec une forte couleur verte; (b) $V^{+4}$–$ZrSiO_4$, stable thermiquement et avec une couleur bleue obtenue par méthode sol–gel et avec des quantités de $V_2O_5$ inférieures à 0·03 mole par poids de formule; et (c) $Na^+,F^-,V^{+4}$–$ZrSiO_4$, solution solide avec une forte couleur bleue–turquoise obtenue par*

*addition de NaF au système $V_2O_5$–$ZrO_2$–$SiO_2$. De manière similaire, la substance verte est obtenue de la substance bleutée synthétisée à basse température (800°C) par à la fois introduction d'ions $V^{+5}$ dans le réseau de zircone et par migration des ions $V^{+4}$ des sites tétraèdriques aux sites dodécaèdriques quand la température augmente.*

## 1 Introduction

It is well known that the zircon network has capacity to accept replacement of its cations by foreign cations in a substitutional solid solution.[1] The zircon is a highly stable structure (it decomposes to yield zirconium and silicon oxides at 1667°C), whose principal structural unit is a chain of alternating edge-sharing $SiO_4$ tetrahedra and $ZrO_8$ triangular dodecahedra extending parallel to the $c$ axis. The chains are joined laterally by edge-sharing dodecahedra. Similar chains occur in the garnet structure, extending in three mutually perpendicular directions, but they are cross-linked by $YO_6$ octahedra as well as by $XO_8$ dodecahedra. In zircon, octahedral sites are present but contain no cations.[2] Therefore, the foreign cation, depending on its ionic radius, could occupy the $Si^{+4}$ (0·40 Å) position, or the $Zr^{+4}$ (0·80 Å) position or, less likely, it could be incorporated interstitially into the zircon structure.

The discovery of the zircon–vanadium blue pigment in 1948 by Seabright[3] was the most significant advance in the ceramic pigments field in recent years. Other ceramic pigments based on the zircon structure were developed: lattice pigments, where the dopant or colorant ion occupies a zircon lattice site in solid solution (as would be the case for zircon–vanadium turquoise and zircon–praseodymium yellow); encapsulated or protected pigments, where the colorant ($Fe_2O_3$ or CdSSe particles) is encapsulated as discrete particles in the zircon structure and does not form part of the oxide lattice (as would be the case for zircon–iron coral, zircon–cadmium sulphoselenide red, zircon–vanadium (or molybdenum) sulphide grey and zircon–carbon grey); and, lastly, mordant pigments, where the colloidal particle of the chromophore agent is held on the host particle by Van der Waals forces; the gold–violet in zircon is an example of this pigment type. However, the difference between mordant and encapsulated pigments is not clear.

V–$ZrSiO_4$ solid solutions have already been studied and different authors indicate that the vanadium ion could be $V^{+3}$ (0·78 Å), $V^{+4}$ (0·73 Å) or $V^{+5}$ (0·68 Å) and it could occupy octahedral or

tetrahedral sites in the zircon lattice.[4-6] In the $V_2O_5$–$SiO_2$–$ZrO_2$ system, the sample fired at 800°C and washed shows a soft blue colour that changes to green when the firing temperature is increased, and this colour can be yellowish when there is a low $V_2O_5$ amount in the composition. Different explanations of this fact have been published in the literature.

Matkovich & Corbett[4] indicate that the salts with $V^{+4}$ ions have a similar blue colour and because of this it is thought that the $V^{+4}$ ion is introduced in solid solution in the zircon (a 4% $V_2O_5$ amount according to mass loss in TG measurements); the presence of yellow free $V_2O_5$ is not eliminated by washing, which would explain the gradual development of a greenish colour in the sample. Similarly, tested measurements of the crystallographic unit cell parameters indicate higher or lower values compared to the value in the undoped zircon. Therefore, according to the octahedral environment ionic radius reported by Shannon & Prewitt[16] (in parentheses in the previous paragraph), $V^{+4}$ replaces both $Si^{+4}$ and $Zr^{+4}$ ions in the zircon lattice.

Cini[5] attributes the green colour to the presence of both $V^{+4}$ (blue) and $V^{+5}$ (yellow) ions in the solid solution; however, the preservation of the electrical neutrality in the zircon lattice could be due to the presence of $V^{+3}$ ions or to a cationic defective zircon lattice.

Demiray et al.,[6] after an optical spectrum analysis of the samples, concluded that only $V^{+4}$ ions are present and that they occupy the octahedral sites, since unit cell parameters in V-doped zircon are the same as those in undoped zircon. Similarly, an optical spectra comparison between the green sample and an artificial green pigment made by mixing a blue–turquoise pigment and a yellow zirconia pigment indicates a similar form of the spectra, therefore leading to the conclusion that the green sample is a mixture of these two pigments.

In the NaF–$V_2O_5$–$SiO_2$–$ZrO_2$ system, a deep blue–turquoise pigment is synthesized,[1] and several authors[6,7] consider that a solid solution of NaF in $ZrSiO_4$ is achieved; in effect, analysis of both $Na^+$ and $F^-$, carried out on these blue–turquoise samples, indicated either a large quantity of $F^-$ or a portion of $Na^+$, which are combined as NaF, are retained into $ZrSiO_4$. However, although this entrance must effect a change in $ZrSiO_4$ unit cell dimension, Demiray et al.[6] do not find any differences between the unit cell parameters of blue–turquoise pigment and undoped zircon.

The aim of this paper is the investigation of the process of turning green observed in the $ZrO_2$–$SiO_2$–$V_2O_5$ system and the identification of the different

solid solutions available. Similarly, the effect of NaF addition and its role is studied.

For this purpose sol-gel synthesis techniques are used. These methods, developed over 30 years ago, allow the thermodynamic equilibrium of a solid-state reaction to be reached rapidly because of the high homogeneity achieved in the mixture of the component ions in solution followed by gelation,[8] thereby achieving a mixture on a 0·5 nm scale instead of a 50 $\mu$m solid particle scale, a gain in homogeneity of $10^4$-$10^5$. Making use of the sol-gel methods and working with the adequate composition both blue and green solid solutions can be stabilized and can be compared with the blue-turquoise pigment obtained by addition of NaF.

## 2 Preparation of Xerogels

Compositions and sample preparation methods for the $V_2O_5$-$SiO_2$-$ZrO_2$ system are shown in Table 1. Two types of xerogels were prepared: colloidal gel (CG) and polymeric gel (PG). For the preparation of CG, colloidal silica (Aerosil 200, industrial quality, Degussa, Castellón, Spain), zirconium(IV) acetate (industrial quality, Aldao-Julia, Barcelona, Spain) and vanadium(IV) oxyacetylacetonate (analytical grade, Merck, Darmstadt, Germany) were used as raw materials. In the PG method, tetraethylorthosilicate (TEOS) (analytical grade, Fluka, Berlin, Germany), zirconium(IV) propoxide (analytical grade, Merck, Darmstadt, Germany) and vanadium-(IV) oxyacetylacetonate were used as raw materials.

In the colloidal gel method, the sample was prepared following the method described in Ref. 9. Colloidal silica was dispersed in water (100 ml per 10 g end-product) by vigorous stirring. The vanadium(IV) oxyacetylacetonate was added into this suspension and stirred vigorously at 70°C. Then the zirconium(IV) acetate previously dissolved in 100 ml water was added to it. After that a solution of ammonium hydroxide was added dropwise until gelation (pH = 5-6) occurred. Finally, the gel obtained was dried by an infrared lamp.

**Table 1.** Sample composition (mol%) and preparation techniques

| Sample | $V_2O_5$ | $SiO_2$ | $ZrO_2$ | NaF | Methods |
|--------|----------|---------|---------|-----|---------|
| A | 0·02 | 1·00 | 0·96 | — | CE, CG, PG |
| B | 0·05 | 1·00 | 0·90 | — | CE, CG, PG |
| C | 0·10 | 1·00 | 0·80 | — | CE, CG, PG |
| D | 0·05 | 1·00 | 0·90 | 0·20 | CE, CG, PG |

CE: Ceramic method; CG: colloidal gel method; PG: polymeric gel method.

In the PG method, absolute ethanol was used. Ethanol was refluxed with continuous stirring at 70°C and the necessary TEOS and 3M $HNO_3$, containing both acid catalyst and water (per 7 g end-product), were added, keeping the molar ratios at TEOS:ethanol = 1:13, TEOS:$H^+$ = 1:0·05 and TEOS:$H_2O$ = 1:0·8. The process conditions were maintained for 2 h (TEOS prehydrolysis time), then zirconium(IV) propoxide was added and the sample was maintained under the same conditions for 24 h. The gelation and drying were performed at room temperature in the open air.

In the CG process, a homogeneous yellow opaque gel was obtained, and in the PG method a very homogeneous, bulky, coffee-coloured translucent xerogel was synthesized. In the CG method, gelled sol particles of silica, hydrated $ZrO_2$ and precipitated vanadium oxide were homogenized to a sol particle scale (1 nm to 1 $\mu$m). In the same way, the hydrolysis and condensation of alkoxides in the PG method can produce a homogeneity degree in the components in the dry gel between 1 and 1000 Å. Thereby, in order to achieve an ultrahomogeneous gel, a TEOS prehydrolysis time was used according to the hydrolysis kinetics of both TEOS and zirconium(IV) propoxide.

These results were compared to a sample obtained by a ceramic method (CE). In this case vanadium(IV) oxyacetylacetonate, zirconium(IV) oxide (baddeleyite) and silicon dioxide (quartz), the last two of industrial quality, were mixed and homogenized in acetone in a ball mill.

The raw materials were selected after a study of several precursors in the $V_2O_5$-$SiO_2$-$ZrO_2$ system.[10]

## 3 Firing and Characterization of the Samples

The xerogels and ceramic samples were calcinated in an electric kiln at a temperature between 500 and 1200°C with a soaking time of 12 h. Chemical and structural evolution of the dried gels after the thermal treatments were followed by several techniques.

X-Ray diffraction (XRD) analyses were obtained with a Philips X-ray diffractometer using nickel-filtered and Cu$K_\alpha$ radiation. Zircon unit cell parameters were measured using LSQC (least-squares-calculation) and POWCAL (powder-calculation) programs from the Department of Chemistry, University of Aberdeen (United Kingdom). The former refined $d$ values of tested polycrystals with an internal standard mixed with sample; the latter calculates the crystallographic unit cell parameters

of the sample by comparing their refined $d$ values with the standard values.[11] For that $\alpha$-$Al_2O_3$ was used to refine $d$ values as internal standard in an X-ray diffractogram run between 20 and 80 (°$2\theta$) at low goniometer speed and measuring the values in the middle of the X-ray peaks.

UV–visible (UV–V) spectroscopy (diffuse reflectance) at the range between 200 and 2000 nm allowed information to be obtained about the oxidation state and coordination environment of the chromophore in the fired samples. Lab colour parameter measurements, following the CIELAB colorimetric method recommended by the CIE (Comission International de l'Eclairage),[15] were carried out with a colorimeter using a standard lighting $C$. On this method, $L$ is the lightness axis (black (0) → white (100)), $b$ is the blue (−) → yellow (+) axis and $a$ is the green (−) → red (+) axis. Similarly, on an $x$–$y$ CIE cromatic diagram, the dominant reflected wavenumber ($\lambda$) was measured. Differential thermal analyses were carried out with a Perkin–Elmer spectrophotometer in air, using a platinum crucible and a heating rate of 20°C/min. Finely powdered alumina was used as the reference substance.

## 4 Results and Discussion

### 4.1 X-Ray diffraction
Table 2 shows the most important results obtained by XRD analysis together with the sample colour measurements.

According to Refs 9 and 10 it is observed that:

(1) Gel samples crystallize in the tetragonal zirconia and cristobalite system at low temperatures, developing a hard yellow composite.

(2) In gel samples, when the monoclinic zirconia crystallizes, zircon that crystallizes at a narrow range of firing temperatures rapidly appears. This range is narrower when the vanadium amount increases.

(3) The ceramic samples and gel samples (with vanadium amounts higher than 0·02 mol $V_2O_5$ per formula weight) show a blue colour (that appears after washing the samples with 0·3m $HNO_3$) at low temperatures (800°C), and the sample colour changes to a deep green colour (that is yellowish in ceramic samples), when the firing temperature increases.

(4) Gel samples containing 0·02 mol $V_2O_5$ per formula weight stabilize a blue colour at high temperatures.

(5) The NaF stabilizes a blue–turquoise colour stable during the thermal treatments.

The considerations mentioned lead to the taking into account of three different kinds of substances in the systems studied:

(a) A deep green-coloured substance obtained by gel methods, with $V_2O_5$ amounts higher than 0·02 mol per formula weight, after being washed with 0·3m $HNO_3$. The only crystalline phases detected in this substance are zircon and a small amount of cristobalite (substance I).

(b) A soft blue-coloured substance synthesized by gel methods and containing a $V_2O_5$ amount of 0·02 mol per formula weight. XRD analysis shows zircon as the only crystalline phase present (substance II).

(c) A deep blue–turquoise substance obtained by NaF addition to the samples. This substance, depending on the method, presents zircon, monoclinic zirconia and cristobalite as crystalline phases (substance III).

### 4.2 Lab colour parameter measures and UV–V spectroscopy
The Lab colour parameter measurements for the previously mentioned substances and their homologous ceramic samples are shown in Table 3. With the aim of obtaining the best comparison, measurements were carried out on an enamelled surface with a commercial $PbO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ frit in a weight ratio of frit:colourant = 100:3.

An increase from red and blue amount values is observed in the sequence substance I < II < III. Likewise, the dominant reflected wavenumber ($\lambda$) decreases in the same sequence. Similarly, the comparison of gel samples with their homologous ceramic samples, fired at the same temperature (1000°C/12 h), indicate yellow $b$ values, and high lightness ($L$) and $\lambda$ values for ceramic samples. This fact shows the different colour levels achieved when gel methods are used.

The optical spectrum of the $V_2O_5$–$SiO_2$–$ZrO_2$ system has been analysed by several authors and an interesting discussion about the assignment of the absorption bands is described in the literature. Demiray et al.,[6] considering tetrahedral and octahedral environments for the $V^{+4}$ with $D_{2d}$ symmetry, have calculated the distribution of energy levels. Comparison between experimental and theoretical values leads the authors to conclude that the $V^{+4}$ ion only occupies the dodecahedral sites in the lattice, replacing the $Zr^{+4}$ ion. Di Gregorio & Greenblatt,[12]

**Table 2.** X-Ray phases detected and colours of the samples

| Temperature (°C) | Sample A | | | Sample B | | |
|---|---|---|---|---|---|---|
| | CE | CG | PG | CE | CG | PG |
| 700 | | T(vs) ye | | ZV(vw), Q, M(s) grey-ye | Z, T, M(m) gr-ye | Amorphous, ye |
| 800 | Z(m), Q, M(s) gr | T(s), M(m) ye | | Z(s), Q, M(m) bl | Z(vs), M(vw) gr-br | Z(vs), C(vw) gr |
| 900 | Z(m), Q, M(m) bl | Z(vs), M(w), C(vw) grey-bl | | Z(s), Q, M(m) gr-bl | Z(vs), M, C(vw) gr-br | Z(vs), C(vw) gr |
| 1000 | Z(s), Q, M(w) gr | Z(vs), M, C(vw) grey-bl | { 24 h: Z(vs) bl / 12 h: Z, T(s), M(w) bl | Z(vs), M(w) gr-br | Z(vs), C(vw) gr-br | gr-br |
| 1100 | Z(s), M(w) gr | Z(vs), M, C(vw) grey-bl | | gr-ye | Z(vs), C(w) gr-br | |
| 1200 | | Z(vs) bl | | | Z(vs), C(w) gr-br | |

| Temperature (°C) | Sample C | | Sample D | | |
|---|---|---|---|---|---|
| | CE | CG | CE | CG | PG |
| 700 | | ZV, Z(w), M(vs) ye | Q, M(s) w | T(s), M, C(m) ye | T(s), M, C(m) ye |
| 800 | Z(vs), M(w) br | Z(vs), C, V(w) gr | Z, M, Q(m) w-bl | Z(vs), T, M, C(vw) tu | T(s), Z, M, C(m) ye-gr |
| 900 | Z(vs), M(w) br | Z(vs), C, V(w) gr-br | Z(s), M(m), Q(w) tu | Z(vs), T, M(vw) tu | Z(vs), T, M, C(w) tu |
| 1000 | Z(vs), M(w) br | Z(vs), C(m) gr-br | Z(vs), M(w) tu | tu | tu |
| 1100 | br | Z(vs), C(m) gr-br | | | |
| 1200 | | Z(vs), C(m) gr-br | | | |

Sample colours: ye (yellow), bl (blue), grey (grey), gr (green), oc (ochre), br (brown), w (white), tu (blue–turquoise).

Crystalline phases: Z (zircon), ZV (zirconium(IV) pyrovanadate), M (monoclinic zirconia), T (tetragonal zirconia), Q (quartz), V (vanadium(V) pentoxide), C (cristobalite).

Peak intensity: vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

by means of monocrystal measurements, calculation of the energy level diagram by the punctual charge model and ESR data, conclude that the $V^{+4}$ ion would preferentially occupy the tetrahedral environments, replacing the $Si^{+4}$ ion. Lastly, Hong Xiayou et al.,[13] using the experimental results of Demiray et al.[6] and Di Gregorio & Greenblatt[12] and calculating, by another model, the energy levels indicated in Fig. 1, have concluded that $V^{+4}$ replaces both $Si^{+4}$ and $Zr^{+4}$ in the zircon lattice.

The assignment of bands made by Hong Xiayou et al. is shown in Table 4. The UV–V spectra of several samples are presented in Fig. 2, where all the bands assigned by Hong Xiayou et al. are observed. Figure 3 shows the UV–V spectra thermal evolution of the B(CG) sample that is observed to become green when firing temperature increases. Almost all bands are maintained with thermal treatment, except the band that appears at $1400\,cm^{-1}$, the only

band assigned solely to the tetrahedral environment. It is shown, therefore, that the $V^{+4}$ ion occupies initially both tetrahedral and dodecahedral environments, but when the temperature increases the $V^{+4}$ ion occupies preferentially the dodecahedral sites.

A comparison between the UV–V spectra of substances I, II and III in an expanded range between 190 and 800 nm is made in Fig. 4. It is observed that in the green sample (substance I) a broad band appears at 400 nm; this band can be assigned to a charge transfer band of the $V^{+5}$ ion. Therefore, according to Cini,[5] $V^{+5}$ is present in the green sample.

At this point it is important to take into account a secondary result in the sample colours. Sample A(CG) in Table 2 presents a grey–blue colour which can be associated with carbon from organics entrapped in the fired gel matrix. This phenomenon is known in the sol–gel process and in the literature[14]

**Table 3.** Lab colour parameter measurements

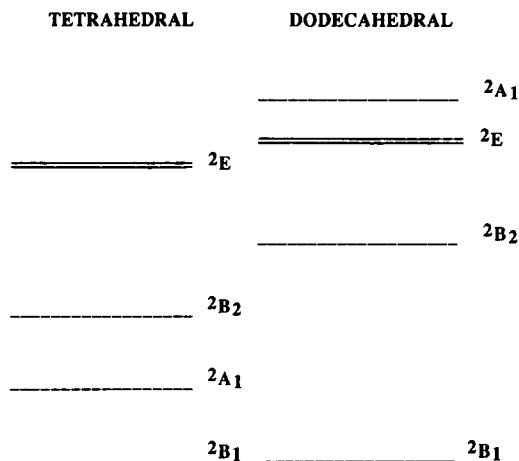| | Sample (preparation method) | | | | |
|---|---|---|---|---|---|
| | B(CG) | A(CG) | D(CE) | B(CE) | A(CE) |
| Substance | I | II | III | — | — |
| Firing temperature (°C) | 1000 | 1000 | 800 | 1000 | 1000 |
| L | 55·53 | 74·93 | 65·38 | 70·04 | 79·93 |
| a | −10·70 | −12·65 | −12·78 | −2·99 | −4·73 |
| b | 4·48 | −5·19 | −16·73 | 14·09 | 11·60 |
| λ (nm) | 520 | 500 | 480 | 570 | 560 |

TETRAHEDRAL          DODECAHEDRAL



Fig. 1. Energy levels distribution for tetrahedral and dodeca-hedral environments.[13]
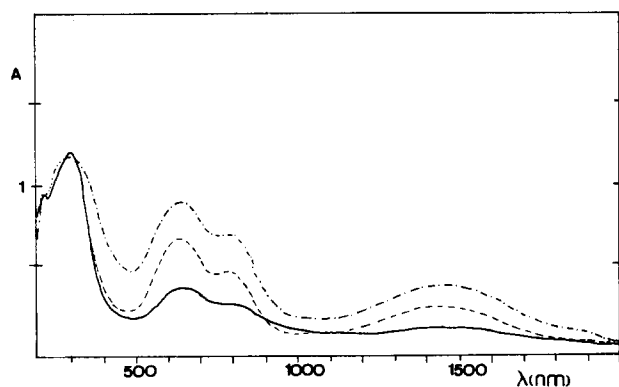


Fig. 2. UV–V spectra (180–2000 nm) of samples B(CE) (———), D(CE) (– – –) and B(CG) (–·–·) fired at 800°C.



Fig. 3. UV–V spectra evolution with temperature in sample B(CG): ———, 900°C; – – –, 1000°C; –·–·, 1100°C.



Fig. 4. UV–V spectra comparison for substances I (–·–·), II (– – –) and III (———) (B(CG)/1000°C, A(CG)/1200°C and D(CE)/800°C, respectively). $V_2O_5$ raw material spectrum (·····) is also shown.

is sometimes associated with the stabilization of tetragonal zirconia above 650°C. In this case carbon is entrapped but its effect does not seem important (method and vanadium amount used in the sample are more decisive in this case, see Table 2).

## 4.3 Measurements of zircon unit cell parameters and DTA results

The zircon unit cell parameter variation in the three green samples with the temperature is shown in Table 5, and the cell volume evolution with the
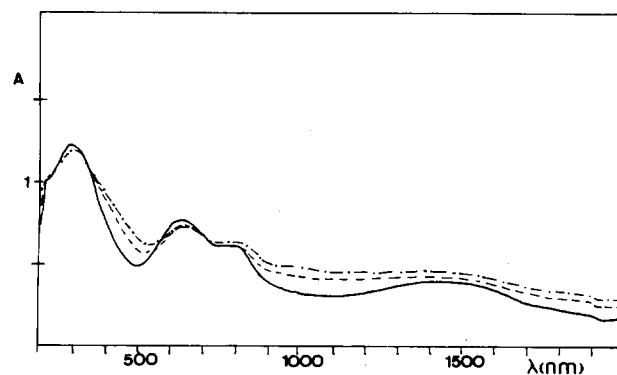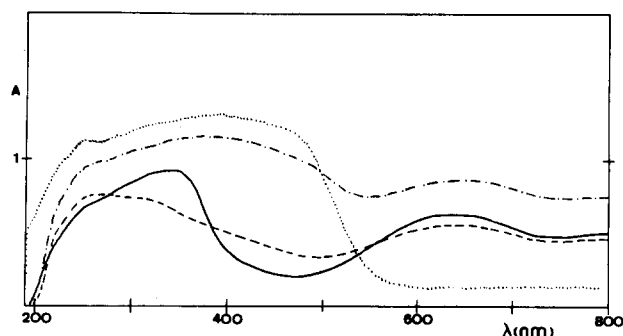
temperature is represented in Fig. 5. It is observed that both $a$ and $c$ parameters continuously decrease when the firing temperature increases, and therefore the unit cell volume also decreases (Fig. 4). This fact is in good agreement with the UV–V results: in the green substance, when $V^{+4}$ moves from the tetrahedral site, replacing $Si^{+4}$, to the dodecahedral site, replacing $Zr^{+4}$, the unit cell volume decreases. In the same way, the introduction of $V^{+5}$ into the dodecahedral site must produce another reduction in unit cell volume.

The DTA curves for D(PG) and B(PG) samples are shown in Fig. 6. At the temperature range between 50 and 250°C a strong broad endothermic

Table 4. UV–V band assignation from Hong Xiayou et al.[13] model

| λ (nm) | v (cm⁻¹) | Assignation |
|---|---|---|
| 190–212 | 52·631–47·170 | Forbidden transition |
| 290–297 | 34·483–33·670 | $^2B_1 \rightarrow {}^2A_1$ (dodecahedral) |
| 640–644 | 15·625–15·528 | $^2B_1 \rightarrow {}^2E$ (dodecahedral and tetrahedral) |
| 922–927 | 10·846–10·787 | $^2B_1 \rightarrow {}^2B_2$ (dodecahedral and tetrahedral) |
| 1 381–1 405 | 7·241–7·117 | $^2B_1 \rightarrow {}^2A_1$ (tetrahedral) |
| 750–770 | 13·333–12·987 | Shoulder (forbidden transition) |
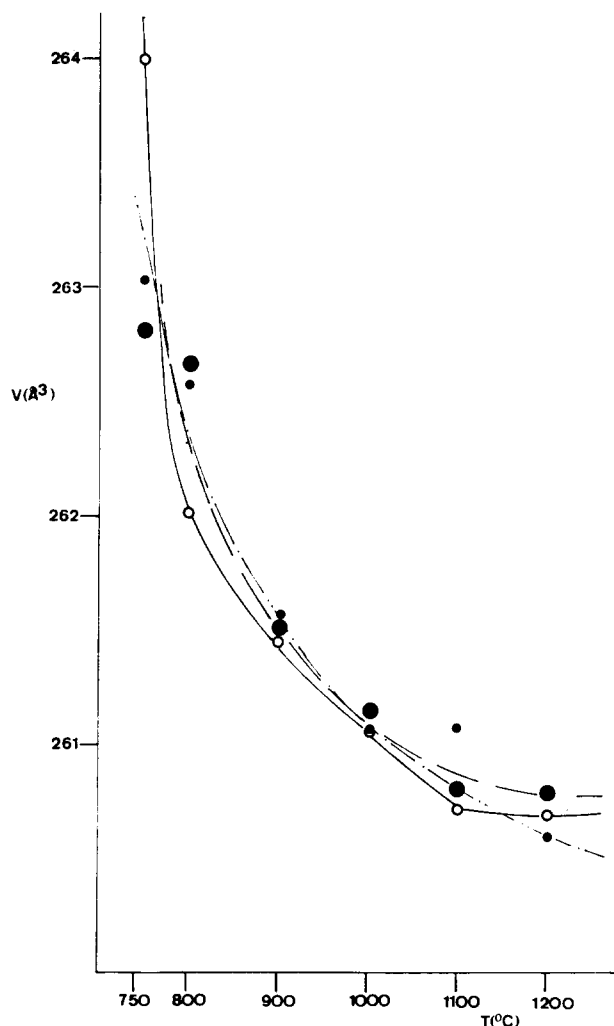
**Fig. 5.** Zircon cell volume evolution with firing temperature for sample 1 (○), 2 (●) and 3 (●) as in Table 5.



**Fig. 6.** DTA curves of samples in air and scan rate of 20°C/min: (a) B(PG); (b) D(PG); (c) raw NaF.

peak appears, due to the evaporation of residual water and ethanol entrapped in micropores of the gel. Both samples show an exothermic peak in the temperature range between 350 and 550°C, which can be associated with the oxidation of organic compounds introduced in the precursors. In sample D(PG), only a peak at 700°C can be assigned to tetragonal zirconia and zircon crystallization, observed by XRD in the samples after DTA treatment; however, in B(PG) samples, a strong peak at 700°C can be associated with the tetragonal zirconia (dominant crystalline phase detected by XRD in this sample), and a little peak at 850°C can be ascribed to zircon formation (minor crystalline phase in the XRD diffractograms). Thereby DTA shows that no NaF evaporation occurs (DTA run with NaF sample under the same conditions shows an exothermic peak at about 1000°C), and this fact might indicate that NaF remains in the zircon, allowing a NaF solid solution in zircon lattice, according to Marchesini & Ramous[7] and Demiray *et al.*[6]
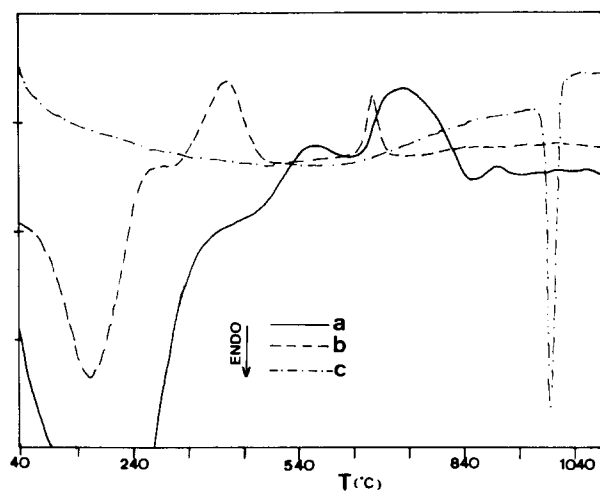
The variation of zircon unit cell parameters for samples D(CE), B(CG) and D(CG) with the soaking time at 750°C are presented in Table 6. In order to follow the evolution of XRD peaks intensity with firing temperature, in Table 6 an $I_Z$ parameter defined by eqn (1) is used:

$$I_Z = \frac{i_Z}{i_T + i_M + i_{ZV} + i_Z} \tag{1}$$

where $i_Z$, $i_T$, $i_M$ and $i_{ZV}$ are the heights of the XRD peaks measured from the diffractograms at $°2\theta = 27$, 30·2, 28·2 and 20·1, respectively. These peaks correspond to zircon, tetragonal zirconia, monoclinic zirconia and vanadium pyrovanadate, respectively. The zircon cell volume variation with the soaking time at 750°C is shown in Fig. 7.

From Table 6 it can be inferred that both $a$ and $c$ parameters continuously decrease with the firing soaking time and therefore the cell volume also decreases. Similarly, parameters tend to rise compared to the reference values for undoped zircon in sample D; moreover, green sample B without NaF addition remains with high values. Figure 7 explains this fact better, which is in agreement with the previously mentioned results: NaF addition leads to a higher reactivity in zircon formation, according to the DTA results, and likewise, this addition decreases the zircon unit cell size according to the NaF retention, probably with $O^{-2}$ replacements by $F^-$. In the green sample B(CG), the $V^{+4}$ migration is not effective at this low temperature and its cell parameter remains relatively high.

The unit cell parameters of the three substances are compared in Table 7. It is observed that all parameters decrease in the order substance I > II > III. The green substance I, with the $V^{+4}$ and $V^{+5}$ ions

**Table 5.** Zircon unit cell parameter evolution with temperature for three green gel colloidal samples

| Sample | Temperature ($^\circ C$) | $I_Z$ (%) | $a = b$ ($\AA$) | $c$ ($\AA$) | $V$ ($\AA^3$) |
|---|---|---|---|---|---|
| 1[a] | 750 | 89 | $6\cdot625 \pm 0\cdot002$ | $6\cdot010 \pm 0\cdot003$ | $263\cdot8 \pm 0\cdot2$ |
| | 800 | 98 | $6\cdot611 \pm 0\cdot001$ | $5\cdot995 \pm 0\cdot002$ | $262\cdot1 \pm 0\cdot1$ |
| | 900 | 98 | $6\cdot608 \pm 0\cdot001$ | $5\cdot989 \pm 0\cdot001$ | $261\cdot5 \pm 0\cdot1$ |
| | 1000 | 100 | $6\cdot603 \pm 0\cdot001$ | $5\cdot981 \pm 0\cdot001$ | $260\cdot8 \pm 0\cdot1$ |
| | 1100 | 100 | $6\cdot601 \pm 0\cdot001$ | $5\cdot983 \pm 0\cdot001$ | $261\cdot1 \pm 0\cdot1$ |
| | 1200 | 100 | $6\cdot602 \pm 0\cdot001$ | $5\cdot982 \pm 0\cdot001$ | $260\cdot7 \pm 0\cdot1$ |
| 2[a] | 750 | 82 | $6\cdot618 \pm 0\cdot001$ | $6\cdot005 \pm 0\cdot003$ | $263\cdot0 \pm 0\cdot2$ |
| | 800 | 93 | $6\cdot615 \pm 0\cdot001$ | $5\cdot999 \pm 0\cdot003$ | $262\cdot5 \pm 0\cdot2$ |
| | 900 | 97 | $6\cdot609 \pm 0\cdot001$ | $5\cdot989 \pm 0\cdot001$ | $261\cdot6 \pm 0\cdot1$ |
| | 1000 | 99 | $6\cdot605 \pm 0\cdot001$ | $5\cdot984 \pm 0\cdot001$ | $261\cdot1 \pm 0\cdot1$ |
| | 1100 | 99 | $6\cdot605 \pm 0\cdot001$ | $5\cdot984 \pm 0\cdot001$ | $261\cdot1 \pm 0\cdot1$ |
| | 1200 | 100 | $6\cdot602 \pm 0\cdot001$ | $5\cdot981 \pm 0\cdot001$ | $260\cdot7 \pm 0\cdot1$ |
| 3[a] | 750 | 80 | $6\cdot613 \pm 0\cdot002$ | $6\cdot010 \pm 0\cdot004$ | $262\cdot8 \pm 0\cdot3$ |
| | 800 | 90 | $6\cdot617 \pm 0\cdot001$ | $5\cdot999 \pm 0\cdot002$ | $262\cdot7 \pm 0\cdot1$ |
| | 900 | 95 | $6\cdot608 \pm 0\cdot001$ | $5\cdot988 \pm 0\cdot001$ | $261\cdot5 \pm 0\cdot1$ |
| | 1000 | 97 | $6\cdot605 \pm 0\cdot001$ | $5\cdot986 \pm 0\cdot001$ | $261\cdot1 \pm 0\cdot1$ |
| | 1100 | 98 | $6\cdot602 \pm 0\cdot001$ | $5\cdot983 \pm 0\cdot002$ | $260\cdot8 \pm 0\cdot1$ |
| | 1200 | 98 | $6\cdot603 \pm 0\cdot001$ | $5\cdot983 \pm 0\cdot001$ | $260\cdot8 \pm 0\cdot1$ |
| ASTM card[11] | — | — | $6\cdot604$ | $5\cdot979$ | $260\cdot76$ |
| b | 1400$^\circ$C/24 h | 87 | $6\cdot594 \pm 0\cdot006$ | $5\cdot972 \pm 0\cdot007$ | $259\cdot7 \pm 0\cdot6$ |

[a] $1 = B(CG)$; $2 =$ gel colloid of $ZrO_2 \cdot SiO_2 \cdot (V_2O_5)_{0\cdot05}$ composition; $3 =$ gel colloid of $ZrO_2 \cdot (SiO_2)_{0\cdot9} \cdot (V_2O_5)_{0\cdot05}$ composition.
[b] $ZrO_2 \cdot SiO_2$ composition treated by CG method with Aerosil 200 and zirconium(IV) oxychloride as raw materials.

**Table 6.** Zircon cell volume parameter variation for samples D(CE), B(CG) and D(CG) with the soaking time at a firing temperature of 750°C

| Sample | $t$ ($h$) | $I_Z$ (%) | $a = b$ ($\AA$) | $c$ ($\AA$) | $V$ ($\AA^3$) |
|---|---|---|---|---|---|
| D(CE) | 36 | 35 | $6\cdot607 \pm 0\cdot007$ | $5\cdot980 \pm 0\cdot009$ | $261\cdot0 \pm 0\cdot9$ |
| | 72 | 78 | $6\cdot599 \pm 0\cdot004$ | $5\cdot980 \pm 0\cdot004$ | $260\cdot4 \pm 0\cdot5$ |
| | 168 | 93 | $6\cdot599 \pm 0\cdot004$ | $5\cdot978 \pm 0\cdot005$ | $260\cdot3 \pm 0\cdot5$ |
| B(GC) | 12 | 76 | $6\cdot613 \pm 0\cdot005$ | $6\cdot017 \pm 0\cdot009$ | $263\cdot1 \pm 0\cdot7$ |
| | 36 | 100 | $6\cdot622 \pm 0\cdot009$ | $5\cdot994 \pm 0\cdot009$ | $262\cdot9 \pm 0\cdot9$ |
| | 72 | 100 | $6\cdot606 \pm 0\cdot006$ | $5\cdot988 \pm 0\cdot009$ | $261\cdot3 \pm 0\cdot8$ |
| | 168 | 100 | $6\cdot605 \pm 0\cdot004$ | $5\cdot990 \pm 0\cdot006$ | $261\cdot3 \pm 0\cdot6$ |
| D(GC) | 1 | 90 | $6\cdot605 \pm 0\cdot001$ | $5\cdot986 \pm 0\cdot002$ | $261\cdot1 \pm 0\cdot2$ |
| | 12 | 100 | $6\cdot598 \pm 0\cdot006$ | $5\cdot974 \pm 0\cdot007$ | $260\cdot0 \pm 0\cdot7$ |
| | 36 | 100 | $6\cdot602 \pm 0\cdot001$ | $5\cdot981 \pm 0\cdot001$ | $260\cdot7 \pm 0\cdot1$ |
| | 72 | 100 | $6\cdot600 \pm 0\cdot004$ | $5\cdot975 \pm 0\cdot005$ | $260\cdot3 \pm 0\cdot5$ |
| | 168 | 100 | $6\cdot596 \pm 0\cdot005$ | $5\cdot971 \pm 0\cdot006$ | $259\cdot8 \pm 0\cdot6$ |
| ASTM card[11] | — | — | $6\cdot604$ | $5\cdot979$ | $260\cdot76$ |
| a | 1400$^\circ$C/24 h | 87 | $6\cdot594 \pm 0\cdot006$ | $5\cdot972 \pm 0\cdot007$ | $259\cdot7 \pm 0\cdot6$ |
| b | 1400$^\circ$C/24 h | 83 | $6\cdot597 \pm 0\cdot004$ | $5\cdot975 \pm 0\cdot004$ | $260\cdot1 \pm 0\cdot5$ |

[a] $ZrO_2 \cdot SiO_2$ composition treated by CG method (colloidal silica and zirconium(IV) oxychloride as raw materials).
[b] The same composition made by CE method (quartz and baddeleyite as raw materials).
Both samples were fired at 1400°C/24 h after firings at 800, 900, 1000, 1100 and 1200°C with a soaking time of 8 h at each temperature.
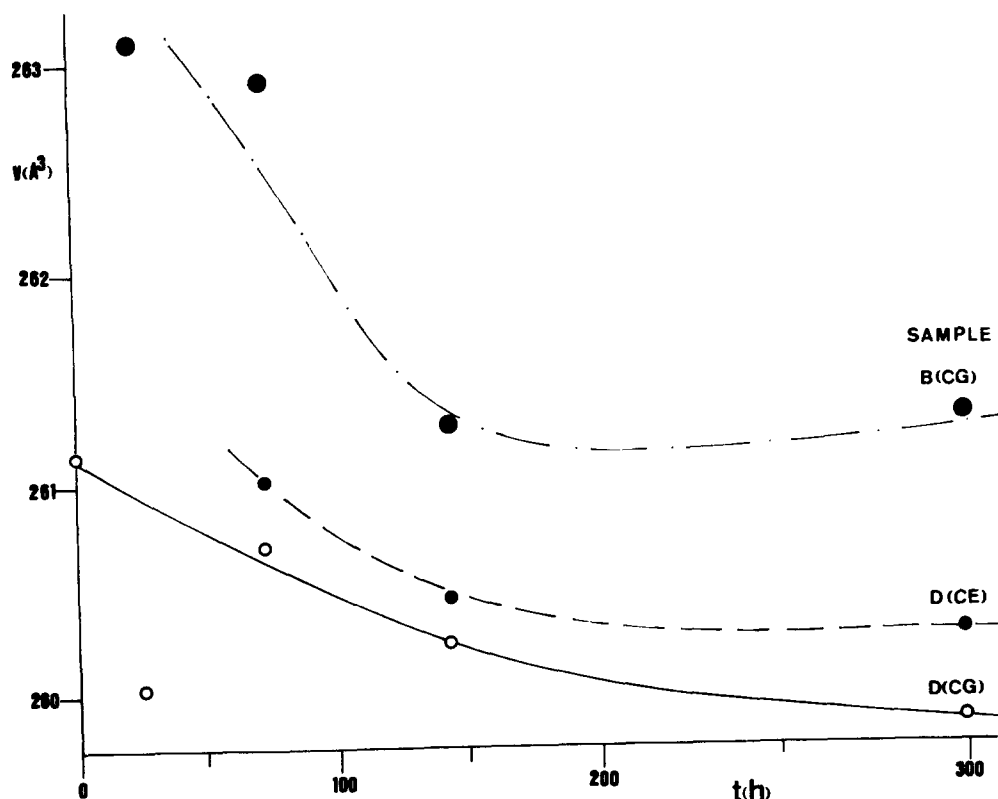
**Fig. 7.** Zircon cell volume variation with the soaking time at a firing temperature of 750°C.

(and therefore anionic vacancies) preferentially in the dodecahedral sites replacing the $Zr^{+4}$ ion in the zircon structure, presents the highest unit cell size. The blue substance II, with $V^{+4}$ in the dodecahedral position, presents intermediate values, and the deep blue–turquoise substance III, in which $V^{+4}$ and $F^-$ are replacing the $Zr^{+4}$ and $O^{-2}$ in zircon respectively, presents the lowest values. Moreover, the differences are not large between these three substances and the undoped zircon, because the amount of vanadium in the solid solution is not large. In this sense it is possible not to find any differences in the zircon unit cell parameters working at high temperatures.[6]

## 5 Conclusions

The different kinds of solid solutions in the NaF–$V_2O_5$-$SiO_2$-$ZrO_2$ system have been investigated by sol–gel techniques and the following facts from the results of this study might be inferred:

(1) Sol–gel techniques allow a thermal stabilization of the blue colour which appeared at low firing temperatures in the $V_2O_5$-$SiO_2$-$ZrO_2$ system when the $V_2O_5$ amounts are lower than 0·03 mol per formula weight.

(2) Sol–gel techniques produce a deep green colour in the $V_2O_5$-$SiO_2$-$ZrO_2$ system with $V_2O_5$ amounts in the samples over 0·03 mol per formula weight.

(3) Three kinds of V–$ZrSiO_4$ solid solutions can be identified:

(I) $V^{+4},V^{+5}$-$ZrSiO_4$ solid solution, which presents a deep green colour and is obtained working with high $V_2O_5$ amounts in the $V_2O_5$-$SiO_2$-$ZrO_2$ system. In the thermal treatments, the

**Table 7.** Unit cell parameter comparison for the three substances (I, II and III) and undoped zircon

| | *Substance* | | | |
|---|---|---|---|---|
| | *I* | *II* | *III* | *Undoped zircon* |
| Sample | B(CG)/1200°C | A(CG)/1200°C | D(CG)/750°C/100 h | $ZrO_2$ . $SiO_2$/CG/1400°C |
| $a = b$ (Å) | 6·602 ± 0·001 | 6·601 ± 0·001 | 6·596 ± 0·005 | 6·594 ± 0·006 |
| $c$ (Å) | 5·981 ± 0·001 | 5·978 ± 0·001 | 5·971 ± 0·006 | 5·972 ± 0·007 |
| $V$ (Å³) | 260·7 ± 0·1 | 260·5 ± 0·1 | 259·8 ± 0·6 | 259·7 ± 0·6 |

sample, initially blue, turns green by the introduction of $V^{+5}$ in the lattice and migration of $V^{+4}$ from tetrahedral to dodecahedral sites.

(II) $V^{+4}$–$ZrSiO_4$, a thermally stable solid solution with a soft blue colour, is synthesized by sol–gel techniques and with $V_2O_5$ amounts lower than 0·03 mol per formula weight in the $V_2O_5$–$SiO_2$–$ZrO_2$ system.

(III) $Na^+,F^+,V^{+4}$–$ZrSiO_4$ solid solution, with a deep blue–turquoise colour, is obtained by addition of NaF in the $V_2O_5$–$SiO_2$–$ZrO_2$ system.

## Acknowledgement

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