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Low temperature synthesis of zircon from silicone resins and oxide nano-sized particles

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Abstract

In this paper we present a new route for the realization of crack-free zircon monoliths, at very low temperature (1200 °C). Zircon ceramics are for the first time synthesized from a mixture of preceramic polymers, consisting of silicone resins, filled with active nano-sized fillers, being ZrO_2 nano-particles. The introduction of small quantities (up to 10 mol%) of TiO_2 as a sintering aid, and of zircon micro-powders, as seeds, has been also considered. The additives demonstrated to be extremely effective in increasing the zircon yield, with a synergistic effect when used together. Moreover, an appropriate mixture of different preceramic polymers as SiO_2 source was found to be critical for the obtainment of crack-free monoliths. This simple methodology demonstrated kinetic features comparable to those of sol–gel processes, but coupled with the possibility of an easy shaping of the desired ceramic before heat treatment.

Keywords: Precursors-organic; Silicate; Refractories; Shaping

1. Introduction

Zircon (zirconium silicate, $ZrSiO_4$ or $ZrO_2{\cdot}SiO_2$) is a ceramic material which is suitable for multiple applications, although most of them have been rather unexplored so far. The classical application is in the field of refractory materials, where zircon is appreciated mainly for its very low CTE, although the performance is generally lowered by the presence of impurities.[1] More recent high-technology applications are in the nuclear and electronic fields. In fact, zircon has been considered a promising nuclear waste host material,[2–4] owing to the possibility of introducing large amounts (up to 20 wt%) of radionuclide cations inside its crystal structure.[4] Electronic applications are in relation to the possibility to replace SiO_2 in silicon-based MOSFET, thanks to its relatively large dielectric constant, high band gap, high breakdown field, and good thermal stability in contact with silicon.[5–7]

According to several studies in the literature, zircon synthesis from SiO_2 and ZrO_2 raw materials is characterized by a very slow kinetic, and achieving high zircon yield through this reaction sintering is possible only at high temperatures (above 1500 °C). High synthesis temperatures, however, hinder the applicability: as an example, the hosting of nuclear waste may be compromised, due to the risk of volatilization of some radionuclides, lowering the immobilization efficiency.[4] The possibility of lowering the synthesis temperature of zircon has been explored in several studies, most of them based on the sol–gel route,[8–11] well known to be hardly applicable to the manufacturing of monoliths.

In the recent years, the use of Polymer Derived Ceramics (PDCs) in conjunction with nano-sized particulate fillers has proved to be a straightforward methodology for the realization of advanced ceramic monoliths, featuring a kinetic comparable, if not better, to the sol–gel method. In particular, silicates and sialons have been successfully obtained by the reaction between oxide particles, introduced in commercially available silicone resins, and the polymer-derived silicate matrix, at generally lower temperatures than those necessary in other common ceramic processing routes.[12–14] The coupling of the high reactivity of nano-sized particles with that of amorphous silica, provided by the ceramic conversion of silicones, leads to a high phase purity and to an interesting microstructure. In particular, it has been shown the possibility to produce nano-structured ceramics, i.e. fine grained monophasic ceramics or ceramic matrix nano-composites, such as zirconia-toughened mullite.[15]

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In this work we discuss for the first time the application of the method of nano-sized filled silicones to the manufacturing of zircon ceramics. The approach was found to enable the synthesis of crack-free and high purity zircon monoliths at low temperature (1200 °C), starting from a silicone and zirconia nano-sized particles, through a careful control of additional secondary fillers and seeds.

2. Experimental

A commercially available polysilsequioxane (Silres MK, Wacker-Chemie GmbH, Munchen, Germany) was dissolved in isopropanol under stirring. ZrO_2 nano-sized powders (VP Zirconium Oxide PH, 13 nm mean particle size, Evonik Industries AG, Essen, Germany) were subsequently dispersed into the solvent/polymer solution, without the addition of any chemical dispersant. A pure ZrO_2/MK system, where the ZrO_2/MK weight ratio was kept constant and equal to 1.682 was investigated first. The weight ratio value of 1.682 was calculated by considering both the stoichiometry of zircon (SiO_2 and ZrO_2 in equal molar concentration) and the ceramic yield of the polysiloxane, which is equal to 82 wt%. Although it should be considered that, in some cases, the introduction of secondary fillers could have some influence on the chemical composition of the final ceramic residue (particularly in the case of active fillers), during the present work calculations were made with the assumption that a pure SiO_2 ceramic residue from the polysiloxane(s) is obtained, thus neglecting possible polymer–fillers interactions during the pyrolysis step. This assumption seems to be reasonable, since heat treatments were carried out in oxidative atmosphere and only oxides were used as fillers. In other formulations, TiO_2 nano-powders (VP P90, 13 nm mean particle size, Evonik Industries AG) and/or zircon seeds (0.8 μm mean particle size, Industrie Bitossi SpA, Vinci, Italy) were also introduced. Considering the possibility that Ti^{4+} cations could enter into the zircon crystal lattice by substituting Zr^{4+} cations,[16] in all the dispersions containing TiO_2 the original ZrO_2/MK weight ratio was adjusted according to the relation $n_{SiO2} = n_{ZrO2} + n_{TiO2}$, with n_x = moles of species x. Samples were labeled "X-Y", where "X" and "Y" represent the molar TiO_2 and seeds concentrations in the final ceramic, respectively. All the dispersions were homogenized by magnetic stirring for 10 min, and then ultrasonicated for 20 min to reduce the size of the residual particles agglomerates, thus obtaining homogeneous and stable dispersions. After the evaporation of the solvent in oven at 90 °C, the material obtained was finely ground in a mortar with a pestle and sieved (75 μm aperture). Powders were uniaxially compacted at room temperature under a pressure of 40 MPa. Pellets were subsequently heat treated in air in the 1100–1500 °C range for 1 and 4 h (10 °C/min heating rate).

For some samples, part of Silres MK was substituted by another polysiloxane (Silres H62C, Wacker-Chemie GmbH, Munchen, Germany), which is characterized by a different SiO_2 yield (approx. 58 wt%) and does not releases gaseous products during the curing step. For these samples, a partial pre-curing treatment (250 °C, 30 min) was necessary before the grinding step.

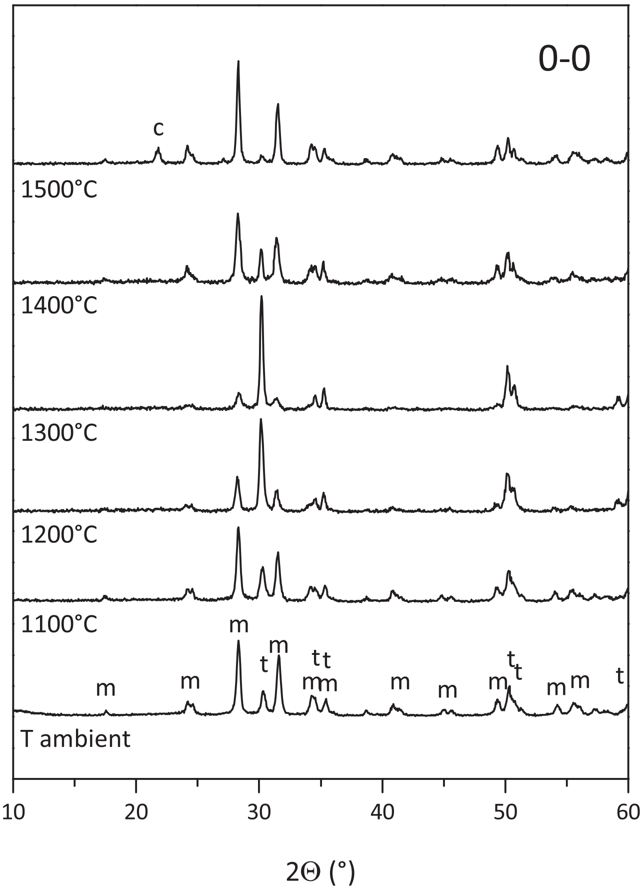

Fig. 1. XRD patterns as a function of the treatment temperature of 0-0 sample. m = m-ZrO_2, t = t-ZrO_2, c = cristobalite.

The identification of crystalline phases was performed by means of X-ray diffraction analysis (XRD; Bruker AXS D8 Advance, Bruker, Germany). All XRD pattern were collected in 10–60 °C 2-theta range (0.05 °C step-size). Rietveld refinement was applied on all the patterns by the MAUD software package,[17] thus obtaining the volumetric fractions and an estimate of the mean crystallite size of the phases present in the final ceramics. After Rietveld refinement, a zircon yield parameter was calculated as $vol\%_{zircon}/(vol\%_{zircon} + vol\%_{m\text{-}ZrO2} + vol\%_{t\text{-}ZrO2})$. Differential thermal and thermo-gravimetric analysis (DTA/TG) were done up to 1500 °C in air (DTA/TGA, STA409, Netzsch GmbH, Selb, Germany). Microstructural investigations were carried out by Scanning Electron Microscopy (SEM; FEI Quanta 200 FEG, FEI Company, The Netherlands).

3. Results and discussion

In Fig. 1, XRD data for a pure MK/ZrO_2 system are reported as a function of the temperature (1 h soak time). As it can be observed, zircon is virtually absent even at 1500 °C, as a confirmation of the already reported extremely slow nucleation kinetic, and unreacted ZrO_2 and SiO_2 continue to be the predominant phases. Below 1500 °C, ZrO_2 is the only crystalline phase, and the SiO_2 component deriving from the pyrolysis of

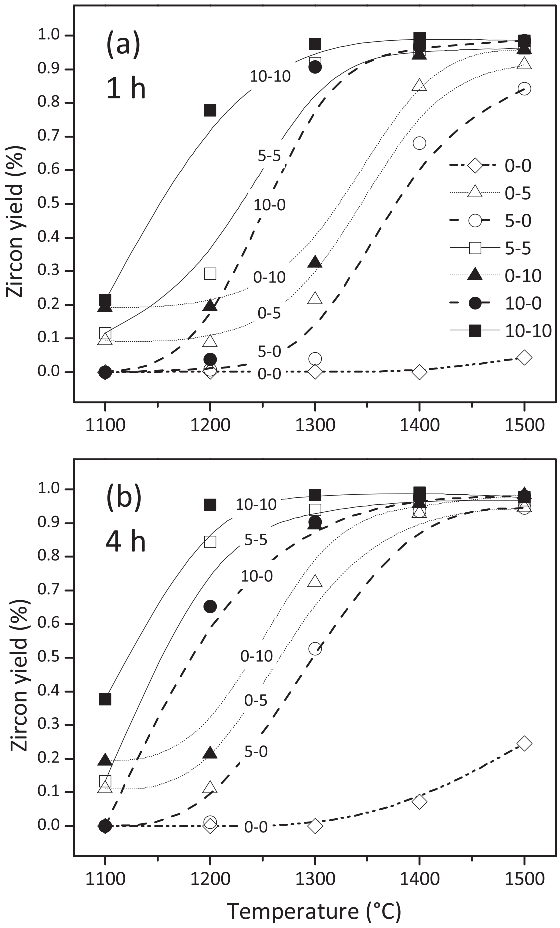

Fig. 2. Zircon yield as a function of the treatment temperature for all the different systems studied. (a) 1 h soak, (b) 4 h soak.

the silicone resin is still present as an amorphous phase. The t-ZrO_2/m-ZrO_2 ratio first increases up to 1300 °C, and then decreases until 1500 °C: the first increase, from one hand, is probably due to the well-known mechanical constraint effect of the matrix on the t-ZrO_2 phase; the decrease, on the other hand, could be associated with an progressive increase in the dimension of the ZrO_2 grains, counteracting the mechanical constraint provided by the matrix.[18]

An approximate but rapid evaluation of the kinetic of the system, in the form of MK and ZrO_2 nano-particles, with or without additives, comes from the evolution curves reported in Fig. 2. It is evident that the formation of zircon was effectively enhanced by the introduction of small quantities (5 and 10 mol%) of TiO_2 and/or zircon seeds, since the zircon yield is much higher than that from only MK and ZrO_2, in any condition of concentration of additive, temperature and soak time. Specific features, however, should be noted. First of all TiO_2 may be seen as a key additive, as testified by the evolution curves for samples 5-0 (5% TiO_2, no seeds) and 10-0 (10% TiO_2, no seeds), for both 1 and 4 h treatments, shown in Fig. 2, and by the XRD patterns as a function of the treatment temperature, at a constant soak time of 1 h, for samples 10-0 and 10-10 (10% TiO_2, 10% seeds), shown in Fig. 3. TiO_2 nanoparticles accomplish their beneficial effect by providing a reduction of the viscosity of the SiO_2 phase (deriving from the pyrolysis of the polymeric phase) before the reaction of the latter with ZrO_2 nanoparticles to give the formation of zircon. The reduction of SiO_2 viscosity by the introduction of Ti^{4+} cations, which was also observed in previous works in the literature,[19,20] is associated with a breakage of the silica network produced upon pyrolysis, thus leading to a lower network connectivity. The improved mobility of silicon and oxygen ions, upon rupture of siloxanic network, as a triggering event, is also consistent with the observation that silicon and oxygen ions are the mobile species in zircon formation.[21]

If TiO_2 may be seen as an actual catalyst, the sigmoidal curves for samples 5-0 and 10-0 being shifted towards lower temperatures with increasing TiO_2 content, the role of seeds is less clear. The zircon yields were simply shifted up by a constant quantity, below a “critical temperature”, 1300 °C for 1 h soak time or 1200 °C for 4 h, according to the different quantity of seeds added to the starting mixture, compared to the yields for pure MK and ZrO_2. The seeds reasonably provided some heterogeneous nucleation, but with a much less marked effect on the temperature for extensive zircon formation than TiO_2.

Interestingly, a synergistic effect of TiO_2 addition and seeding occurs, testified by the high zircon yields for the 5-5 and 10-10 systems even below 1200 °C. In the presence of both TiO_2, after 4 h at 1100 °C, the effect of seeding starts to be significant already at 1100 °C, and gives almost phase pure zircon at 1200 °C (sample 10-10). The synergy is further illustrated by the DTA analysis reported in Fig. 4 whereas for pure MK and ZrO_2 there is no practical evidence of crystallization exothermic peak, the sample with both TiO_2 and seeds shows a well-defined peak at about 1320 °C (the other peaks are all attributable to the decomposition of the silicone resin, evident also from the weight loss in the thermo-gravimetric plot, TG).

The phase purity, in the newly developed zircon ceramics, is not accompanied by mechanical consistency. SEM analysis revealed many cracks in all samples, as it could be observed, as an example, for sample 0-0 (Fig. 5a and b) and sample 10-10 (Fig. 5c and d). Compact regions are separated one from each other, leading to very poor mechanical properties. This effect is very likely to be associated with the lacking compensation of the significant shrinkage and gas release occurring upon polymer decomposition at high temperature.[22]

To increase the integrity of the samples, part of Silres MK was replaced with Silres H62C, in order to have an equal SiO_2 contribution from both the polymers. Sample 10-10 was realized with this new formulation (referred as “10-10H”). As shown by Fig. 6, the formation of zircon does not seem to be affected by the new source for silica (as a representative example, only patterns for the condition 1300 °C/1 h are reported, and these are virtually identical). The new samples, although much improved compared to those from only MK, being visibly not cracked and hard to be powdered, were not actually fully dense, as reported by Table 1. No significant increase in apparent density and decrease of open porosity could be observed in the 1200–1400 °C range, while a certain densification seems to start at 1500 °C. SEM images in Fig. 5e,f confirm the presence of residual porosity, but also show, significantly, a much different structure from 0-0 and 10-10 samples. Long cracks are replaced by a system of micro-cracks,

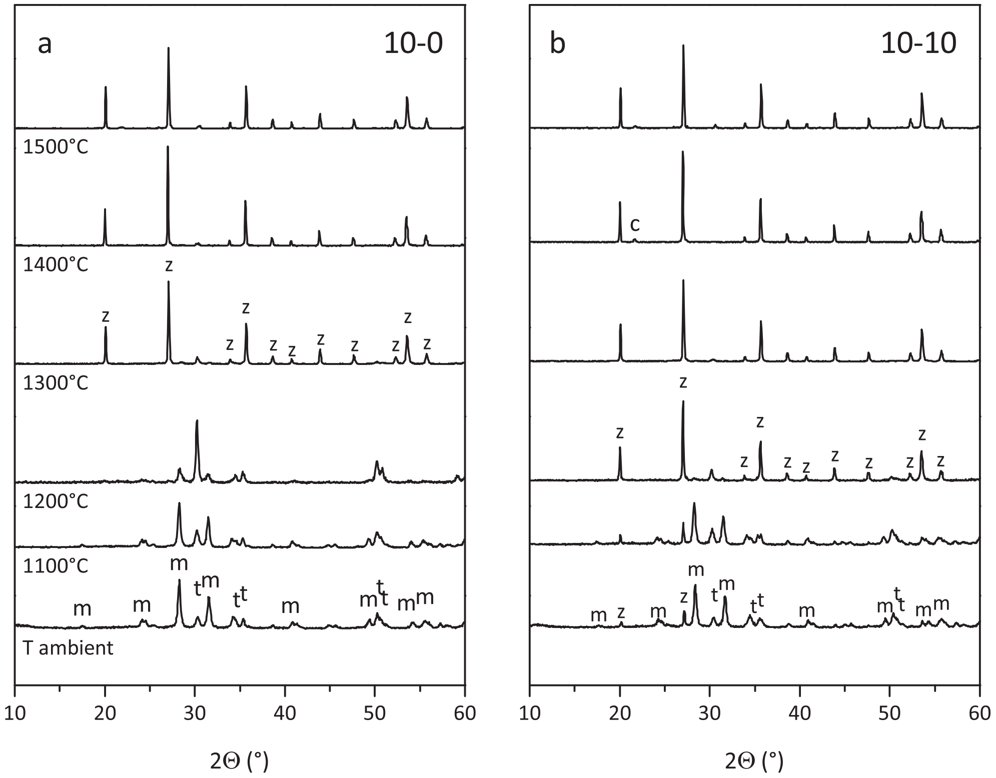

Fig. 3. XRD patterns as a function of treatment temperature (1 h soak) of 10-0 (a) and 10-10 (b) samples. m = m-ZrO_2, t = t-ZrO_2, z = zircon, c = cristobalite.

Table 1
Apparent density and open porosity values for sample 10-10H as a function of the treatment temperature.

Treatment temperature (1 h soak)	Apparent density (g/cm^3)	Open porosity (vol%)
1200 °C	3.74	12.92
1300 °C	3.75	14.27
1400 °C	3.79	14.22
1500 °C	3.97	9.25

likely determining a much lower weakening effect, owing to crack branching.[18] A clear explanation for this phenomenon is still not very clear. One contribute could be connected with the pre-curing step before powders compaction, which can eliminate (at least partially) the contribute of both shrinkage and gaseous products release during cross-linking. In any case, this does not seem to be the only reason. In fact, samples containing only Silres MK which have been pre-cured with the same methodology before compaction (data not shown for the seek of brevity) still suffer cracking after heat treatment. The authors, on the basis of similar results for different ceramic systems,[23] suggest that the molecular structure of the starting polymer could influence the characteristics of the amorphous SiO_2 network (i.e. connectivity, number of defects) after pyrolysis, and specific studies (regarding tests with many different weight proportions between MK and H62C) are currently being planned for the future.

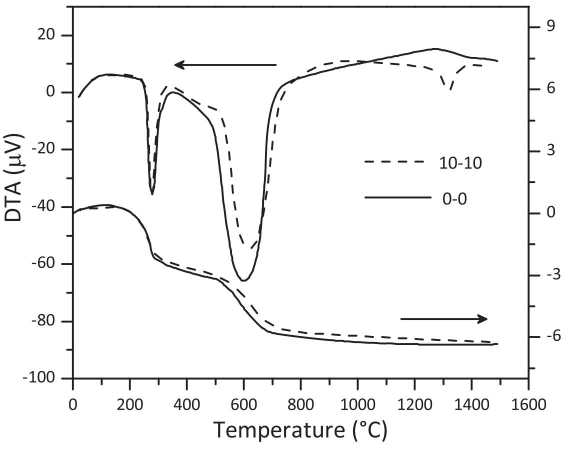

Fig. 4. DTA/TG analysis of samples 0-0 and 10-10.

A final remark concerns the possible applications of the developed ceramics. The very low synthesis temperature is attractive for the realization of monoliths to be used as refractory components or as dielectrics (e.g. the possibility of shaping in the preceramic state could be interesting, for the manufacturing of electronic micro-components); in addition, considering the low coefficient of thermal expansion, zircon anti-oxidation coatings could be proposed on SiC substrates (analogous coatings, in which filled silicones are exploited for their intrinsic

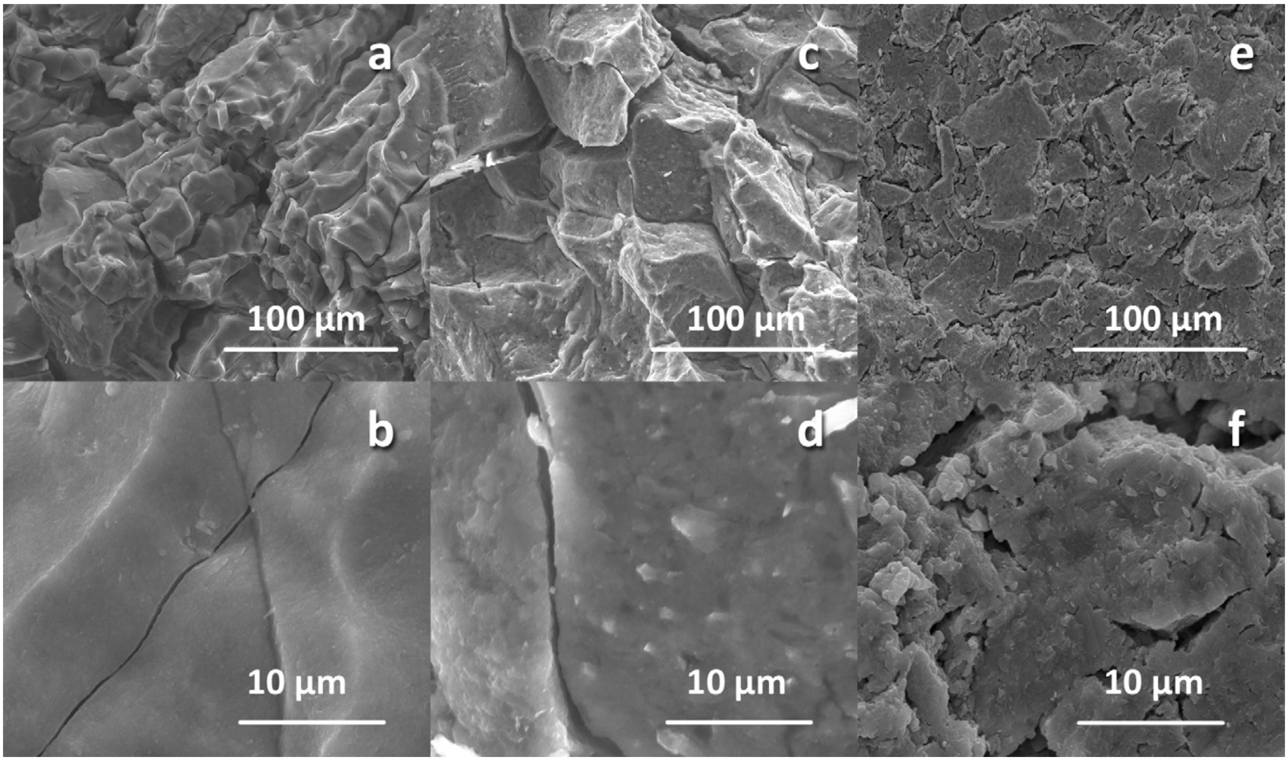

Fig. 5. SEM images of samples (a, b) 0-0, (c, d) 10-10 and (e, f) 10-10H (1300 °C, 1 h).

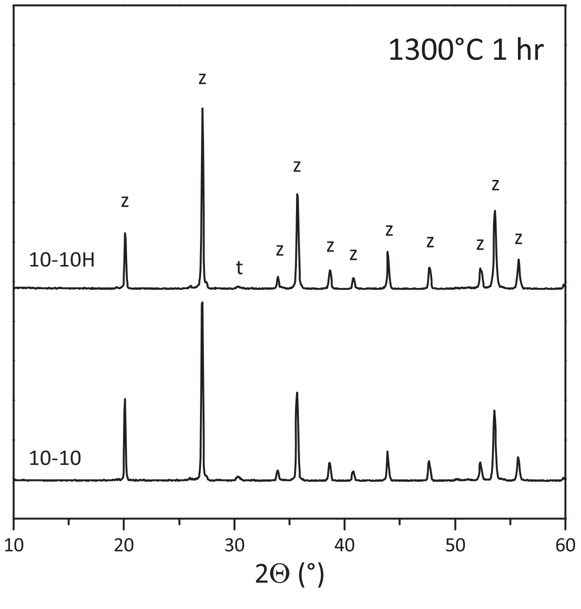

Fig. 6. XRD patterns of samples 10-10 and 10-10H (1300 °C, 1 h). z = zircon, t = t-ZrO_2.

shaping capability, have been already developed with a mullite composition[24]: the low firing temperature could allow zircon formation without extensive oxidation of the substrate).

4. Conclusions

We may conclude that:

- silicone resins, properly filled with oxide nano-particles, are suitable for the preparation of zircon monoliths, starting from the very low temperature of 1200 °C;
- TiO_2 nano-particles are very effective in promoting low temperature synthesis of zircon, reasonably by operating a decrease in viscosity of the amorphous phase provided by the ceramic conversion of silicones;
- zircon seeds are particularly appreciated in their synergistic effect with TiO_2; an optimum composition comprises 10 mol% TiO_2 and 10 mol% seeds;
- variations in the silica source, i.e. changes in the formulation of the starting silicone, do not seem to affect the formation of zircon, rather than the density and integrity of the obtained monoliths;
- the low firing temperature is promising for extending the applications of zircon ceramics.

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