

Suspensions on the basis of stabilised zirconium oxide for three-dimensional printing

P S Sokolov¹, D A Komissarenko¹, I A Shmeleva¹, I V Slyusar¹, G A Dosovitskiy¹, P V Evdokimov², V I Putlyaev², and A E Dosovitskiy³

¹ NRC «Kurchatov Institute» – IREA, Bogorodskiy val str. 3, Moscow, 107076, Russia

² Moscow State University, Vorobiev Gory 1, Moscow, 119991, Russia

³ NeoChem, Profsoyuznaya str. 115-2-331, Moscow, 117647, Russia

E-mail: sokolov_ps@irea.org.ru

Abstract. Present work considers the first results on rheological and photo-curing behaviour of suspension consisting of nanocrystalline stabilised zirconium dioxide powders (19 - 27 vol. %) and a liquid UV-photosensitive organic monomer. At ambient temperature compositions showed a viscosity of 2.5 and 0.8 Pa·s at 10 and 100 s⁻¹ shear rates, respectively. Printability of these compositions was subsequently investigated by using an stereolithography machine Ember (Autodesk). 3D objects were later sintered in a separate furnace into dense translucent ZrO₂ ceramics.

1. Introduction

Stereolithography (SLA) is a technology that opens the possibility to fabricate complex 3D construction and functional ceramic components without tooling and with a good dimensional resolution. There have been some reports [1 - 6] on successful using the SLA method for production of complex-shape ceramic, such as Al₂O₃ [1], ZrO₂ [2, 3], yttrium aluminium garnet [4] and calcium phosphates [1, 5, 6]. This has been done via ultraviolet curing of a highly concentrated suspension of ceramic particles in a photopolymerisable liquid. The suspension must contain as much as possible (at least 30 vol %) ceramic powders to provide subsequent sintering with a viscosity less than 3 Pa·s at low shear rates to promote self-leveling and recoating. In this paper, the rheological and photo-curing behavior suspensions and the influence of the ZrO₂ particle size on viscosity, have been investigated.

2. Experimental

2.1. Starting materials

High-purity, homogeneous stabilised zirconia powders were synthesised by co-precipitation method and then annealed at different temperatures [7]. Their main properties are presented in Table 1. Four grades of 8 mol% Y₂O₃ stabilised ZrO₂ powders with different particle size and specific surface area (SSA) were prepared. Average crystallite size (*D*) was calculated from the broadening of X-ray diffraction peaks. The SSA and pore volume (*V_{pore}*) were measured using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) method, respectively. The medium aggregate size (*d₅₀*) was measured by the laser diffraction. Tap density (*ρ_{tap}*) of powders was estimated according to GOST



25279-93 (ISO 3953). The moisture (*MC*) of the zirconia powders was determined from weight loss on annealing at 378-383 K for 8 h, an average from three experiments was used for each sample.

A photopolymerisable suspension (slurry) usually consists from acrylic monomer, ceramic powder, dispersant and photoinitiator (PI) [1-6]. In the present work 1,6-hexanediol diacrylate (HDDA, technical grade, Aldrich) was chosen as a monomer. HDDA is a fast curing monomer with a low-viscosity (below 9 mPa*s at 293 K) and relatively high refractive index ($n = 1.46$). It has low volatility and low odour. The commercially available substances Triton X-100 (Aldrich) and w969 (BYK) were selected as a dispersant due to their good wetting and dispersing properties. Triton X-100 is a nonionic surfactant that has a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group. BYK w969 is a mixture of 2-Phenoxyethanol and alkanolammonium salt of an acidic polyester. Dispersant with 0.5-12.0 wt% concentration was added into the mixture, on a dry weight of stabilized ZrO_2 powders. The PI was Irgacure 2100 (BASF). Irgacure 2100 is a liquid blend of acylphosphine oxides for radical polymerisation. We used 0.5 or 1.0 wt% of PI with respect to the mass of monomer. No dye or UV light absorber or additional inhibitor of polymerisation was used.

Table 1. Main physical properties of stabilised zirconium dioxide powders

	SSA (m^2/g)	V_{pore} (cm^3/g)	D(nm)	d_{50} (μm)	ρ_{tap} (g/cm^3)	MC (%)
8YSZ1	48.5	0.205	14	1.09	1.04	1.57
8YSZ2	21.7	0.120	25	0.91	1.19	0.61
8YSZ3	12.4	0.092	36	0.83	1.29	0.44
8YSZ4	5.9	0.016	124	0.81	1.49	0.18

2.2. Preparation of UV-curable suspensions

The preparation method of the UV-curable suspension used in this work contains a few steps. First, photoinitiator and calculated amount of dispersant were added to the HDDA. The mixture was kept under stirring at room temperature and in the dark for 1 h. Second, the stabilised ZrO_2 powder, after sieving through a 70 μm mesh and dried for 8 h at 373 K, was added in small increments to mixture using a laboratory magnetic stirrer. Then the suspensions were mixed additional 1 h to produce a well-blended system. The stir bar was of 25 mm in length and of 5 mm in diameter, and the mixing speed was 100 rpm. The mixing process was carried out in a 25 ml glass. Finally, bubbles were removed from the completed suspension by vacuum deairing under 10-30 mbar pressure about 10 min under continued stirring.

2.3. 3D printer

A commercially available open-source desktop 3D printer [8], the Ember (Autodesk, USA), was used for this study. The Ember uses a 3D printing method in vat photopolymerisation known as digital light processing. The main difference with classical laser stereolithography is a digital light projector which is used as a UV light source. The projector shines light below the vat through an optical window. The optical window in the bottom of the vat has layer of polydimethylsiloxane. The projector has a wavelength of 405 nm with a total optical powder of 5 W. The Ember's UV light source was monitored using special UV light meter, the model 222 (G&R Labs, USA). Ember has a resolution of 50 μm [8] in the plane parallel to printing surface (XY resolution). The photo-curing behaviour of prepared ceramic suspensions was examined on the same printer.

2.4. Washing, binder burnout and sintering

After printing, the green body was rinsed with inert solvent in a heated ultrasonic bath to remove any uncured residual monomers, dried at room condition and then post-cured using a 36 W UV nail exposure chamber with Hg bulb (365 nm) for a minimum of 2 min. The debinding of green body was performed with a heating rate of 1 K/min up to 1073 K in air. Finally green body was sintered at 1873 K for 2 h with a heating rate of 6 K/min. The microstructure of sintered samples was observed by scanning electron microscopy (SEM) using JSM 7100 F (Jeol, Japan) instrument.

2.5. Rheometric measurement

Rheological characterisation of the suspension was performed at room temperature with rheometer Physica MCR 52 (Anton Paar, Austria). A plate-and-plate geometry with a measuring disk with diameter of 25 mm and a gap of 0.200 mm was used.

2.6. TGA-DSC measurement

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of cured suspensions of 5-10 mg in alumina crucibles was carried out on a simultaneous analyser SDT Q600 (TA Instruments, USA) under dynamic air atmosphere, at a constant heating rate of 2, 3, 5, 10 and 20 K/min from room temperature up to 1073 K. The DSC-TGA samples are flat disk with dia. of 4 mm and thickness of 100 μm .

3. Results and discussion

3.1. Rheological behaviour of the ceramic suspensions

Suspensions containing cubic ZrO_2 with various amount of dispersant showed different viscosities (Figure 1). It was observed that the optimal concentration of dispersant was about 3 wt%. The relation between shear stress and shear rate is not linear. Viscosity strongly depends on shear rate. All HDDA suspensions with 8YSZ as a filler showed the non-Newtonian (pseudoplastic or shear-thinning) behavior). Thus, 8YSZ3 powder containing suspension with a lowest viscosity was chosen for further experiments.

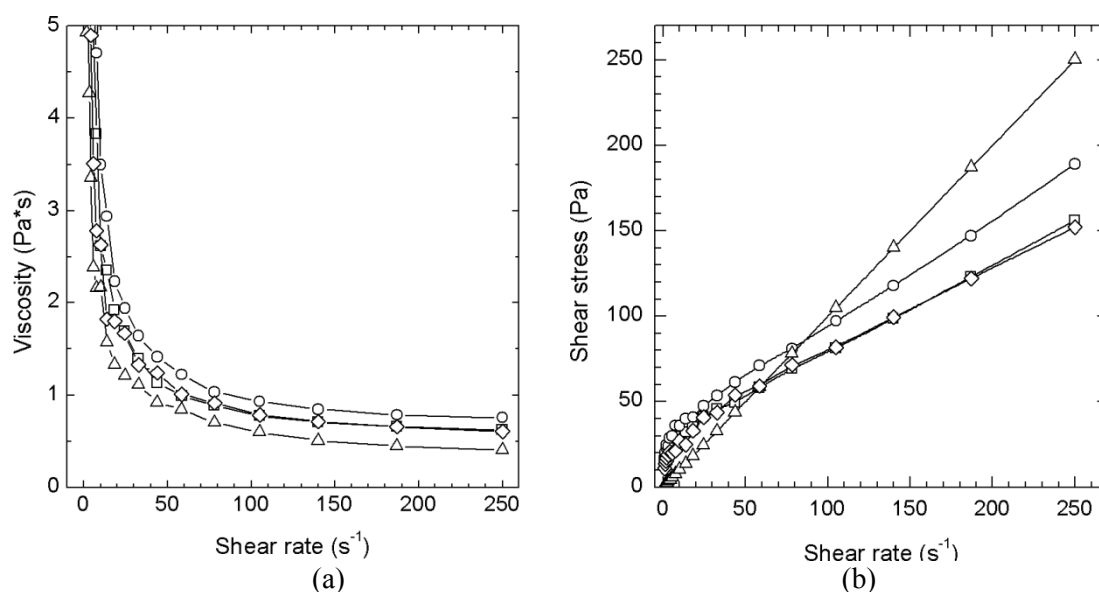


Figure 1. Representative rheological curves. (a) Viscosity curves and (b) flow curves of HDDA/Triton X-100 with stabilised zirconia powders: squares – 8YSZ1 (21 vol%), circles – 8YSZ2 (23 vol%), triangles – 8YSZ3 (27 vol%) and diamonds – 8YSZ4 (26 vol%).

No use degassing under vacuum leads to an increase of suspensions viscosity at a low shear rate up to 50 Pa*s. The dispersants Triton X-100 and BYK w969, in spite of their different nature, showed a similar reducing effect on the viscosity of suspensions. Without a dispersant the highest loading of ceramic fillers did not exceed 10-12 vol%. Addition of PI did not change the viscosity of the suspensions but slightly decrease loading. Addition of the inert diluents (ethylene glycol, diethylene glycol, polyethylene glycol 400 and polypropylene glycol 1025 in the amount of 1-10 wt%) did not effect the viscosity of suspensions but could reduce the filler loading.

3.2. Curable of the ceramic suspensions

The turbidity of highly concentrated ceramic suspensions induces light scattering and limits light penetration into the suspension. One aim of this study was to verify that the cured depth in the ceramic suspension is sufficient to SLA process. Then, the curing ability will be compared to that obtained with the pure monomer.

The polymerisation depth (C_p) is expressed by the Jacob equation (Beer-Lamber law) [6]:

$$C_p = D_p \ln(E/E_c) \quad (1)$$

where D_p is the depth of penetration, E – the exposure energy and E_c - the critical (or minimal) exposure energy to provide polymerisation of the monomer. For a load monomer D_p is a function of the particle size, concentration and refractive index difference between monomer and ceramic powder [6]. E_c is only depends on the PI/monomer system. So for a high refractive index difference (cubic ZrO_2 $n = 2.15$) of the cured depth is more attenuated and can becomes insufficient for SLA process [6].

Two suspensions with 0.5 or 1.0 wt% of photoinitiator with respect to the HDDA were characterized for curable. Experimental cure depths curves are plotted in Figure 2 on a semi-logarithmic scale. For comparison pure HDDA without powder loading have the depth of cure more 1 mm in the same condition. The D_p values calculated from the slopes are found to be 59 ± 2 and 69 ± 6 μm for 0.5 and 1.0 wt% of PI, respectively. The average E_c values are to be 49 ± 4 and 46 ± 4 mJ/cm^2 , for 0.5 and 1.0 wt% of PI, respectively. These curves allow us to choose the optimal print settings (time and dose of irradiation, Z-layer thickness – 100 μm , etc).

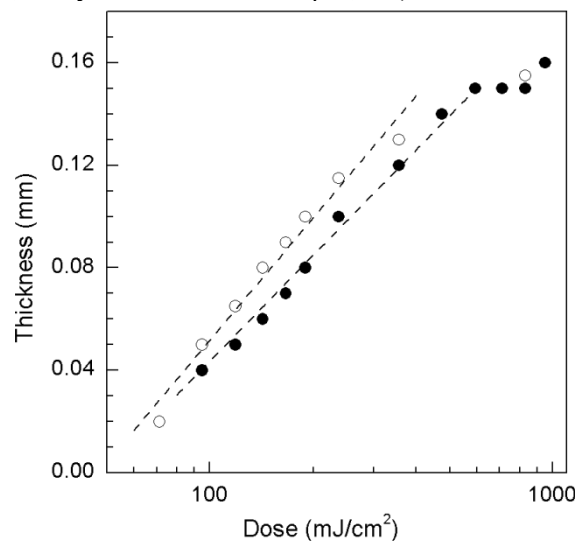


Figure 2. Dependence of polymerisation depths *versus* energy dose for 26 vol% 8YSZ3 suspensions with 3.6 wt% of BYK w969. Open symbols are suspension with 1 wt% of PI, solid — 0.5 wt% of PI.

Cure depth measurement was performed using 405 nm source with 23 ± 0.5 mW/cm^2 UV light intensity.

3.3. Thermal decomposition of cured 8YSZ/HDDA suspensions

TGA was applied to identify temperature regions of rapid mass loss of the green body of ceramic mold. Figure 3 represents the weight loss and DSC curve as a function of temperature for constant heating rate of 2 K/min. Noticeable weight loss was observed in the range of 400-700 K. All the organic binders are removed below 800 K in air (Table 2). The exothermic events demonstrate that the degradation involves oxidation reaction. The samples after DSC-TGA measurement with heating rate above 3 K/min have cracks.

Table 2. Thermal events of decomposition of cured 8YSZ/HDDA suspensions (0.5 wt% PI).

Rate	First event			Second event		
	T_{b1} (K)	T_{p1} (K)	ΔQ_1 (kJ/g)	T_{b2} (K)	T_{p2} (K)	ΔQ_2 (kJ/g)
2	602	634	1.349	668	683	0.295
3	713	650	1.172	681	694	0.266
5	626	668	0.779	693	706	0.195
10	601	696	2.290	–	728	0.572
20	598	715	2.23	–	753	0.567

Note: T_b - temperate of the beginning of the thermal event, T_p – peak temperate; ΔQ – heat effect.

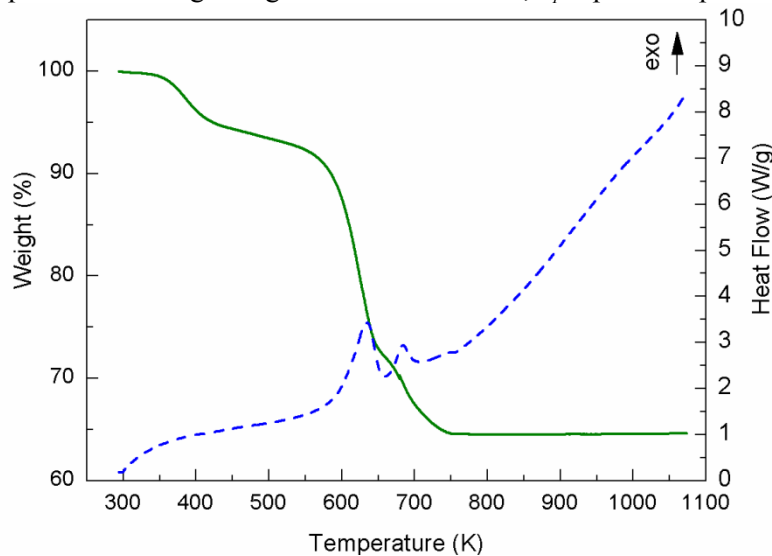


Figure 3. TGA and DSC curve at 2 K/min of pyrolysis of cured suspension 8YSZ3/BYK/HDDA with 0.5 wt% of PI in 25 vol% stabilised ZrO_2 printed by stereolithography showing mass loss accompanied by two exothermic reactions.

The kinetic investigation of thermal degradation was achieved from DSC data by the application of Kissinger [9] and Takhor [10] methods. The activation energy (E_a) is an important parameter associated with nonisothermal decomposition. The E_a can be derived from the peak temperature T_p with heating rates by the Kissinger approach [9] as follows:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (2)$$

and by the Takhor model [10] as:

$$\frac{d[\ln(\phi)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (3)$$

where ϕ is the heating rate, T_p is the thermal decomposition peak temperature, and R is the universal gas constant. Plots of $\ln(\phi)$ versus $1/T_p$ are shown in Figure 4a (Takhor model) and plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ are shown in Figure 4b (Kissinger model), and they are fitted to straight lines. The E_a values calculated from the slopes are found to be 94 ± 6 and 130 ± 6 kJ/mole for 0.5 wt% of photoinitiator (for first and second thermal event respectively) for Kissinger model. The comparable E_a of 0.5 and 1.0 wt % of PI suggested that polymer structure did not significantly affect the energy required to decomposition.

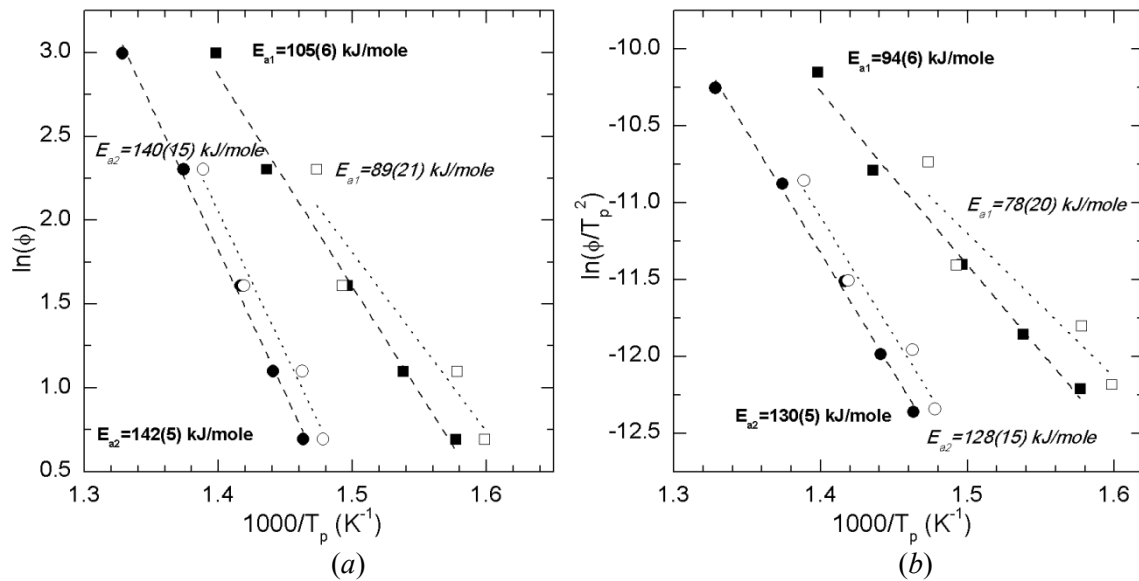


Figure 4. Kinetic of thermal decomposition of cured 8YSZ3/BYK/HDDA suspensions. Open symbols are suspension with 1 wt% of PI, solid — 0.5 wt% of PI. Squares are first thermal events, circle — second thermal events. (a) Takhor plot, (b) Kissinger plot with various heating rate. E_a activation energy for 0.5 wt% of PI, E_a — for 1.0 wt% of PI.

In order to verify the printability of the best suspension (8YSZ3 powder with load 26 vol%) the reticulated variant of the Kelvin structure [6] was prepared (Figure 5). As disadvantages of suspensions based on HDDA, it is important to note the interaction with polydimethylsiloxane and the some brittleness of the green body after polymerisation, it may be necessary to modify the suspension composition or add plasticizer. One can see some cracks in the green body which also present in the sintering ceramic. According to SEM study the 3D printed ceramic material shows the typical fine grained microstructure of Y_2O_3 -stabilised zirconia with grain a few micrometers.

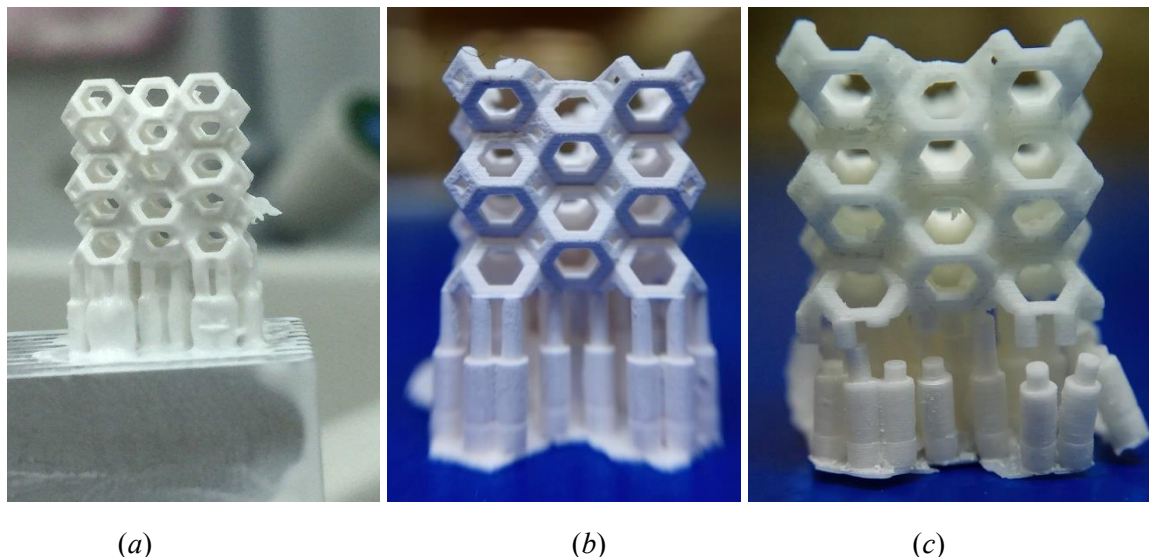


Figure 5. (a) The green body immediately after printing; (b) after post-curing and (c) sintering ceramic. The XY dimension of 9.8×9.8 mm (a,b), linear shrinkage is about 33% (c).

4. Conclusions

Suspensions of HDDA and fine zirconia powders with dispersant show good loading (of around 25 vol.% stabilised zirconia), good viscosity and stability 24-48 h at least, that allows to use them for stereolithography 3d printing.

The dispersants Triton X-100 and BYK w969 show the good liquefier properties. The optimal concentration of dispersant is about 3 wt% according to dry weight of zirconia powder. The better concentration of the photoinitiator Igracure 2100 is 0.5 wt% by weight of HDDA.

Acknowledgments

The authors would like to thank E.I. Panarina, S.K. Belus and M.A. Timokhin for technical assistance and A.M. Nemeryuk for valuable discussions. Measurements were performed using equipment of IREA shared analytical facilities center. This work was supported by Ministry of Science and Education of the Russian Federation, subsidy agreement N° 14.625.21.0040 dated 29.09.2016, project identifier RFMEFI62516X0040.

References

- [1] Pfaffinger M, Mitteramskogler G, Gmeiner R and Stampfl J 2015 Thermal debinding of ceramic-filled photopolymers *Mater Sci Forum* **825-826** 75
- [2] Mitteramskogler G, Gmeiner R, Felzmann R, Gruber S, Hofstetter C, Stampfl J, Ebert J, Wachter W and Laubersheimer J 2014 Light curing strategies for lithography-based additive manufacturing of customized ceramics *Additive Manufacturing* **1-4** 110
- [3] Harrer W, Schwentenwein M, Lube T and Danzer R 2017 Fractography of zirconia-specimens made using additive manufacturing (LCM) technology *J Eur Ceram Soc* **37** 4331
- [4] Dosovitskiy G A, Karpyuk P V, Evdokimov P V, Kuznetsova D E, Mechinsky V A, Borisevich A E, Fedorov A A, Putlyaev V I, Dosovitskiy A E and Korjik M V 2017 First 3D-printed complex inorganic polycrystalline scintillator *CrystEngComm* **19** 4260
- [5] Putlyaev V I, Evdokimov P V, Safronova T V, Klimashina E S and Orlov N K 2017 Fabrication of osteoconductive $\text{Ca}_{3-x}\text{M}_{2x}(\text{PO}_4)_2$ (M= Na, K) calcium phosphates bioceramics by stereolithographic 3D printing *Inorg Mater* **53** 529
- [6] Ievlev V M, Putlyaev V I, Safronova T V and Evdokimov P V 2015 Additive technologies for making highly permeable inorganic materials with tailored morphological architectonics for medicine *Inorg Mater* **51** 1295
- [7] Sokolov P S, Karpyuk P V, Dosovitskiy G A, Volkov P A, Lyskov N V, Slyusar I V and Dosovitskiy A E 2018 Nanostructured stabilized zirconia powders for solid oxide fuel cells *Russian Journal of Electrochemistry* Accepted for publication
- [8] Adzima B 2015 The Ember Printer: An Open Platform for Software, Hardware, and Materials Development. uv.ev WEST Conference; Redondo Beach, CA.
- [9] Kissinger H E 1956 Variation of peak temperature with heating rate in differential thermal analysis *J Res Natl Inst Stand Technol* **57** 2712
- [10] Takhor R L 1971 Advance in nucleation and crystallization of glasses; American Ceramics society, Columbus