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Direct inkjet printing of miniaturized luminescent YAG:Er^{3+} from sol-gel precursor

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ABSTRACT

This work focuses on demonstrating the fabrication of miniaturized scintillators based on rare earth activated YAG ceramics using the direct inkjet printing method. Erbium was chosen as the activator, and YAG sol-gel precursor inks were prepared under precise hydrolysis and polycondensation reactions. The precursors showed excellent control over rheology and surface tension, resulting in good printability. One of the most important challenges of inkjet printing of lines is the stability of lines. Line stability during printing is highly dependent on the printing frequency, drop spacing and substrate temperature. When a line was printed drop by drop, bulges were always observed during printing at 25 °C. This instability was significantly suppressed when the substrates were slightly heated. Adding polyvinylpyrrolidone to the precursor helped eliminate pores and cracks during firing. Crack-free YAG lines with ~200 nm thickness were obtained after firing. The photoluminescence of YAG:Er heat-treated at 1200 °C for 1 h was optimized for an Er concentration of 2 wt%. X-ray induced radioluminescence was dominated by emission lines at 398 and 567 nm.

1. Introduction

Polycrystalline ceramic and single-crystal scintillators are widely used in medical imaging, security inspection and high energy physics [1–3]. In many applications, the scintillator needs to be fabricated into specific geometries, *e.g.*, sheets [4] and fibers [5], to allow the optimal performance or to satisfy specific needs. For example, fiber scintillators have been used to measure the particle radiation dose for local cancer treatment [5]. Thus, it is highly desired to be able to fabricate miniaturized ceramic scintillators into complex geometries for specific applications, or as a part of integrated smart devices. However, due to the high hardness and brittleness of ceramics, they are difficult to fabricate into complex shapes in small dimensions (*e.g.* smaller than 100 μm) using the traditional bulk sintering and machining method [6].

Direct inkjet printing is a promising method to fabricate complex ceramic features because the ceramic precursors can be directly deposited at specific positions with high spacial resolution [7]. Many ceramic systems have been directly printed on substrates using the inkjet printing method [8–14]. Some complex parts, such as ZrO_2 mazes [8] and Si_3N_4 gear wheels [14], have been successfully fabricated using this method. However, commonly used inks are made of dispersed nanopowders in a liquid medium [8–10]. Besides the challenge of dispersion, the ceramic nanoparticles tend to concentrate at the edge of the drop during drying. This effect is known as the 'coffee ring' effect [15] and it results in uneven depositions of ceramic powder on the substrates. One can avoid the coffee ring effect by using a ceramic sol-gel precursor instead of a nanopowder dispersion as the ink for direct inkjet printing. Ceramic sol-gel precursors allow one to uniformly mix the solute molecules [16] thus avoiding concentration gradients in the printed drops. However, there are no systematic studies of the stability of the printed lines formed by the sol-gel inks. In addition, post processing and sintering efficiency of the printed sol-

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Table 1
The compositions of inks.

Ink	YW	YWP	YWEP
YAG yield	2.5%	2.5%	2.5%
Solvent	DI water	DI water	DI Water: ethanol = 7:1 by weight
PVP addition	No	Yes	Yes

gel lines have not been studied.

In this work, we aimed at demonstrating the use of direct inkjet printing to fabricate miniaturized rare earth activated YAG-based scintillators. Toward this goal, we used sol-gel derived YAG:Er^{3+} precursor to create lines of ~100 μm width. To obtain stable lines without bulges, we studied the effect of drop spacing, substrate moving speed and substrate temperature. Finally, the luminescence of sintered YAG:Er^{3+} was characterized by means of photo- and radioluminescence measurements.

2. Experimental procedure

The YAG precursor was prepared from aluminum isopropoxide (AIP, $Al(C_3H_7O)_3$, 98%, Alfa Aesar, MA, USA), aluminum nitrate nonahydrate (AN, $Al(NO_3)_3{\cdot}9H_2O$, 98%, Alfa Aesar, MA, USA) and yttrium nitrate hexahydrate (YN, $Y(NO_3)_3{\cdot}6H_2O$, 99.9%, Alfa Aesar, MA). Erbium nitrate pentahydrate (EN, $Er(NO_3)_3{\cdot}5H_2O$, 99.9%, Sigma, MO) was used as the starting material of the activator, and deionized (DI) water was used as the solvent. The molar ratio of AIP: AN: YN: DI water was 3.5:1.5:3:100 in order to make stoichiometric YAG. AN and YN were first dissolved in deionized water at room temperature by vigorously stirring for 30 min. Then AIP was added into the solution and stirred for 20 h. The solution was then refluxed at 80 °C for 5 h. Approximately 2/3 of the solvent was removed using a rotary evaporator (IKA RV 10 digital, China). The resultant solution was dried in an oven at 80 °C until viscous sols were obtained. The hydrolyzed sols were diluted with DI water or water-ethanol mixture solution using an ultrasonic processor. The YAG yield w is defined as $= m/m_0 \times 100\%$, where m is the mass of product after firing at 1200 °C for 1 h and m_0 is the mass of the ink before firing. The YAG yield in the inks was diluted to 2.5%. Polyvinylpyrrolidone (PVP, M_w 58,000 Da, Sigma-Aldrich, MO, USA) was added to relax stresses during srying. The PVP weight to the YAG yield was set to be 30%. Three different inks were investigated: YAG sol in water (YW); YAG sol in water with PVP (YWP); and YAG sol in water and ethanol with PVP (YWEP). The compositions of the final inks are shown in Table 1.

Fused silica plates were used as substrates. To clean them, they were ultrasonicated in the following sequence: DI water, ethanol and acetone, each for 10 min. After sonication, substrates were dried in an oven. A piezo-electric drop-on-demand printhead (MJ-AT-01-40, orifice diameter 40 μm, MicroFab Inc., Plano, TX, USA) was used in this study. The diameter of the generated droplet was about 60 μm, as measured using a high speed camera. The printing frequency was set to 200 Hz. To study the effect of droplet spacing, p, on the printing stability, the moving speed of the substrate was set as: $v = pf$ for a given p, where f is the printing frequency. The

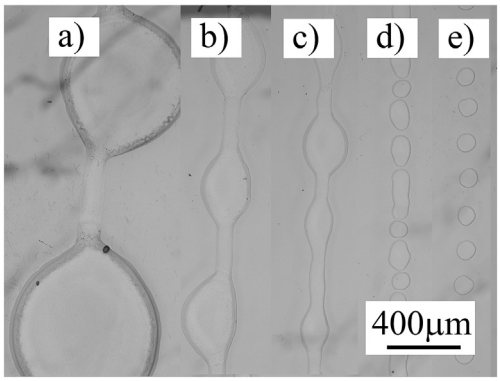

Fig. 1. Optical microscopy images of printed lines using YWP ink at room temperature with different drop spacing: a) 5 μm; b) 25 μm; c) 50 μm; d) 100 μm; d) 200 μm.

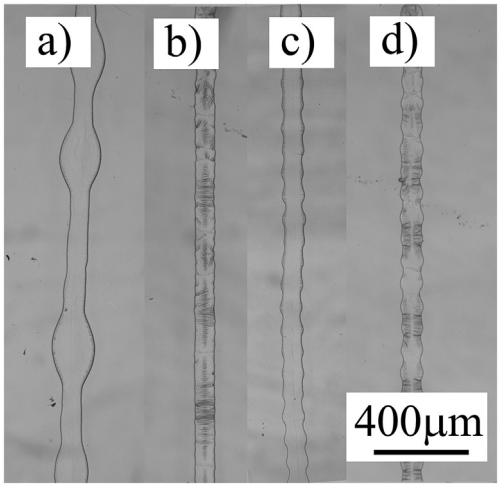

Fig. 2. Optical microscopy images of printed lines using YWP ink on heated substrates at different temperature and drop spacings: a) 57 °C, 50 μm; b) 95 °C, 50 μm; c) 76 °C, 100 μm; d) 95 °C, 100 μm.

viscosities of the inks were measured using an Ubbelohde viscometer (Cannon instrument, PA, USA) under water bath. The advancing and receding contact angles, and surface tension were measured using a Kruss drop shape analyzer (DSA100, Hamburg, Germany).

After printing, the samples were dried in an oven at 80 °C for 24 h and then fired at 1200 °C for 1 h with heating rate of 10 °C/min. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of YAG gel were carried out using a DTA7 analyzer (Perkin Elmer, MA) and a TGA7 analyzer (Perkin Elmer, MA). In order to identify the phases using X-ray diffraction (XRD, Rigaku Co., Ltd., Tokyo, Japan), YAG powder was prepared from YAG gel by firing at a target temperature for 1 h. The fully-dried printed patterns were characterized using optical microscope (Olympus BX60). The microstructure of printed patterns after firing was characterized using scanning electron microscope (SEM, Hitachi S4800, Hitachi,

Table 2
The rheology data and Z values of the inks.

Ink	Density (g/cm^3)	Viscosity (10^{-3} Pa·s)	Surface tension (mN/m)	Z	Advancing contact angle (°)	Receding contact angle (°)
YW	1.04	1.09	61.72 ± 0.08	5.17	47 ± 1	19 ± 2
YWP	1.04	1.11	64.94 ± 0.08	5.10	45 ± 1	15 ± 2
YWEP	1.01	1.51	42.50 ± 0.05	3.23	37 ± 2	15 ± 2

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