

## EXECUTIVE SUMMARY

The combinatorial approach for the discovery of new scintillating materials has been investigated using the wet-chemical (sol-gel) synthesis methods. Known scintillating compounds  $\text{Lu}_2\text{SiO}_5$  (LSO) and  $(\text{LuAl})\text{O}_3$  (LAO) and solid solutions in the systems of  $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$  ( $\text{CeO}_2$ -doped) (LYSO) and  $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$  ( $\text{CeO}_2$ -doped) (LYAO) were synthesized from sol-gel precursors. Sol-gel precursors were formulated from alkoxides and nitrates and acetates of the cations. Sol-gel solution precursors were formulated for the printing of microdot arrays of different compositions in the above oxide systems. Microdot arrays were successfully printed on C-cut and R-cut sapphire substrates using Biodot printer at Los Alamos National Laboratory (LANL). The microdot arrays were adherent and stable after heat-treating at  $1665^\circ\text{C}$  and had an average thickness of around  $2\mu\text{m}$ . X-ray fluorescence elemental mapping showed the arrays to be of the correct chemical composition. Sintered microdots were found to be highly crystalline by microscopic observation and x-ray diffraction. Scintillation was not clearly detectable by visual observation under UV illumination and by video observation under the scanning electron beam of an SEM. The microdots were either poorly scintillating or not scintillating under the present synthesis and testing conditions. Further improvements in the synthesis and processing of the microdot arrays as well as extensive scintillation testing are needed.

## EXPERIMENTAL

Experimental work involved two parts. First, the well known scintillating compounds, Ce-doped  $\text{Lu}_2\text{SiO}_5$  (or LSO) and Ce-doped  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  (LAO) [usually referred to as  $(\text{LuAl})\text{O}_3$  (LAO)], were synthesized by sol-gel method. Second, a combinatorial approach was applied to print by the same sol-gel method microdot arrays of the systems  $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$  ( $\text{CeO}_2$ -doped) (LYSO) and  $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$  ( $\text{CeO}_2$ -doped) (LYAO). Formation of the crystalline phases was confirmed by x-ray diffraction (XRD) and thickness of the heat treated dots was measured using surface profilometry (Alpha Step). The arrays were examined visually using an optical microscope at magnifications of 75 and 150X.

### Materials

**Chemicals:** Lutetium(III) nitrate hydrate:  $\text{Lu}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , FW 360.98 (Aldrich #436429-5G). Lutetium(III) acetate hydrate, 99.9% :  $(\text{CH}_3\text{CO}_2)_3\text{Lu} \cdot x\text{H}_2\text{O}$ , FW 352.10 (Aldrich # 325783-5G). Cerium (III) acetate hydrate, 99.9% :  $(\text{CH}_3\text{CO}_2)_3\text{Ce} \cdot x\text{H}_2\text{O}$  ( $x=1-3$ ) FW: 317.26 for  $x=0$ ; FW = 353.26 for  $x=2$  (Aldrich # 367753-50G). Aluminum nitrate nonahydrate, 99.997% :  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , FW 375.13 (Aldrich # 229415-10G). Tetraethylorthosilicate (TEOS), 98% :  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , FW 208.33 (Aldrich # 131903-500ML). Yttrium (III) acetate tetrahydrate, 99.9% (REO):  $\text{Y}(\text{OOCCH}_3)_3 \cdot 4\text{H}_2\text{O}$ , FW 338.09 (Alfa-Aesar Stock # 14565).

**Substrates:** Arrays were deposited onto optically polished fused silica and sapphire circles. The characteristics of the sapphire substrates were as follows:

**Table 1: Characteristics of Sapphire Substrates**

	<b>Sapphire R-Cut</b>	<b>Sapphire C-Cut</b>
Orientation	R-plane (1102)	C-plane (0001)
Diameter	19mm	19mm
Thickness	0.53mm	0.5mm
Epi-polish	One side	One side
Surface roughness	Ra < 0.3nm P-V < 3 nm	Ra < 0.3nm P-V < 3 nm

The substrates were cleaned (degreased) by Huang’s cleaning method. This cleaning method involves heating of the substrates in Solution A (water: ammonium hydroxide: hydrogen peroxide = 5:1:1) followed by heating in Solution B (water: hydrochloric acid: hydrogen peroxide = 5:1:1) at 80°C for 10 minutes in each solution and cleaning in de-ionized (DI) water.

**Microdot Array Deposition:**

The microdot arrays were printed using the Biodot system (Figure 1) which employs a positive displacement high resolution syringe pump that yields picoliter resolution of deposited solutions.

**Figure 1: Biodot Printer at Los Alamos National Lab**

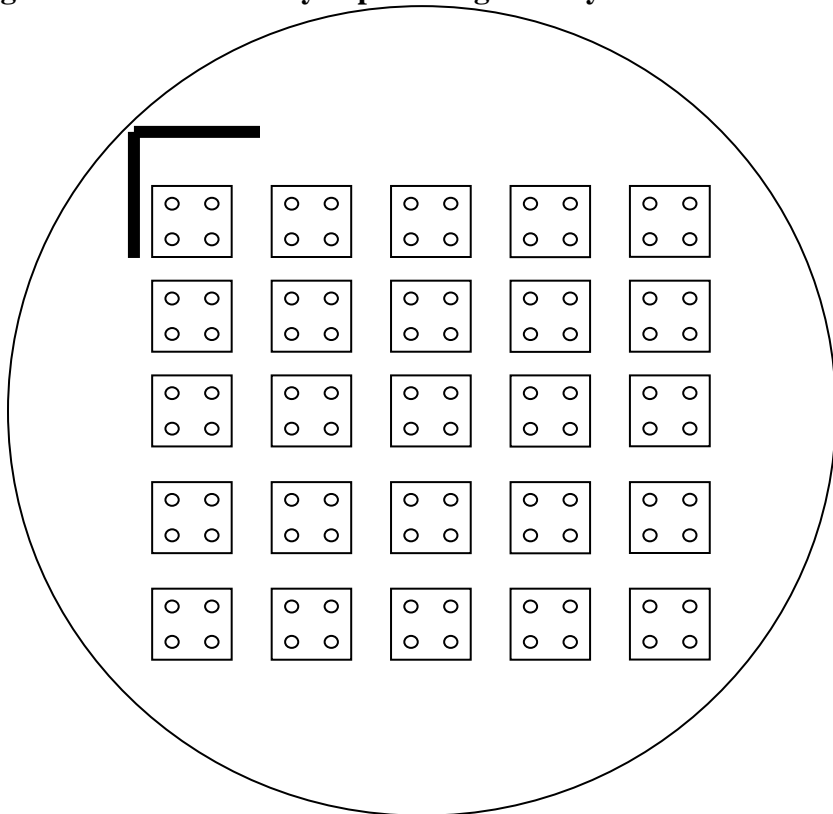


The pump is used in conjunction with a solenoid valve which opens and closes (opening times) to form the droplets and give them inertia to be released from the print tip. The printing tip size used was 100 microns which resulted in 20nL drops. For consistency and accuracy in drop formation the solution viscosities were kept water like with viscosities in the 50 centipoise range. The solutions were filtered prior to deposition down to 0.2µm which is the limit in particle size the dispensing tip can accommodate. The solution pH was kept between 3 and 10 which was within the stability range of the Biodot printing process.

The arrays were deposited in 2 x 2 “mini” arrays with 25 mini arrays per substrate as shown in the Figure 2. Each mini array represents a particular composition deposited in a 2 x 2 array of 20nL. Depositions started at the top left hand corner (beside right angle marking in Figure 2) and

then across five samples. This was repeated to complete the 10 x 10 array of drops. To correctly orientate the substrate the top left hand corner was scribed with a black 90° angle.

**Figure 2: Microdot array deposition geometry on circular substrate**



**Heat-Treatment Conditions for Deposited Arrays:**

The samples were first given a preheating to 750°C under a slow heating rate to maximize organic burn out and minimize cracking. The samples were then given a final heat treatment to 1665°C. The heat treatment atmosphere was air and the conditions were as follows:

**Table 2: Thermal Treatment of Arrays. Atmosphere Air**

	<b>Pre-Heating</b>	<b>Final Heating</b>
<b>Furnace</b>	Lindberg/Blue M box furnace (Max temp. 1100°C)	CM Furnace (MoSi <sub>2</sub> heating elements, 1700°C max)
<b>Atmosphere</b>	Air	Air
<b>Heating Rate</b>	6.9°C/min to 750°C	8.3°C/min to 1665°C
<b>Soaking</b>	0.5 hours at 750°C	2.0 hours at 1665°C
<b>Cooling Rate</b>	10°C/hour to 25°C	10°C/hour to 25°C

## RESULTS AND DISCUSSION

### Sol-Gel Synthesis of the Precursor Solutions:

Initial studies were done to demonstrate that scintillating compounds of interest could be easily prepared by sol-gel synthesis methods so that the same approach can be readily applied for the combinatorial synthesis of new compositions. At first, the well-known scintillating phases  $\text{Lu}_2\text{SiO}_5$  (Ce-doped) (LSO) and  $(\text{LuAl})\text{O}_3$  (Ce-doped) (LAO) were synthesized from solution (sol-gel) precursors.

Several wet-chemical (or sol-gel) approaches were considered.

Approach 1: Pechini or modified Pechini process involves using nitrates (or acetates) in aqueous solutions with complexing agents such as citric acid, acetic acid, ethylene glycol, etc. The pH of the solution - highly acidic and basic solutions – could cause problems in the microarray printer. Rapid decomposition of nitrate-organic components could lead to cracking of the films or the microdots becoming powder.

Approach 2: All-organic solution or mixture of alkoxides and some soluble salts can be used. Moisture sensitivity is a potential concern but may be stabilized with organic chelating agents like acetyl acetonate or acetic acid for example.

Approach 3: Colloidal oxide/hydrous oxide suspensions of the component. The stability of the suspension containing different colloids of the metal oxides could be an issue.

Due to the availability and/or the moisture sensitivity of some of the chemicals, the selected method was a combination of the modified Pechini process with alkoxide precursor tetraethyl orthosilicate (TEOS) for silica and acetates or nitrates for other oxides. Both acetates and nitrates can be used to prepare the sol-gel precursors to yield the phases LSO or LAO. However, acetates were found to be relatively more compatible for depositing uniform thin layers on substrates. Lu-Y-Si-Ce-Oxide compositions were prepared from lutetium acetate, yttrium acetate, cerium acetate and TEOS. Lu-Y-Al-Ce-Oxide compositions were prepared from lutetium acetate, yttrium acetate, aluminum nitrate and cerium acetate.

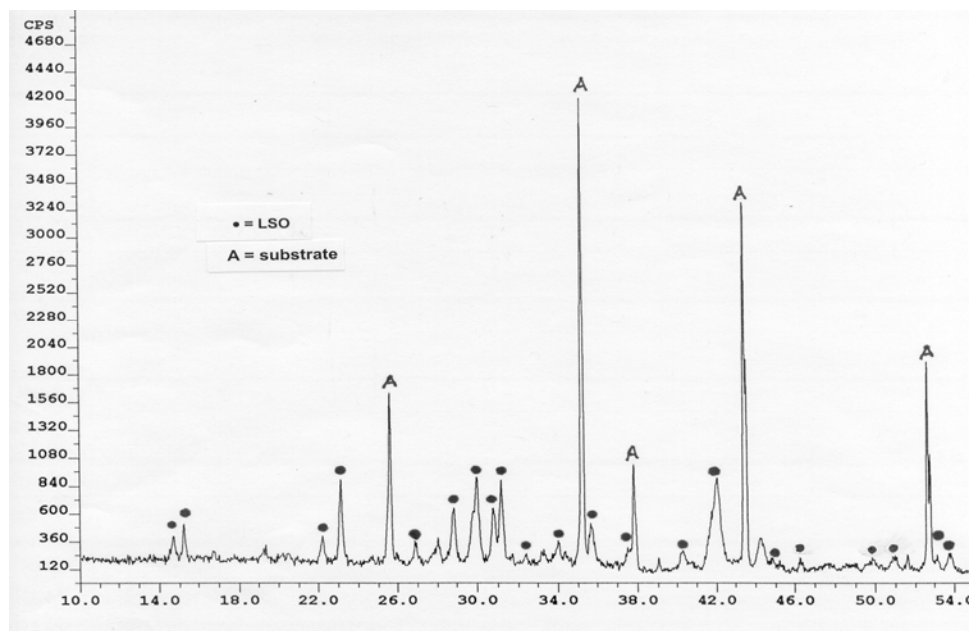
A summary of chemical compositions, sol-gel synthesis conditions and the phase development results are given in Table 3.

**Table 3: Sol-gel preparation conditions for LSO**

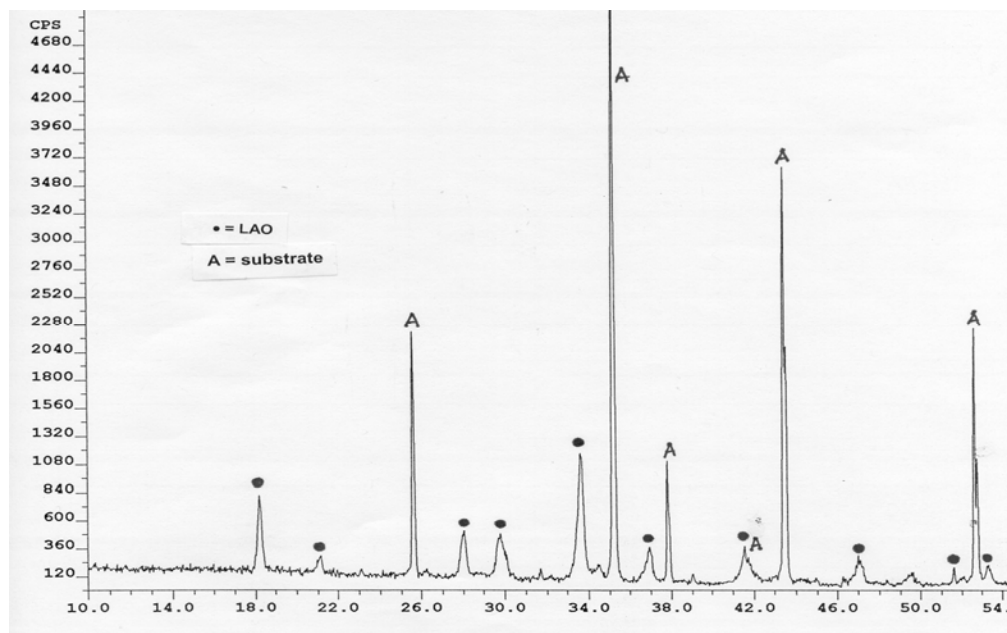
Sample #	Material form and Substrate	Description	Heating conditions	XRD Results
LSO-1	Powder	Lu-nitrate, TEOS, Ce-nitrate, Citric acid, Ethylene Glycol (clear soft gel)	1100 C ~30min & 1090 2 hrs	$\text{Lu}_2\text{SiO}_5$ (small), $\text{Lu}_2\text{Si}_2\text{O}_7$ (Large) $\text{Lu}_2\text{O}_3$ (large)
LSO-2	Layer deposited	Lu-nitrate, TEOS,	1090 C, 45	$\text{Lu}_2\text{Si}_2\text{O}_7$

	on Al <sub>2</sub> O <sub>3</sub> subs	Ce-nitrate, Ethylene Glycol (clear solution)	min	(Large) Lu <sub>2</sub> O <sub>3</sub> (large)
LSO-3	Layer deposited on Al <sub>2</sub> O <sub>3</sub> subs	Lu-nitrate, TEOS, Ce-nitrate, Ethylene Glycol (clear solution)	1090 C, 45 min	Lu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (Large) Lu <sub>2</sub> O <sub>3</sub> (large)
LSO-4	Layer deposited on silica glass (quartz glass) subs (layer not very adherent)	Lu-nitrate, TEOS, Ce-nitrate, Ethylene Glycol (clear solution)	1090 C, 45 min	Lu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (Large) Lu <sub>2</sub> O <sub>3</sub> (large)

The temperature at which the samples are heat-treated (calcination temperature) is very important. It appears that the Lu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> phase is dominant over the desired Lu<sub>2</sub>SiO<sub>5</sub> phase at shorter heating times and at temperatures below 1100°C. Heating at ~1100°C for three hours produced >90% of the LSO phase. It is found that the calcination temperature should be above 1100°C and the calcination times should be longer than 2 hours to form the scintillator phase (LSO). Effect of substrate (Al<sub>2</sub>O<sub>3</sub> and silica glass) was negligible, if any, in favor of the crystallization of the Lu<sub>2</sub>SiO<sub>5</sub> phase. XRD pattern of a layer of LSO on alumina substrate heat treated at 1200°C for 2 hours is presented in Figure 2. Similarly, a layer of LAO compositions heat-treated at 1200°C for 2 hours is given in Figure 3. It is clear from both the figures that the correct scintillating phase has formed.

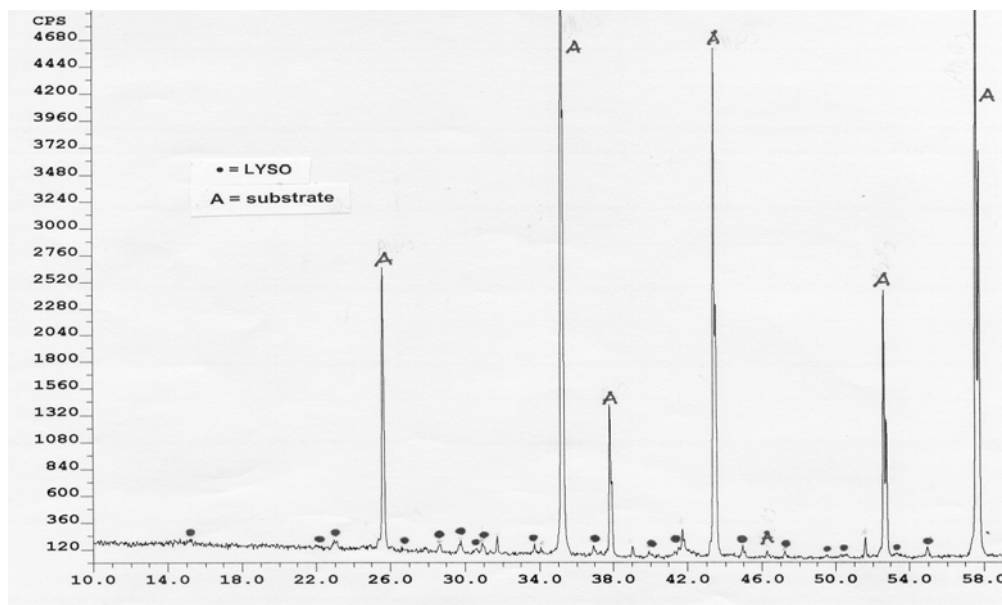


**Figure 2.** X-ray diffraction pattern for sol-gel film of composition Lu<sub>2</sub>SiO<sub>5</sub> (LSO) on alumina substrate. Film was deposited from a solution of TEOS-Lu-acetate and with cerium nitrate doping. Heated in air at 1200°C for 3 hours. Lines marked with • correspond to the scintillator phase Lu<sub>2</sub>SiO<sub>5</sub>.

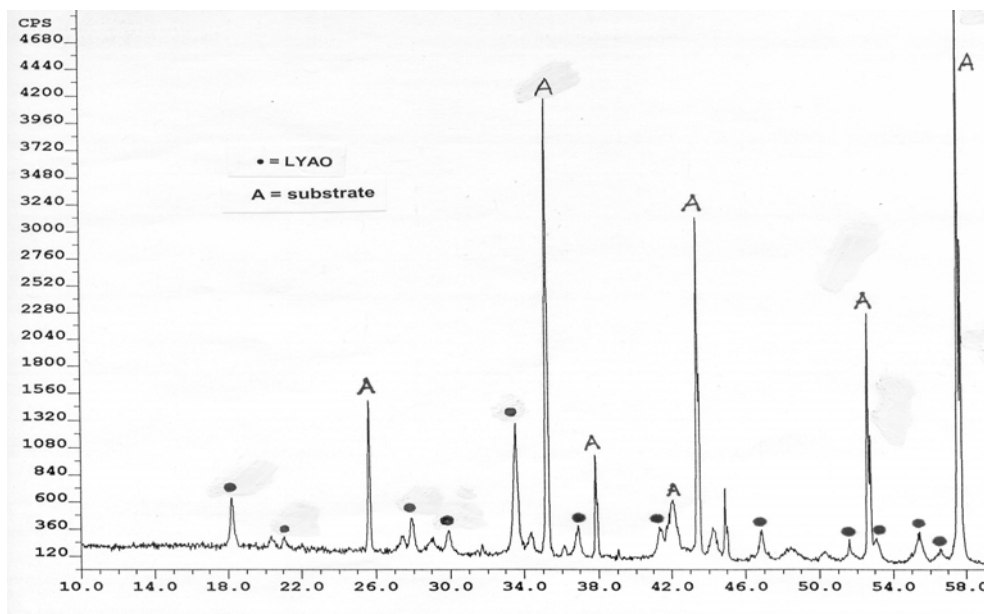


**Figure 3.** X-ray diffraction pattern for sol-gel film of composition  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  (LAO) on alumina substrate. Film was deposited from a solution of Lu-acetate and aluminum nitrate and with cerium nitrate doping. Heated in air at  $1200^\circ\text{C}$  for 3 hours. Lines marked with • correspond to the scintillating phase  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ .

The sol-gel approach was also employed for the solid solutions in the systems Lu-Y-Si-O (Ce) (i.e., LSO with  $\text{Y}_2\text{O}_3$ ) and Lu-Y-Al-O (Ce) (i.e., LAO with  $\text{Y}_2\text{O}_3$ ). Compositions corresponding to formulae  $(\text{Lu}_{0.48}\text{Y}_{0.48}\text{Ce}_{0.04})_2\text{SiO}_5$  and  $(\text{LuY})_{0.48}\text{Ce}_{0.04}\text{AlO}_3$  were prepared. The acetates were used for Lu, Y and Ce while nitrate was used for Al. TEOS was used for Si. The formation of the phases was confirmed by XRD. Figures 4 and 5 show the XRD patterns of the major phases of LSO and LAO on aluminum substrates (E. Bescher et al. *J. Sol-Gel Sci. and Technol.* 19,325-328, 2000). Apparently, the solid solutions are essentially of the same crystalline structure as the pure phases of the LSO or LAO.



**Figure 4.** X-ray diffraction pattern for sol-gel film of composition  $(\text{Lu}_{2-x}\text{Y}_x)\text{SiO}_5$  (LYSO) on alumina substrate. Film was deposited from a solution of TEOS-Lu-acetate and with cerium nitrate doping. Heated in air at  $1400^\circ\text{C}$  for 2 hours. Lines marked with • correspond to the scintillating phase  $\text{Lu}_2\text{SiO}_5$ .



**Figure 5.** X-ray diffraction pattern for sol-gel film of composition  $(\text{Lu}_{3-x}\text{Y}_x)\text{Al}_5\text{O}_{12}$  (LAO) on alumina substrate. Film was deposited from a solution of Lu-acetate, Yttrium acetate, and aluminum nitrate and cerium nitrate doping. Heated in air at  $1200^\circ\text{C}$  for 3 hours. Lines marked with • correspond to the scintillating phase  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ .

The above results demonstrate that the sol-gel approach chosen (modified Pechini process with alkoxide, acetates or nitrates) can be used to form scintillating materials in the Lu-Y-Si-O (Ce) or Lu-Y-Al-O (Ce) systems.

### Preparation of Solutions for Combinatorial Printing Microdot Arrays

For testing of the deposition of arrays the standard solutions for LAO and LSO were deposited by Biodot printing at LANL. The solutions used are listed in Table 3.

**Table 3: Solutions of Lao and LSO Prepared for Inkjet Printing at Los Alamos National Laboratory (LANL)**

Material	Solution code	Total solution volume	Main components of the solution	Composition <sup>1</sup>
Lutetium Silicon Oxide (Lutetium Orthosilicate) (Ce-doped)	LSO	20 ml	Lutetium acetate, Cerium acetate, Hydrolyzed TEOS, water, glacial acetic acid, ethanol, HCl	Lutetium acetate: 1.2215g Cerium acetate: 0.04238g Tetraethylorthosilicate [Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]: 0.3125g EtOH: 0.75 ml; HCl (0.1M): 0.1 ml H <sub>2</sub> O: 15 ml Glacial acetic acid: 5 ml
Lutetium Aluminum Oxide (Lutetium Aluminate) (Ce-doped)	LAO	20 ml	Lutetium acetate, Cerium acetate, Aluminate nitrate	Lutetium acetate: 0.8144 Cerium acetate: 0.0283 Aluminum nitrate: 0.7502 H <sub>2</sub> O: 12.5 ml Glacial acetic acid: 7.5 ml

<sup>1</sup> Amount of chemicals (mass or volume) given in table are calculated values. Actual amounts measured (weighed) are as close as possible to these values (weighed to ± 0.0005g).

### Characteristics of Microdots

Microdot arrays were initially deposited for the basic compositions LSO and LAO onto quartz and sapphire as shown in Table 4:

**Table 4: LAO and LSO Array Depositions**

Substrates	Composition	Array
Fused Silica	LAO	10 x10 array 20nL
Fused Silica	LSO	10 x10 array 20nL
C-Cut Sapphire	LAO	10 x10 array 20nL
C-Cut Sapphire	LSO	10 x10 array 20nL
R-Cut Sapphire	LAO	10 x10 array 20nL
R-Cut Sapphire	LSO	10 x10 array 20nL

For all the arrays scanned the distance between each spot (center to center) was 1 mm and the drop volume was 20nL. The arrays were heat treated to 1100°C for three hours. The compositions of the dots were determined using x-ray fluorescence (XRF) elemental mapping.



Figure 6 shows the array deposited on fused silica for the LAO system. The figure shows a well formed 10 x 10 array as seen by the magnification of one spot of the array.

**Figure 6: LAO array on fused silica**

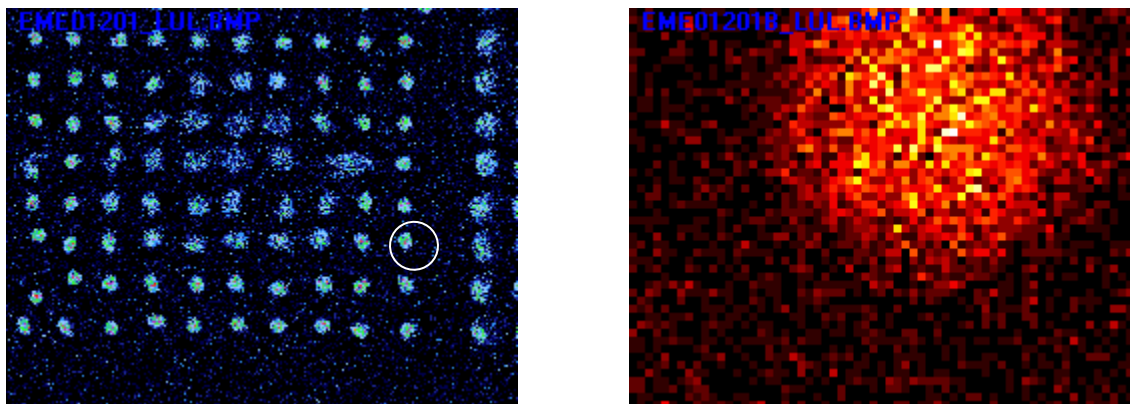


Figure 7 shows the XRF mapping of the dots shown in Figure 6. The Al, Lu and Ce peaks are present the Al is masked by the Si peak from the substrate and the rhodium peak is due to the x-ray source.

**Figure 7: XRF Elemental Mapping of LAO Array on Fused Silica**

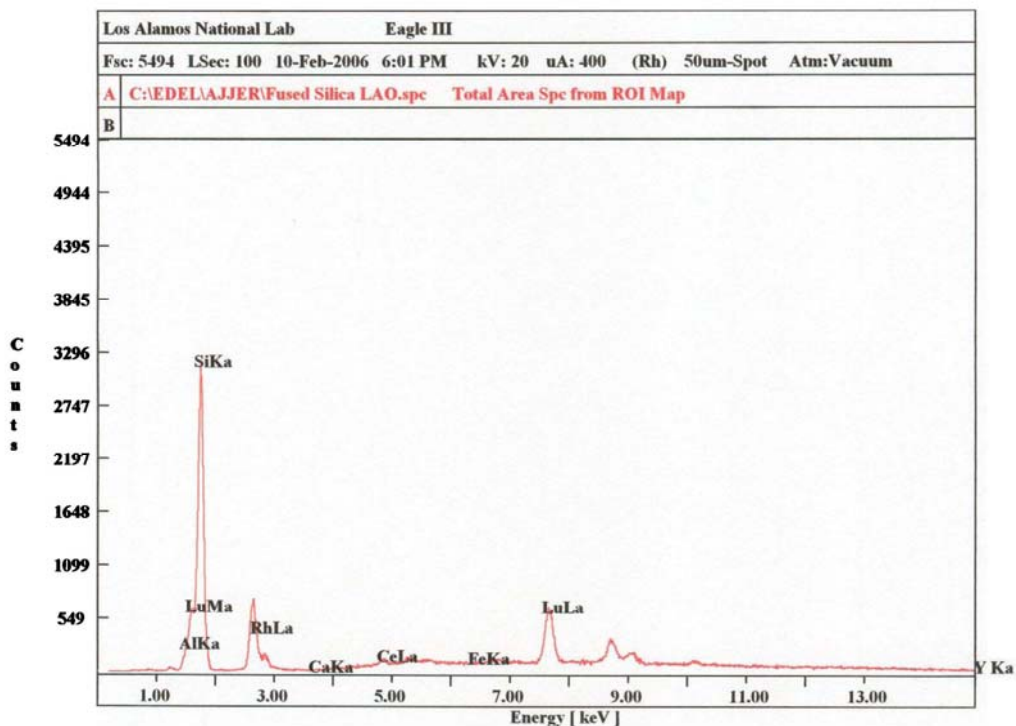
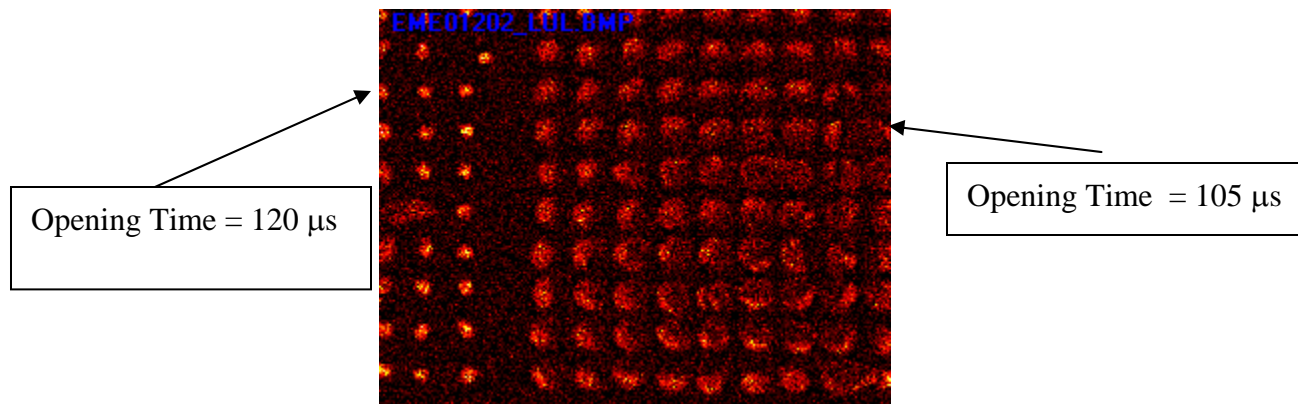


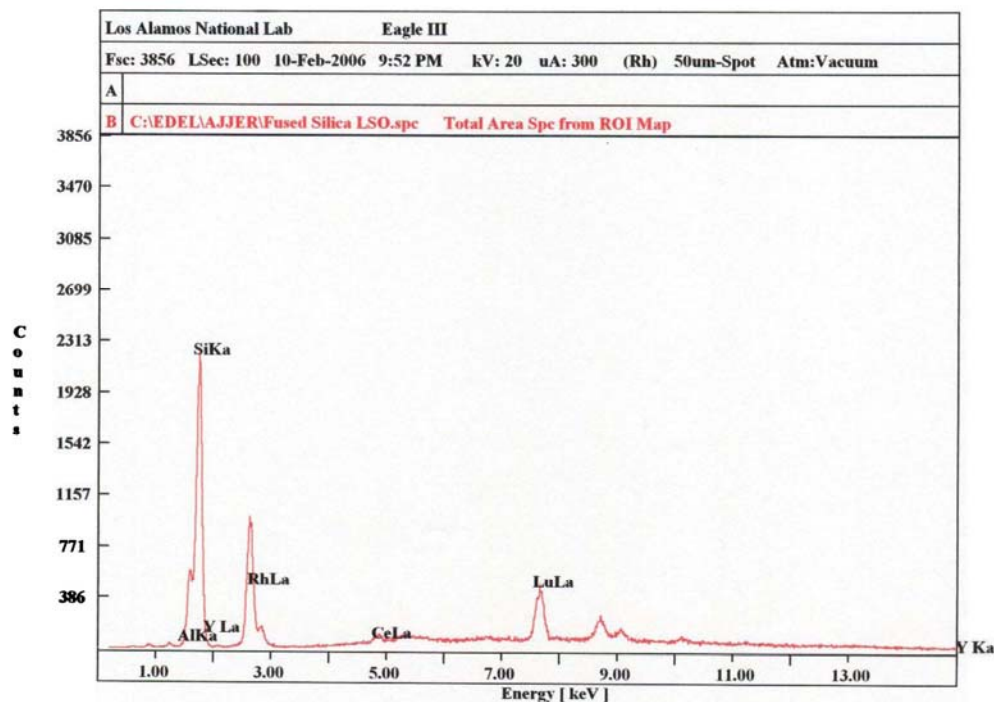
Figure 8 shows the effect of micro drop size as a function of opening times of 120 and 105 microseconds for the LSO deposited arrays on fused silica. As can be seen in Figure 8 the

opening times have an enormous effect on the size of the drop. The XRF elemental mapping of the dots is shown in Figure 9 which shows all the elements present.

**Figure 8: LSO array deposited on fused silica at opening times of 120 and 105 $\mu$ s.**

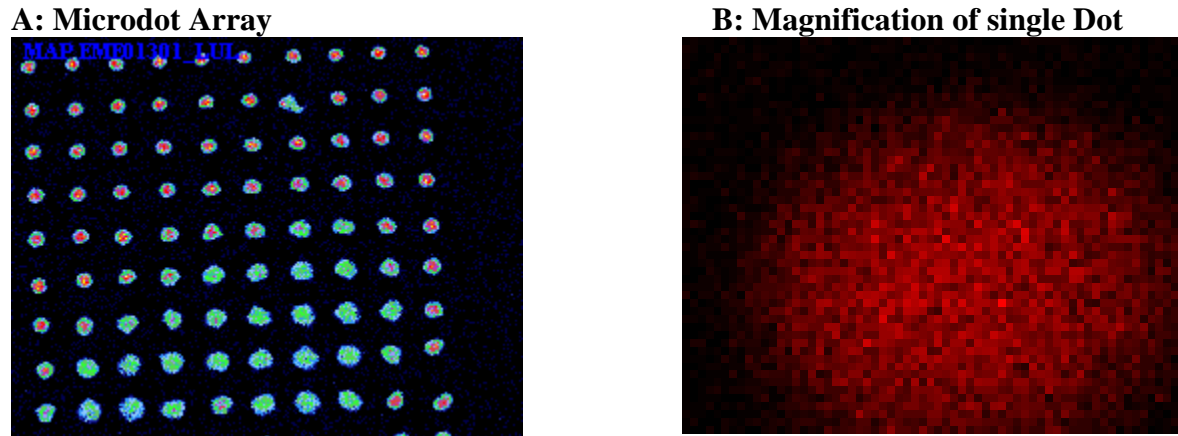


**Figure 9: XRF Elemental Mapping of LSO Array on Fused Silica**

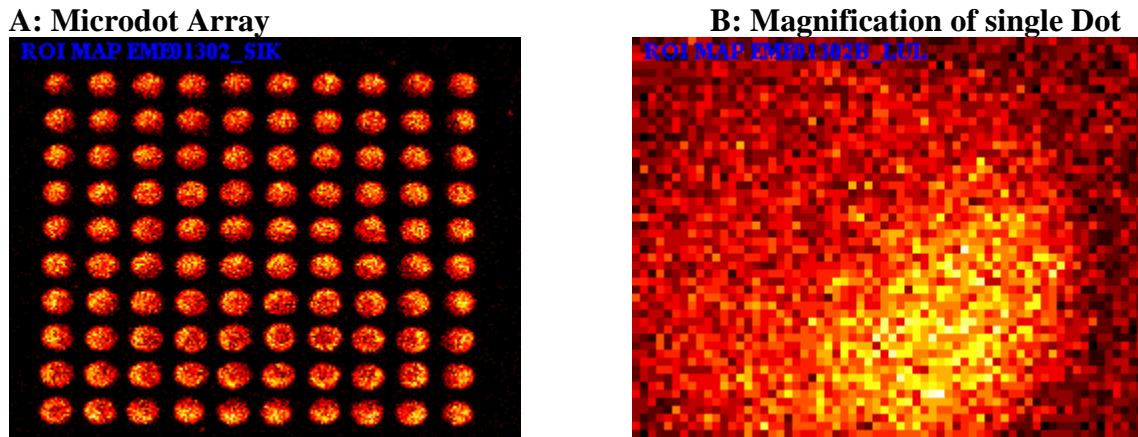


Figures 10, 11, 12 and 13 show the arrays for both LAO and LSO deposited on C and R cut sapphire. Both substrates give well defined spots after heat treatment. The sapphire R-cut seems to affect a higher surface tension on the droplets causing them to dry to smaller spots. This allows for more uniform drying as seen in the magnified spot in Figure 12.

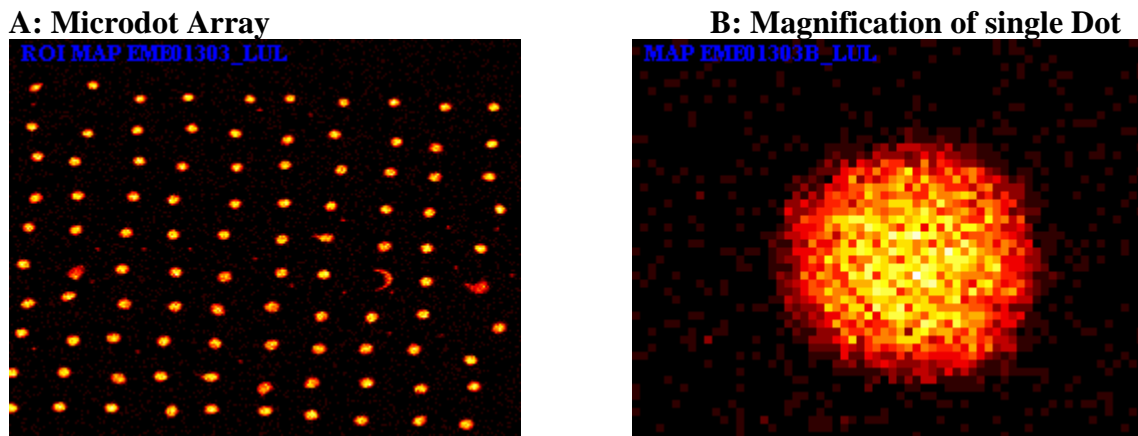
**Figure 10: LAO array deposited on C-cut Sapphire**



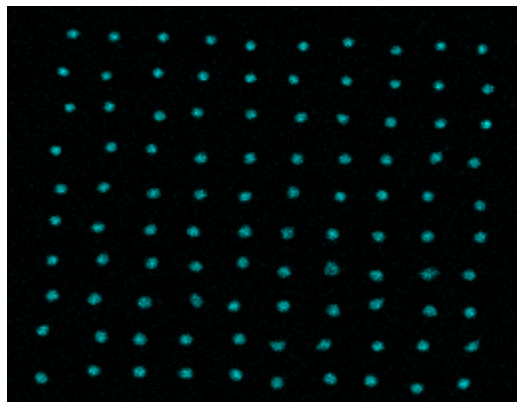
**Figure 11: LSO array deposited on C-cut Sapphire**



**Figure 12: LAO array deposited on R-cut Sapphire**



**Figure 13: LSO array deposited onto R-cut Sapphire**



Figures 14, 15 and 16 show the spectra for the XRF elemental mapping for the LAO, LSO on C-cut sapphire and LAO on R-cut sapphire respectively.

**Figure 14: XRF Elemental Mapping of LAO Array on C-cut Sapphire**

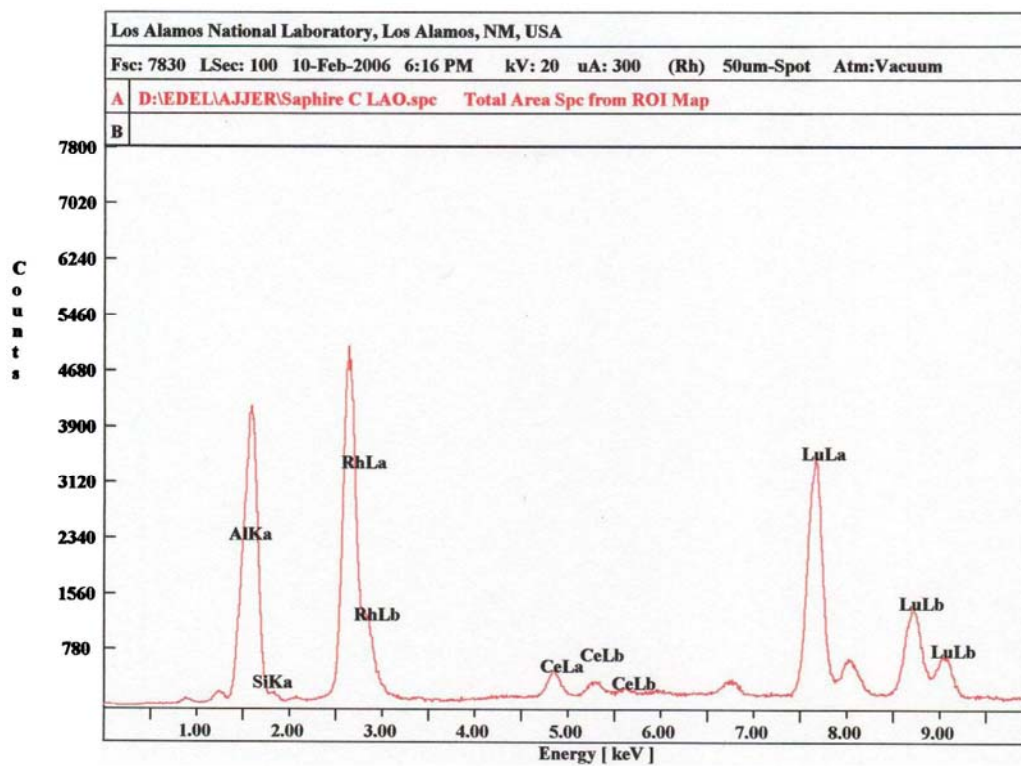


Figure 15: XRF Elemental Mapping of LSO Array on C-cut Sapphire

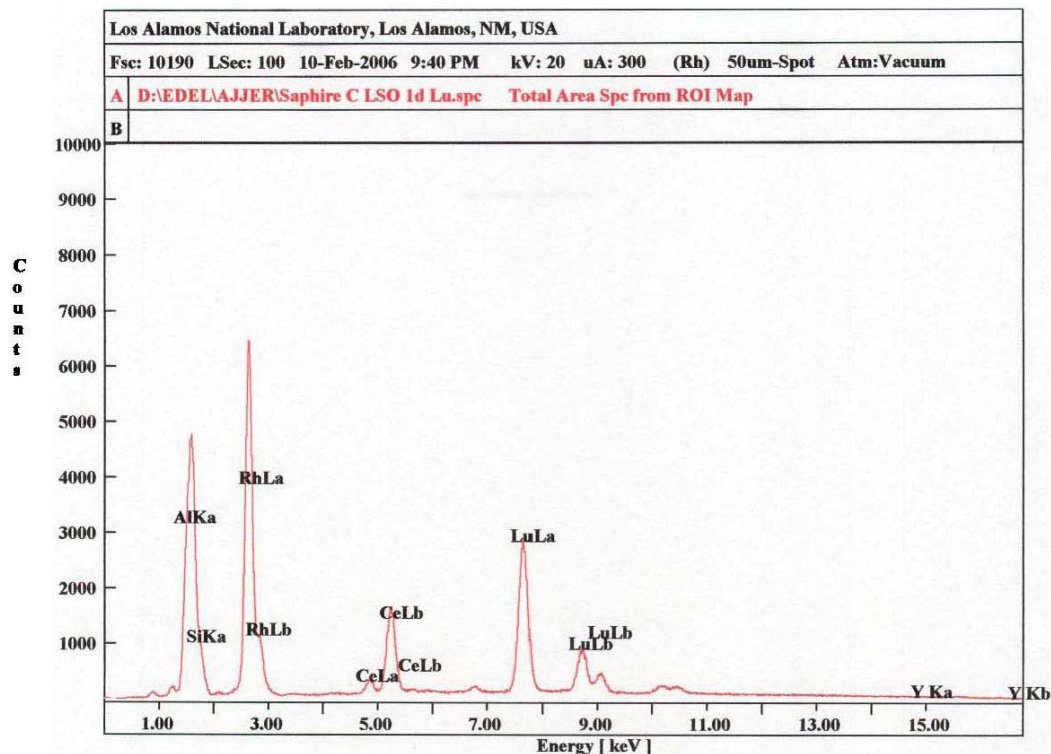
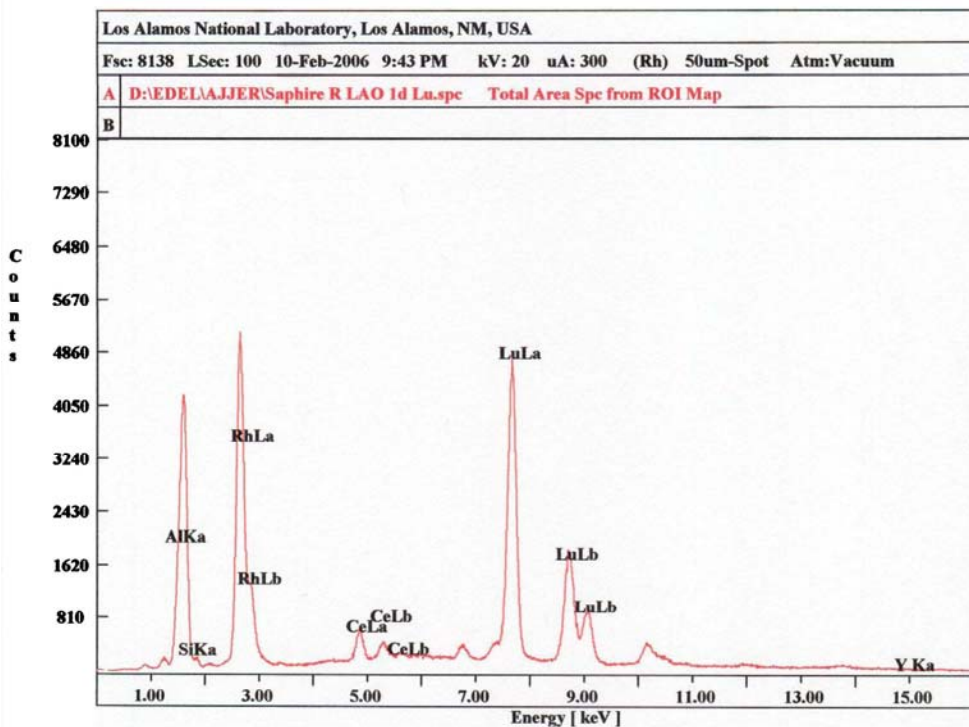


Figure 16: XRF Elemental Mapping of LAO Array on R-cut Sapphire

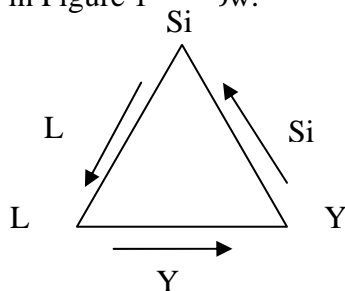


The sintered microdots were found to be highly crystalline by microscopic observation; however, scintillation was not clearly detectable by visual observation under UV illumination and by video observation under the scanning electron beam of a SEM.

Having successfully deposited arrays of LAO and LSO by Biodot printing using sol-gel solutions we used this technique to deposit Phase I proof of concept combinatorial arrays of LYSO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$ : Ce-doped) and LYAO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$ : Ce-doped).

### LYSO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$ : Ce-doped) System

The first class of materials prepared to deposit a combinatorial microdot array were the silicates, where both yttria-silicates lutetium silicates (LS) were doped with cerium. The ternary system is shown schematically in Figure 17.



**Figure 17: Schematic diagram of the system LYSO**

Both binary (along the edges of the triangle) and ternary (inside the triangle) compositions were prepared. Table 5 lists the mole ratios of the main oxides ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$ : Ce-doped) in the microdots and in the final sintered mixed oxide solid phase.  $\text{Ce}_2\text{O}_3$  dopant level was kept constant at 0.014 mole %. Each concentration from Table 5 was deposited on the substrates in 2 x 2 mini arrays of 20nL droplets. Twenty five different concentrations were deposited on individual C and R-cut sapphire substrates. Depositions started at the top left hand corner beside right angle as shown in Figure 2 to form the mini arrays.

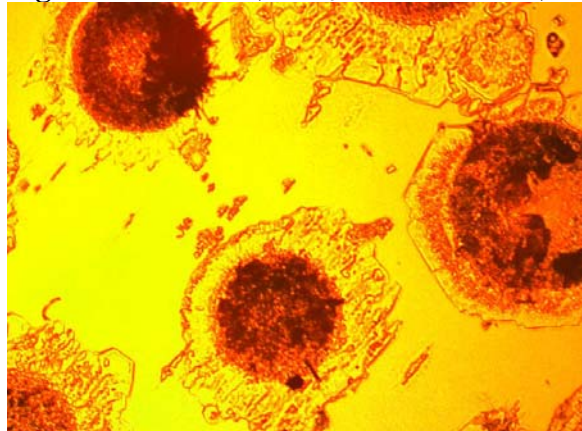
**Table 5: Molar ratios of the oxides in the compositions prepared by combinatorial method LYSO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$ : Ce-doped at 0.014 mole%)**

Composition #	$\text{Lu}_2\text{O}_3$ (mole)	$\text{Y}_2\text{O}_3$ (mole)	$\text{SiO}_2$ (mole)
1	0.1	0.9	0
2	0.1	0.8	0.1
3	0.1	0.7	0.2
4	0.1	0.6	0.3
5	0.1	0.5	0.4
6	0.1	0.4	0.5
7	0.1	0.3	0.6
8	0.1	0.2	0.7
9	0.1	0.1	0.8
10	0.1	0	0.9
11	0.2	0.8	0
12	0.2	0.7	0.1
13	0.2	0.6	0.2
14	0.2	0.5	0.3
15	0.2	0.4	0.4
16	0.2	0.3	0.5
17	0.2	0.2	0.6
18	0.2	0.1	0.7
19	0.2	0	0.8

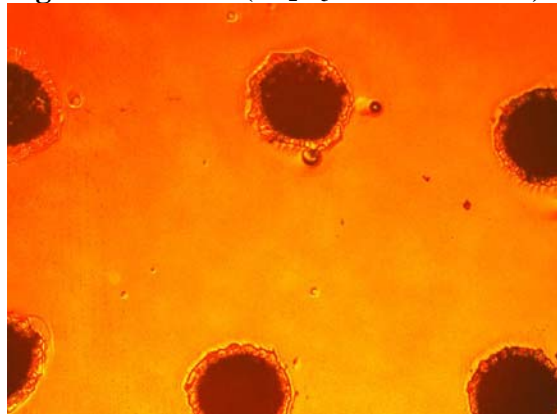
20	0.3	0.7	0
21	0.3	0.6	0.1
22	0.3	0.5	0.2
23	0.3	0.4	0.3
24	0.3	0.3	0.4
25	0.3	0.2	0.5
26	0.3	0.1	0.6
27	0.3	0	0.7
28	0.4	0.6	0
29	0.4	0.5	0.1
30	0.4	0.4	0.2
31	0.4	0.3	0.3
32	0.4	0.2	0.4
33	0.4	0.1	0.5
34	0.4	0	0.6
35	0.5	0.5	0
36	0.5	0.4	0.1
37	0.5	0.3	0.2
38	0.5	0.2	0.3
39	0.5	0.1	0.4
40	0.5	0	0.5
41	0.6	0.4	0
42	0.6	0.3	0.1
43	0.6	0.2	0.2
44	0.6	0.1	0.3
45	0.6	0	0.4
46	0.7	0.3	0
47	0.7	0.2	0.1
48	0.7	0.1	0.2
49	0.7	0	0.3
50	0.8	0.2	0
51	0.8	0.1	0.1
52	0.8	0	0.2
53	0.9	0.1	0
54	0.9	0	0.1
55	0.33	0.33	0.33
56	0.45	0.25	0.3
57	0.4	0.25	0.35
58	0.35	0.25	0.4
59	0.35	0.35	0.3
60	0.35	0.30	0.35
61	0.3	0.25	0.45
62	0.3	0.45	0.25
63	0.5	0.35	0.15
64	0.5	0.15	0.35
65	0.55	0.25	0.2
66	0.25	0.25	0.5
67	0	0.5	0.5
68	0	0.7	0.3
69	0	0.3	0.7

Figures 18 and 19 show typical examples of the arrays (at a magnification of 75X) from Table 5 deposited on C and R cut sapphire respectively. The arrays were in the composition range up to 0.3 mole  $\text{Lu}_2\text{O}_3$  (#1-25 as listed in the table). The arrays were heat treated to 1665°C as described in Table 2. On C cut sapphire the dots have spread more and are not as well defined as on R-cut sapphire. However, in both cases the dots are well adhered to the substrate and had an average thickness of about 2 $\mu\text{m}$  as determined by surface profilometry.

**Figure 18 : LYSO ( $\text{Lu}_2\text{O}_3$  0.14 to 0.3 mole) # 1-25 on C-cut sapphire at 75X**



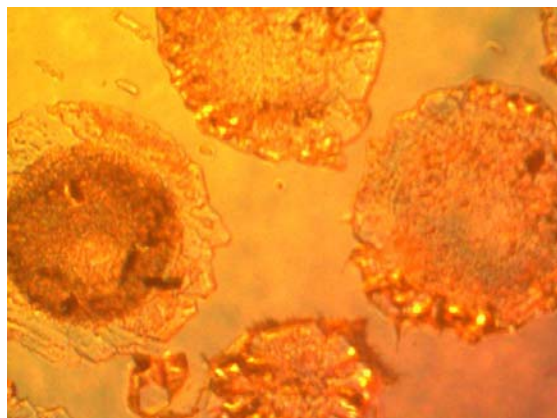
**Figure 19: LYSO ( $\text{Lu}_2\text{O}_3$  0.14 to 0.3 mole) # 1-25 on R-cut sapphire at 75X**



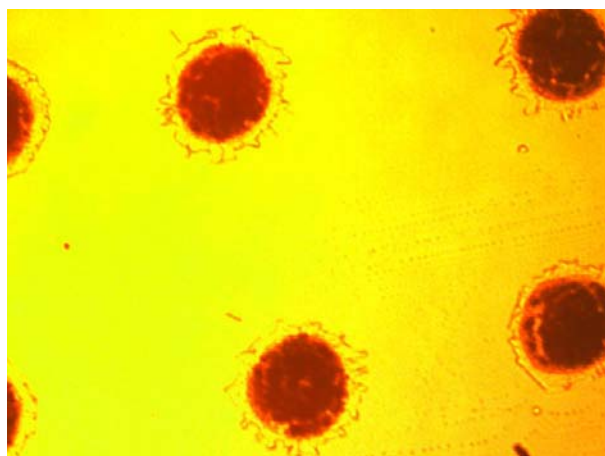
Increasing the mole concentration of  $\text{Lu}_2\text{O}_3$  to between 0.4 to 0.9 mole decreased the quality of the array dot as shown in Figure 20 where the dots spread more and were not as well defined on C-cut sapphire. This was not the case on R-cut sapphire as shown in Figure 21 which has a much smaller spot size which is well defined. Figure 22 shows an example of the crystalline nature of the dots.



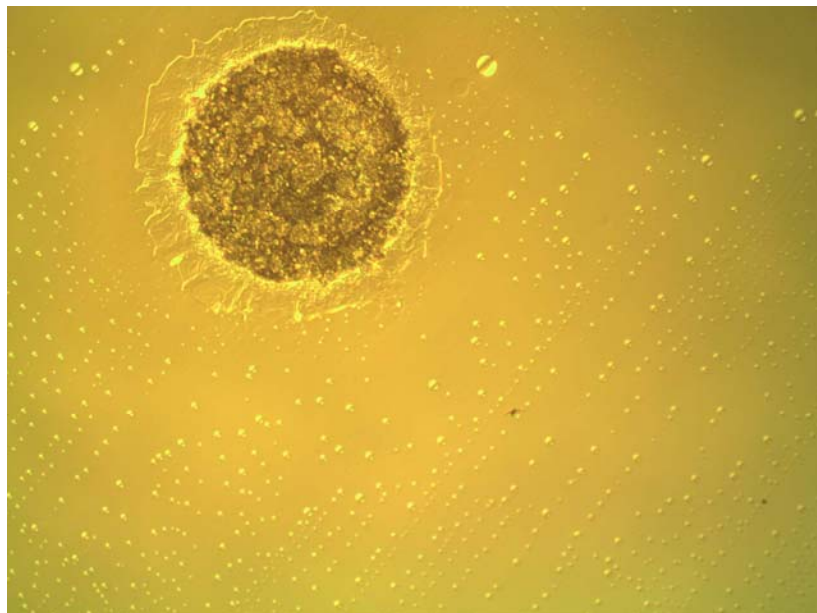
**Figure 20: LYSO ( $\text{Lu}_2\text{O}_3$  0.4 to 0.9 mole) # 28-53 on C-cut sapphire at 75X**



**Figure 21: LYSO ( $\text{Lu}_2\text{O}_3$  0.4 to 0.9 mole) # 28-53 on C-cut sapphire at 75X**

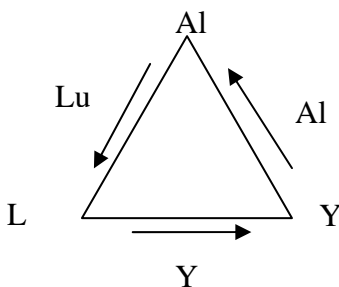


**Figure 22: LYSO dot at 150X on R-cut Sapphire showing crystalline properties**



### **LYAO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$ : Ce-doped) System**

The second class of materials deposited in microdot combinatorial arrays was the aluminates, where cerium doped yttria alumina matrix and lutetium alumina matrix were mixed. A schematic diagram of the system is shown in Figure 23 and the mole concentration of the deposited arrays is shown in table 6. The  $\text{Ce}_2\text{O}_3$  dopant level was kept constant at 0.014 mole%.



**Figure 23: Schematic of LYAO System**

Each concentration from Table 6 was deposited on the substrates in 2 x 2 mini arrays of 20nL droplets. Twenty five different concentrations were deposited on individual C and R-cut sapphire substrates. Depositions started at the top left hand corner beside right angle as shown in Figure 2 to form the mini arrays.

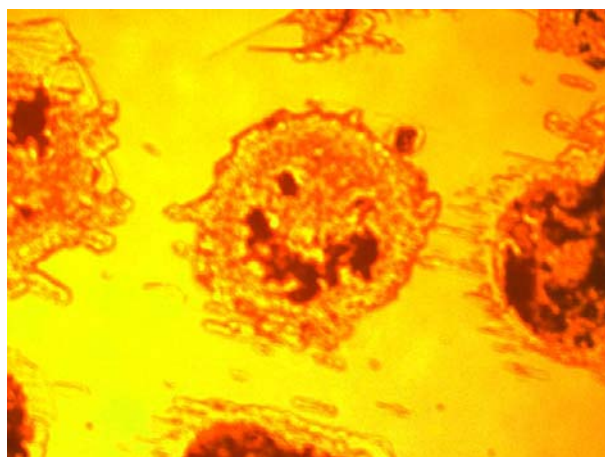
**Table 6: Molar ratios of the oxides in the compositions prepared by combinatorial method  
 LYAO:Ce (Lu<sub>2</sub>O<sub>3</sub> – Y<sub>2</sub>O<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub>: Ce-doped 0.014 mole%)**

Composition #	Lu <sub>2</sub> O <sub>3</sub> (mole)	Y <sub>2</sub> O <sub>3</sub> (mole)	Al <sub>2</sub> O <sub>3</sub> (mole)
1	0.1	0.9	0
2	0.1	0.8	0.1
3	0.1	0.7	0.2
4	0.1	0.6	0.3
5	0.1	0.5	0.4
6	0.1	0.4	0.5
7	0.1	0.3	0.6
8	0.1	0.2	0.7
9	0.1	0.1	0.8
10	0.1	0	0.9
11	0.2	0.8	0
12	0.2	0.7	0.1
13	0.2	0.6	0.2
14	0.2	0.5	0.3
15	0.2	0.4	0.4
16	0.2	0.3	0.5
17	0.2	0.2	0.6
18	0.2	0.1	0.7
19	0.2	0	0.8
20	0.3	0.7	0
21	0.3	0.6	0.1
22	0.3	0.5	0.2
23	0.3	0.4	0.3
24	0.3	0.3	0.4
25	0.3	0.2	0.5
26	0.3	0.1	0.6
27	0.3	0	0.7
28	0.4	0.6	0
29	0.4	0.5	0.1
30	0.4	0.4	0.2
31	0.4	0.3	0.3
32	0.4	0.2	0.4
33	0.4	0.1	0.5
34	0.4	0	0.6
35	0.5	0.5	0
36	0.5	0.4	0.1
37	0.5	0.3	0.2
38	0.5	0.2	0.3
39	0.5	0.1	0.4
40	0.5	0	0.5
41	0.6	0.4	0
42	0.6	0.3	0.1
43	0.6	0.2	0.2
44	0.6	0.1	0.3
45	0.6	0	0.4
46	0.7	0.3	0
47	0.7	0.2	0.1
48	0.7	0.1	0.2
49	0.7	0	0.3
50	0.8	0.2	0
51	0.8	0.1	0.1
52	0.8	0	0.2
53	0.9	0.1	0
54	0.9	0	0.1
55	0.33	0.33	0.33
56	0.45	0.25	0.3
57	0.4	0.25	0.35
58	0.35	0.25	0.4
59	0.35	0.35	0.3
60	0.35	0.30	0.35
61	0.3	0.25	0.45
62	0.3	0.45	0.25

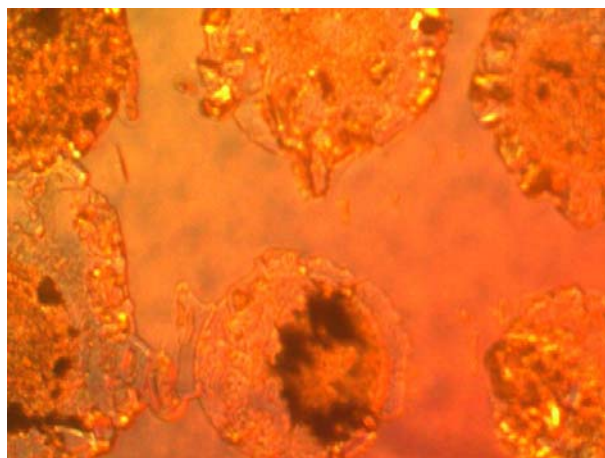
63	0.5	0.35	0.15
64	0.5	0.15	0.35
65	0.55	0.25	0.2
66	0.333	0.333	0.333
67	0	0.5	0.5
68	0	0.7	0.3
69	0	0.3	0.7

Figures 24 and 25 show the arrays on both C and R cut sapphire after firing to 1665°C for Lu<sub>2</sub>O<sub>3</sub> concentrations (mole) between 0.3 to 0.9. The LYAO system did not form well defined arrays as for the LYSO system and as seen in Figure 24 and 25 changing the substrate from C to R cut did improve or change the microdot geometry. However, the arrays that formed had good adhesion to the substrate and had an average thickness of about 2µm.

**Figure 24: LYAO (Lu<sub>2</sub>O<sub>3</sub> 0.3 to 0.9 mole) # 20-54 on C-cut sapphire at 75X**

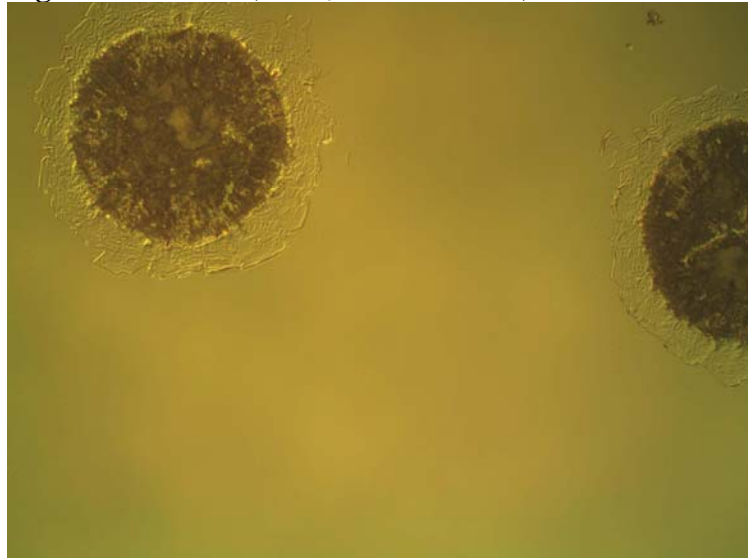


**Figure 25: LYAO (Lu<sub>2</sub>O<sub>3</sub> 0.3 to 0.9 mole) # 20-54 on R-cut sapphire at 75X**



On close microscopic examination of the array dots at 150X as shown in Figure 26 they appeared to be highly crystalline.

**Figure 26: LYAO ( $\text{Lu}_2\text{O}_3$  0.3 to 0.9 mole) # 20-54 on R-cut sapphire at 150X**



### **Scintillating Properties**

We had planned to get the micro-dot arrays analyzed at Lawrence Berkeley Laboratories (LBL) for scintillating properties using a scanning electron microscope fitted with a pulsed electron source and a photomultiplier tube to look at the optical emission but unfortunately LBL informed us that they were unable to do the analysis with their current set up.

As a result we were only able to visually inspect the arrays for scintillating behavior. For both the LYSO and LYAO arrays scintillation was not clearly detectable by visual observation under UV illumination and by video observation under the scanning electron beam of a scanning electron microscope. The microdots were either poorly scintillating or not scintillating under the present synthesis and testing conditions. Further improvements in the synthesis and processing of the microdot arrays as well as extensive scintillation testing are needed.

### **Conclusion:**

During Phase I of this program we were successful in demonstrating that scintillating materials in the  $\text{Lu}_2\text{SiO}_5$  (LSO) and  $(\text{LuAl})\text{O}_3$  can be prepared by the sol-gel method. Phase I proof of concept was demonstrated for a combinatorial approach to the deposition of microarray dots for the systems LYSO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{SiO}_2$ : Ce-doped) and LYAO:Ce ( $\text{Lu}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$ : Ce-doped). Extensive and more detailed testing of the arrays are needed to determine the scintillating materials of interest.