# Combinatorial Inorganic Chemistry

M. Anji Reddy
CY03D023

# Introduction

**Combinatorial chemistry-a technology for creating molecules en masse and testing them rapidly for desirable properties-continues to branch out rapidly. Compared with conventional one-molecule-at-a-time discovery strategies, combinatorial chemistry is a better way to discover new drugs, catalysts, and materials.**

# History

Combinatorial chemistry began with amino acids. In 1963, R. Bruce Merrifield developed a way to make peptides by solid-phase synthesis. But the field in its modern dimensions only began to take shape in the 1980s, when H. Mario Geysen, developed a technique to synthesize arrays of peptides on pin-shaped solid supports and Houghten developed a technique for creating peptide libraries in tiny mesh "tea bags" by solid-phase parallel synthesis.

**It becomes the basis for the explosion of solid phase organic synthesis, whereby molecular diversity can be introduced by producing a nearly infinite variety of heterocycles, steroids, carbohydrates, and soon, organometallics, all while tethered by one reversible link to a suitable polymeric support.**

## Now

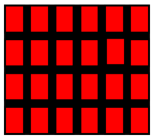
**The mass of a protein library….would exceed that of the universe by more than two hundred order of magnitude.**

# Combinatorial approach to inorganic materials

**Soon after the discovery of high –$T_c$ superconductors (HTSC),a huge number of investigators in many fields of science and technology expended huge amounts of energy and time on the preparation and characterization of mixed and sintered compounds with the presumed possibilityof a higher $T_c$. Some groups started applying the combinatorial approach to identify the superconductive materials. Thus the application of combinatorial chemistry to inorganic materials started here.**

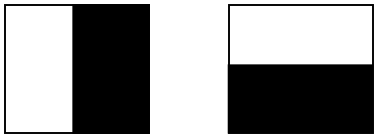
# Common terms

- Combinatorial Library



- Substrate

- Physical Mask

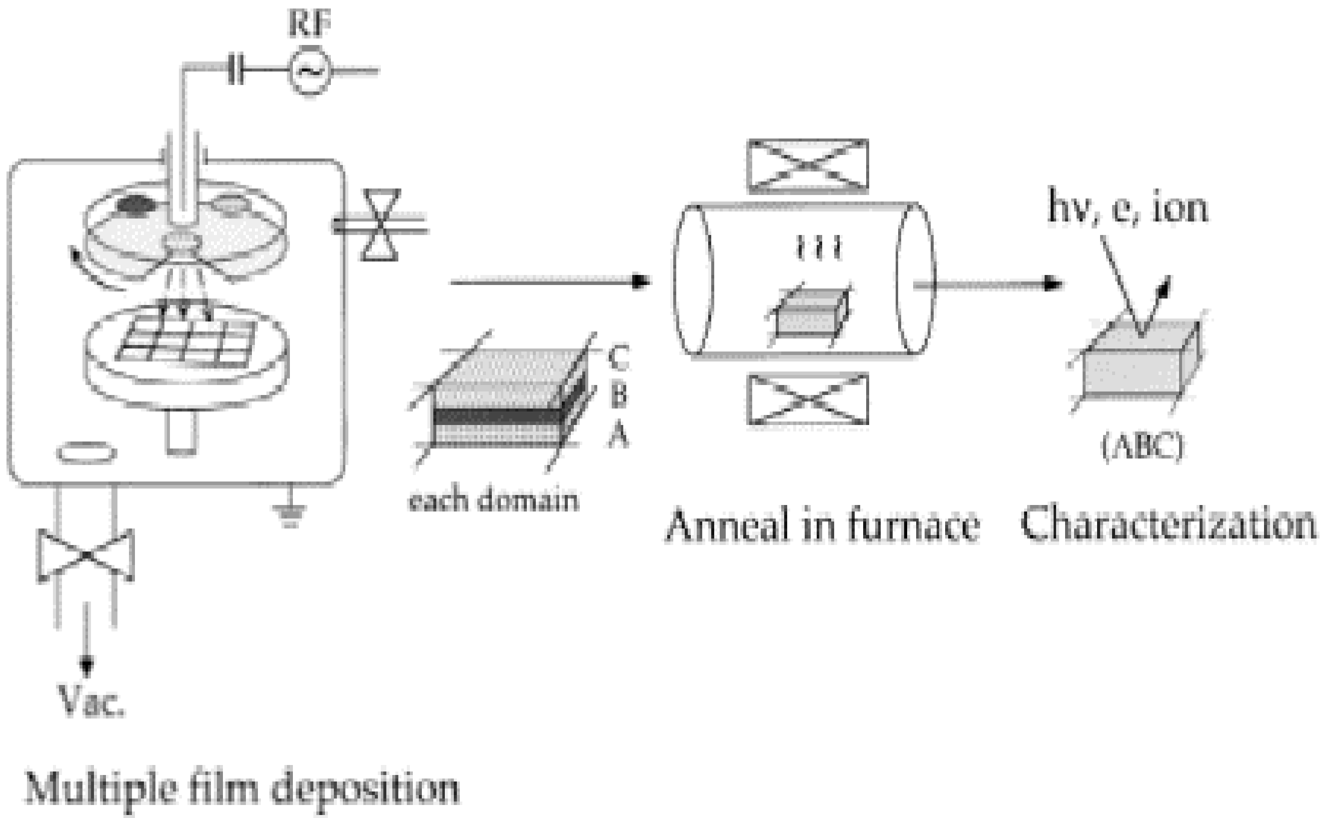


## Process

- Deposition of multiple solid state materials as thin - films

- Thermal processing of the Library

- High – throughput screening




**Reaction sequence for the conventional Combinatorial synthesis of oxide films**

Hideomi koinuma., Solid State Ionics108,1-7 (1998).

# Combinatorial Approach to Discover

**Superconductive**

**Magnetoresistance and**

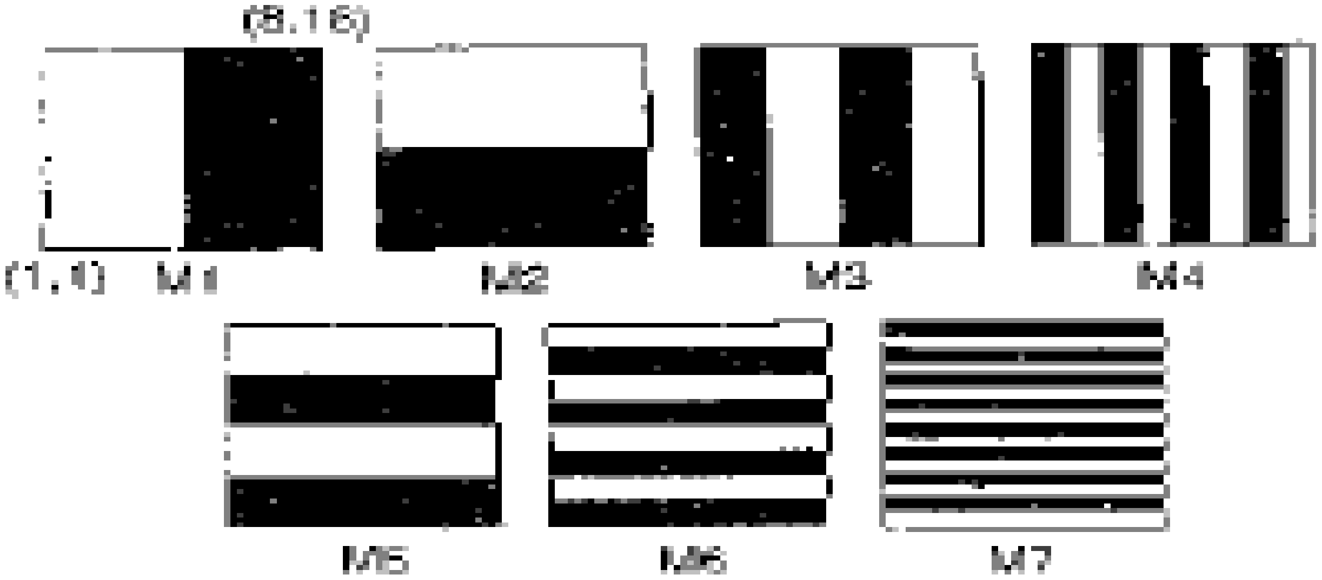
**Luminescent Materials**

# Identification of Superconducting Materials

**Substrates : MgO, $LaAlO_3$**

**Sputtering targets : CuO, $Bi_2O_3$, CaO, PbO, $SrCO_3$, $Y_2O_3$ $BaCO_3$**

**Masks :**




Peter G. Schultz et al., Science 268, 1738 (1995).

# Synthesis of 16-Member Library

- 1, Bi, M1; 2, Pb, M2; 3,Cu, M0; 4, Ca, M3; 5, Sr, M4. (deposition step, element, mask number).

- Each site 2mm by 2mm size

- 1:1 ratio relative to Cu

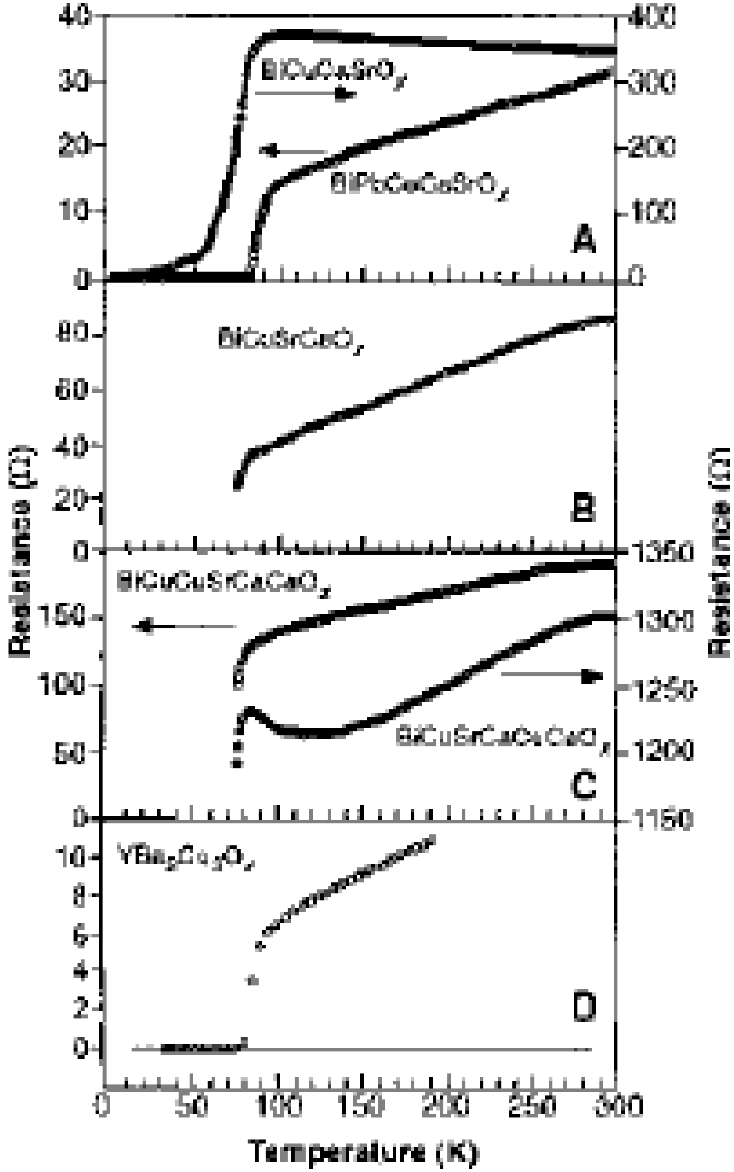
- Sintered at 840$^{o}$C

- Superconductivity found in $BiCuCaSrO_x$ ($T_c$=80K) and $BiPbCuCaSrO_x$ ($T_c$=90K).

- Then 128 member library was generated for further examine deposition sequence on the properties of $BiSrCaCuO_x$ .

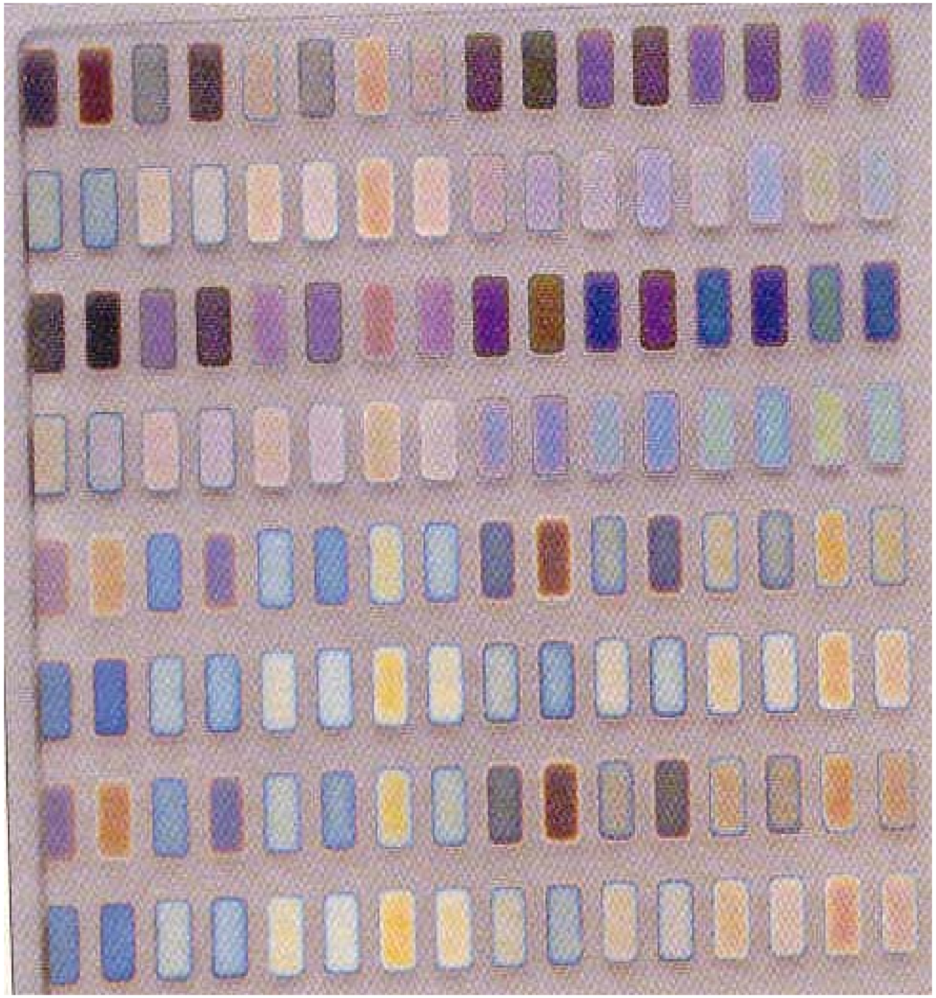
- Some films displayed distinct profiles of resistance Vs temperature.

  Ex; $BiCuSrCaCuCaO_x$ and $BiCuCuSrCaCaO_x$.



# Deposition sequence

1, Bi, M0; 2, Bi, M1;
3, Cu, M0; 4, Cu, M2;
5, Cu, M3; 6 Sr, M0;
7, Sr, M5; 8, Ca, M6;
9, Cu, M4; 10, Ca, M7;



# Identification of Magnetoresistance Materials

- **Colossal Magnetoresistance (CMR), with MR ratios [R(H=0)-R(H)]/R(H=0)**

  **$La_{0.60}Y_{0.07}Ca_{0.33}MnO_X$ - 99.0%**

  **$La_{0.67}Ca_{0.33}MnO_x$ - 99.9%**

  **$Nd_{0.7}Sr_{0.3}MnO_{3-x}$ - 99.99% are reported**

- **Combinatorial method is applied to examine the Mn analog of Co compounds**

# Synthesis of 128-Member Library

- Substrate: $LaAlO_3$ (001)
- Sputtering targets : $La_2O_3$, $Y_2O_3$,$BaCO_3$,$SrCO_3$,$CaCO_3$ and Co.
- Site Size : 1mm by 2mm
- L1 : RT to 200$^{o}$C; 300$^{o}$C 12h;cooled to RT;650$^{o}$C 1h; 850$^{o}$C 3h;900$^{o}$C 3h;cooled to RT.
- L2 : RT to 200$^{o}$C; 300$^{o}$C 15h;Cooled to RT; to 650$^{o}$C 2h; to 740$^{o}$C 13h;to 850$^{o}$C 1h; to 900$^{o}$C 0.5 h.

X.-D. Xiang et al., Science270,237 (1995).

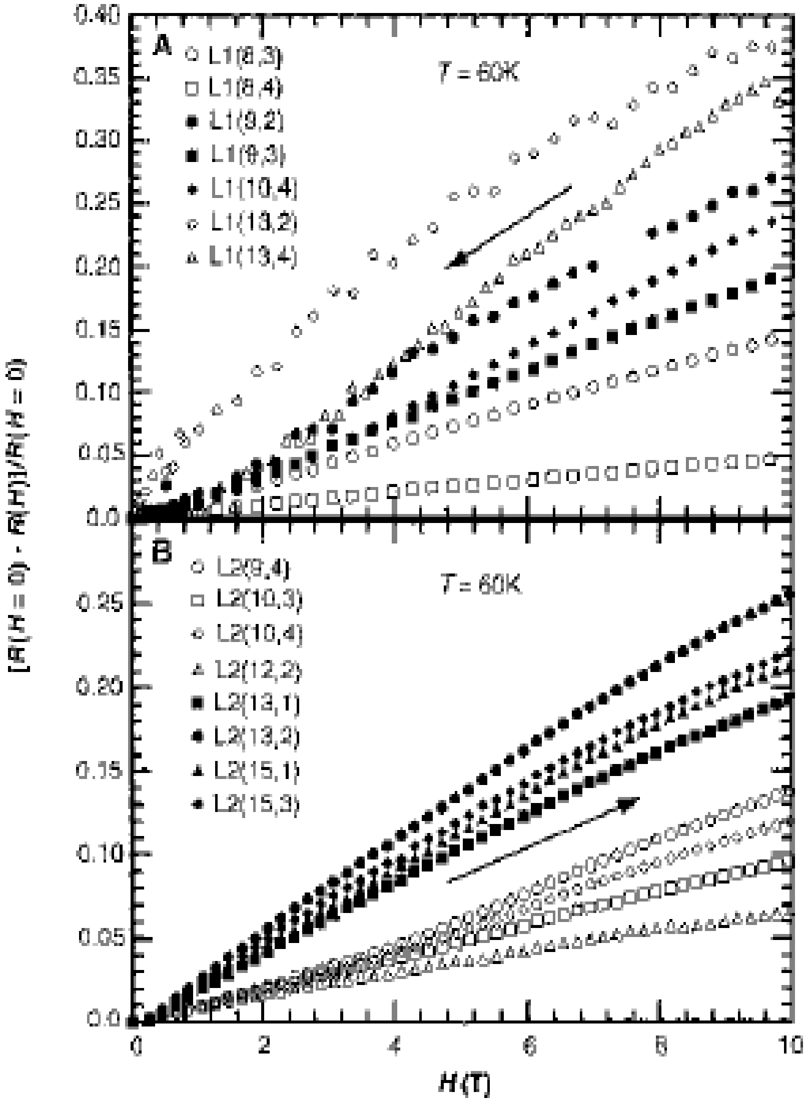
| | | La | | | | Y | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ba | | 1.38 / 0.62 | 1.14 / 0.62 ● | 0.89 / 0.62 | 0.64 / 0.62 | 0.5 / 0.62 | 1.0 / 0.62 | 0.74 / 0.62 | 1.24 / 0.62 | 16 |
| | | 1.0 / 0.45 ● | 0.83 / 0.45 ● | 0.65 / 0.45 ● | 0.47 / 0.45 | 0.36 / 0.45 | 0.72 / 0.45 | 0.54 / 0.45 | 0.9 / 0.45 | ↑ |
| | | 0.73 / 0.33 ● | 0.6 / 0.33 ● | 0.47 / 0.33 ● | 0.34 / 0.33 | 0.36 / 0.33 | 0.52 / 0.33 | 0.4 / 0.33 | 0.66 / 0.33 | |
| | | 0.61 / 0.27 ● | 0.5 / 0.27 ● | 0.39 / 0.27 ● | 0.28 / 0.27 ● | 0.22 / 0.27 | 0.45 / 0.27 | 0.33 / 0.27 | 0.55 / 0.27 | |
| Sr | | 1.38 / 0.62 | 1.14 / 0.62 ● | 0.89 / 0.62 ● | 0.64 / 0.62 ● | 0.5 / 0.62 | 1.0 / 0.62 | 0.74 / 0.62 | 1.24 / 0.62 | |
| | | 1.0 / 0.45 | 0.83 / 0.45 ● | 0.65 / 0.45 ● | 0.47 / 0.45 ● | 0.36 / 0.45 | 0.72 / 0.45 | 0.54 / 0.45 | 0.9 / 0.45 | |
| | | 0.73 / 0.33 | 0.6 / 0.33 ● | 0.47 / 0.33 ● | 0.34 / 0.33 ● | 0.26 / 0.33 | 0.52 / 0.33 | 0.4 / 0.33 | 0.66 / 0.33 | |
| | | 0.61 / 0.27 | 0.5 / 0.27 ● | 0.39 / 0.27 ● | 0.28 / 0.27 ● | 0.22 / 0.27 | 0.45 / 0.27 | 0.33 / 0.27 | 0.55 / 0.27 | |
| Ca | | 1.38 / 0.62 | 1.14 / 0.62 | 0.89 / 0.62 ● | 0.64 / 0.62 ● | 0.5 / 0.62 | 1.0 / 0.62 | 0.74 / 0.62 | 1.24 / 0.62 | |
| | | 1.0 / 0.45 | 0.83 / 0.45 | 0.65 / 0.45 | 0.47 / 0.45 ● | 0.36 / 0.45 | 0.72 / 0.45 | 0.54 / 0.45 | 0.9 / 0.45 | |
| | | 0.73 / 0.33 | 0.6 / 0.33 | 0.47 / 0.33 | 0.34 / 0.33 | 0.26 / 0.33 | 0.52 / 0.33 | 0.4 / 0.33 | 0.66 / 0.33 | |
| | | 0.61 / 0.27 | 0.5 / 0.27 | 0.39 / 0.27 | 0.28 / 0.27 | 0.22 / 0.27 | 0.45 / 0.27 | 0.33 / 0.27 | 0.55 / 0.27 | |
| Pb | | 1.38 / 0.62 | 1.14 / 0.62 | 0.89 / 0.62 | 0.64 / 0.62 | 0.5 / 0.62 | 1.0 / 0.62 | 0.74 / 0.62 | 1.24 / 0.62 | |
| | | 1.0 / 0.45 | 0.83 / 0.45 | 0.65 / 0.45 | 0.47 / 0.45 | 0.36 / 0.45 | 0.72 / 0.45 | 0.54 / 0.45 | 0.9 / 0.45 | |
| | | 0.73 / 0.33 | 0.6 / 0.33 | 0.47 / 0.33 | 0.34 / 0.33 | 0.26 / 0.33 | 0.52 / 0.33 | 0.4 / 0.33 | 0.66 / 0.33 | |
| | | 0.61 / 0.27 | 0.5 / 0.27 | 0.39 / 0.27 | 0.28 / 0.27 | 0.22 / 0.27 | 0.45 / 0.27 | 0.33 / 0.27 | 0.55 / 0.27 | 1 |
| | | 1 → | | | | | | | 8 | |

- **Computer controlled multichannel switching system used for resistivity measurements as a function of magnetic field and temperature**

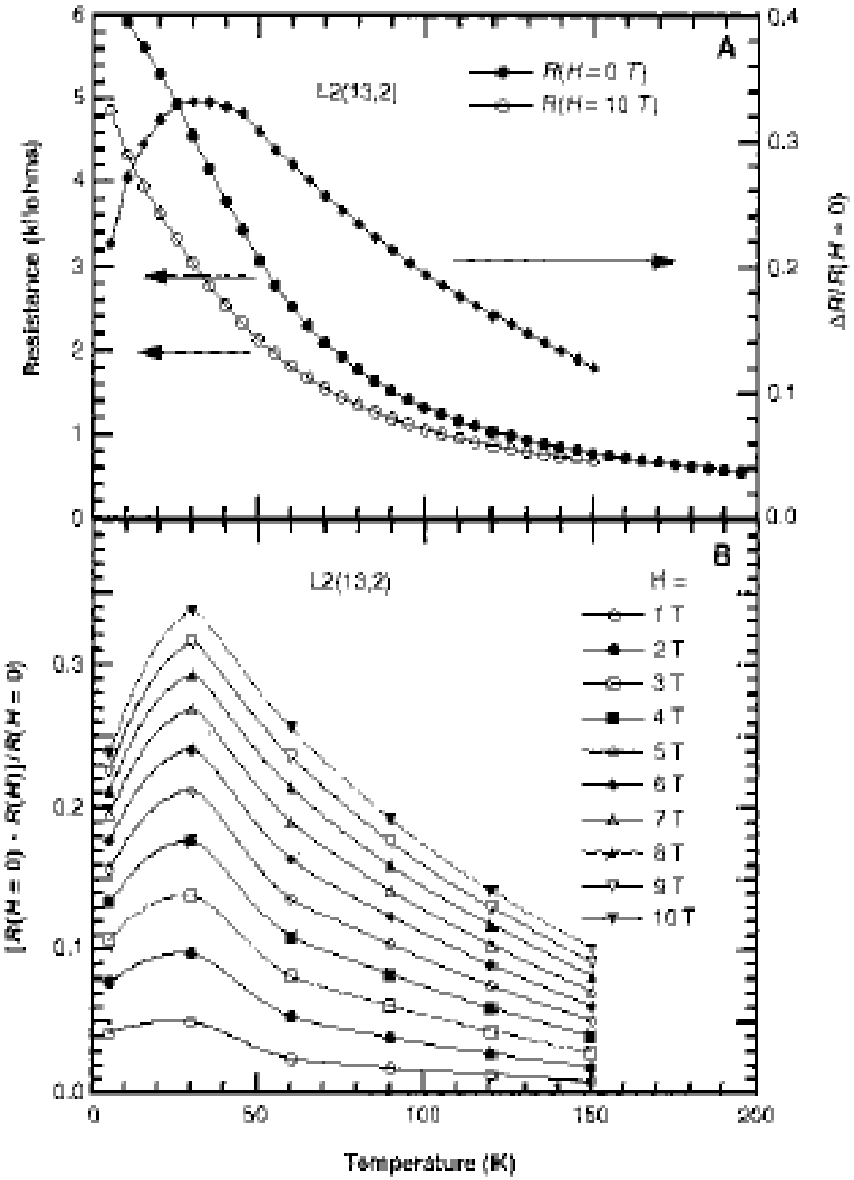
- **Large giant – MR effect identified in $La_xM_yCoO_\delta$; M=Ca,Sr,Ba**

- **The largest MR ratio measured in this library was 72%, obtained for sample L1 (15, 2) at T = 7K and H = 10T.**

- **The MR of the Co – containing compounds increases as the size of the Alkaline earth ion increases, in contrast to Mn containing compounds.**



A
B
T = 60K
L1(6,3)
L1(6,4)
L1(9,2)
L1(9,3)
L1(10,4)
L1(13,2)
L1(13,4)
L2(9,4)
L2(10,3)
L2(10,4)
L2(12,2)
L2(13,1)
L2(13,2)
L2(15,1)
L2(15,3)
[R(H = 0) - R(H)]/R(H = 0)
H (T)

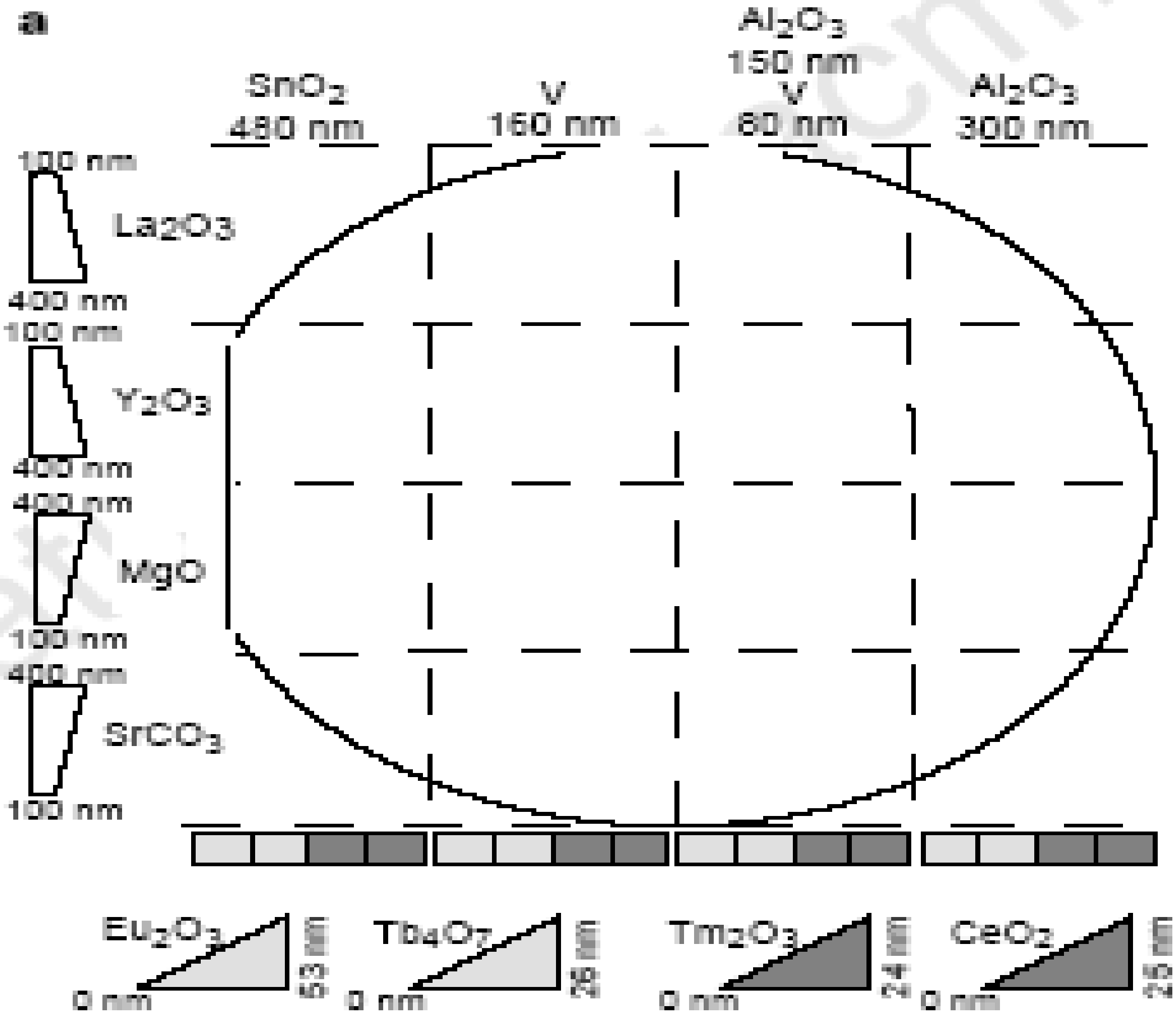
A
B
L2(13,2)
R(H = 0 T)
R(H = 10 T)
Resistance (kOhms)
ΔR/R(H = 0)
H =
1 T
2 T
3 T
4 T
5 T
6 T
7 T
8 T
9 T
10 T
[R(H = 0) - R(H)]/R(H = 0)
Temperature (K)

# Discovery and optimization of Luminescent Materials

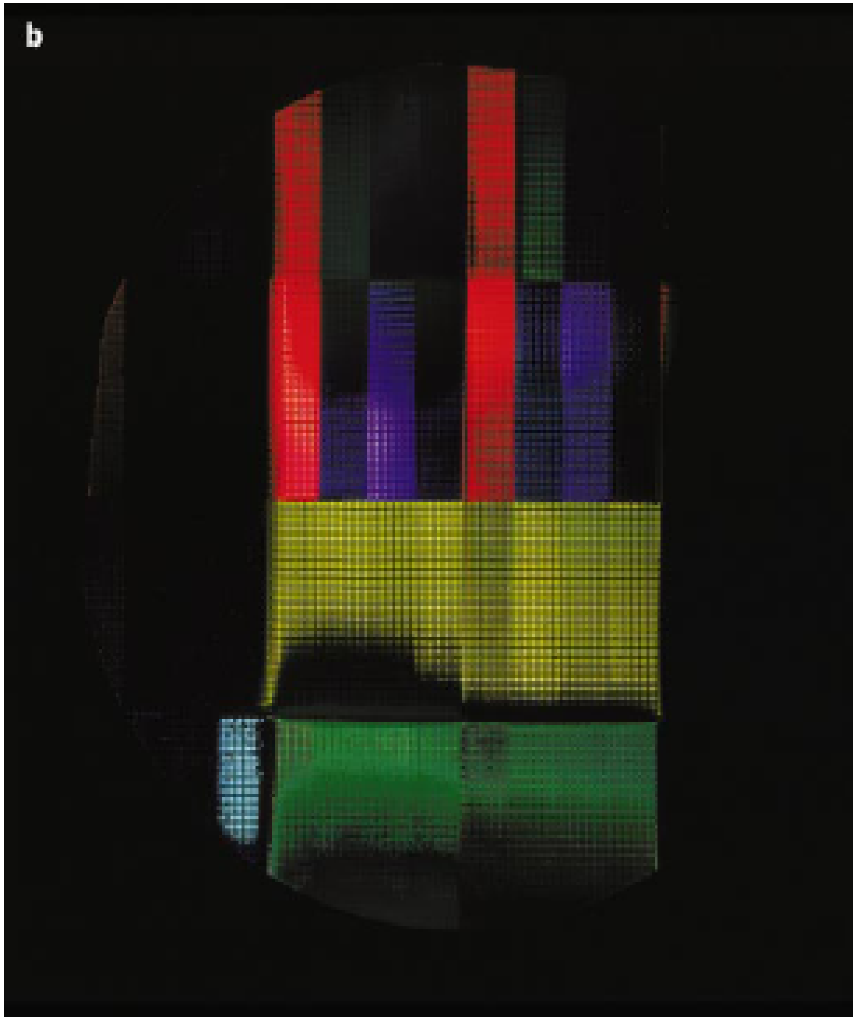
- Electron gun with $La_2O_3$, $Y_2O_3$, MgO, $SrCO_3$, $SnO_2$,V,$Al_2O_3$, $Eu_2O_3$,$Tb_4O_7$,$Tm_2O_3$ and $CeO_2$ Solid pellet target was used.

- Each site size 230ɥm and 420ɥm apart from each other.

- TP: 500°C 2h; 850°C 5h.


a
$Al_2O_3$
150 nm
$SnO_2$
480 nm
V
160 nm
V
80 nm
$Al_2O_3$
300 nm
100 nm
$La_2O_3$
400 nm
100 nm
$Y_2O_3$
400 nm
400 nm
MgO
100 nm
400 nm
$SrCO_3$
100 nm
$Eu_2O_3$
0 nm
53 nm
$Tb_4O_7$
0 nm
26 nm
$Tm_2O_3$
0 nm
24 nm
$CeO_2$
0 nm
25 nm

- Screening of Library was performed by imaging the visible emission of library with a CCD camera While exciting Luminescence with a 254nm source.




- Regions of library with the highest Luminescence were selected.

Xin Di Wu et al.,Nature389,944 (1997)

# Compositions, relative intensities, CIE chromaticity coordinates of selected red, green, blue phosphors

**Table 1 High-throughput screening results for extrinsic phosphor properties**

| CIE Chromaticity ($x$, $y$) | Ranks in library within colour group | Relative luminosity | Location in library ($i$, $j$) | Elemental components (molar ratio) |
|---|---|---|---|---|
| Red ($x$ = 0.6–0.7, $y$ = 0.3–0.4) | | | | |
| (0.65, 0.35) | 1 (out of 1,754) | 1.00 | 72, 58 | Y : V : Eu (0.34 : 0.60 : 0.06) |
| (0.65, 0.35) | 4 | 0.95 | 73, 58 | Y : V : Eu (0.35 : 0.59 : 0.06) |
| (0.64, 0.35) | 149 | 0.53 | 66, 106 | Y : V : Eu (0.37 : 0.29 : 0.30 : 0.04) |
| (0.64, 0.34) | 380 | 0.27 | 26, 110 | Al : La : V : Eu (0.34 : 0.31 : 0.28 : 0.07) |
| (0.64, 0.35) | 516 | 0.21 | 4, 606 | La : V : Eu (0.51 : 0.43 : 0.06) |
| Green ($x$ = 0.0–0.4, $y$ = 0.4–0.8) | | | | |
| (0.40, 0.51) | 1 (out of 121) | 1.00 | 102, 140 | Al : Mg : V : Ce (0.21 : 0.61 : 0.17 : 0.01) |
| (0.38, 0.53) | 1 | 1.00 | 103, 115 | Al : Mg : V : Tb (0.22 : 0.60 : 0.17 : 0.01) |
| (0.37, 0.51) | 6 | 0.73 | 144, 54 | Mg : V : Eu (0.34 : 0.63 : 0.03) |
| (0.36, 0.44) | 44 | 0.59 | 51, 119 | Al : Y : V : Tb (0.43 : 0.19 : 0.35 : 0.03) |
| (0.35, 0.41) | 93 | 0.50 | 42, 117 | Al : La : V : Tb (0.32 : 0.26 : 0.40 : 0.02) |
| Blue ($x$ = 0.0–0.3, $y$ = 0.0–0.2) | | | | |
| (0.18, 0.09) | 1 (out of 728) | 1.00 | 82, 78 | Y : V : Tm (0.41 : 0.57 : 0.02) |
| (0.18, 0.08) | 3 | 0.94 | 84, 78 | Y : V : Tm (0.42 : 0.56 : 0.02) |
| (0.19, 0.11) | 29 | 0.76 | 68, 126 | Al : Y : V : Tm (0.38 : 0.31 : 0.30 : 0.01) |
| (0.19, 0.11) | 37 | 0.73 | 70, 126 | Al : Y : V : Tm (0.37 : 0.30 : 0.32 : 0.01) |
| (0.21, 0.13) | 307 | 0.32 | 70, 80 | Y : V : Tm (0.35 : 0.63 : 0.02) |

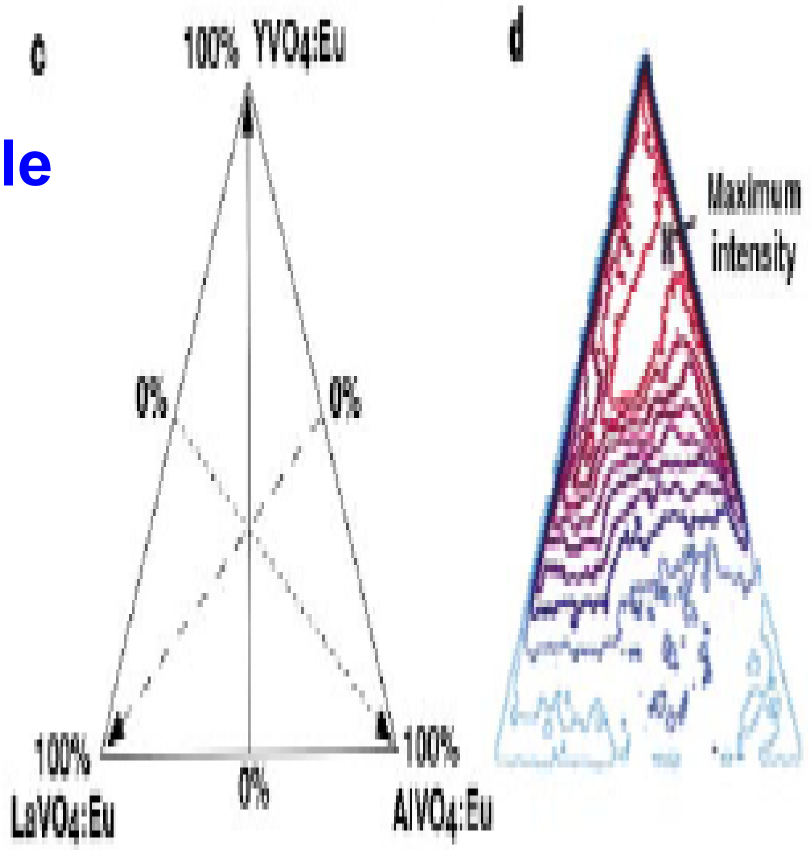


**The highest efficiency materials with desirable chromaticity identified in the initial high-density exploration library were red phosphors with ($Eu^{3+}$ doped)$Y_{1-m}Al_mVO_4$ as the host.**

- To optimize these compounds second library was designed and synthesized to focus on best host compositions. It includes La.

- This library explored all possible $Y_{0.95-m-n}Al_nLa_mEu_{0.05}VO_4$.

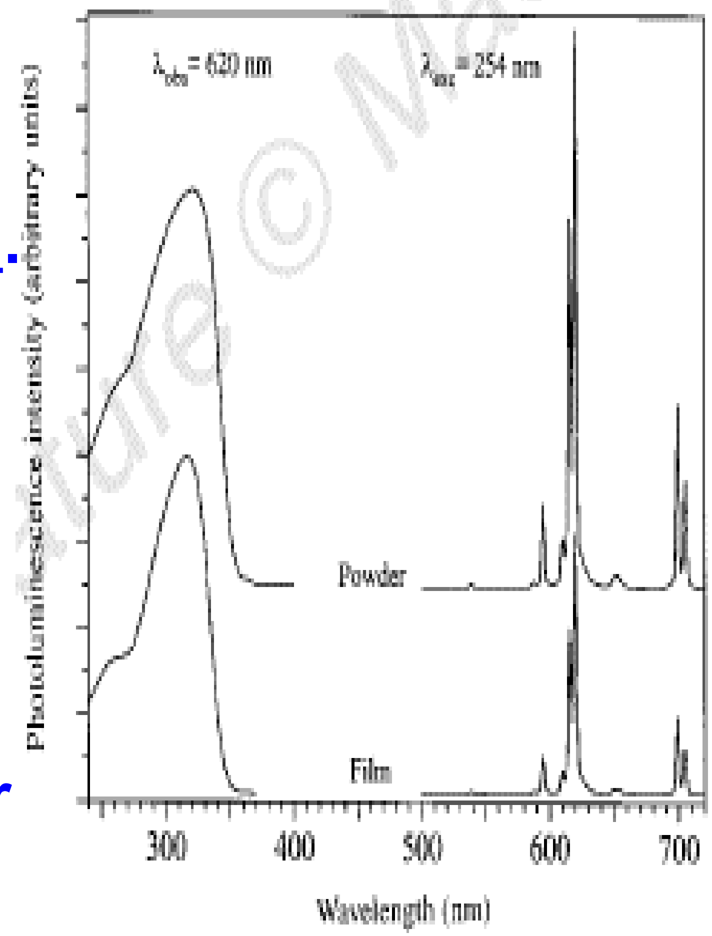
- Maximum red chromaticity observed in$Y_{0.82}Al_{0.07}La_{0.06}Eu_{0.05}VO_4$



- On the host was optimized The activator concentration with third library with variable $Eu^{3+}$ , in $Y_{0.87-m}Al_{0.07}La_{0.06}Eu_mVO_4$.

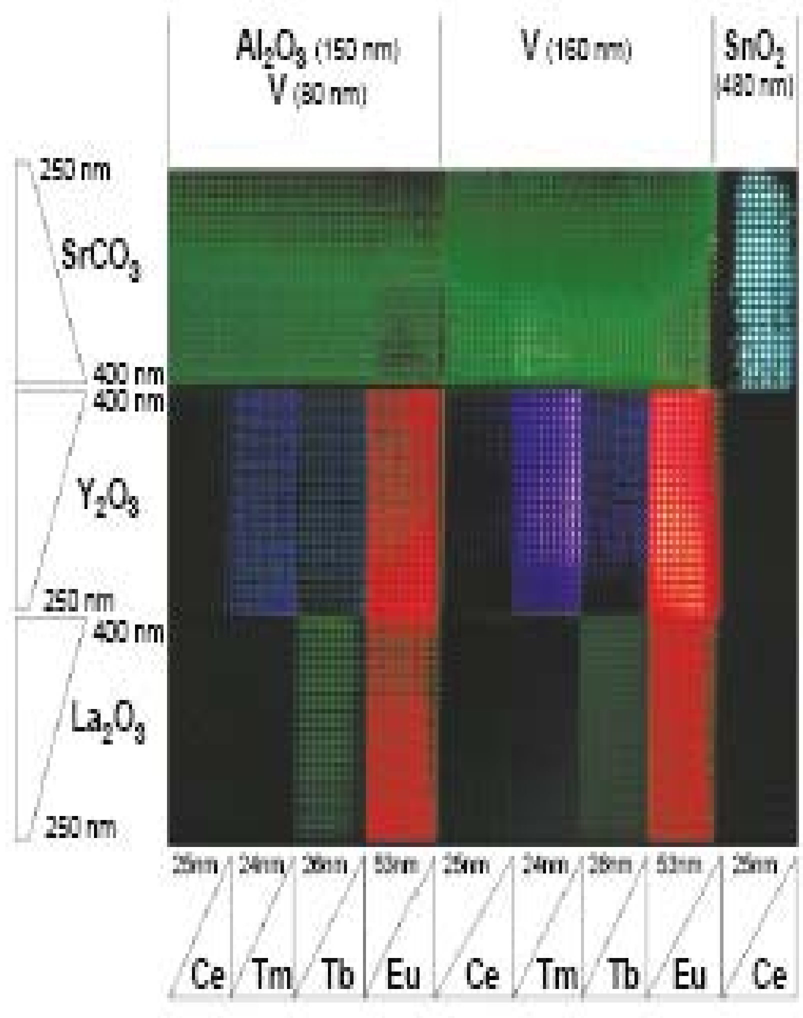
- In this library maximum red chromaticity observed in $Y_{0.845}Al_{0.07}La_{0.06}Eu_{0.25}VO_4$ (x=0.67, y=0.32).

- $Y_{0.845}Al_{0.07}La_{0.06}Eu_{0.25}VO_4$ powder contains single phase, iso structural with $YVO_4$.



# $Sr_2CeO_4$ An Unusual Luminescent Inorganic Oxide

- Blue – white emission observed From Sr, Sn, Ce containing region.
- Second library containing Sr, Sn, Ce revealed Sn was not need for the observed emissive properties.

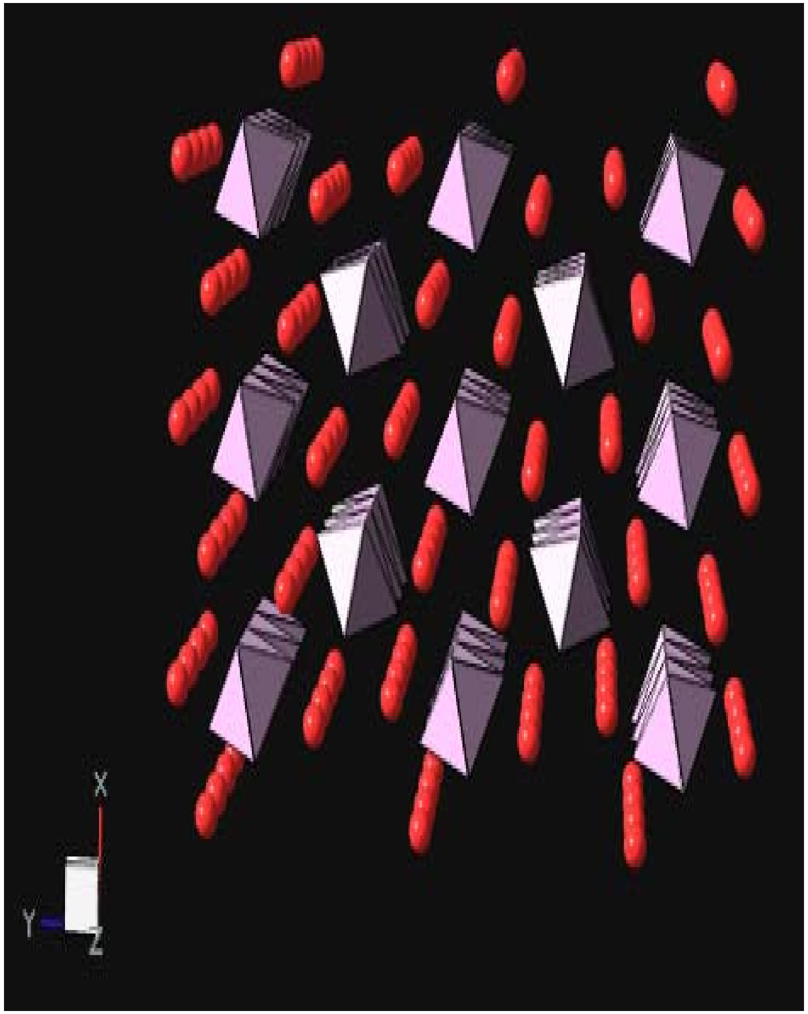



Xin Di Wu et al., Science 279,837 (1998)

- $Sr_2CeO_4$ was prepared by solid state reaction.

- Orthorhombic cell witha=6.11897, b=10.3495,c=3.5970 and Pbam space group .

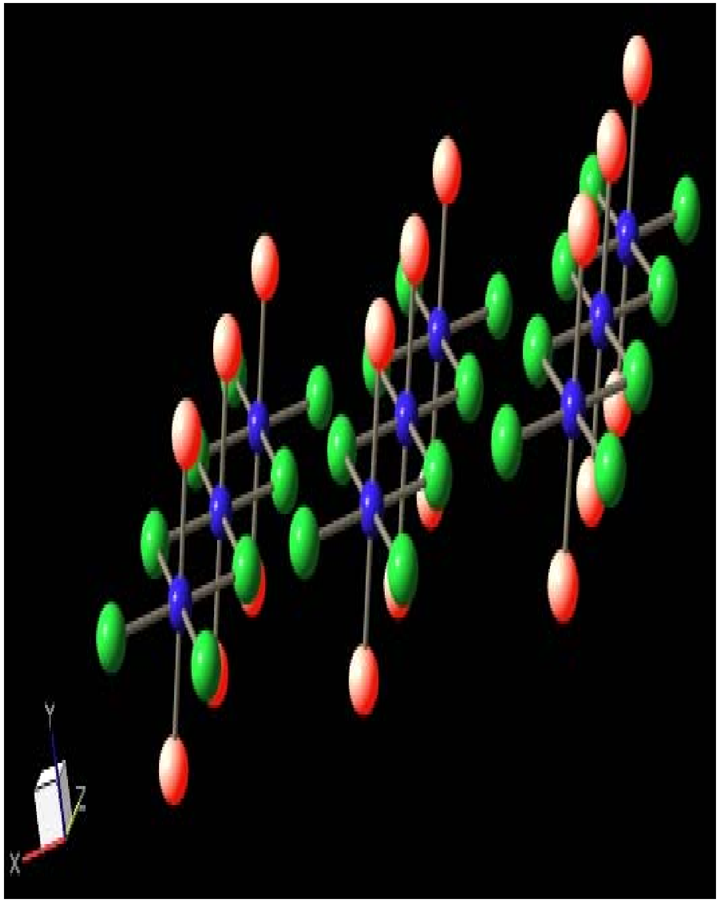
- Excitation-310nm,Emission-485nm Exited life time 51.3ųs CIE chromaticity coordinates x=0.198,y=0.292.



- Magnetic susceptibility and ESR measurements confirm no $Ce^{3+}$.

- Excitation is due to charge transfer from $O^{2-}$ to $Ce^{4+}$ .

- Terminal Ce-O bond is shorter (0.1) than equatorial.



- A triangular library was prepared with $M_2CeO_4$ (M=Ba, Ca and Sr) compositions at each corner.

- This library was prepared by sol-gel method.

- Sr containing region has the brightest emission.

# Summary

- Thin film deposition and physical masking techniques has been used for the spatially addressable libraries of Solid state materials.

- Combinatorial approach is successfully applied to discover the Superconductive, Magnetoresistance and Luminescent materials

# References


Hideomi koinuma., Solid State Ionics 108,1(1998).

Peter G. Schultz et al., Science 268, 1738 (1995).

X.-D. Xiang et al., Science 270,237 (1995).

Xin Di Wu  et al., Nature 389,944 (1997).

Xin Di Wu  et al., Science 279,837 (1998).

Peter G. Schultz et al., Science 279, 1712 (1998).

Peter G. Schultz., Applied Catalysis 254, 3 (1995).