INTEMATIX CORPORATION

Combinatorial Screening of Advanced Scintillators for High Resolution X-Ray Detectors

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Final Technical Report

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Executive Summary

The lack of efficient scintillators is a major problem for developing powerful x-ray detectors that are widely used in homeland security, industrial and scientific research. Intematix has developed and applied a high throughput screening process and corresponding crystal growth technology to significantly speed up the discovery process for new efficient scintillators. As a result, Intematix has invented and fabricated three new scintillators both in powder and bulk forms, which possess promising properties such as better radiation hardness and better matching for silicon diode.

1. Identification of Significance of the Problem or Opportunity, and Technical Approach

1.1. Significance and Background Information

Scintillators have been used for several decades as the primary technique for detecting charged particles such as protons, electrons, alpha particles, and heavy ions, as well as neutrons, X-rays, and gamma rays. The early history, theory, and application of scintillation counters have been reviewed by J. B. Birks[1]. As described by Birks, many different materials have been used as scintillators; these include gases, liquids and solids. Gases and liquids have generally occupied large volumes and very specialized applications. The solid scintillators have fallen into three categories; organics or polymer, glass, and inorganic crystals. Organic scintillators have been applied primarily as electron and fast neutron detectors [2]. Because of their low densities, their efficiencies are usually low for gamma rays and heavy particles. Glass scintillators are easy to fabricate in almost any useable shape. However, because of the absence of any long-range order in these systems, their efficiencies are more than an order of magnitude below that of the inorganic crystal scintillators.

For gamma-rays and X-rays, the inorganic crystal systems have generally been used because of their high densities and high atomic numbers that result in high efficiencies. The NaI(Tl) scintillator is the most widely used crystal system. This crystal has played a part in some of the most important physical discoveries of the past 50 years. Some of these are: 1) Deutsch's[3] discovery of positronium; 2) Fitch and Rainwater's [4] verification of the existence of μ-mesic atoms; 3) the demonstration by Wu, et. al. [5] of the nonconservation of parity in weak interactions; 4) the Mossbauer effect [6], 5) Pound and Rebka's [7] verification of Einstein's prediction of the equivalence effect; and 6) the verification of the predictions of quantum electrodynamics at distances as small as ~ $4\text{x}10^{-15}$ cm [8]. These systems have also been applied to a wide variety of problems in science, technology and medicine.

However, due to a member of serious shortcomings with the existing scintillators, there is still a great need for new scintillators that are efficient, fast, heavy, and low cost. Unfortunately, the conventional methods used to search for new and efficient scintillator materials are very slow and expensive. This can be readily understood by a brief description of the process normally used for the development of new crystalline materials. First the researcher must, to some degree, intuitively select the crystalline material composition. He must then collect the component materials and mill them into fine powders. After weighing out the proper amounts, the materials must be mixed and ground further. The crucible must then be charged and the material brought up to the melting point and soaked for several hours. It then may be necessary to cool the crucible down to room temperature and recharged. This process may have to be repeated several

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[1] J. B. Birks, The Theory and Practice of Scintillation Counting, MacMillan, New York, 1964

[2] J. A. Harvey & N. W. Hill, Nuclear Instr. & Methods 162, 507 (1979)

[3] M. Deutsch, Phys. Rev. 82, 455 (1951)

[4] V. L. Fitch & J. Rainwater, Phys. Rev. 92, 789 (1953)

[5] C. S. Wu, et. al., Phys. Rev. 105, 1413 (1957)

[6] R. L. Mossbauer, Naturwissenschaften 45, 538 (1958)

[7] R. V. Pound & G. A. Rebka, Phys. Rev. Lett. 4, 337 (1960)

[8] C. J. Biddick, et. al., Phys. Rev. Lett. 38, 1324 (1977)

times. At this point the crucible may be placed in the growth furnace and brought back up to the melting point or above and allowed to soak for several hours. Finally the crystal growth process can begin. The growth can take between two and four weeks. Therefore, the average growth time is over four weeks for each crystal sample. This explains that almost a century of search in scintillators after the discovery of X-ray only produces very limited number of choices of good scintillators. Clearly there is a need to significantly speed up the R&D of advanced scintillators.

1.2 Overall Technical Approach

In this project, Intematix proposes to fulfill three tasks based on the success of Phase I project.

The Task One is to expand the highly efficient combinatorial discovery process for advanced scintillators developed in Phase I to ternary and pseudo-quaternary compound systems. Over 1,000 samples will be screened to determine which crystalline compositions are of interest. Ternary and quaternary compounds should provide more possibility to yield superior scintillators.

The scientists of Intematix have pioneered a series of technologies that allow scientists and engineers to dramatically speed up the discovery and development of functional materials by integrating thousands of different materials or an entire ternary phase diagram on a single chip since 1994 [9]. These technologies and related studies have formed a new field known as combinatorial materials sciences. This method has been used to search advanced functional materials, including superconductors[9a], magneto-resistance materials[9b], luminescent materials[9c] and dielectric materials [9d]. Intematix Corporation was founded based on the extensive experience and knowledge of its founders in this area. Intematix has recently developed a complete line of proprietary technologies for high-speed development of functional materials. **During Phase I program, we have demonstrated that various combinatorial methods can be successfully applied to screen of binary compound system for advanced scintillators**. Five new scintillator materials in powder form have been identified as a result. We will expand our capability and effort search ternary and pseudo-quaternary compound systems for new scintillator materials.

Table 1.1 is a summary of the existing state-of-the-art fast decay scintillator materials. Although some scintillators in Table 1 already have better light yield than BGO, they have other problems (marked by *italic* font in Table 1), such as longer decay time, less density and therefore longer radiation length. Lu_2SiO_5 is better than BGO in speed, light output, and density; however, it is an expansive material (i.e. Lu element) to grow large pieces of crystals.

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[9] (a) *A Combinatorial method to material discovery* X.-D. Xiang, X.Sun, G. Briceño, Y.Lou, K.-A. Wang, H. Chang, W.G. Wallace-Freedman, S.-W. Chen, P.G. Schultz, *Science* Vol. 268, 1738-1740 (1995); (b). *A class of cobalt oxide magnetoresistance materials discovered by combinatorial synthesis* . G. Briceno, H. Chang, X. Sun, P.G. Schultz, X.-D. Xiang, *Science* Vol. 270 , 273-275 (1995); (c), *Solution-phase synthesis of luminescent materials libraries* X. Sun, K.A. Wang, Y.Yoo, W.G. Wallace-Freedman, C. Gao, X.D. Xiang, P. Schultz, *Advanced Materials* Vol.9, 1046 (1998); (d) Combinatorial synthesis and high throughput evaluation of ferroelectric/dielectric thin-film libraries for microwave applications. Chang, H.; Gao, C.; Takeuchi, I.; Yoo, Y.; Wang, J.; Schultz, P.G.; Xiang, X.-D.; Sharma, R.P.; Downes, M.; Venkatesan, Applied Physics Letters, vol.72, (no.17), AIP, 27 April 1998

Host Lattice	Concentration Ce^{3+} (mol%)	Emission maximum	Light yield (Photon/Mev)	Decay Time(ns)	Density (g/cm^{-3})
BGO	0	480 nm	9,000	300	7.13
$ZnWO_4$	0	480 nm	10,000	*5,000*	7.87
$CdWO_4$	0	480 nm	14,000	*5,000*	7.99
$YAlO_3$	0.1	350 nm	17,000	30	*5.55*
Gd_2SiO_5	0.5	440 nm	9,000	60	*6.71*
Lu_2SiO_5	0.5	420 nm	25,000	40	7.4
$Y_3Al_5O_{12}$	0.4	550 nm	14,000	65	*5*

Table 1.1. Comparison of the existing advanced fast scintillators

After examining the literatures and the result of Phase I, we decide to focus on two types of scintillator materials:

1. Undoped self-activated scintillators, e.g. ternary and pseudo-quaternary Tungstates, Niobates, Zirconate and lanthanide compound.
2. Ternary and pseudo-quaternary hosts doped with luminescent ions with fast decay time or high light output, such as Ce^{3+}, Eu^{2+} and Bi^{3+}.

For the 1st category, we will study other potential self-activating scintillators, such as mixed cations and/or mixed anions. For the 2nd category, we will study various doping elements, such as Ce^{3+}, Eu^{2+} and Bi^{3+}, in the hosts of first category.

The Task Two is to grow single crystals of those compositions selected in Phase I and Task One of Phase II program. From the experimental results of combinatorial libraries and powders studied in Phase I and Task One of Phase II program, we determine new scintillator materials that have superior properties to grow single crystal. Powder samples have much more optical defects than corresponding single crystal samples. These defects will trap emitted photons within the samples and dramatically deteriorate the light output. Therefore, in most practical applications, single crystal scintillators are used. In order to further confirm the true scintillator performance and ultimately produce realistic scintillator products, we will try to grow single crystals of selected compositions from combinatorial screening. Two of the frequently applied melt growth methods, Bridgman-Stockbarger method and Czochralski method, will be adopted in this project.

The Task Three is to prepare the transparent ceramic scintillators of the compositions determined in Phase I and Task One of Phase II program. One way to overcome the optical defects and photon trapping in non-transparent ceramics is to fabricate transparent ceramics. The first polycrystalline ceramic scintillator was developed by combining carefully controlled phosphor composition and doping with innovative techniques to produce transparent, polycrystalline ceramics[10]. A wet chemistry co-precipitation process will be used for producing powder and hot-pressing sintering process will be used for transforming powder compacts into transparent luminescent ceramics. The ceramic route offers uniform co-doping on a molecular level. Complex compositions that cannot be grown by single-crystal methods can be synthesized by the relatively inexpensive ceramic process.

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[10] Greskovich C., etc., Am. Ceram. Soc. Bull., 1992, 71 (7), 1120-30

We will determine the best method to make either single crystal or transparent ceramic scintillator for each of these compositions. These compositions possess high atomic number, high density, and therefore high stopping power and light output under x-ray excitation. Meanwhile, all of these compositions are self-activated scintillators and doped with luminescent ions Eu^{2+} and Bi^{3+} with fast decay time. Since scintillator materials must be used in the form of either single crystal or transparent ceramics, we will characterize and validate the scintillators performance, including decay time, light output, radiation hardness, under their realistic application environment.

1.3 Anticipated Public Benefits

The development of new scintillator materials with faster response times, higher density, greater radiation hardness and higher energy efficiencies will have significant benefits to areas, such as security (airport and seaport) inspections, medical diagnosis, well-logging, industrial non-destructive evaluation (NDE), physics and chemistry research, and etc.

Security and industrial inspections are an important area that could make wide use of the materials we are investigating. If we reached the goal of the project, which is to develop a heavy and fast scintillator with greater light output than for BGO [11] and higher density than $PbWO_4$, it will great improve the current technology used in airport luggage and cargo inspection. This will help to enhance our homeland security.

Better scintillators would have great potential to be used in medical diagnostics such as in X-ray CT (computed tomography) and PET (positron emission tomography). The potential market size in the medical arena for the scintillator crystals should be in a range of hundreds of millions. The improvement in scintillator materials will help to reduce radiation exposure and improve reliability of medical diagnosis, both greatly benefiting to public health.

These new materials may also be used in nuclear and high-energy physics experiments. Because of their short radiation lengths, short decay constants and radiation hardness, they will be ideal as EM calorimeters for γ-rays. These materials should also be useful as active shielding materials in Compton-suppressed spectrometers. Because of the attractive physical parameters just listed, and their potential for high efficiency and large crystal sizes of greater than $20xX_o$, these new materials have the potential for replacing $NaI:Tl^+$, $CsI:Tl^+$, BGO and other materials in a wide variety of physics experiments. As facilities such as SLAC and CERN use hundreds or thousands of crystals, the commercial potential for these materials to be used in physics experiments is good.

2. The Phase II Project

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[11] C. L. Melcher, et al, IEEE Trans. Nucl. Sci., NS-38, 506 (1991)

2.1. Technical Objectives

The primary objective of the Phase II program is to reproduce the scintillators discovered in Phase I in transparent ceramics or single crystal form under various processing conditions. With sufficient crystal sizes available we will be able to measure the efficiency and time resolution of the most promising crystals and compare them to the standard BGO and $PbWO_4$ crystals. In addition, the searching of new scintillator materials will be expanded from binary system to ternary and pseudo-quadric systems using similar combinatorial methods as in Phase I program. The single crystal and ceramic samples will be characterized with XRD, X-ray laser to determine the structure and radiation properties. These thin film specimens will be investigated using our scanning fluorescence spectroscopy and scanning X-ray microbeam XRD (X-ray diffraction) and XRF (X-ray fluorescence) methods to select the most promising candidates.

Successful completion of this phase II program could be judged by the fulfillment of the following technical objectives and milestones in this project:

1. Establish combinatorial synthesis capability of multi-components scintillator materials with ion-beam sputtering.
2. Establish combinatorial synthesis capability of multi-components scintillator materials with wet chemical process.
3. Establish a scanning spectrometer based high throughput screening (HTS) capability for rapid evaluation of fluorescence and energy efficiency of libraries of thin film scintillators under short UV exposure
4. Establish a HTS method based on X-ray microbeam XRD and XRF to measure the structures and elemental compositions of thin film scintillators in a high density library,
5. Develop the single crystal growth technology to prepare the single crystals from the designed and new found scintillator materials.
6. Develop the transparent ceramics processing technology to prepare the transparent ceramics from the designed and new found scintillator materials.
7. Measure the scintillators properties under x-ray radiation, such as light output, decay time, after glow, radiation damage etc.
8. Measure the scintillators properties under high energy radiation, such as light output, decay time, after glow, etc.

2.2. Phase II Work Procedure

2.2.1. Exploration new scintillator materials with combinatorial methods

Intematix's innovative combinatorial process for searching new scintillator materials can be summarized in Figure 2.1, note that it is a closed loop process with the end deliverable of "Hits for validation" from each combinatorial cycle. We start from the design of a high-density scintillator materials library, which usually contains hundreds to thousands of different elemental compositions. We can fabricate either a thin film library using our proprietary **combinatorial ion beam sputtering (CIBS)** technology (**Fig. 2a**), or polycrystalline library using our in-house chemical solution robot. After a simultaneous synthesis of the large collection of material libraries under various conditions, the samples in the material library can be rapidly analyzed using various high throughput optical and materials characterization methods. The information on elemental composition of samples in a library, the library processing conditions, and the various properties of a scintillator library can be stored and sorted in a custom-developed combinatorial database. The database can be integrated with data mining capability to help digesting the information and designing the next library cycle.

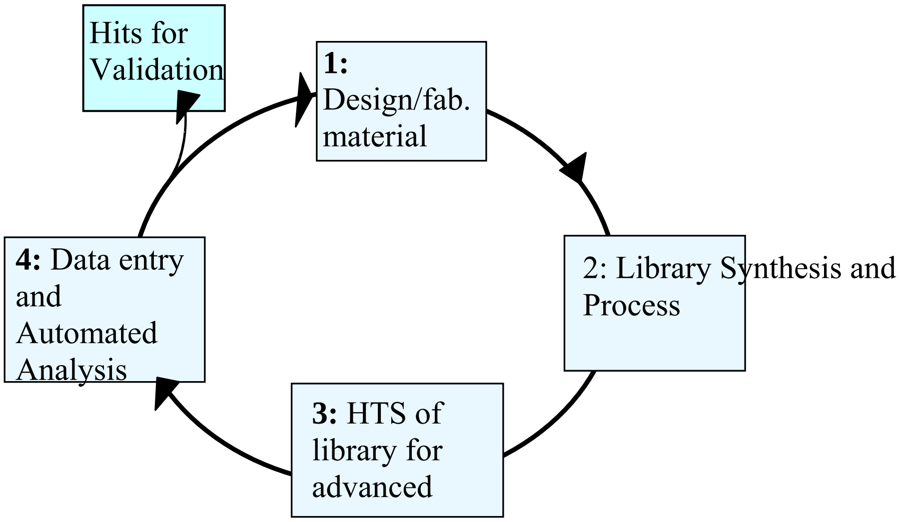

Fig. 2.1 Diagram of Intematix's proposed combinatorial (HTS) cycle for searching advanced scintillators

Therefore, three steps are adopted and validated in the Phase II to complete the cycle of combinatorial scintillator process, which covers the combinatorial synthesis, high throughput screening (HTS), and combinatorial informatics. By completing these steps, we finished a comprehensive screening of advanced scintillators from the possible scintillator elements in periodic table in the Phase II.

2.2.1.1 Combinatorial Method with Ion Beam Sputtering

The scintillator materials in a thin film library can be made either in "discrete" or in "continuous" forms, namely "Discrete materials library"[9] (DML) and "Continuous phase diagram libraries" (CPDL), respectively[12]. We used a combination of both methods to discover (using DML) and optimize (using CPDL) advanced scintillator materials in this SBIR program. DML is designed and fabricated using various combinatorial mask patterns (e.g. **Fig. 2.2b**) to effectively search through large compositional spaces. CPDL is designed to cover every composition of a multiple-elements phase diagram. CPDL is fabricated using linear shutter masks that move at a controlled rate during each precursor deposition (**Fig. 2.2c**), and a gradient of solid deposit can be created with a constant vapor deposition. This method can easily generate precisely controlled composition profiles within a small area.

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[12] *Combinatorial Screening and Optimization of Luminescent Materials and Organic LED,* Ted X. Sun and G. Jabbour, MRS Bulletin, April, 2002

Intematix has recently developed an effective ultra high vacuum (UHV) combinatorial ion beam sputtering system (CIBS) with a base vacuum pressure of 10^{-10} Torr to fabricate high-density libraries of thin film materials (**Fig. 2.2a**). The system is attached to a glove box to handle air sensitive materials without contamination. It consists of an automated 8-targets carousel and an x-y precision shutter for making CPDL. CIBS provides an ideal solution for high throughput synthesis and evaluation of various scintillator compositions on the same substrate. After a library with hundreds to thousands of different thin film compositions is deposited, usually in a matter of days, they will be synthesized at high temperature under variable atmospheres to generate a library of scintillator candidates. **Fig. 2.3a** is the picture of a high-density thin film phosphor library we made on Silicon substrate under the ambient light, using the discrete quaternary mask of **Fig. 2.2b**. **Fig. 2.3b** is the picture of a CPDL with 3 elements, made by shutter mask (**Fig. 2.2c**), which covers the whole compositional range of the ternary phase diagram of the 3 elements.

Fig. 2.4a is the luminescent photograph (taken under 254 nm UV exposure) of the 1,024-member thin film DML shown in **Fig. 2.3a**, made by CIBS. **Fig. 2.4b** is the X-ray excited luminescent photograph (taken under 254 nm UV exposure) of two sets of 128 members thin film DML in two columns, with different processing conditions. We have discovered a few highly efficient and novel blue and green phosphors using such DML [9]. **By simply replacing UV lamp with an X-ray source, the scintillating properties (intensity and color) of 1,024 different phosphor candidates can be studied simultaneously.**

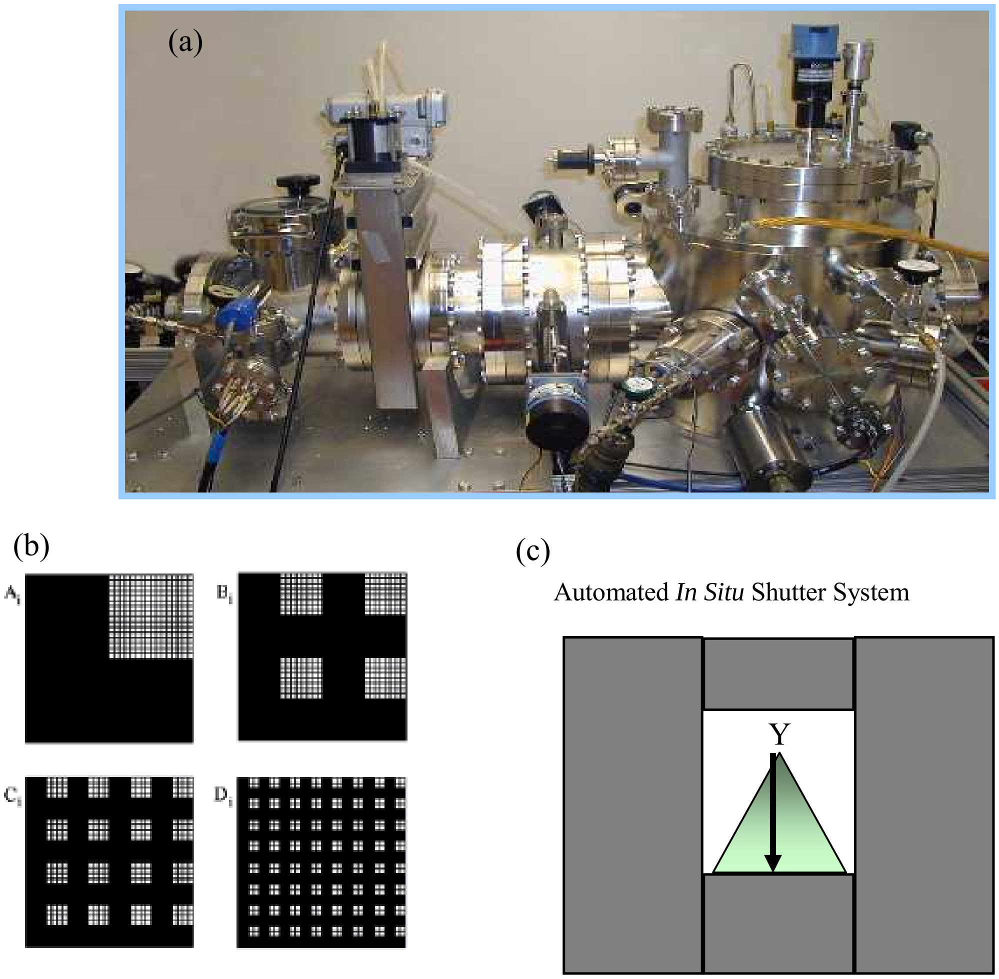
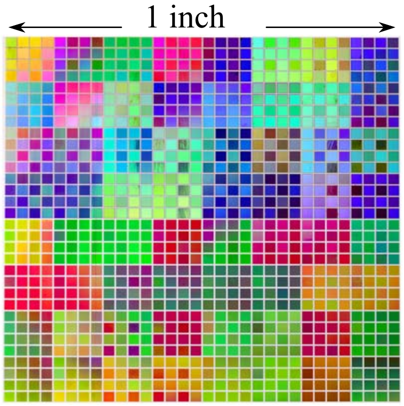


Fig. 2.2a. Photograph of the Combinatorial Ion-Beam Materials library Synthesis System **Fig. 2.2b**. Schematic of shadow mask patterns for making DML. **Fig. 2.2c** Schematic of the *in-situ* shutter mask for making CPDL



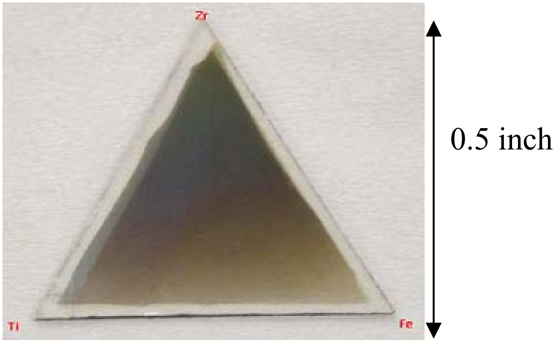


Fig. 2.3a. The photo of a high-density thin film oxides DML library, each thin film sample is ~650 micron in size. **Fig. 2.3b.** The photo of a thin film CPDL, which covers all the complete compositions of the ternary elemental Ti-Zr-Fe series.

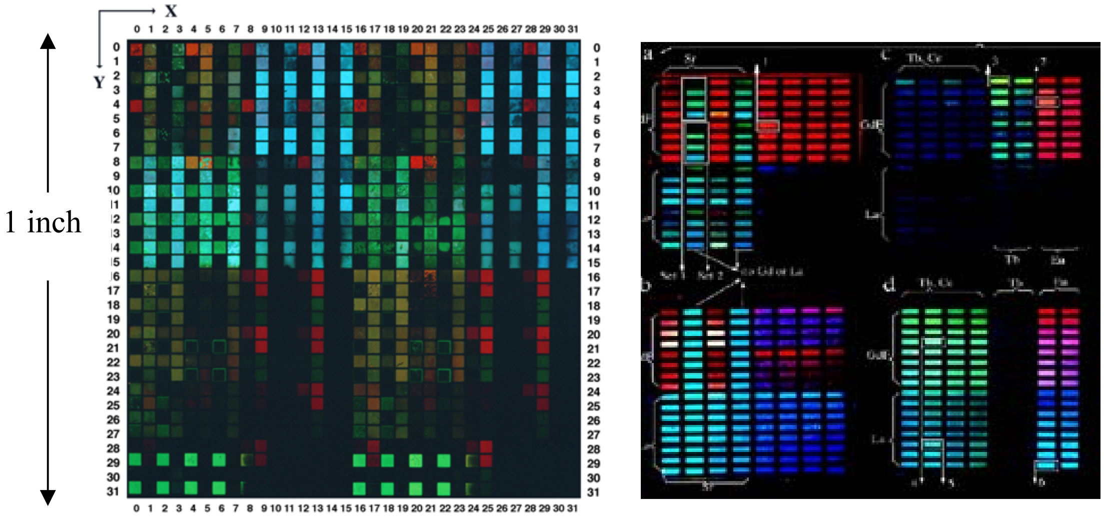


Fig. 2.4. UV-luminescent emission image of high-density thin film phosphor library

2.2.1.2.Combinatorial Method with Wet Chemical process

The scintillator materials in a thin film library can be also prepared in discrete form by wet chemical solutions method. Most low valence elements can be prepared into water solution. For high valence elements (W, Ta, Nb, Zr, Hf, etc.) can be encapsulated with specific organics and prepared as aqueous solution. By using our innovative printing technology, we can prepare ternary and quadratic libraries on silicon substrates easily. After baking by IR light, these libraries are fired in a furnace in various conditions to acquire polycrystalline thin films. Figure 2.5 is the luminescent photograph (taken under 365 nm UV exposure) of the LED quadratic library made by wet chemical process. The advantages of this method include easy fabrication, short processing time and fewer requirements on substrate.

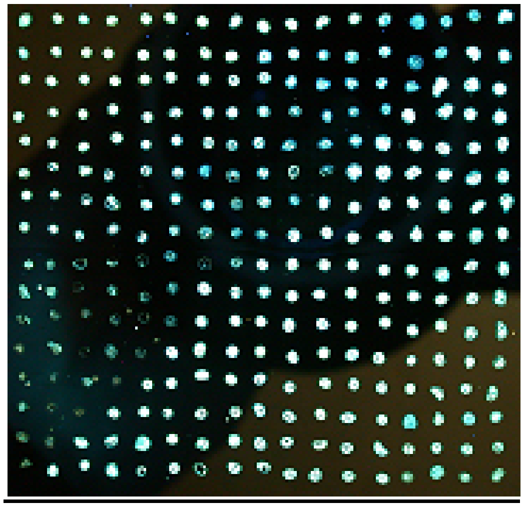


Fig. 2.5. UV-luminescent emission image of high-density thin film phosphor library with wet chemical process.

2.2.1.1 High Throughput Screening Methods on Scintillator Properties

The following scintillating properties, including light output, or X-ray luminescence intensity and color; luminescent decay time; scintillator structure and compositions; and density are of interest for this project. The density of scintillator can be readily calculated with the knowledge of scintillator lattice structure and elemental compositions. Therefore, we need to develop and validate the high throughput screening (HTS) tools for the first two properties in the Phase II. The reliable decay time will be characterized after the single crystal or transparent ceramics are fabricated.

A. Multi-functional Scanning X-ray system for HTS of scintillator light output, fluorescent spectrum, structure and composition

Intematix has recently developed an extremely versatile X-ray characterization station on high-density material libraries. The overall schematic of the system is shown in **Fig. 2.6**. It comprises of a common X-ray source, which is focused and introduced to the sample via a novel X-ray capillary tube of 0.5 mm ID. Therefore the X-ray output from the capillary is significantly higher than a conventional 0.5 mm X-ray slit, and sample spots of 0.5 mm in size can be readily probed with the X-ray. A library with multiple samples is mounted on a X-Y scanning stage to switch the sample in a library without changing the relative spatial positioning of target sample with probe.

Three detection modules are installed into this system: They are

i. X-ray detector mounted on goniometer and can process with target sample in a library for a θ-2θ measurement of sample crystal structure by X-ray diffraction.

ii. An Amptek Si-PIN diode X-ray fluorescent detector, which is used to measure the X-ray fluorescence from the target sample with an energy resolution of ~160 eV. This module can measure the elemental composition of target sample in library beyond Mg in periodic table.

iii. Ocean Optics spectrophotometer, the X-ray induced UV-Vis fluorescence from scintillator or phosphors can be introduced into the spectrometer to determine the color and the intensity of the target luminescent material in a library.

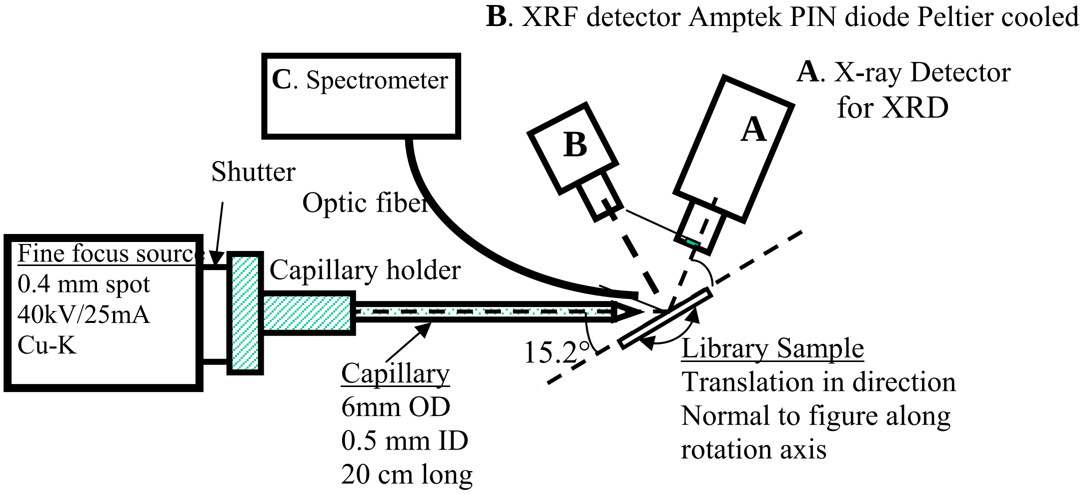


Fig. 2.6. Intematix's proprietary multifunctional X-ray based characterization system for the high throughput screening of scintillator libraries.

2.2.2 Preparation of Single Crystal

Scintillators that are used for the detection of strongly ionizing radiation are practically always applied as single crystals. The reason for this is that the scintillator should have a high optical transmission in the emission region, so that the emission can escape efficiently. This sometimes requires very large crystals without gas bubbles or precipitate, since these would result in light scattering. It is probable that certain imperfections in the crystal will also be detrimental for radiation hardness. When dopants have to be used, for example Tl^+ in NaI, the dopant will never have a uniform distribution over the whole crystal volume.

2.2.2.1 Single Crystal Growth Methods

All commercially available scintillator crystals are grown from the melt. But crystals can only be grown from the melt if 1) the compound has a congruent melting point, 2)does not decompose before melting, and 3) has no phase transition between the melting point and room temperature.

Two of the frequently applied melt growth methods are the Bridgman-Stockbarger method and the Czochralski method. In the Bridgman-Stockbarger technique both crystal and melt are confined within a solid container such that the three-phase boundary is between crystal, melt and container material. This technique can be divided into three situations:1) a crystal-melt interface is propagated vertically or horizontally, 2) the whole charge is melted initially and subsequently crystallized progressively, 3) a molten zone is established and traversed along and ingot. Generally, quartz and Pt ampoules are used in the Bridgman-Stockbarger method.

Fig. 2.7 shows a schematic view of the vertical directional solidification. The resistance-heated furnace is composed of several separate heating zones, the temperature of which can be programmed and controlled separately. The cylindrical ampoules containing the charge are supported or the furnace can be lowered during the crystal growth process.

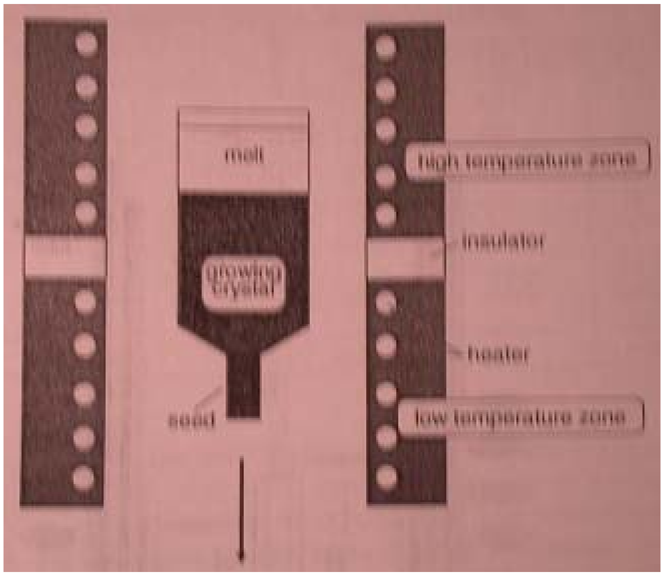


Fig. 2.7. Crystal growth according to the Bridgman-Stockbarger method

With this methods growth rates of about one millimeter per hour can be obtained. Alkali halide crystals ranging up to 30 inches in diameter and half a ton of mass can be grown. Such crystals are not truly single, but rather contain five to ten components as delineated by small-angle grain boundaries which crop out at the surface or are evident under strong illumination due to scattering by impurities on the boundaries If doped scintillators are desired, the dopant has to be mixed with the starting material and dissolved in the melt. Generally, if the dopant is volatile at the melt point, some of the dopant may be lost by evaporation. This means that the dopant concentration in a given crystal will not be constant over the crystal volume. Thus, the relationship of luminescence intensity with dopant concentration will be determined to avoid the loss.

The elements of the Czochralski technique are shown schematically in **Fig. 2.8**. The melt is contained in the crucible that is heated either by radio-frequency-induction heating or by resistance heating. The pull rod with a chuck containing the seed crystal at its lower end is positioned axially above the crucible. The seed crystal is dipped into the melt and the melt temperature adjusted until the meniscus is supported. The poll rod is rotated slowly and then lifted. By careful adjustment of the power supplied to the melt, the diameter of the crystal is controlled as it grows. Rotation rates are commonly in the range of 1-100rpm. Pulling rates can vary from one millimeter per hour for certain oxide crystals to several tens of millimeters per hour for halide crystals. The whole assembly is enclosed within an envelope that permits control of the ambient gas. The principal advantages of the technique include the fact that the crystal remains unstrained when it cools, so that a high structural perfection can be obtained. To yield material of high and controllable purity, it is necessary to fabricate the crucible from a material that is not attacked by the molten charge.

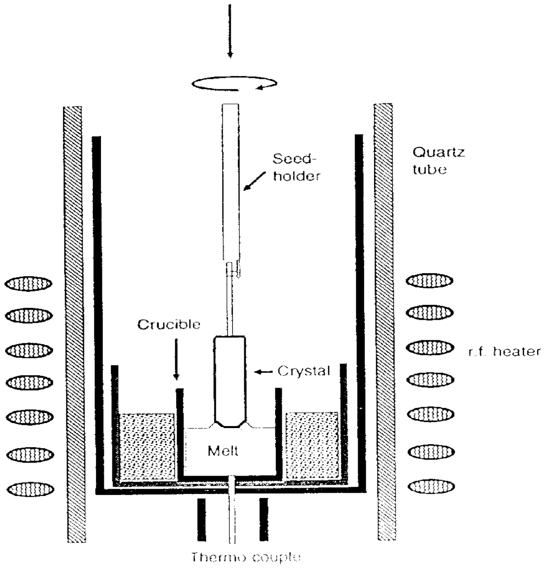


Fig. 2.8. Crystal growth according to the Czochralski method

For oxide crystals liked $Bi_4Ge_3O_{12}$ (T_m: 1044°C) and $CdWO_4$ (T_m: 1272°C) Pt crucibles are normally used. For crystals with a higher melting temperature, such as Gd_2SiO_5:Ce (T_m: 1950°C), Ir crucibles are applied. Oxide crystals are usually grown by the Czochralski technique. The perfection of these crystals is high, but the size is normally limited to 3-4 inches diameter.

2.2.2.2 Single Crystal Growth

One of the main goal of this project is to prepare the single crystals with the compositions determined from library screening. These advanced scintillator materials are expected to possess reduced luminescent decay time, increased light output and X-ray stopping power. For this program, we will focus on the material properties and corresponding growth technology. Therefore, there are two major subtasks in this Phase II project:

Following compositions are used to prepare single crystal:

$CdWO_4$:Gd
Sr_3SiO_5:Eu^{2+}

Czochralski technique is used. These compositions possess different melting point, vapor pressure and atmosphere requirement. For $Sr_3SiO_5:Eu^{2+}$, we prepared the single crystal in reduced atmosphere.

Task 2: Determining the proper growth processing conditions for each composition

After determining the growth method for each composition, proper growth processing technology is critical to acquire single crystal with high quality. This is a process of error and try and time consuming. At last, $CdWO_4$:Gd is successfully prepared as single crystal.

2.2.3. Ceramic Scintillator Processing

2.2.3.1 Powder preparation and processing

A variety of powder preparation routes and ceramic processing procedure can be used to produce high quality, high purity powders that can be consolidated into highly-dense, transparent/translucent ceramics. Each ceramic scintillator composition typically requires special processing conditions specific to that material. In general, the desirable physiochemical, characteristics of the special powder are high purity (≥99.99%), high specific surface area of ≥5 m^2g^{-1} and median particle (agglomerate) size less than 3μm with no particles greater than 7 μm[13]. The selected methods of powder synthesis and ceramic processing to produce such a desirable powder mush also ensure high material yields, permit multicomponent codoping on a molecular scale for control of scintillation properties, and produce uniformly reproducible powders for subsequent powder compaction and consolidation steps.

Some preferred methods of powder preparation and processing will be briefly described. In the case of $(Y,Gd)_2$:Eu,Pr, an oxalate coprecipitation process is conveniently employed[14]. In this method a nitrate solution of proper proportions of Y, Gd, Eu and Pr is added to an oxalic acid solution to coprecipitate the respective oxalates. The precipitate is washed to remove nitric/oxalic acids, filtered, and dried. This powder is then thermally decomposed at 800°C in air to convert the oxalate into oxide powder. The oxalate or oxide powder should be de-agglomerated by milling (ball, colloid or fluid energy) to enhance optical clarity of the final product.

$Gd_3Ga_5O_{12}:Cr^{3+}$,Ce garnet powder may be prepared by an ammonium hydroxide process[15]. High purity (≥99.99%) oxides of the correct proportions are dissolved in hot, concentrated hydrochloric acid. Separately, an NH_4OH solution is prepared by diluting 30% NH_4OH with an equal volume of de-ionized water. This NH_4OH solution is added to the Gd, Ga, Cr and Ce chloride solution while stirring vigorously. During this process a gel-like precipitate forms as the pH increases up to the end point of about 8.The ultrafine precipitate is then washed with water to remove the NH_4Cl and excess NH_4OH. After drying, this fine powder is thermally decomposed in air at 900°C to convert the hydroxide into a crystalline garnet powder. De-agglomeration of

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[13] Greskovich C., Dynys F.W., 1990. Presented at the conf. ceramic powder processing science., San Diego

[14] Kostler W., etc, J. Phys. Chem. Solids., 56(7):907-13

[15] Blasse G., etc, J. Alloys and Compounds, 200(1-2):17-18

the garnet powder can be accomplished by a ball-milling method using zirconia grinding media and a liquid vehicle such as water or methyl alcohol.

We prepare two kinds of powders Sr_3SiO_5:Eu and $Bi_{7.38}Zr_{0.62}O_{12.31}$ powders with coprecipitation method.

2.2.3.2 Densification processes for transparent/translucent ceramic scintillators

For high density transparent/translucent ceramics, the residual porosity must be reduced to <0.1 vol% by high temperature sintering. Such minute amounts of residual porosity are often controlled by the state of agglomeration of the starting powder, the amount of organic contamination during ceramic processing, and rapid grain growth during sintering. Sintering processes have been successfully used to make $Y_{1.34}Gd_{0.60}Eu_{0.06}O_3$[15] and $Gd_3Ga_{4.96}Cr_{0.04}O_{12}$[16] scintillator materials. Typically, the processed powders are pressed into powder compacts with relative densities 50% by die-pressing and /or cold isostatic pressing at pressure up to 300 MPa. $Bi_{7.38}Zr_{0.62}O_{12.31}$ is pressed in to powder compact by die-pressing and sintering at 720 °C in the air. Due to high vapor pressure of Bi at sintering temperature, the fired body is not dense enough to look translucent.

The hot isostatic pressing (HIP) method of consolidation of powders is useful when a very high driving force is required to densify the powder into a ceramic body. The Gd_2O_2S:Pr,Ce powder with a large particle size of 40 μm requires a HIP process[16]. After the Li_2GeF_6 densification aid is added to the powder, the mixture is loaded into an iron cylindrical capsule and sealed off in a vacuum. The encapsulated powder is then heated at 1300°C for 10 hours under 200 MPa of argon pressure. We utilized the same process to sinter Sr_3SiO_5:Eu. The powder is encapsulated in Nb capsule and sealed off in a vacuum. The encapsulated powder is then heated at 1500 °C for 10 hours under 200 MPa of argon pressure. The final product looks some dark spots on the surface. It is possible the atmosphere is not reduced enough.

2.2.3.3 Scintillator properties

Following properties are often critical to their performance in high energy detection systems.

Light output

The relative light output is an extrinsic property typically measured as the current out of a diode attached to the scintillator. For accurate relative light output measurements it is important that x-ray energy and dose, as well as scintillator geometry, be held constant. Light output depends on (1) the absorption coefficient of the scintillator at the x-ray excitation energy, (2) the efficiency of exciton creation and capture at the luminescent centers, (3) the intrinsic emission quantum efficiency of these centers, (4) the scintillators geometry (surface structure and reflectors) and transparency, and (5) the quantum efficiency of the diode at the emission wavelength.

Decay time and afterglow

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[16] Yamada A., etc., J. Electrochem. Soc., 136(9):2713-16

In certain applications the response time of the scintillator is critical. Delayed emission from the scintillator after the incident x-ray bean is highly attenuated by the object being imaged, can degrade image quality and reduce image resolution. Two mechanisms play a role in such delayed emission. The first, primary speed is the intrinsic decay time of the emitting site or activator. The second, afterglow, is the delayed excitation and emission of activators due to the trapping of electrons or holes by lattice defects and their delayed thermal release.

Radiation damage

Stability and reproducibility of light output of a scintillator is critical to many applications. Radiation damage refers to the change of scintillation efficiency due to defect creation by the radiation dose. These defects are commonly color centers whose electronic structure imparts optical absorption bands at the scintillator emission wavelengths. As in the case of afterglow, the binding energy of the color center determines the longevity of the damage. In general, this energy is sufficiently large that damage can last from seconds to days at room temperature.

Radiation damage is characterized experimentally by exposing the scintillator to a relevant dose of radiation and measuring the change in light output taken before and after the damage dose. The recovery can be plotted as a function of time after the end of damage pulse. For accurate measurements it is important to compensate for variations in the source creating the measurement pulses. Scintillators with high afterglow must be compensated for residual afterglow from the damage dose. Since the absorption of the scintillation light depends on path length through the crystal, the measured damage can depend on details of the scintillator geometry, such as crystal thickness and transparency. Details of the radiation damage mechanism can be determined by also measuring the changes in optical transmission after the damage dose. This information is used to distinguish radiation damage due to color center absorption or other defect centers that decrease activator emission efficiency.

3. Degree to which Phase II has completed

One of the primary purpose of the Phase II program is to further develop and demonstrate that new scintillator materials can be prepared and selected by the combinatorial synthesis and screening technique, which can lead to the rapid development of new and efficient scintillators with increased energy and time resolution, radiation hardness and sensitivity and decreased radiation length, and prepare bulk materials with single crystal technique and sintering of transparent ceramics.

Combinatorial synthesis with ion beam sputtering and wet chemical method has been successfully applied in exploring the new binary doped and undoped scintillator materials. In combinatorial synthesis with ion beam sputtering, we adopted both continuous and discrete composition libraries, in which we prepared the libraries including rare earth element to V, Nb, Ta, W; more than 500 discrete undoped and doped compositions, and the dopants are Ce, Bi and Eu. In combinatorial synthesis with wet chemical method, we developed the printing technology and encapsulation technology, which can effectively overcome the present difficulties in wet chemical library. We prepared two kinds of libraries. The first library includes all binary doped compositions (more than 1100 compositions) that have crystal structure and the possibility to be used as a phosphor host, and the dopant is Ce and Eu. The second library includes various doped and undoped combination of vanadate, niobate, tantalite, tungstate, and so on. From these libraries, more than twenty new compositions are selected by UV (254 nm) excitation and reproduced in the form of powder. At last $CdWO_4$:Gd with superior radiation hardness and Sr_3SiO_5:Eu with near red wavelength (600 nm) were screened out and prepared in bulk form. We will focus on these achievement and relative preparations and properties.

3.1 Printing liquid solution arrays for inorganic combinatorial libraries

Combinatorial arrays of materials are useful, e.g., in screening compositions for unique or improved characteristics. In the biosciences, combinatorial arrays can be useful in discovery of molecules with desirable binding or catalytic activities. In materials sciences, combinatorial arrays have been constructed to discover materials with useful physical, catalytic, chemical, mechanical, or optical characteristics. Combinatorial technologies can provide efficient ways to create and screen materials useful in medicine, electronics, optics, packaging, machinery, and more.

In inorganic materials science, arrays have been prepared using continuous or discrete application of different inorganic materials for reaction on a substrate. For example, in Combinatorial Synthesis of Novel Materials, U.S. Pat. No. 5,985,356, to Shultz, et al., multiple different inorganic materials are applied to multiple regions of an array before reaction of the mixtures to form a combinatorial array of inorganic materials. Shultz, et al., discusses the use of robotics to discretely apply the different materials for combination on the substrate, using masks to direct application of materials to specific regions of a substrate, use of gradients to apply materials to substrates in changing proportions, and spacing array locations to reduce cross contamination. Still, problems remain in providing well defined, homogenous, and repeatable arrays having the same combinations in the same proportions on a substrate. Again, replication of an array in Shultz, et al., requires complete reconstruction of a duplicate array from scratch. This invention can be applied to liquid solution processes for synthesis of a combinatorial array of inorganic materials. However, liquid combinatorial libraries can be difficult to prepare. The general methods of preparation of liquid combinatorial libraries known in the art have problems with stability, homogeneity, and uniformity, especially if the members of the array comprise metal ions with high valence, such as Ti^{+4}, Ta^{+5} and Nb^{+5}. Generally, it is only possible to solvate ions having low valences (e.g., alkaline and alkaline earth metal ions). Although certain organic solvents may occasionally work in this regard, more often than not the ions precipitate to form non-homogeneous solutions, or an otherwise unstable solution. Even if one is able to produce a solution containing these metal ions, including high valence rare earth metal ions, there is still a potential for precipitation of the ionic species or the instability of the solution if new solvents or reagents are added, or if the solvents from different libraries are combined or mixed. This is especially true for aqueous solutions.

What is needed in the liquid solution processes for synthesis of a combinatorial array of inorganic materials, therefore, is a way of stabilizing liquid arrays of materials, including solutions of high valence ions, such that the array may be stored for further processing. It is contemplated that such an intermediate array may be commercialized in that stabilized condition, such that another investigator or commercial entity may further process the array according to its own proprietary interests.

3.1.1 Preparation of stable liquid solution

We have developed systems and methods for controlling and maintaining a stable distribution of metal ions in solution at the molecular level, thus ensuring a homogeneous mixture, and these techniques are particularly useful when processing or transferring a liquid master array either to a substrate or to an intermediate liquid array. According to these methods, a metal precursor and a soluble polymer are reacted to form a solution that does not suffer from the conventional problems of gelling or precipitation. The polymer actively binds the metal ion(s) and serves to encapsulate the metal, prevent chemical reactions between constituent ions of the mixture, and maintain the ions in a uniform distribution within the solution. In other words, the polymer functions to ensure a homogeneous metal ion distribution in the solution, and to isolate ions from one another to prevent unwanted reactivity between the metal ion constituents.

Inorganic materials can be, e.g., any materials that do not include carbon-hydrogen bonds. The inorganic materials can be produced from metal compounds in solution in an aqueous and/or organic solvent liquid. In many cases, the inorganic materials can be metal compounds associated with stabilizing polymers in solution. Typical inorganic materials are metals, metal ions, metal salts and/or metal oxides. The materials can be a compounds of, e.g., Aluminum, Antimony, Barium, Bismuth, Boron, Cadmium, Calcium, Carbon, Cerium, Chromium, Cobalt, Copper, Dysprosium, Erbium, Europium, Gadolinium, Germanium, Gold, Hafnium, Holmium, Indium, Iridium, Iron, Lanthanum, Lead, Lithium, Lutetium, Magnesium, Manganese, Molybdenum, Neodymium, Nickel, Niobium, Palladium, Platinum, Polonium, Praseodymium, Rhenium, Rhodium, Ruthenium, Samarium, Scandium, Selenium, Silicon, Silver, Strontium, Tantalum, Tellurium, Terbium, Thallium, Thulium, Tin, Titanium, Tungsten, Vanadium, Ytterbium, Yttrium, Zinc, Zirconium, oxidized forms thereof, and/or ionized forms thereof.

Polymers useful in the present invention can stabilize the inorganic materials in solution. Stabilizing refers to interactions with inorganic materials of interest so that they can be applied consistently. In general, in at least one stage of the processing of the present combinatorial array(s), a polymeric solution is mixed with a metal ion solution to effect the stabilized array. The polymeric solution may be prepared by dissolving a polymer such as polyethylenimine $(C_2H_5N)_n$ in water. Other components such as ethylenediaminetetraaceticacid (EDTA, $C_{10}H_{16}N_2O_8$) may be added to this solution. Next, the corresponding salt of the metal ion under investigation in the combinatorial library is prepared by dissolving the salt in water. In one embodiment of the present invention, nitrates may be used. The metal ion solution is then mixed with the polymer solution such that the polymer/EDTA encapsulates the metal ion(s). In some instances, it may be necessary to add either an acid or a base to the polymer/EDTA metal salt solution to assist with the encapsulation.

Other polymers that may be used in conjunction with EDTA to encapsulate the metal ion and stabilize the liquid array include a polyanionic polymer, a polycationic polymer, mixed ionic polymers, a peptide, polyethyleneimine (PEI) and carboxylated polyethyleneimine (PEIC).

Virtually any metal in the periodic table may be used by the present method. For example, the metal may comprise a group IA element, such as Li, Na, K, Rb, or Cs. These ions are monovalent. Alternatively, the metal may comprise a divalent ion from the group IIA alkaline earth metal column such as Ca, Sr, Ba, Mg, or other divalent metal ions such as Co, Mn, Zn, and Pb. Trivalent metal ions include Al, Ga, La, Ce, Pr, Nd, Po, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Bi, and Cr. Metal ions and/or semiconducting elements having a quaternary valence include Ge, Zr, Hf, and Sn. Metal ions and inorganic non-metal elements having a valence of V that may be stabilized according to the present embodiments include V and P, metals with a valence of VI are Mo and W.

For example, the stabilizing polymer are soluble in the application liquid of choice, and can have ionic properties, chelating properties, and/or viscosity enhancing properties that interact with the inorganic material to promote uniform distribution in the liquid. Stabilizing polymers can help retain uniform distribution of the materials while the liquids are handled during application processes and/or while liquids are held in storage between processes. Some stabilizing polymers can have the useful property of reducing oxidation and/or precipitation of the inorganic material.

Inorganic material is associated by ionic interaction with a charged polymer; the material will avoid reacting with other materials at the location until the polymer is removed by heat. In other word, the homogeneity can be kept all the time.

3.1.2. Printing liquid solution arrays for inorganic combinatorial libraries

Methods of preparing arrays of inorganic material combinations include, e.g., preparing a master array of well mixed and homogenous liquid solutions with the composition designed for final inorganic material combinations and transferring a replicate array of the master array onto a substrate to provide a replicate array of liquid solution combinations. The master array can be stored for use at another time to prepare an identical second, third, or fourth replicate array. The replicate arrays can be treated, e.g., by exposure to certain chemical reactive processes under certain physical conditions to form an array of final single phase or multiphase materials. Reaction product compositions can be analyzed to define useful process conditions and/or to identify compositions with desirable characteristics. An advantage of this method is the ability to readily and accurately produce a set of identical arrays of various composition materials on the same kind of substrates for individual testing under different chemical or physical conditions.

Master arrays can be prepared manually or by automated techniques. Stock solutions of inorganic material solutions are typically prepared manually to have known concentrations (molarities) of inorganic materials. Stabilizing polymers can be included, e.g., to chemically stabilize the materials or to help maintain homogenous distribution of the materials in the solution. Combinations of two or more inorganic materials can be prepared, e.g., by mixing two or more stock solutions at locations in a master array.

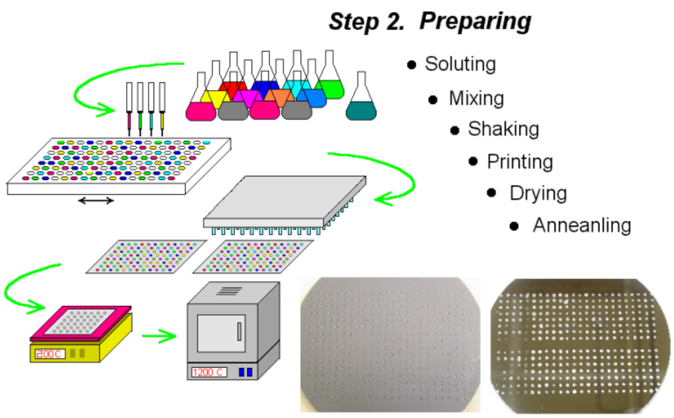

FIG. 3.1 Schematic diagram to prepare replicate arrays .

Fig. 3.1 shows schematic diagrams and images showing process steps to prepare replicate arrays by parallel transfer of liquid solutions from a master array to a replicate array on a substrate.

Methods of preparing arrays of inorganic material product compositions can generally include the steps of preparing a master array of liquid solutions, transferring samples of master array combinations to locations on a substrate to provide a replicate array of materials combinations, and reacting the combinations to form combinatorial arrays of product inorganic compositions. The reactions can include chemical and/or physical reactions between the materials in the combinations. Signals emitting from materials or products at array locations can be detected for analysis.

3.2 Doped cadmium tungstate scintillator with improved radiation hardness

New compositions and processing method for making doped cadmium tungstate scintillator materials are presented, which have a higher radiation hardness than that of undoped cadmium tungstate under UV, X-ray and other high-energy irradiation. The scintillator materials can be used in a variety of applications including, but not limited to X-ray detectors, e.g., for X-ray CT, digital panel imaging, screen intensifier etc. The scintillator materials of the invention can be used in bulk, sheet and film forms of ceramics, single crystals, glasses, and composites.

To acquire high resolution and quality picture, high dose radiation is required. Unfortunately, high dose radiation generally causes radiation damage to the scintillator material (i.e., the transmittance of scintillator crystal decreases with time), which inevitably leads to the loss of resolution and performance. One approach to solving this problem has been to lower the radiation dose. This approach requires better scintillators that provide higher light output to maintain the detector resolution and quality.

Recently, there has been an increasing demand for transparent, high atomic density, high speed and high light-output scintillator crystals and ceramic materials as detectors for computed X-ray tomography (CT) and other real time X-ray imaging systems. Many transparent ceramics like $(Y,Gd)_2O_3:Eu^{3+}$, $Gd_2O_2S:Pr,F,Ce$, etc. have been developed for this purpose. Their slow response, however, and lack of single crystal form have limited their applications for X-ray explosive detection systems and X-ray panel displays.

Another approach to providing improved scintillator materials has been to improve the radiation hardness of the scintillator crystals so they can withstand high dose radiation. Scintillators typically used for x-ray explosive detection systems are mainly CsI and $CdWO_4$ single crystals. Even though CsI provides a higher light output, its use has been problematic due to slow scan speeds associated with afterglow problems and low density for CsI,

$CdWO_4$ crystals are more popular for X-ray explosive detection. $CdWO_4$ possesses shorter afterglow times and demonstrates lower radiation damage than CsI. Unfortunately, the radiation damage of $CdWO_4$ crystal also depends on the radiation dose. The higher the dose, the greater the radiation damage. For example, the radiation damage of CdWO4 crystal can reach as high as 40% when radiation dose is high enough.

Various approaches have been taken to reduce the radiation damage of tungstates. One approach has involved doping the scintillator material with other elements. Thus, for example, U.S. Patent Publication US 2003/0020044 A1, describes scintillator compositions formed from alkali and rare-earth tungstates, that have a general formula of $AD(WO_4)_n$. The composition $CsY_{0.25}\,Gd_{0.75}\,W_2O_8$ doped with Ca, showed improved radiation tolerance.

Another approach to improving radiation tolerance of scintillators has involved annealing the scintillator crystal in a controlled atmosphere. For example, the damage mechanism of $PbWO_4$ has been analyzed, and it was found the damage was caused by oxygen vacancies. By annealing the $PbWO_4$ crystal in an oxygen atmosphere, the defects in the crystal structure decreased significantly and the resistance to radiation damage improved.

This project pertains to the use of doping to improve the radiation resistance of $CdWO_4$. It was found that doping provides a better method of increasing radiation hardness (e.g., as compared to annealing) as the doping can stabilize the scintillator crystal structure in air, which is convenient for material preparation. Moreover the doping does not substantially interfere with the light output and other desirable properties of the material.

In particular, it was discovered that doping of cadmium tungstate with trivalent metal ions or monovalent metal ions is particularly effective in improving radiation hardness of the scintillator material.

3.2.1 Powder preparation and characterization

One of the method of making a scintillator composition typically involves combining essentially equal amounts of CdO and WO_3 and minor amounts of a dopant that comprises at least one oxygen-containing compound of a monovalent metal selected from the group consisting of Li, Na, K, Rb, Cs, Ag and TL, or/and at least one oxygen containing compound of a trivalent element selected from the group consisting of Bi, Y, La, Ce, Pr, Nd, Gd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb, where the dopant(s) comprise less than about 0.1 mole percent of the amount of cadmium; and firing the mixture at a temperature and for a time sufficient to convert the mixture to a solid solution of cadmium tungstate. Another method of making a scintillator composition comprises preparing a solution of a cadmium compound, a tungsten compound, and an amount of a monovalent metal ion selected from the group consisting of Li, Na, K, Rb, Cs, Ag, T, and/or a trivalent metal ion selected from the group consisting of Bi, Y, La, Ce, Pr, Nd, Gd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu, where the monovalent ion and the trivalent ion when present are less than about 0.1 mole percent of the amount of cadmium; precipitating the compounds in a basic solution to obtain a mixture of oxygen-containing compounds; calcining the precipitate in an oxidizing atmosphere; and heating the precipitate at a temperature and for a time sufficient to convert the mixture to a solid solution of cadmium tungstate.

In a conventional ceramic process, essentially equal amounts of CdO and WO.sub.3 are combined, and to this combination is added the desired amount of the desired dopant(s), e.g., oxygen-containing compounds of at least one trivalent element selected from the group consisting of Bi, Y, La, Ce, Pr, Nd, Gd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb or/and at least one oxygen-containing compound of at least one monovalent metal selected from the group consisting of Li, Na, K, Rb, Cs, Ag and Tl. The compounds with are wet-mixed together with ethanol alcohol to form a slurry. The slurry is dried, e.g., at 100.degree. C. for 2 hours. The mixture is then fired at temperature and for a time sufficient to convert the mixture to a solid solution of cadmium tungstate (e.g. at a temperature from 900.degree. C. to 1100.degree. C., for several hours).

In a gelation/coprecipitation process, a solution comprising a compound of Cd, a compound of tungsten, and the desired dopant(s), e.g., at least one trivalent element selected from the group consisting of Bi, Y, La, Ce, Pr, Nd, Gd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm and Yb, or/and at least one monovalent metal selected from the group consisting of Li, Na, K, Rb, Cs, Ag and Tl is prepared with dilute HNO_3 solvent, and then gelatinized by adding ammonia to the solution to obtain a gel of oxygen-containing compounds. The gel is dried, e.g., at 100.degree. C. for 3 hours and then calcined, e.g., at 700.degree. C. for 1 hour in an oxidizing atmosphere. The calcined sample is fired at a temperature ranging from 900.degree. C. to 1200.degree. C. and for a time sufficient to convert the mixture to a solid solution of cadmium tungstate.

Doped cadmium tungstates having the formulas $Cd_{0.9995}Na_{0.0005}WO_4$, $Cd_{0.9995}Gd_{0.0005}WO_4$, and $Cd_{0.9995}(KBi)_{0.0005}WO_4$were fabricated were fabricated using conventional ceramic processing methods. Briefly, proper amounts of raw materials from CdO, WO_3, Na_2CO_3, K_2CO_3, Gd_2O_3, and Bi_2O_3 were selected. The compounds were wet-mixed together with ethanol alcohol to form a slurry. The slurry was dried at 100C for 2 hours. The mixture was then fired at 1100C for 3 hours in air.

The susceptibility to radiation damage of these materials was calculated based on the percentage change of scintillating peak intensity before and after X-ray exposure (145 KeV) for 5 hours. The distance between the samples and the x-ray source was 10 cm. After irradiation, the samples were immediately measured for luminescence properties immediately to eliminate any recovery effect.

Table 1 lists the light output before radiation and radiation damage of One $CdWO_4$ single crystal sample (milled to powder), one commercial $CdWO_4$ and the three different doped tungstates.

Radiation damage was defined as the difference in light output before and after radiation divided by the light output before radiation.

Table 1. light output and radiation damage data of various $CdWO_4$ powder samples.

Sample	Peak value (no rad.)	Radiation damage (%)
Single Crystal	888	37.5
Polycrystalline Powder	342	30
$Cd_{0.9995}Na_{0.0005}WO_4$	416	13.1
$Cd_{0.9995}Gd_{0.0005}WO_4$	414	2.2
$Cd_{0.9995}(KBi)_{0.0005}WO_4$	571	6.8

The doped samples were sintered at 1000C for 3 hours.

Emission spectra of the powdered samples before and after irradiation were determined by exciting the sample with an X-ray source having peak energy of 8 keV produced from a copper anode at a power of 40 kV and 20 mA. Since all emission spectra of all of the samples had almost the same peak position and shape, we used peak height as the measure of light output.

Usually the radiation damage of scintillator crystals is measured from the change of transmittance of visible light before and after irradiation. Powder samples, however, are not transparent and thus this method is not feasible.

The high intensity radiation caused defects in crystal structure, and these defects trap the visible light excited by X-ray. Consequently the radiation damage lowers the light output of the scintillator materials. Therefore, the radiation damage can also be measured by the change of light output of the scintillator(s) (when exposed to a defined energy source) before and after irradiation. From the data in table 1, the radiation damage, up to 37.5% for the single crystal powder sample, was consistent with the data measured by transmission method, indicates that the data presented in the Table is a valid measure of radiation damage.

The light output of crystal samples was much higher than the other powder samples indicating that the radiation-induced defects in the in single crystals was less than the powder samples. The light output of all of the doped samples was greater than the commercial $CdWO_4$ powder sample indicating that the doping reduced radiation damage.

As shown in Table 1, Gd^{3+} doping was the most effective. Co-doping of K^{1+} and Bi^{3+} was better than single Na^{1+} doping. Without being bound to a particular theory, it is believed the doping of trivalent ions can introduce excess oxygen ions to the crystal lattice, which later supplements the oxygen vacancy caused by radiation and thereby reduces the radiation damage. In conclusion, the doping described herein, especially trivalent ion doping of $CdWO_4$ improves the radiation hardness of the tungstate scintillator while maintaining the scintillator light output and other desirable properties.

3.2.2 Single crystal preparation and characterization

The Czochralski method is used for the single crystal growth process for producing a scintillator composition.

Typically, seed crystal of $CdWO_4$ is introduced into a saturated solution containing appropriate compounds and new crystalline material is allowed to grow and add to the seed crystal using Czochralski method.

The starting materials, typically comprising a cadmium compound, a tungsten compound and one or more of the dopant materials and heated to form a reactant melt. The crucible is typically located in a housing, such as a quartz tube, and heated, e.g. by r.f. or resistance heaters. The melt temperature is determined by a thermocouple. A single crystal seed attached to a seed holder is lowered into the melt (the melt is the high temperature zone). As the seed is rotated about its axis and lifted from the melt, a single crystal scintillator boule forms below the seed. The size of the crystal boule increases as the seed is lifted further away from the melt toward the low temperature zone above the heaters. The boule can then be sliced and polished into scintillator crystals.

$Cd_{0.9995}Gd_{0.0005}WO_4$ was selected to grow the single crystal. The growth temperature is 1325^oC and pulling rate is 2mm/hour. Fig. 3.2 display the single crystal boule with 60 mm diameter. It looks transparent and no defects.

Fig. 3.2. $Cd_{0.9995}Gd_{0.0005}WO_4$ single crystal boule with 60 mm diameter

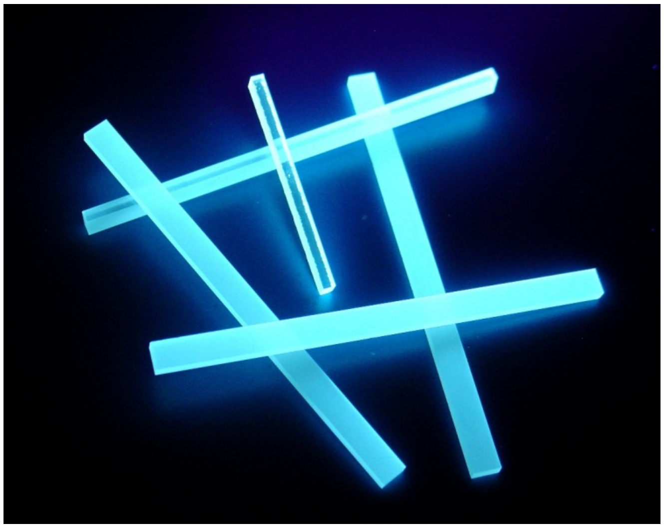

Fig. 3.3 $Cd_{0.9995}Gd_{0.0005}WO_4$ single crystal bars (polished)

We prepared single crystal bars with various spec. from the boule for different application. The typical bars are showed in Fig. 3.3. We mounted these bars on specific module to test the radiation damage. The susceptibility to radiation damage of these materials was calculated based on the percentage change of scintillating peak intensity before and after X-ray exposure (145 KeV) for 2 hours. The distance between the samples and the x-ray source was 10 cm.

The result is the same as the powder sample. It proves the doping indeed improve the radiation damage.

3.3 Silicate- based orange scintillators

Scintillators are phosphors that show luminescence under X-ray and high energy radiation. They are commonly used in today's X-ray imaging detectors for medical diagnostics, security inspection, industrial non-destructive evaluation (NDE), dosimetry, and high-energy physics. Recently, there has been an increasing demand for high atomic density, high speed and high light-output scintillator crystals and ceramic materials in above mentioned applications. As the silicon photo diode is widely used in these detector, the spectra response of silicon photo diode requires the scintillator material can emit long wavelength visible light, especially red light. So far, most red scintillators are from the doping of Eu^{3+}, which decay time is in the range of millisecond and can not be used in security and high energy detection. The currently used scintillators for X-ray Explosive Detection system are mainly CsI and $CdWO_4$ single crystals. Even though CsI has high light output, $CdWO_4$ crystal is more popular for X-ray Explosive Detection due to slow scan speed associated with afterglow problem for CsI. Low light output and toxicity are the disadvantages for $CdWO_4$.

Europium as a di-valence primary activator in orthosilicate is known to have high emission efficiency, exhibiting broad-band luminescence, and has a superior advantage of very short luminescence decay time of a few µs in comparison to the rare earth elements such as Eu^{3+}, Nd^{3+}, Tb^{3+} doped scintillators which have a decay time in the order of ~ 1ms. Unfortunately, its emission light is from blue to yellow and can not match the spectral response of silicon photo diode. If red orthosilicate scintillators can be developed with di-valence europium as an activator and high emission efficiency, it might turn out to be an ideal material of choice as a detector for X-ray and high energy detection. It is extensively studied for Eu^{2+} doped silicate. So far, the longest emission peak for Eu^{2+} doped silicate with an acceptable optical output is located around 580nm. It is reported Eu^{2+} doped Ba_3SiO_5 possesses the red emission light, but the light output is too low for any commercial application.

The search thus continues for Eu^{2+} doped M_3SiO_5 luminescent material having orange to red emission light in combination with the aforementioned other advantageous properties.

With the help of library technology, we develop Eu^{2+}-activated Ca, Sr, and Ba silicates configures to emit in the orange to red region of the spectrum for use in a x-ray detection system such as security inspection in airports. In particular, the orange scintillators comprise a silicate-based compound having at least one divalent alkaline earth element M that is Mg, Ca, Ba, or Zn in a stoichiometric relationship generally represented by the formula $(Sr_{1-x}M_x)_3SiO_5:Eu^{2+}$.
In particular, the present orange scintillators have the formula $(Sr_{1-x}M_x)_yEu_zSiO_5$, where M is at least one of a divalent metal selected from the group consisting of Ba, Mg, Ca, and Zn; $0 \le x \le 0.5$; $2.6 \le y \le 3.3$; and $0.001 \le z \le 0.5$. These scintillators are configured to emit visible light having a peak emission wavelength greater than about 590 nm.

The present orange scintillators may be used in a x-ray detection system. Such a system comprises a radiation source configured to emit x-ray, an object to be detected and a detector with silicate-based orange scintillators configured to absorb the radiation from the radiation source and penetrating x-ray from the object, and emit light with peak intensity in a wavelength greater than about 590 nm.

3.3.1 Powder preparation and characterization

Methods of producing the present orange scintillators include two steps: powder preparation and bulk fabrication. sol-gel methods, solid reaction methods, and co-precipitation methods can be used for powder preparation. The scintillator bulk can be prepared as single crystal and transparent ceramics with the sintered powder. An exemplary co-precipitation method includes the steps of:

a) dissolving $Sr(NO_3)_3$ in water;
b) dissolving Eu_2O_3 in nitric acid;
c) dissolving NH_4F in water;
d) mixing the resulting solutions of steps a), b), and c);
e) adding $(CH_3O)_4Si$ to the resulting solution of step d), and then adding oxalic acid to the mixture to cause precipitation;
f) adjusting the pH of the mixture of step e) to about 9 with ammonium hydroxide;

g) drying the reaction product of step f), and then calcining the reaction product to decompose the precipitant; and

h) sintering the precipitant of step g) in a reducing atmosphere.

The effect of varying the ratio of the alkaline earth metal to the silicon in the host lattice, the type of alkaline earth metal, the effect of the content of the Eu activator, and the role of the halogen dopant are discussed in the following.

As taught by G. Blasse et al. in Philips Research Reports Vol. 23, No. 1, pp. 1-120, the host lattice in a phosphor belonging to the system Me_3SiO_5, where Me is either Ca, Sr, or Ba, has the crystal structure (or is related to the crystal structure) Cs_3CoCl_5. That the host lattice of the phosphors of the present invention is also crystalline is demonstrated by the x-ray diffraction pattern shown in FIG. 3.4. The exemplary phosphor in FIG. 3.4 is $(Sr_{0.97}Eu_{0.03})_3SiO_5F_{0.18}$, which was prepared by co-precipitation and sintering at 1250°C in H_2 for 6 hours).

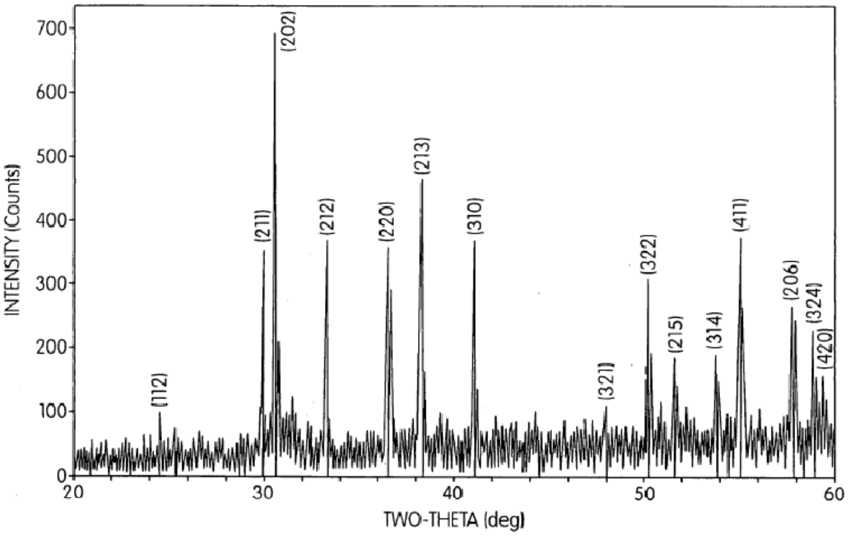

FIG. 3.4. An X-ray diffraction pattern of $(Sr_{0.97}Eu_{0.03})_3SiO_5F_{0.18}$ prepared by co-precipitation and sintering at 1250°C in H_2 for 6 hours.

Excitation spectra are prepared by observing changes in the emitted light intensity at a set wavelength while varying the excitation energy (see, for example, the Phosphor Handbook, edited by S. Shionoya and W.M. Yen, CRC Press, New York, 1999, p. 684. The excitation spectrum of exemplary orange phosphors of the present invention are shown in FIG. 3.5, where the exemplary phosphors are Ba_3SiO_5, Sr_3SiO_5, and $(BaSrMg)SiO_5$. The emission intensity of the phosphors was recorded at a wavelength of 590 nm.

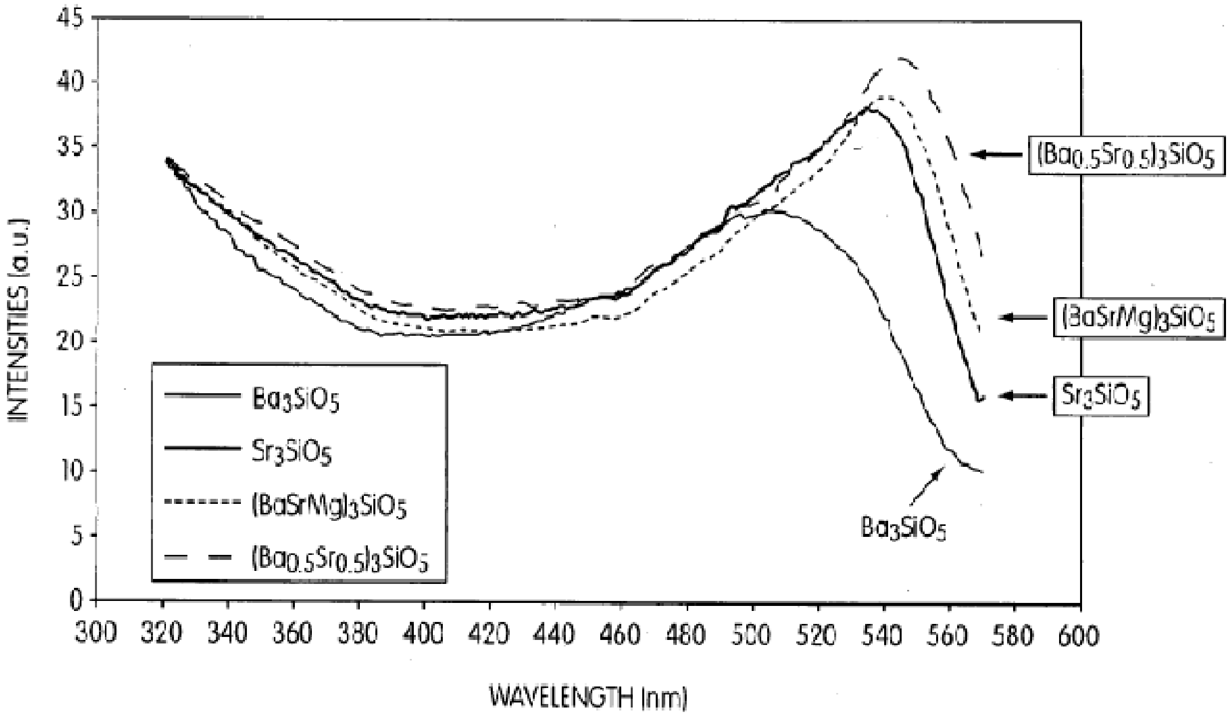

Fig. 3.5. Excitation spectra of various M_3SiO_5:Eu

The excitation spectra in FIG. 3.5 shows that these phosphors are efficient at fluorescing when excited at wavelengths ranging from about 480 to 560 nm. The intensity of the light emitted at 590 nm is greatest for the phosphor $(BaSrMg)SiO_5$, and this occurs when the wavelength of the excitation radiation is a little greater than 540 nm. Virtually equally intense in emission is the phosphor Sr_3SiO_5, where its maximum emission occurs for excitation radiation having a wavelength a little less than 540 nm. Of the three phosphors in this exemplary series Ba_3SiO_5 has the lowest intensity emission; the peak of this emission occurs when the wavelength of the excitation radiation is about 510 nm.

The present orange phosphors offer emission characteristics that have advantages over the present scintillators. These characteristics include both the spectral position of the emission peak, as well as the maximum intensity of the peak. FIG. 3.6 shows emission spectra of $CdWO_4$ and $(Ba_{0.1}Sr_{0.9})_3SiO_5$ excited by 40kev x-ray.

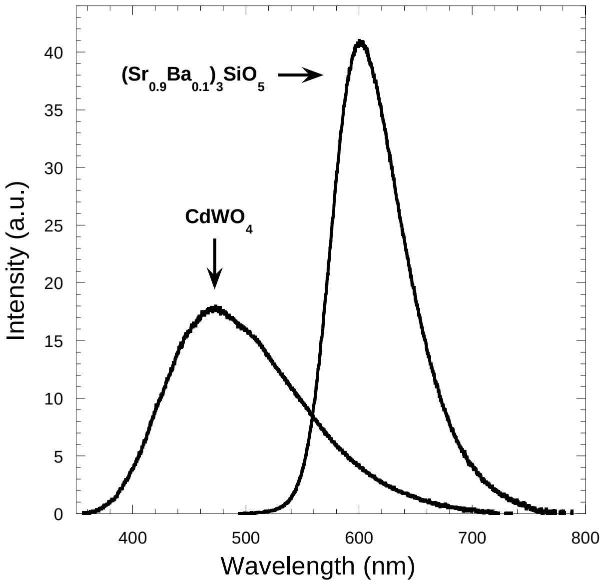

FIG. 3.6 Emission spectra of $CdWO_4$ and $(Ba_{0.1}Sr_{0.9})_3SiO_5$ excited by 40kev x-ray

Referring to FIG. 3.6, the phosphor $(Ba_{0.1}Sr_{0.9})_3SiO_5$ demonstrating not only the longer wavelength 9600 nm), but also much higher intensity than t $CdWO_4$.

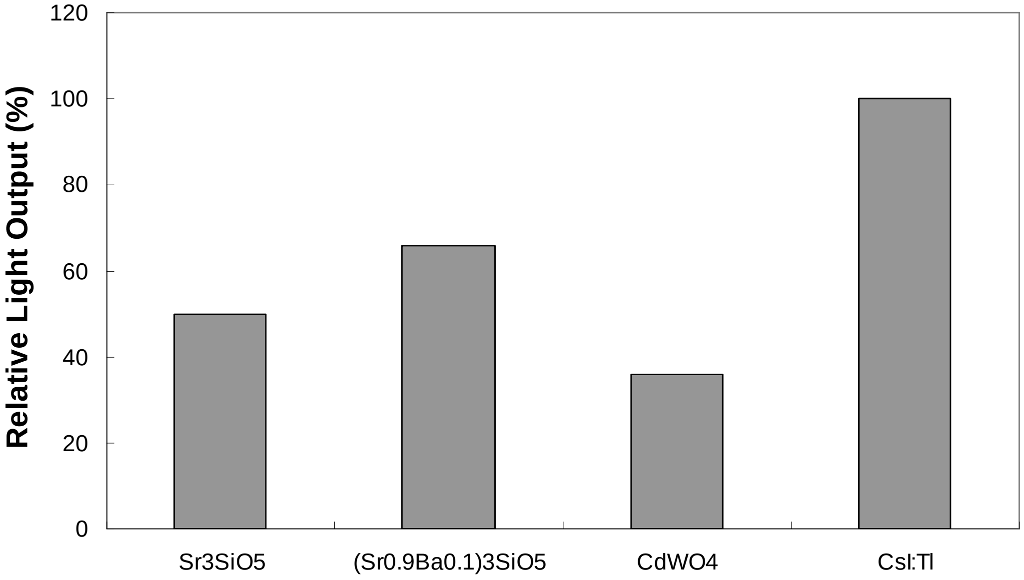

FIG. 3.7. Comparison of light output of various scintillators excited by 40kev x-ray and measured with silicon photo diode

FIG. 3.7. shows the comparison of light output of various scintillators excited by 40kev x-ray and measured with silicon photo diode. It can be seen the the light output of $(Ba_{0.1}Sr_{0.9})_3SiO_5$ is much better than $CdWO_4$. Though the light output of $(Ba_{0.1}Sr_{0.9})_3SiO_5$ is lower than CsI:Tl, the wavelength of $(Ba_{0.1}Sr_{0.9})_3SiO_5$ is at least 40nm longer than CsI:Tl, which is an advantage in the detector with Si photo-diode.

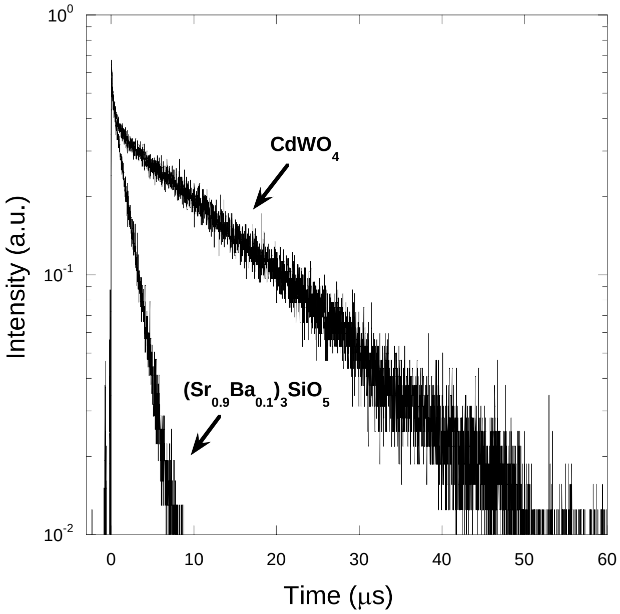

FIG. 3.8 Decay time pattern of $CdWO_4$ and $(Ba_{0.1}Sr_{0.9})_3SiO_5$

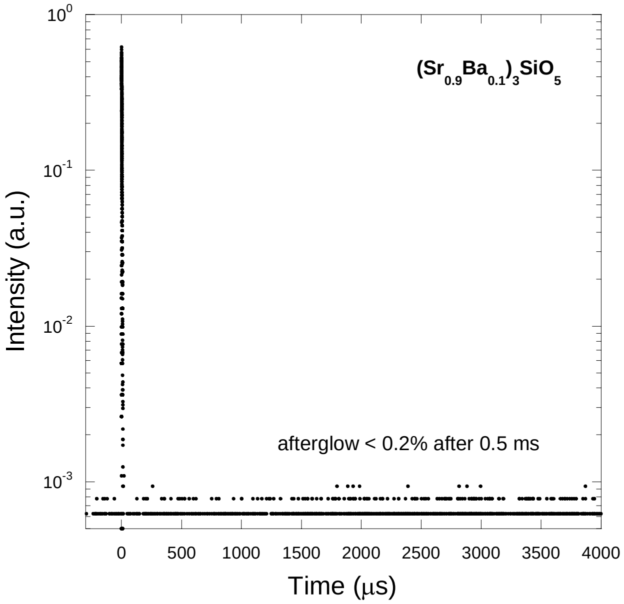

FIG 3.9. Afterglow measurement of $(Ba_{0.1}Sr_{0.9})_3SiO_5$

From Fig.3.8 and Fig. 3.9, the afterglow of $(Ba_{0.1}Sr_{0.9})_3SiO_5$ is much shorter than $CdWO_4$. From these data, we can conclude the M_3SiO_5:Eu is a promising scintillator material.

3.3.2 Single crystal preparation and characterization

The Czochralski method is used for the single crystal growth process for producing a scintillator composition.

Iridium bar is used as seed to grow the single crystal. $(Ba_{0.1}Sr_{0.9})_3SiO_5$ was selected to grow the single crystal. The growth temperature is 1800°C and pulling rate is 2mm/hour. Fig. 3.10 displays the result of single crystal growth. This is not single crystal and phase segregation occurs, which may be due the two kind of element Ba and Sr in M position. Single element (Sr) is supposed to have a better result.

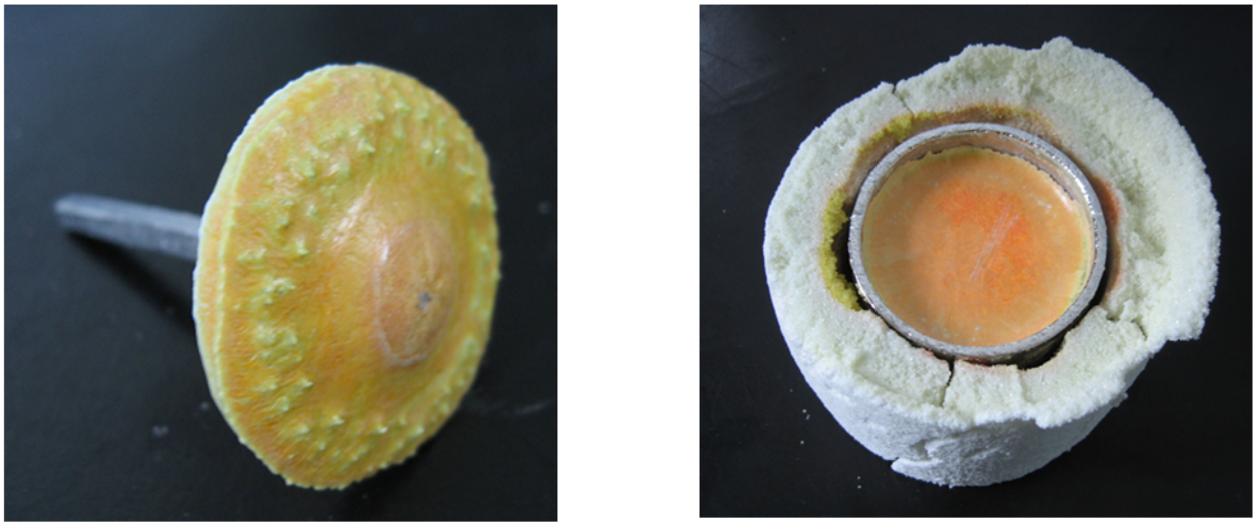

Fig. 3.10. The result of single crystal growth of $(Ba_{0.1}Sr_{0.9})_3SiO_5$

3.3.3 Transparent preparation and characterization

Since the melting point of M_3SiO_5 is higher than 2000°C, single crystal growth with Czochralski method is not plausible. We tried to fabricate the transparent ceramics with $(Ba_{0.1}Sr_{0.9})_3SiO_5$.

We used centrifugal method to collect fine particles. Fig. 3.11 is the particle size distribution of the powder collected for transparent ceramics. We collected the particle size between 1 to 3μm and the pattern verifies our expectation.

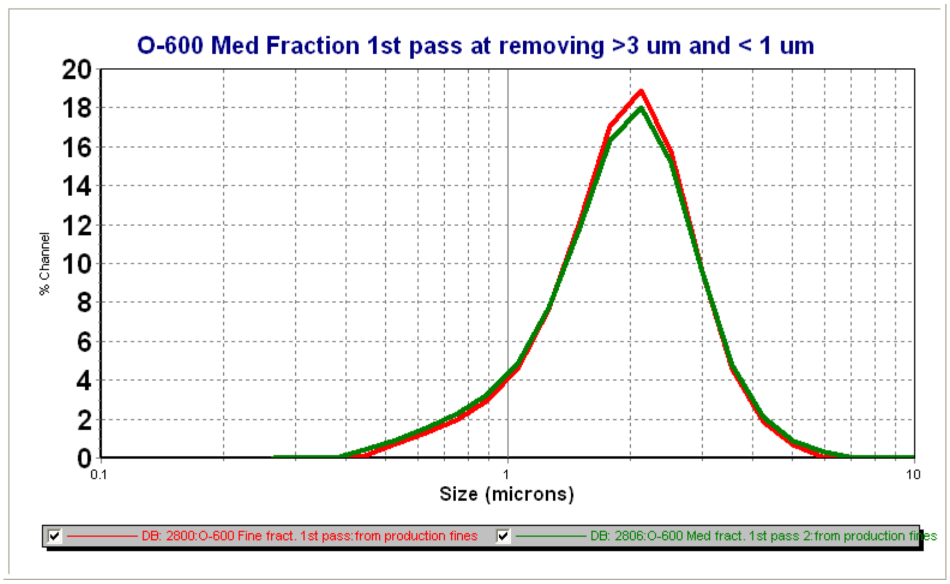

Fig. 3.11 The particle size distribution of the powder collected for transparent ceramics

Cold isostatic-press was carried out with vacuum sealing in Nb sheet and stacking compact under 15000 psi. Hot isostatic-press was carried out at 30000 psi, 1400^{o}C, Ar and 2h holding time. The microstructure of sintered bulk is showed is Fig. 3.12. There is still pores and gray spot on the surface. Adjustment of atmosphere and sintering temperature is needed to improve the quality.

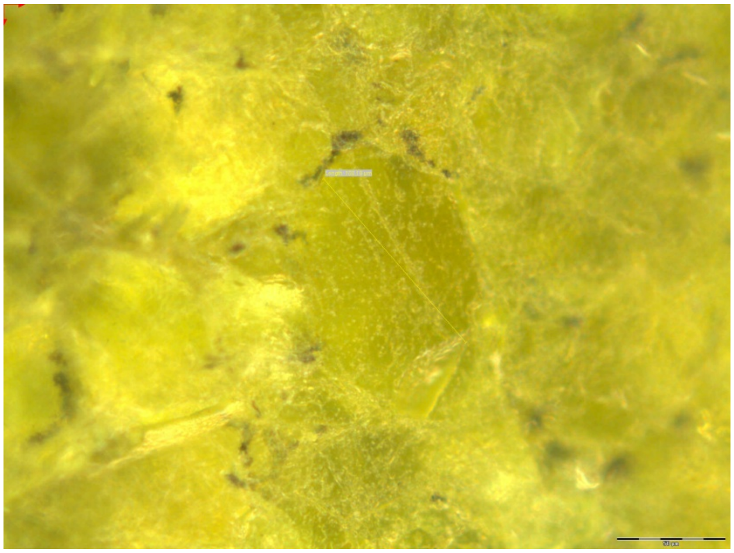

Fig. 3.12. The microstructure of sintered bulk of $(Ba_{0.1}Sr_{0.9})_3SiO_5$.

4. Conclusions

1. We successfully developed stable liquid solution for almost all useful metal ions.

2. We developed printing liquid solution arrays for inorganic materials libraries, which can not only screen out the scintillator candidates, but also make unlimited replica easily for processing test.

3. Doped $CdWO_4$ are developed both in powder and single crystal, which possesses superior radiation hardness.

4. Silicate-based orange scintillator is developed, which is especially suitable for Si photodiode due to its long emission wavelength. Single crystal growth and transparent ceramic preparation are also carried out.