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M.J. Weber

September 1994

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## Scintillator Materials for Calorimetry

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**SCINTILLATOR MATERIALS FOR CALORIMETRY**

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**ABSTRACT**

Requirements for fast, dense scintillator materials for calorimetry in high energy physics and approaches to satisfying these requirements are reviewed with respect to possible hosts and luminescent species. Special attention is given to cerium-activated crystals, core-valence luminescence, and glass scintillators. The present state of the art, limitations, and suggestions for possible new scintillator materials are presented.

**1. Introduction**

The past decade has witnessed a veritable renaissance in research and development of scintillator materials, prompted to a major degree by the need for scintillators for precision calorimetry in high energy physics, but also by the needs for high light output scintillators for medical imaging, geophysical exploration, and numerous other scientific and industrial applications. Improved experimental techniques for studying scintillator materials and more knowledgeable, systematic surveys of have led to the development and better understanding of many promising scintillator materials for calorimetry and numerous other applications. The current state of the art and progress in the search for improved scintillator materials is well documented in the published proceedings of a recent workshop<sup>1</sup> and a symposium<sup>2</sup> devoted to scintillator materials.

Scintillators may be in the form of crystals, glasses, liquids, and gases and composed of organic and inorganic materials.<sup>3</sup> Here we restrict consideration to inorganic solids. A history of the discovery of important inorganic scintillator materials—important in the sense that they either became commercially available and widely used (or have the potential of becoming so in the case of recently discovered materials) or triggered further developments or new research directions—is shown in Fig. 1. The century of discovery may be divided into three phases. The first phase included the earliest scintillators:  $\text{CaWO}_4$  first used in the year following Roentgen's discovery of x-rays, uranyl salts used by Becquerel in 1896 to discover radioactivity, and  $\text{ZnS}$  used by Crookes to detect and count radioactivity and by Rutherford to study alpha particle scattering. This period of visual scintillation counting ended with the development of photomultiplier tube and the discovery of scintillation in naphthalene and led in mid-century to the second phase and Hofstadter's discovery of  $\text{NaI(Tl)}$ . In a burst of exploration during the next few years, the scintillation properties of most pure and activated alkali halide crystals were investigated. Lithium containing compounds to detect neutrons and the first glass scintillators were

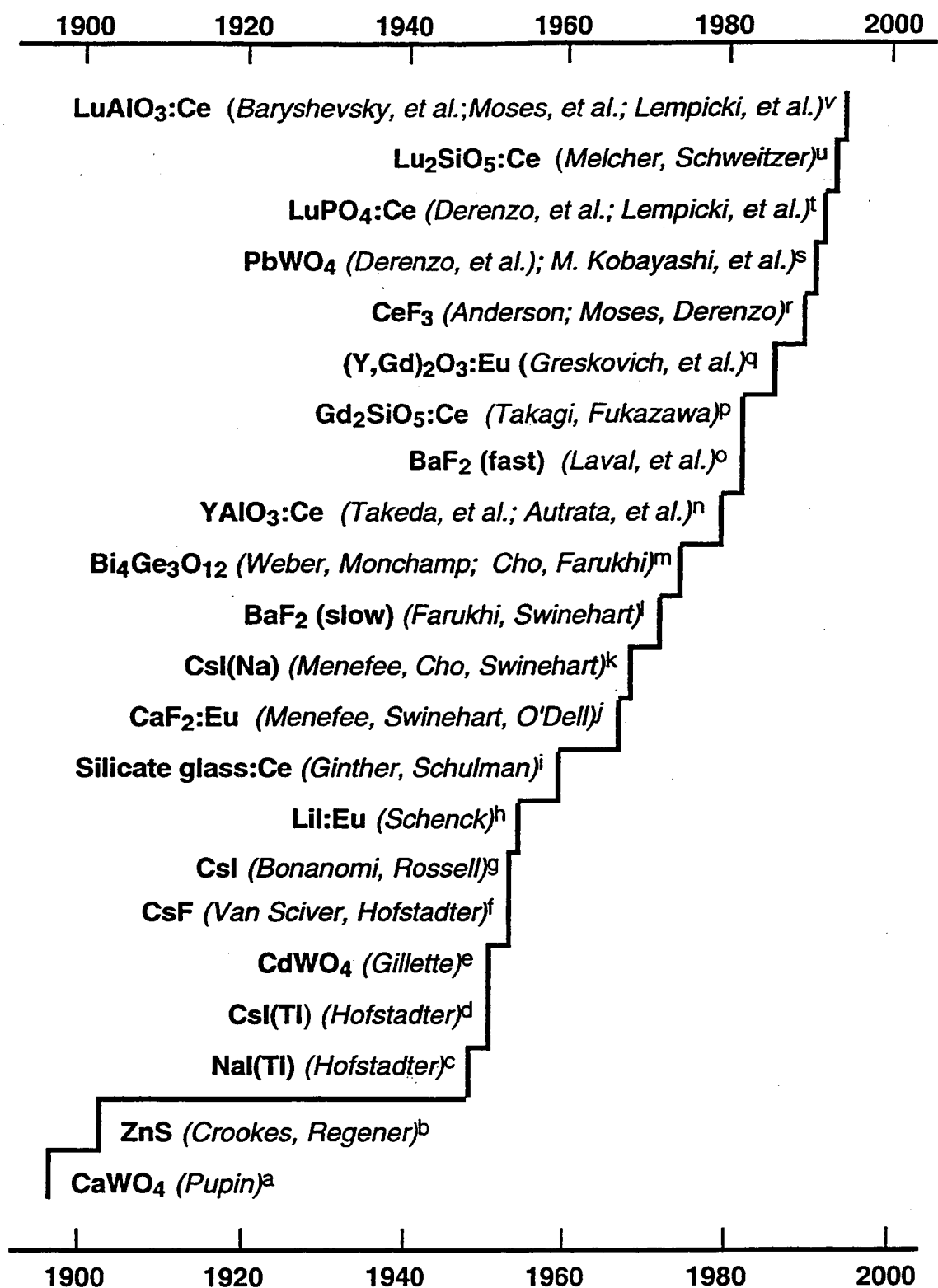


Figure 1. Discovery of major inorganic scintillator materials.

also developed in the 1950s. A steady precession of material discoveries followed leading to the third phase and the explosive growth of activity during the past decade. These discoveries and improvements in scintillator material benefited throughout by concurrent research on photoluminescence, cathodoluminescence, and x-ray phosphors.

Current scintillator materials of choice for calorimetry and their properties are reviewed in several articles in references 1 and 2 and in many papers in this volume and will not be repeated here. Instead we address the following questions. Are there still better scintillators to be found? What do we mean by better? How much better could scintillators be? Have we exhausted the Periodic Table? We do this by considering the requirements for calorimetry, the processes governing scintillation efficiency, and various luminescent species and host compounds that may have the potential for satisfying the requirements of high energy physics calorimetry.

## 2. Properties of Scintillator Materials

### 2.1 Requirements

Today we have a large number of well-characterized scintillator materials including crystals, glasses, plastics, and liquids. No single material is superior for all applications; in most cases improvements in one or more properties are desirable. Properties that one must keep in mind in selecting a material for a specific application are shown in Fig. 2. The material may be a crystal or glass in bulk, fiber, or sheet form. The emission wavelength and the light yield will determine the best photodetector to use. Fast signal rise and decay times are important for timing and high event rate applications or time-of-flight (TOF) modes of operation; the absence of afterglow is important in medical imaging. Stability includes several factors that must be known or controlled: environmental or chemical durability, ruggedness and mechanical shock resistant, and variation of light output with temperature and time. Radiation damage, which may be irrelevant for detectors for most imaging applications, is extremely important in high radiation environments such as in detectors for use with high luminosity colliders. High density and stopping power (i.e., large effective atomic number) are important for reducing the amount of material needed. Whereas for detecting very energetic particles light yield may not be too critical, for applications where the particle energy is smaller or fixed, e.g., in positron emission tomography, increased light yield is important for improving accuracy and spatial resolution. Energy resolution is also dependent on light yield. The price of raw materials, the method of preparing the scintillator material, and fabricating the material into the desired size and shape all enter into the final cost. These and other factors not included in Fig. 2 (we rarely have a lobotomy) differ in their relative importance in selecting materials for a particular application.

Some specific requirements for calorimetry and other applications are compared in Table 1. High density and high  $Z$  materials are of almost universal because increased stopping power reduces the amount of scintillator material needed. For shower containment, the radiation length and the Moliere radius, which are proportional to  $Z$ , are of special interest.<sup>5</sup> High energy physics (HEP) calorimetry differed from low- or intermediate energy calorimetry and most other applications in the requirements for (1) light

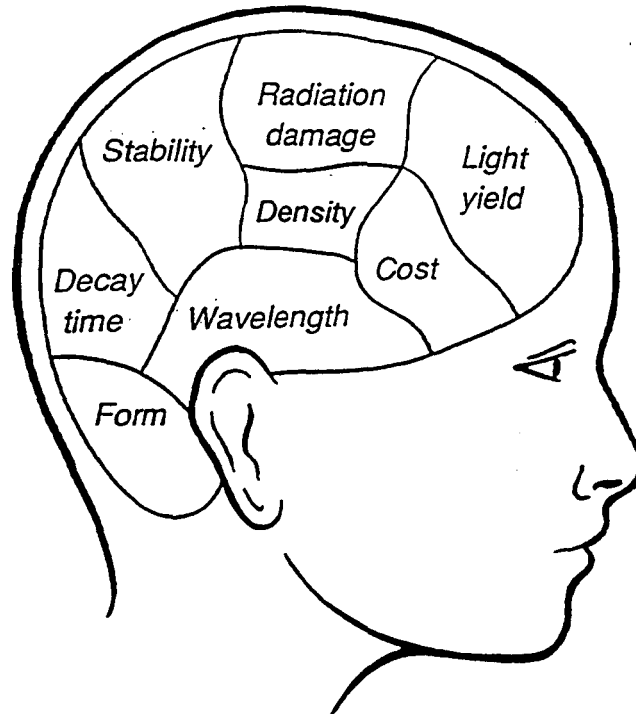


Figure 2. Properties of scintillators to be considered when selecting materials.

yield, (2) decay time, and (3), for high-luminosity, high-intensity colliders, radiation hardness. Because of the high energies of the incoming radiation, which may be 100 GeV or more, light yields in terms of luminescent photons per MeV can be very modest. In general an output of  $>200$  photons/MeV (about 0.5% of that of NaI(Tl)) is sufficient to provide adequate accuracy and energy resolution. The light yield also affects the type of photodetector required (e.g., photomultiplier tube, photodiode, avalanche photodiode). The decay time must be short and consistent with the event rate. For precision calorimetry, uniformity of light output is essential. Therefore accumulated radiation damage, which appears as induced optical absorption bands that absorb part of the scintillation light, must be controlled.

TABLE 1 Requirements for various scintillator applications (adapted from ref. 4).

Application	Density (g/cm <sup>3</sup> )	Z	Light yield (phot./MeV)	Decay time (ns)	Radiation hardness (Mrad)
HEP calorimetry	high	high	$> 200$	$< 20$	$> 10$
Low-int. energy calor.	high	high	high	varies	+/-
Nuclear physics	high	high	high	varies	-
Astrophysics	high	high/low	high	less import.	-
Medical imaging	high	high	high	$\leq 1$ (TOF)	-
Industry	high	high	high	less import.	-
Neutrons	high	B, Li, Gd	high	10 - 100	-



With present and proposed detectors for high energy physics experiments having grown to gargantuan dimensions requiring thousands of crystals with quantities of materials measured in cubic meters, the cost of the scintillator materials has become a major concern.<sup>6,7</sup> Low- or moderate-cost crystal production methods such as Bridgman or Czochralski growth are highly desirable. Glass, because of its low-cost, large-volume production, is attractive for scintillator materials but has other limitations that are discussed later.

Below we consider possible luminescent species and host materials that may provide the high density, fast decay, and light output required for HEP calorimetry. Although radiation hardness is a prime consideration, because of space limitations it will not be discussed here (the reader is referred to papers in references 1 and 2 for details of this issue).

## 2.2 Scintillation Efficiency

The basic processes in scintillation may be divided into three stages:<sup>8-11</sup> (i) the absorption of the incident radiation or particle by the host and conversion of the energy into thermalized electrons and holes, (ii) transfer of some fraction of the electron and hole excitation to luminescence centers, and (iii) the luminescence process. The quantum efficiency of the scintillation process is given by

$$\eta = \beta \cdot S \cdot Q, \quad (1)$$

where  $\beta$  is the conversion efficiency for creating electron-hole pairs,  $S$  is the transfer efficiency, and  $Q$  is the radiative efficiency of the luminescence centers. Because the incident energy  $E_m$  of a particle will usually be very much bigger than the band gap  $E_g$  of the material, the number of electron-hole pairs and resultant scintillation photons may be very large, thus yielding huge quantum efficiencies. In terms of energy efficiency, however, the performance of scintillators is less impressive. For a scintillation photon of energy  $E_s$ , this efficiency is given by

$$\eta(E_s/E_m) \sim (E_m/\alpha E_g) S \cdot Q (E_s/E_m) = (E_s/\alpha E_g) S \cdot Q. \quad (2)$$

In Eq. (2) it is assumed that it takes on the average an energy  $\alpha$  times the band gap to create a thermalized electron-hole pair. Various treatments of polaron and plasmon models and electron-phonon scattering losses have shown that  $\alpha$  is typically about 2-3 for semiconductor and insulator materials (see Ref. 12 for an good review of this problem). Thus from Eq.(2), for a material having transfer and luminescence efficiencies  $S$  and  $Q$  of unity and a scintillation photon energy approaching that of the band gap, the energy efficiency should be ~25-30%, which is about what has been obtained for the best phosphor materials. For one of the best scintillators, NaI(Tl),  $E_s$  is equal to approximately  $E_g/2$  and the reported efficiency is 12%, therefore  $S$  and  $Q$  must again be near unity. CsI(Tl) has an even higher efficiency than NaI(Tl).<sup>13</sup> Thus scintillator

materials already exist with near the maximum achievable efficiency and only small improvements in light yield are possible. For HEP calorimetry, however, light yield is usually not the main issue. Rather, a fast decay time, good stopping power for shower containment, radiation hardness, and reasonable cost are the principal concerns for the scintillator material.

### 2.3 Luminescent Species

Table 2 summarizes the wide variety of luminescent species possible for inorganic scintillators. The luminescence of many of these, such as transition metal ions, f-f transitions of lanthanides ions, and filled shell ions, involve transitions of varying degrees of forbiddenness and hence are generally slow ( $>1 \mu\text{s}$ ). Exciton decay rates may be fast but vary widely with exciton type and host. To ensure the requirement of fast decay, we consider luminescence involving only allowed electric-dipole transitions of  $\text{Ce}^{3+}$  and core-valence transitions.

TABLE 2. Inorganic luminescent species.

Type	Transition	Examples
Transition metal	nd - nd	$\text{Ti}^{3+}$ , $\text{Cr}^{3+}$ , ... $\text{Cu}^{2+}$ , $\text{Mo}^{3+}$
Lanthanide/actinide	nf - nf	$\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ , ... $\text{Yb}^{3+}$ , $\text{U}^{3+}$
Lanthanide/actinide	nf - (n+1)d	$\text{Ce}^{3+}$ , $\text{Eu}^{2+}$
Filled shell	$\text{nd}^{10}$ - (n+1)s	$\text{Cu}^+$ , $\text{Ag}^+$
Post-transition group	$\text{ns}^2$ - $\text{nsnp}$	$\text{Sn}^{2+}$ , $\text{Sb}^{3+}$ , $\text{Tl}^+$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$
Molecular complex	charge transfer	$\text{WO}_4^{2-}$ , $\text{TaO}_4^{3-}$
Exciton	e - h recombination	$\text{CsI}$ , $\text{BaF}_2$ (STE)
Core-valence	$\text{np}(\text{cation})$ - $\text{n}'\text{p}'(\text{anion})$	$\text{BaF}_2$ , $\text{CsF}$

The dependence of scintillation on temperature is a further consideration for precision calorimetry. At room temperature ( $T_R$ ) the luminescence and decay of  $\text{Ce}^{3+}$  and core-valence transitions exhibit little variation with temperature. In contrast, most excitonic, post-transition-group ion, and molecular complex luminescence processes are temperature dependent and the scintillation yield may vary by more than 1%/K, thus requiring a temperature stabilized environment for reliable accurate calibration.

The decay times and emission intensities from molecular complexes and post transition group elements depend on the degree of thermal quenching and or changing level populations with temperature and can vary greatly with the structure and chemical composition of the host material. This accounts for the large variation in scintillation yields of different tungstate, bismuth, and lead compounds. The decay time of such materials can be reduced, if necessary for calorimetry, by increasing the temperature to increase the rate of nonradiative decay but with a concomitant loss of light output. The scintillation of  $\text{PbWO}_4$  is an example of a material that naturally exhibits the features of fast decay and low light output at room temperature and is a candidate for a planned HEP detector.<sup>7</sup>

IA												VIII A																																	
H	IIA												III A	IV A	V A	VIA	VII	He																											
Li	Be											B	C	N	O	F	Ne																												
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII			IB	IIB	Al	Si	P	S	Cl	A																												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																												
Fr	Ra	Ac	<table border="1"> <tr> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lw</td> </tr> </table>															Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw																																

Figure 3. Cations used in dense scintillator materials.

#### 2.4 Host Materials

Cations that have been exploited for dense scintillator materials are indicated in Fig. 3. The post transition group elements Tl, Pb, and Bi are the highest Z, nonradioactive elements in the Periodic Table which accounts for the wide spread use of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) and the current interest in  $\text{PbWO}_4$ . These materials have densities of 7.1 and 8.3  $\text{g/cm}^3$  and radiation lengths of 1.1 and 0.9 cm., respectively. There are, however, many more dense Pb and Bi containing compounds with densities in the range 9-10  $\text{g/cm}^3$  (for some representative examples, see Table 3 of Ref. 14). These may either be Pb or Bi emitting materials or hosts for other activator ions or luminescent species.

As noted above, although the light yields of many compounds containing post transition group elements or molecular complexes such as tungstate or tantalate groups may be small at room temperature, they may still be adequate for high energy calorimetry. Since many of these are very dense materials, they warrant further investigation to quantify their yields and dependences on temperature.

The refractive index  $n$  of the host material is a further consideration. Since the probability of electric-dipole transitions of an activator is proportional to  $n(n^2 + 2)^2$ , the radiative lifetime is reduced if a high-refractive-index host is used. The refractive index also enters into the transport and coupling of the scintillation light to the photodetector.

Lutetium compounds have become favorite hosts for high-efficiency  $\text{Ce}^{3+}$ -activated scintillators because of their high density and high light yield, although they have a background count rate due to radioactive  $^{176}\text{Lu}$  which may be detrimental for some applications. Many lutetium aluminate, silicate, and phosphate compounds have been investigated (see Section 3). Crystals of simple Ce-doped  $\text{Lu}_2\text{O}_3$  (density 9.4  $\text{g/cm}^3$ ) have been prepared and its photoluminescence and scintillation properties studied (the results will be reported elsewhere). Another group of compounds that we are studying

are the lutetium borates, i.e.,  $\text{LuBO}_3$  ( $6.9 \text{ g/cm}^3$ ) and  $\text{Lu}_3\text{BO}_6$  ( $7.4 \text{ g/cm}^3$ ). Other dense compounds that are possible hosts for  $\text{Ce}^{3+}$  and have not been reported (to my knowledge include the 2:1 compound of the  $\text{Lu}_2\text{O}_3\text{-Al}_2\text{O}_3$  system  $\text{Lu}_4\text{Al}_2\text{O}_9$  ( $8.4 \text{ g/cm}^3$ ), the 6:1 compound of the phosphate system  $\text{Lu}_{12}\text{P}_2\text{O}_{23}$  ( $9.6 \text{ g/cm}^3$ ),  $\text{Lu}_2\text{O}_2\text{S}$  ( $8.9 \text{ g/cm}^3$ ),  $\text{LuLaO}_3$  ( $9.1 \text{ g/cm}^3$ ),  $\text{LuGaO}_3$  ( $8.8 \text{ g/cm}^3$ ),  $\text{LuInO}_3$  ( $8.3 \text{ g/cm}^3$ ), and  $\text{Lu}_3\text{InO}_6$  ( $10 \text{ g/cm}^3$ ). The  $\text{LnTaO}_4$  group of compounds are known phosphors and can be doped to emit from the ultraviolet to the red.<sup>15</sup> Of these,  $\text{LuTaO}_4$  has a density of  $9.75 \text{ g/cm}^3$ . These are examples of a much larger group of high density compounds including lutetium tantalate, tungstate, and bismuth compounds. The ease of growing large, high-optical-quality crystals of any of the above materials is of course a paramount issue.

A host material with the density and efficiency of lutetium compounds but without the high cost of Lu would be welcomed for those applications involving relatively large quantities of scintillator materials. Although the price of lutetium materials is coming down,<sup>16</sup> it may always be prohibitively expensive for use in large detectors for HEP experiments.

### 3. Cerium Activated Scintillator Materials

Cerium-activated scintillator materials have been known and used for several decades but have received renewed interest for many applications because of the favorable spectroscopic properties of  $\text{Ce}^{3+}$  and the ability to incorporate  $\text{Ce}^{3+}$  into many different host materials.<sup>17</sup> Among the attractive properties of  $\text{Ce}^{3+}$  are (1) its luminescence which occurs in the visible-near ultraviolet region and is well matched to the spectral response of high efficiency photodetectors, (2) the emission which involves an allowed electric-dipole transition and thus is fast for good timing resolution, (3) the luminescence intensity and decay time which are stable and insensitive to temperature for most hosts at room temperatures, (4) there are no long-lived radioactive isotopes, and (5) cerium is the least rare of the rare earths. The density, dominant decay time, and relative light output (photons/MeV) of a number of  $\text{Ce}^{3+}$ -activated materials are given in Table 3. In many instances the optimum concentration of Ce remains to be established.

There is a large variation in the  $\text{Ce}^{3+}$  scintillator efficiencies in Table 3, ranging from values approaching that of  $\text{NaI(Tl)}$  for  $\text{LuAlO}_3$  and  $\text{Lu}_2\text{SiO}_5$  to values two orders of magnitude smaller for some glasses. All of the materials in Table 3—both crystals and glasses—exhibit intense photoluminescence (except for  $\text{PbF}_2$ ) with luminescence lifetimes at room temperature characteristic of the expected probability for radiative decay, thus their radiative quantum efficiencies  $Q$  are near unity. Although the conversion efficiency  $\beta$  may vary somewhat for crystals and glasses of different chemical compositions, the large variation in  $\text{Ce}^{3+}$  scintillation efficiency of these materials is due predominantly to differences in the transfer efficiency  $S$ . Electrons and holes created in the conduction and valence bands may combine radiatively or nonradiatively, be trapped by various defects, form mobile or trapped excitons, or migrate to the vicinity of a  $\text{Ce}^{3+}$

TABLE 3. Properties of cerium-activated scintillator materials.

Material	Density (g/cm <sup>3</sup> )	Decay time (ns)	Relative light yield
<i>Reference</i>			
NaI(Tl)	3.7	230	100
<i>Crystals</i>			
LuAlO <sub>3</sub> (LuAP)	8.3	10-20	80
Lu <sub>2</sub> SiO <sub>5</sub> (LSO)	7.4	~40	75
Gd <sub>2</sub> SiO <sub>5</sub> (GSO)	6.7	30-60	20-25
LuPO <sub>4</sub> (LOP)	6.5	24	33
YAlO <sub>3</sub> (YAP)	5.6	28	40
CeF <sub>3</sub>	6.2	~5, 30	5-9
BaF <sub>2</sub>	4.9	50	6
PbF <sub>2</sub>	8.2		~0
<i>Glasses</i>			
silicate (GS1)	2.5-2.7	~ 60*	~ 5-10
borate	2.4-2.5	~ 30	~ 3
phosphate	~2.6	~ 30	< 1
fluoride (HfF <sub>4</sub> )	~6	10,3 0	< 1

\* Plus slower components.

ion and excite it. The relative probabilities of these processes and the position of the Ce<sup>3+</sup> electronic energy levels in the gap between the valence and conduction bands enter into the transfer efficiency and are material dependent.

The scintillation efficiencies of lutetium aluminum perovskite<sup>18</sup> and lutetium ortho-silicate<sup>19</sup> are the highest reported for any Ce<sup>3+</sup> activated material and nearly equal to that of NaI(Tl), thus they are of interest for many applications. Since for these materials  $E_s \sim (1/2)E_g$ , this efficiency suggests high values for both S and Q. The scintillation outputs of LuAP and LSO have, however, been found to vary significantly with growth and annealing conditions. Lutetium aluminate crystals have shown the presence of both the perovskite and garnet phases which alters the effective light yield.<sup>16</sup> Measurements of light output for a number of different LSO samples have shown a convincing anti-correlation between trap-related integrated thermoluminescence output and scintillation light output over a range of several orders of magnitude.<sup>20</sup> Thus defects and their effect on transfer efficiency can account for the large variation in scintillation found for different LSO crystals. The existence of very deep traps in LSO crystals is also evident from the report<sup>21</sup> of phosphorescence lasting for >2000 s. Therefore if the number of trapping centers in these and other materials can be reduced, slightly higher Ce<sup>3+</sup> light yields may be possible.

The best cerium-activated glasses (silicates) have scintillation efficiencies of only about one-tenth that of NaI(Tl); other glasses (borates, phosphates, fluorides) are reported to have lower efficiencies.<sup>1</sup> This is not surprising given that glass is a disordered medium with a potentially large number of defects and traps to reduce the transfer efficiency. The small scintillation efficiency of Ce-doped glasses is due to the large number of defects that trap electrons and holes and prevent or delay the excitation of and eventual recombination at the activator. Defects in glass are defined as deviations from short-range order and may be intrinsic (for example, three-coordinated Si, oxygen vacancies, or interstitial oxygen in the case of SiO<sub>2</sub>), broken bonds, or extrinsic intrinsic (for example, impurities). Many different thermally-induced defects are also possible. The number and type of traps vary with the glass composition, structure, and the thermal treatment. The low efficiency of heavy metal fluoride glasses is probably associated with the more ionic, weaker bonding in these glasses. These are dense glasses and although their light output is low, the yield is sufficient for HEP calorimetry.<sup>7</sup>

Several years ago Spowart<sup>22</sup> investigated Ce<sup>3+</sup>-activated Li-Mg-Al silicate and found that the scintillation efficiency and thermoluminescence glow curves varied with glass composition but no detailed study was made. Recently Bliss, Craig, et al.<sup>23</sup> have begun a systematic investigation of the effects of composition and microstructure on the scintillation efficiency of Ce-doped silicate glasses. In one study, a large systematic variation in scintillation efficiency was found by varying the alkaline earth component in otherwise identical glasses.<sup>24</sup> Measurements of the absorption and emission spectra and decay curves for these glasses showed only very small changes, as expected for such small compositional variations. That the change in scintillation efficiency is related to defects and their effect on the transfer efficiency was demonstrated by the anti-correlation between integrated thermoluminescence glow curve intensity and the scintillation efficiency.<sup>25</sup>

The effect of defects also appears in the temperature dependence of the scintillation output. At low temperatures,  $\ll 300$  K, much of the electron-hole excitation is trapped before it can reach the Ce<sup>3+</sup> centers and the scintillation yield is low. With increasing temperature the excitation becomes untrapped and the scintillation light output increases. Eventually, usually at temperatures above  $T_R$ , the lowest 5d level of Ce<sup>3+</sup> begins to decay nonradiatively by multiphonon processes and the light output decreases.<sup>26</sup> Thus the scintillation intensity exhibits a peak similar to that observed for Tl-activated crystals.<sup>27,28</sup> For many materials this peak occurs, fortunately, in the vicinity of room temperature (see, for example, reference 29). (CeF<sub>3</sub> shows a different temperature-dependent behavior<sup>30</sup> because of the large fraction of direct excitation of Ce<sup>3+</sup>).

As illustrated above, defects play a dominant role in determining the scintillation efficiency of many activated materials. The overall scintillation process is best investigated and understood by photoluminescence, radioluminescence, and thermoluminescence measurements combined with excitation spectra recorded using synchrotron radiation. Recently the latter was used to examine the relative differences in light output resulting from direct excitation into the 5d bands of Ce<sup>3+</sup> and from excitation

of valence band and core electrons.<sup>31</sup> Large differences in excitation spectra associated with the transfer process were observed for the two extreme cases in Table 3—lutetium crystals and glasses. Theoretical calculations of electronic structure of the host and luminescence centers<sup>32</sup> can also be useful in understanding the behavior of new scintillator materials and in improving our ability to predict and tailor chemical compositions and structures for specific applications.

#### 4. Core Valence Luminescence Materials

In the decade since the first identification of fast scintillation due to core valence transitions, many materials have been reported to exhibit this luminescence and the phenomenon is reasonably well understood.<sup>33</sup> The first and classic example of core-valence luminescence (CVL) is BaF<sub>2</sub> where a hole created in the Ba 5p core band is filled by an electron from the F 2p valence band. Because the energy difference between the valence band and the 5p core levels is less than the band gap of the material, Auger decay is energetically forbidden and the decay is radiative. Since the process involves an anion-cation crossover transition, it has been called cross luminescence (or Auger-free decay).

Core-valence luminescence involving np – n'p transitions have been reported for Ba, K, Rb, and Cs in numerous binary and ternary materials.<sup>34</sup> The emission is in the ultraviolet, fast (~1 ns), and independent of temperature. The light yield is typically about 1500–2000 photons/MeV and thus sufficient for HEP calorimetry if the CVL cation is present in greater than 10 cation percent. Examples of the scintillation properties of CVL materials are given in Table 4. The emission of Cs compounds is particularly attractive because it occurs at wavelengths that are well matched to common photodetectors. The emission of K and Ba compounds is at shorter wavelengths that require appropriate transmissive and photoemissive materials to detect the CVL.

TABLE 4. Examples of core-valence luminescence observed at 300 K (from ref. 34).

Crystal	Density (g/cm <sup>3</sup> )	Wavelength (nm)	Decay time (ns)
KF	2.5	156	
KLuF <sub>4</sub>	5.2	170–200	1.5
RbF	3.6	203, 234	1.3
RbCaF <sub>3</sub>	3.6	240–300	2.8
CsF	4.1	390	2.9
CsCl	4.0	240, 270	0.9
CsBr	4.4	250	0.07
BaF <sub>2</sub>	4.9	195, 220	0.8
BaLiF <sub>3</sub>	5.2	190, 230	≤ 1.0

While the decay rates and light yields of many CVL materials are sufficient for for HEP calorimetry, higher density and radiation hard materials are desirable. The densities of the CVL materials reported to date are low to moderate, thus the radiation lengths are relatively long and large crystals are required to achieve adequate stopping power for high energy calorimetry (for example, 50-cm long crystals were considered for the GEM BaF<sub>2</sub> detector<sup>35</sup>). Examination of the NIST crystal diffraction database<sup>36</sup> reveals a number of more dense, wide band gap materials containing CVL cations. Some examples include Ba<sub>2</sub>YbF<sub>7</sub> (6.1 g/cm<sup>3</sup>), BaThF<sub>6</sub> (6.7 g/cm<sup>3</sup>) (if the radioactivity of Th can be tolerated), and CsPbF<sub>3</sub> (6.0 g/cm<sup>3</sup>). Lutetium containing compounds are again attractive because of their high densities and large band gaps. In addition to KLuF<sub>4</sub> in Table 4, another example of a potential lutetium CVL material is CsLu<sub>4</sub>F<sub>13</sub> (5.8 g/cm<sup>3</sup>). The possibility of CVL in dense lead and bismuth compounds such as RbBiF<sub>4</sub> (6.3 g/cm<sup>3</sup>) or RbPb<sub>2</sub>F<sub>5</sub> (8.5 g/cm<sup>3</sup>) will depend on the various band gaps.

The materials in Table 4 and those discussed above are all halides with large band gaps, but there are a number of oxides that also have large band gaps. For example, BaB<sub>2</sub>O<sub>4</sub> and CsB<sub>3</sub>O<sub>5</sub> (crystals developed for use as nonlinear optical materials) transmit down to 200 nm. We have observed fast (~1 ns) x-ray excited scintillation from these crystals and, in addition, from Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Cs<sub>2</sub>CO<sub>3</sub>, and Cs<sub>3</sub>PO<sub>4</sub>. Excitation and emission spectra are needed to confirm that this is cross luminescence. Some examples of dense oxide materials containing CVL cations are CsLuO<sub>2</sub> (7.8 g/cm<sup>3</sup>), RbYbO<sub>2</sub> (7.4 g/cm<sup>3</sup>), and RbLuO<sub>2</sub> (7.6 g/cm<sup>3</sup>). Possible CVL from glasses is discussed in Section 5.4.

As evident above, there are a number of more dense materials that may be fast CVL scintillators suitable for HEP calorimetry. Other crossover transitions such as np - n'd are potential sources of core-valence luminescence,<sup>33</sup> but thus far none have been reported. In the case of crystalline materials where the CVL ions are intrinsic components of the material, band structure calculations of the positions of the conduction, valence, and core levels can be used to predict CVL. Cluster calculations have also been used to account for general spectral features and decay times of CVL.<sup>33,37</sup>

## 5. Glass Scintillators

As a host material, glass has the advantages that it can be cast in various sizes and shapes, of high optical quality and produced using relatively inexpensive production techniques. Because of its compositional versatility, many physical and spectroscopic properties can be tailored (within limits) for specific applications. However, the number of potential point defects and trapping centers in a disordered medium such as glass is large which, as noted for Ce-activated crystals, can reduce the transfer efficiency and resultant light yield. Although the low light output of glass scintillators is unattractive for many applications, an output of ~1% of NaI(Tl) satisfies the requirement for HEP calorimetry in Table 1. Another consideration for the usage of glass is radiation hardness. Glasses are usually not radiation hard. Ways of attempting to cope with this issue include (1) compositional variations and additives to reduce color center formation, and (2) optical or thermal bleaching.<sup>38</sup>



### 5.1 Cerium-activated Glasses

Of the cerium-doped glasses investigated thus far, silicate glasses have the highest reported light yield of ~1500–5000 photons/MeV.<sup>39,40</sup> The Ce<sup>3+</sup> luminescence decay is nonexponential (as expected due to the existence of physically different sites in a disordered medium) with the principal Ce decay time of ~50 ns characteristic of radiative 5d–4f transitions, but with longer decay components. Measurements of a Li-Mg-Al silicate glass (GS1) by Angelini et al.<sup>40</sup> were fitted with decay components having characteristic times approaching a millisecond. They also showed that only about 60% of the light was emitting in the first microsecond following excitation. This indicated that much of the excitation in glass was stored in deep traps.

While the light output of the best Li-Mg-Al silicates is adequate for HEP calorimetry, the density is low, ~2.5 g/cm<sup>3</sup>, and the radiation length is large, about 10 cm.<sup>39</sup> Other reported phosphate and borate glasses have lower light outputs and similarly low densities and long radiation lengths. Heavier silicate glasses containing lanthanides, lead, and other heavy cations are known but none of these glasses nor bismuth germanate glasses are reported to have any reasonable scintillation output at room temperature. Extremely dense (8.2 g/cm<sup>3</sup>) PbO-Ga<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub> glasses are also known,<sup>41</sup> but visible transmission begins at ~500 nm and, therefore, is unsuitable for Ce<sup>3+</sup> emission. This glass could, however, be a host for activators emitting at longer wavelengths (e.g., Ti<sup>3+</sup>).

Heavy metal fluoride glasses, especially those containing Hf, can have densities in the range ~6 g/cm<sup>3</sup> with radiation lengths of ~1.6 cm. The scintillation light yields are very small, but do just satisfy the criterion in Table 1. Such glasses have been melted in 100 kg batches for infrared optical windows and lenses, therefore they are attractive from the viewpoint of production. Their radiation resistance, however, is low which has thus far made them unacceptable for HEP calorimetry.<sup>7</sup>

### 5.2 Glass Ceramics

Vitroceramics are materials having a mixture of crystalline and glassy. phases. If the crystals are small compared to the wavelength of light or of the same refractive index as the glass, the material may be optically transparent. If cerium can be incorporated into the crystalline phase of such materials, one could preserve the feature of high scintillation efficiency characteristic of a crystal with the potential low-cost, large-scale production of a glass ceramic. The question of radiation hardness remains.

Most known transparent glass ceramics do not have a crystalline phase with a cation site suitable for substitution of a trivalent rare earth. Recently, however, a transparent vitroceramic doped with trivalent lanthanides was reported.<sup>42</sup> The composition (mol.%) was 30SiO<sub>2</sub>-15AlO<sub>1.5</sub>-24PbF<sub>2</sub>-20CdF<sub>2</sub>-11LnF<sub>3</sub>, where Ln was Er and Yb; the density of these materials is about 6.5 g/cm<sup>3</sup>. The lanthanide ions were preferentially segregated from the precursor glass and dissolved into Pb<sub>x</sub>Cd<sub>1-x</sub>F<sub>2</sub> microcrystals of about 20 nm in size, presumably in the form of a LnF<sub>3</sub>-CdF<sub>2</sub>-PbF<sub>2</sub> solid solution. The photoluminescence and scintillation properties of Ce<sup>3+</sup> or Eu<sup>2+</sup> in these materials should be investigated to establish their value for calorimetry and other scintillator applications.

### 5.3 Cross Luminescence Glasses

Core-valence transitions are localized phenomena and do not require long-range order or periodicity of the host,<sup>43</sup> hence they can occur in glass. CVL has been reported in a K-fluoroberyllate glass.<sup>44</sup> Glasses based on BeF<sub>2</sub> as the glass former can have the large band gaps, > 10 eV,<sup>45</sup> therefore CVL involving K, Rb, Cs, and Ba cations in such glasses should all be possible. The light yield of the CVL will be proportional to the content of the CVL cation, which in general will be  $\leq 50$  cation percent. The density of these glasses are low, however,  $\sim 3-4$  g/cm<sup>3</sup>. Heavy metal fluoride glasses, as noted above, can have high densities but their absorption edge is at  $\sim 200$  nm. CVL should be observed from Cs and Rb in these glasses; CVL from Ba is more questionable because of possible competing Auger transitions. Fluoride glasses would combine features of moderately high density with fast ultraviolet scintillation. Cesium and rubidium CVL may also be observable from wide band gap borate, phosphate, and silicate glasses, but these glasses will generally have relatively low densities. As with all glasses, radiation damage is an omnipresent consideration for HEP calorimetry.

### 5.4 Organic Scintillants in Inorganic Glasses.

Organic scintillators are composed of various fluors (aromatic hydrocarbons, organic dyes) in a plastic host.<sup>3</sup> These are generally fast (ns) scintillators but their densities are very low, typically  $\sim 1.0-1.1$  g/cm<sup>3</sup>, and hence of limited usefulness for HEP calorimetry. Incorporating organic molecules into more dense inorganic hosts is limited by the melting temperatures of the latter which are usually well above the decomposition temperature of the organic scintillant. Although various organic materials were introduced into boric acid glasses for luminescence and scintillation studies many years ago,<sup>46-48</sup> these are low density glasses with poor chemical stability.

Several years ago a new class of low-melting temperature tin fluorophosphate glasses was discovered<sup>49</sup> and various organic dyes were incorporated into these glasses for nonlinear optical applications.<sup>50</sup> The glasses are durable with moderate densities (3.5-5.5 g/cm<sup>3</sup>), refractive indices of 1.6-1.9, and Knoop hardnesses of 90-120. Several organic fluors have been incorporated into these glasses and their scintillation properties investigated by Smith, et al.<sup>51</sup> All glasses exhibited intense photoluminescence. Fast ( $\sim 1$  ns) scintillation was observed, but the light output was low. This was due to the small concentration of fluor added and or inefficient transfer from the host. Exactly how the organic molecules are incorporated into the glass and the mechanism and efficiency of host-fluor energy transfer are unknown. The concentration of the organic fluor in the glass represents a fundamental problem for the practical application of these scintillators.

Tin fluorophosphate glasses warrant further investigation for general calorimetry where fast plastic scintillators are now used because they offer the possibility of greater stopping power with increased hardness and physical durability. Glass fibers provide good spatial precision for tracking of ionizing particles in the vicinity of a high energy interaction.<sup>39</sup> Since these glasses can be drawn into fibers with smaller diameters than is now possible with plastics, they could also be useful in certain tracking applications.

## 6. Conclusions

The scintillation light output and decay time of most  $Ce^{3+}$ -activated and core-valence luminescence materials are satisfactory for HEP calorimetry. These materials have the additional advantage that, in contrast to many other scintillator materials, their output is not very sensitive to temperature at ambient temperatures. Materials having higher densities would be beneficial and some suggested approaches to achieving this objective were presented. Further systematic investigation and theoretical treatment of materials incorporating the post transition group elements or molecular complexes are also needed to develop relationships of structure and bonding to scintillation properties and thereby guide the search for improvements in this class of materials. Radiation damage was not dealt with here but is acknowledged to be an extremely important consideration. Finally, after having discovered a promising scintillator material for HEP calorimetry, one of the most significant questions is whether large crystals of high purity can be grown in the sizes required using economically acceptable methods.

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