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Development of glass-ceramic scintillators for gamma-ray astronomy

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Abstract. Scintillators synthesised as glass-ceramics have several potential benefits compared to the currently-used halide scintillators, including non-hygroscopicity, mechanical ruggedness, ease of producing customisable shapes, and the potential for low-cost synthesis. The use of these scintillators is considered for a gamma-ray telescope operating in the 0.2 MeV–50 MeV photon range. Inorganic scintillator compounds suitable for incorporation into glass-ceramics are assessed. In addition, several families of glass suitable for use as hosts for scintillating compounds are also reviewed.

1. Introduction

Scintillation detectors have been used in gamma-ray astronomy telescopes such as the Fermi Gamma-ray Space Telescope and the Compton Gamma Ray Observatory. The requirement to improve the sensitivity of future gamma-ray telescopes, particularly in the 0.2 MeV–10 MeV photon range has motivated an analysis of different scintillator options.

The most commonly used material types for gamma-ray spectroscopy applications are inorganic single crystals, transparent polycrystalline ceramics, glasses, polymers loaded with scintillating compounds, and inert gases, each having advantages and disadvantages [1]. Families of inorganic materials widely-used as scintillators include the alkali, alkaline earth, and rare earth halides, often doped with rare earth elements. These families of materials, which include the most widely used inorganic scintillator NaI(Tl), contain compounds that exhibit high light yield and good timing and energy resolutions. However, they are hygroscopic, and must therefore be hermetically encapsulated. The halide scintillators are normally used in monocrystalline form, and are typically grown by either the Czochralski technique [2, 3], micro-pulling-down technique [4, 5], or by using a Bridgman furnace [6]. The cost of growing single-crystals using these techniques is very high, and can be many times the cost of the raw materials [7].

Transparent ceramic scintillators are produced in polycrystalline form by high temperature sintering of compacts of nano-sized powders, generally followed by hot pressing. While somewhat less expensive than monocrystalline crystal growth methods, production of scintillators by sintering and hot pressing still results in high scintillator costs. Additionally, the hot pressing method is normally limited to production of simple cylindrical shapes. The polycrystalline ceramics produced are generally non-hygroscopic and significantly more rugged than halide

scintillators. Another class of inorganic scintillators are scintillating glasses. ^6Li -doped glasses are widely used for thermal neutron detection and spectroscopy.

Nanocrystalline glass-ceramics are a promising new class of inorganic scintillator. Kang *et al.* and Barta *et al.* demonstrated the feasibility of using glass-ceramic scintillators for gamma-ray spectroscopy [8, 9]. Glass-ceramics possess several advantages over halide and ceramic scintillators.

1.1. Scintillator Requirements

For the current application a scintillator with an energy resolution of less than 5% at 662 keV is required. To achieve this the scintillator must have a high light yield and good light yield linearity. A peak luminescent emission well-matched to the peak sensitivity of silicon photomultiplier detectors (SiPM) is also required. SiPMs are the likely photodetector that will be used for a gamma-ray telescope. A short primary decay constant of < 100 ns is required to make the detector suitable for high count rate applications. To make low count rate experiments feasible a scintillator with low intrinsic activity is required. Scintillators containing significant quantities of long-lived meta-stable radioisotopes such as ^{138}La , ^{176}Lu or ^{87}Rb are therefore unsuitable for the current application. A high density ($> 5 \text{ g} \cdot \text{cm}^{-3}$) and high effective atomic number is required to provide a sufficiently high gamma-ray attenuation coefficient, and to favour photoelectric interaction over Compton scattering. The material should not be hygroscopic as this would require the crystal to be encapsulated, resulting in significant dead space in the telescope. The scintillator material should be available in a wide range of sizes, and be physically robust. Because a large quantity of scintillator material will be required, the specific cost of the scintillator should be moderate. The current cost of producing monocrystalline $\text{LaBr}_3(\text{Ce})$ and CeBr_3 scintillators makes their use prohibitively expensive at the proposed instrument scale.

2. Glass-Ceramics

Glass-ceramics are engineered materials formed by the controlled nucleation and crystallisation of glass. Glass-ceramics are commonly produced by a melt-quench process, followed by annealing, but may be produced by other methods such as the sol-gel process [10]. Controlled crystallisation is achieved by a two-stage heat-treatment process, whereby crystals nucleate and then grow *in situ* from the amorphous glass. As a consequence of this, crystallite distribution can be uniform throughout the glass body. The nature of glass-ceramics allows numerous optical and mechanical properties to be controlled by suitable adjustment of the batch composition and heat treatment regime. Glass-ceramics are widely used for their controllable properties, combining the desirable characteristics of glasses and sintered ceramics.

Unlike crystalline solids, glasses are not thermodynamically stable. Their internal energy is slightly higher than that of a crystalline material of the same composition. A thermodynamic driving force therefore exists for the re-arrangement of the atoms in a glass to form crystalline phases. However, if a material is cooled sufficiently rapidly from the molten state, there will be insufficient time available for atoms to re-arrange themselves to form crystalline phases. Once the material has sufficiently cooled, the atoms possess insufficient thermal energy to rearrange themselves into an ordered lattice, and they will be trapped in the amorphous state. Due to their thermodynamically unstable nature, many glasses may be crystallised in a controlled manner by suitable heat treatment.

The composition of a parent glass may be chosen so that the crystalline phases that are formed upon heat treatment are scintillating compounds. A material so-designed is termed a glass-ceramic scintillator (GCS). The feasibility of using glass-ceramic scintillators for gamma-ray spectroscopy and radiation detection has already been demonstrated by Barta *et al.* and Kang *et al.*, although the energy resolution so far obtained has been low [9, 8, 11, 12].

Glass ceramics have several properties that make them desirable candidate materials for gamma-ray scintillator applications. They are more mechanically rugged and are simpler to synthesise in large volumes than halide scintillators. Glass-ceramics do not cleave, and may be cut and polished with relative ease. The glass matrix of a GCS provides environmental protection to the scintillating compounds, allowing hygroscopic scintillating compounds to be used without encapsulation, while the crystallites act as the luminescent centres. The glass-ceramic production route allows for more compositional flexibility than is possible for monocrystalline crystal growth methods, and may be used to produce crystallites of compounds that do not melt congruently. More significantly, the cost of producing glass-ceramics is typically far less than the crystal growth methods used for halide scintillators, or the hot pressing method used for polycrystalline ceramics, providing the potential to significantly reduce the cost of producing inorganic scintillators.

It is desirable to maximise the volume fraction of scintillating phase crystallites in a glass-ceramic in order to maximise the visible light output. However, excessively high crystallite volume fractions may lead to loss of optical transmissivity [9]. The compositions and heat treatment regimes of GCSs must therefore be carefully optimised to achieve a suitable balance of scintillation and other optical and physical properties. Optical transparency in a glass-ceramic containing a moderately high crystalline volume fraction may be retained by forming crystallites with diameters on the order of 20 nm–50 nm or less [13, 14]. Adjustment of the heat treatment parameters allows the size of the crystallites to be controlled. Matching of the refractive indices of the base glass and crystallites also minimises light scattering.

Polymers loaded with nano-sized scintillating crystallites are also under investigation for scintillation applications. However, glass-matrix nano-structured materials appear more promising as they have higher gamma-ray attenuation than polymer-matrix scintillators [13]. In addition, because the scintillating crystallites in GCSs are formed *in situ*, agglomeration problems that can occur with loaded polymer-matrix scintillators are avoided [13].

Glass-ceramics are preferred to glass for scintillator applications due to the potentially higher light yields obtainable. Glass scintillators exhibit low transfer efficiency of excitation energy from the matrix to the luminescent centres, caused by the abundance of charge carrier trapping sites in glass matrices [15, 14]. These charge carrier traps, which originate from network defects such as non-bridging oxygen and impurities, can lead to non-radiative recombination (phonon emission), and can thereby result in poor light yield. The ordered nature of the crystalline phases in glass-ceramics may lead to more efficient energy transfer to the luminescent centres and a higher probability of radiative recombination [16].

2.1. Glass Systems for Glass-Ceramic Scintillators

Several types of parent glass may be used as a basis for glass-ceramic scintillators. The parent glass should ideally provide a matrix that is capable of incorporating a large volume fraction of scintillating phase in order to maximise light yield. It should provide sufficient chemical stability to protect hygroscopic scintillating compounds from environmental moisture. In addition, the glass matrix should provide good mechanical strength, and should be optically transparent.

Silicate or aluminosilicate glasses are suitable candidate glass families for synthesis of glass-ceramics. Fluxes such as Na_2O and CaO are commonly added to silicate glass to reduce the required processing temperature. These fluxes reduce the connectivity of the glass network, thereby reducing the viscosity of the glass. Some rare earth dopant ions tend to form clusters in silicate glasses, leading to premature concentration quenching [17, 9]. Addition of aluminium cations can prevent rare earth ion clustering, thereby enhancing luminescent efficiency [18, 9].

Oxyfluoride glasses are also suitable parent glass systems for synthesis of glass-ceramic scintillators. Oxyfluoride glasses provide a low phonon energy fluoride environment suitable for rare earth ion doping, while retaining the desirable mechanical and chemical stability of

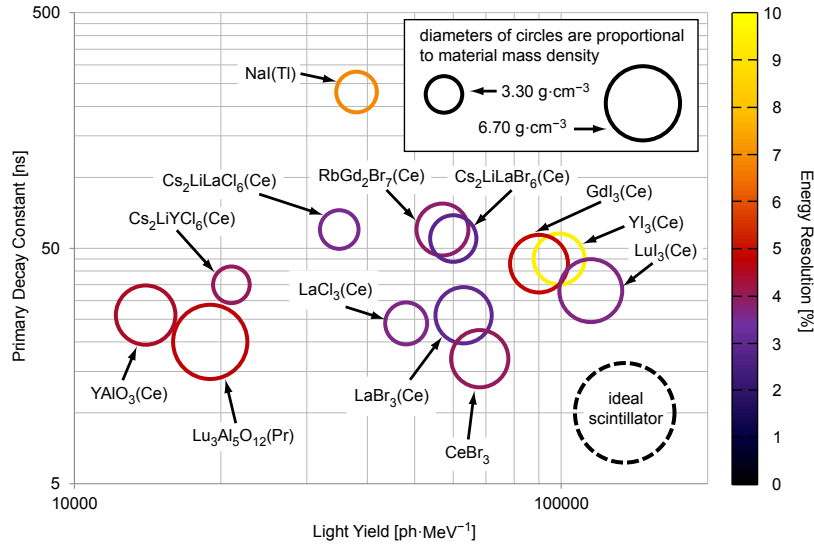


Figure 1. The light yield, primary decay constant, density, and energy resolution of several scintillators.

oxide glasses [19]. Nano-sized crystallites may be precipitated in many oxyfluoride glasses due to the formation of a diffusion barrier surrounding the crystals [20, 21, 22]. In addition to scintillator applications, oxyfluoride glass-ceramics doped with rare earth ions are also of interest for upconversion lasers and telecommunications optical amplifiers [19].

3. Scintillator Compounds

Rare earth halide scintillating compounds such as $\text{LaBr}_3(\text{Ce})$ and CeBr_3 have many desirable properties, including excellent timing and energy resolutions. However, the high cost, hygroscopicity, and difficulty of manufacturing large single crystals of these materials are undesirable. Numerous ceramic scintillators have also been investigated for scintillator applications including aluminium perovskites, aluminium garnets, oxyorthosilicates, and pyrosilicates. Several of these scintillators also exhibit desirable gamma-ray scintillation properties, combined with ruggedness and non-hygroscopicity. However, the energy resolutions so-far demonstrated by ceramic scintillators have been inferior to those of the best rare earth halides. Additionally, despite being less expensive than monocrystalline growth methods, the sintering and hot pressing route used to produce these transparent ceramics still results in rather high scintillator costs.

The light yield, primary decay constant, density, and energy resolution of several promising scintillator compounds suitable for integration into glass-ceramics are illustrated in Figure 1. Several scintillators with high intrinsic activities, which would not be suitable for the current application, are included in Figure 1 for comparison purposes.

4. Glass-Ceramic Scintillators

To-date, a limited number of the known inorganic scintillating compounds have been produced as glass-ceramics. Several of these are listed in Table 1, along with the glass batch composition used. Many of these glass-ceramics have been investigated for applications other than gamma-ray spectroscopy, including photonic and laser upconversion applications. For this reason the scintillation properties of many of these glass-ceramics have not been characterised.

Fu *et al.* produced transparent CaF_2 glass-ceramics doped with 0.1 mol% Eu^{2+} ions [19]. CaF_2 crystallites in the size range 11 nm–18 nm were precipitated from the glass by heat treating at

Table 1. Summary of some known inorganic scintillator compounds that have been produced as glass-ceramics.

Compound	Glass Family	Batch Composition	Reference
BaF ₂	oxyfluoride	(100-x)(2Na ₂ O-16K ₂ O-8Al ₂ O ₃ -74SiO ₂)·xBaF ₂	[22]
Bi ₄ Ge ₃ O ₁₂	bismuthate-germanate	40Bi ₂ O ₃ -60GeO ₂	[23]
CaF ₂ (Eu)	oxyfluoride	45SiO ₂ -20Al ₂ O ₃ -10CaO-25CaF ₂	[19]
CaF ₂ (Eu)	oxyfluoride	49 SiO ₂ -20 Al ₂ O ₃ -30 CaF ₂ -1 EuF ₂	[24]
CeBr ₃	oxyfluoride	50 SiO ₂ -16 Al ₂ O ₃ -19 NaF-13 GdBr ₃ -2 CeBr ₃	[8]
CeF ₃	oxyfluoride	40 SiO ₂ -28 Al ₂ O ₃ -17 NaF-15 CeF ₃	[25]
CeF ₃	fluorophosphate	NaPO ₃ -MF ₂ -CeF ₃ , M = Pb, Zn, Cd, Ba	[26]
GdBr ₃ (Ce)	oxyfluoride	50 SiO ₂ -16 Al ₂ O ₃ -19 NaF-13 GdBr ₃ -2 CeBr ₃	[8]

700 °C. The luminescence intensity of the glass-ceramic was found to be more than twice that of the base glass, caused by the migration of Eu²⁺ dopant ions into the CaF₂ crystallites. Precipitation of crystallites slightly shifted the optical absorption edge to longer wavelength, but did not significantly degrade the transparency of the glass.

Secu *et al.* produced CaF₂(Eu) glass-ceramic in an oxyfluoride glass matrix [24]. Heat treatment at 760 °C for 15 min led to the formation of CaF₂(Eu) nano-crystals with a mean size of 65 nm. Photoluminescence emission for the glass-ceramic was found to peak at 425 nm, ascribed to the Eu²⁺ f-d transition [24]. Neither Fu *et al.* nor Secu *et al.* characterised the scintillation performance of their CaF₂(Eu) glass-ceramics.

Chen *et al.* synthesised a glass-ceramic containing CeF₃ nano-crystals using an oxyfluoride glass matrix [25]. Crystallites were precipitated by heat treating at 630 °C for 2 h. The morphology of the resulting glass-ceramic was a monodisperse arrangement of spherical CeF₃ nano-crystals with diameters of 10 nm–15 nm. The glass-ceramic exhibited a broad luminescent emission spectrum peaking at 407 nm, with a decay constant of 42 ns. Chen *et al.* investigated the glass-ceramic for light emitting diode applications rather than for scintillating applications, and therefore did not characterise the scintillation properties of this CeF₃ glass-ceramic.

Jiang *et al.* investigated ternary phosphate glasses containing cerium for scintillator applications [26]. Of the glass systems investigated, NaPO₃-CeF₃-BaF₂ allowed the highest concentration of cerium to be incorporated into the glass. Jiang *et al.* found that the scintillation light output of this glass increased with increasing cerium concentration, and reached 60 % of that of crystalline CeF₃ with a CeF₃ concentration of 25 mol%.

Kang *et al.* investigated the scintillation performance of GdBr₃(Ce) in an oxyfluoride glass matrix for gamma-ray spectroscopy applications. A full energy photopeak was recorded for the material when exposed to a ¹³⁷Cs source, and an energy resolution of 27 % was obtained for 662 keV gamma-rays. The light yield of the GdBr₃(Ce) activated glass was found to be 1700 ph · MeV⁻¹, and the primary decay constant was found to be approximately 55 ns, attributed to Ce³⁺ emission. In a separate study Kang *et al.* report an improved light yield of approximately 2000 ph · MeV⁻¹–3000 ph · MeV⁻¹ for a GdBr₃(Ce) glass-ceramic [13].

5. Discussion and Conclusions

5.1. Scintillator Compounds for Synthesis of Glass-Ceramics

Promising candidate scintillator compounds for integration into glass-ceramics include: YI₃(Ce), LaCl₃(Ce), LaBr₃(Ce), CeBr₃, GdI₃(Ce), and LuI₃(Ce). The high melting temperatures of ceramic scintillating compounds such as YAlO₃(Ce) makes production of glass-ceramics containing these compounds more challenging.

5.2. Potential of Glass-Ceramic Scintillators

Glass-ceramic scintillators are a promising new class of inorganic scintillator that offer many potential benefits [27, 8]. Glass-ceramic scintillators are non-hygroscopic, mechanically rugged, and are simpler to synthesise in large volumes than monocrystalline halide scintillators. The ruggedness of glass-ceramic scintillators makes them attractive not only for the current application, but also for applications in harsh environments such as oil-well logging. In contrast to nano-structured polymer matrix composites, crystallite distribution can be uniform throughout a glass-ceramic. Most significantly, the cost of producing glass-ceramics is typically far less than the crystal growth methods used for monocrystalline halide compounds, or the hot pressing method used for polycrystalline ceramics, providing the potential to significantly reduce the cost of producing inorganic scintillators.

The main disadvantage of GCSs to-date has been the poor light yields and energy resolutions obtained. However, careful optimisation of the compositions and heat treatment regimes of glass-ceramic scintillators may yield improvements in light yield and energy resolution.

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