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Task 1. Laser Amplified Read-Out at Valence-Modified Luminescence Sites.

To remove the limitation of one signal photon per induced ionization electron, active interrogation with a laser can be used to read out atomic states created by electron capture following passage of ionizing radiation. If such states are sufficiently persistent (~several microseconds), and the ion can be cycled back to the same state with a wavelength different from that of the scintillation, multiple photons per electron can be obtained.

Graphical user interface

Description automatically generatedIn the first year of our research, we found that visible emission can be observed following irradiation of Sr2CeO4 with x-rays or other forms of ionizing radiation. The decay time of the luminescence was exceptionally slow (cf. Fig. 1), reflecting a slow transition of Ce3+ ions formed as ionization products. Although the characteristic d-f emission of Ce3+ was not observed in this oxide host because the *d* levels are in the conduction band, this suggests that in other materials there would be time to recycle the Ce ion in this longer-lived state to produce many *d-f* photons of wavelength ~300-400 nm before hole capture (*i.e.,* the return to the Ce4+ state) occurs at its location.

Figure 1. Sr2CeO4 Decay Time

In earlier research a similar concept was explored in which trivalent Thulium ions in CaF2 were reduced to stable divalent ones following ionization of the host by 60Co gamma irradiation. The reduced ions were subsequently detected by tuning the wavelength of a readout laser to an optical resonance of the long-lived divalent rare earth species. Resonant excitation of the divalent ions resulted in fluorescence at a detection wavelength that was unique to the ionization product. Neither the constituents of the detection medium nor the population of unmodified, trivalent dopant ions were excited in the optical readout process. Hence this generated an output signal that was proportional to the number of host ionization events but could be integrated over time by recycling the long-lived ion state with laser excitation to improve scintillation statistics.

This approach potentially provides an amplified signal from each long-lived (valence-altered) state induced by the radiation, limited only by the integration time. One shortcoming of valence modification as a method of detecting ionization products approach in solids is that, in general, a low concentration of valence-modified ions unavoidably accompanies the incorporation of the main dopant during crystal growth. This leads to a background signal incompatible with single particle detection. However, research proposed for year 2 will focus on stoichiometric media, such as Sr2CeO4, Sr2ZrCeO6, BaCeO3, and the like. In these compounds, no modified-valence species form during ideal material synthesis but would only appear transiently following electron release from an ionization event. It is important to find a host that has low 5d levels of Ce3+ within the forbidden gap.

While Ce4+ is not the only ion that could be used in such experiments, year 2+3 research will initially focus on Ce-containing powders synthesized by a variety of techniques that permit adjustment of chemical composition in the vicinity of stoichiometry. This will not only make available stoichiometric compositions for optimized performance but will also permit the evaluation of the impact of off-stoichiometry. X-ray excitation will be used to produce Ce3+ luminescence following the general scheme of Figure 2. Then, using two very different input wavelengths namely 350 nm and 5.0 microns, we shall investigate (i) the recycling of the Ce3+ ions formed by electron capture by applying laser excitation on the long wavelength Ce3+ *f-d* transition to produce additional photons at the short Ce3+ *d-f* scintillation wavelength, and (ii) demonstrate ways to speed up hole capture after scintillation.

Ce4+

Ce3+

e-

Figure 2. Laser excitation (blue upward arrows) from the “low spin” ground state of Cerium on the long wavelength transition of the trivalent ion generates multiple photons on the d-f scintillation transition (purple downward arrows).

The study of multiple photon generation will seek evidence of signal intensification through the multiplication of photons/electron, with the amplification factor given by the number of achievable re-excitation cycles. As shown in Figure 2, as indicated by blue arrows, intense continuous excitation at 350 nm will cause re-excitation of Ce3+ ions to the emissive state at a rate limited only by input intensity of the laser. Hence during the lifetime of the Ce3+ ground state (~60 μs) many additional scintillation photons will be emitted at a wavelength that is quite distinct from the excitation, permitting an easy separation of laser light from the signal with an appropriate filter. In the study of hole capture, the effectiveness of 5-micron irradiation to flip the captured electron spin will be investigated as described in the next section. The overall decay rate of luminescence should increase with this additional irradiation step, directly reflecting an increase of the hole capture rate due to promotion of an allowed hole transition.

Milestones: 1) Demonstrate the process in one of the material hosts; 2) Demonstrate the capability to generate energy spectrum using the proposed method; 3) Demonstrate improvements to the energy resolution due to photon recycling.

Task 2. Speed up of Hole Capture and Associated Luminescence

To speed up the rate-limiting step of hole capture in scintillators, valence-modified ions in oxides can also undergo internal transitions to alter the selection rules of the final transition in the process of scintillation. Spectroscopic studies of Sr2CeO4 [1] for example have disclosed that hole capture proceeds by a spin-forbidden (charge transfer, CT) transition to the valence band. We propose to render this transition spin-allowed and increase its speed (in principle without limit) using laser light tuned to an *f-f* transition within the ion (2F5/2 🡪 2F7/2).

To illustrate how this will work we note that in conventional scintillators, luminescence in practical scintillators originates from a fast transition of an electron. In the case of trivalent Ce, this takes place on a *d-f* transition which is parity- and spin-allowed. However, to complete the decay of the ionization event, a Ce3+ center must capture a slow-moving hole, thereby finally returning the electron to the valence band. Hole-capture is the rate-limiting step because the effective mass of the hole is much greater than that of the electron and in addition the charge transfer which takes place to oxygen in the valence is spin-forbidden. Hence, this step is extremely slow, often a million times slower than the scintillation decay.

To speed up the rate-limiting hole capture process, laser irradiation can again be used in the case of Ce-oxide crystals. The process is illustrated in Figure 3, where laser excitation is applied between the doublet states of Cerium which are separated by 2000 cm-1, resulting in a spin-allowed transition from the upper state of the doublet to the valence band. The laser should be tuned to resonance at 5 microns, whereupon the charge transfer to oxygen takes place at a rate determined by the input intensity of the laser, rather than the natural rate of the forbidden transition from the lower state of the Ce doublet.

Ce4+

Ce3+

e-

Figure 3. Continuous excitation of the scintillator crystal at 5 microns permits an allowed hole capture transition (green down arrow), thereby speeding up the final step of the decay. In this scheme, hole capture also *adds another photon* to the visible scintillation intensity.

Milestones: 1) Demonstrate the effect of speeding up the charge transfer transition (CTT); 2) Demonstrate the capability to generate two prompt photons (*d-f* and CT) in a selected host; 3) Combine the two methods from Task 1 and Task 2.

Task 3. Readout and signal processing design (Future Years)

The proposed scintillation method will require a novel signal readout and signal processing approach. The system would use at least one laser, depending on the modes of operation. A review of the proposed processes is presented in Figure 4. After the gamma excitation we expect an initial scintillation pulse from the Ce3+ ions. The follow-on sequences are the subject of this research. During Task 3, we shall address questions such as: Should the lasers operate in CW or pulsed modes? Can the initial scintillation pulse be used as a system trigger? Many of these design answers will depend on the results of the previous tasks and the investigated material type.



Figure 4. Physical processes for the scintillation/readout process. The *d-f* Ce3+ emission can be multiplied using a UV laser. The lifetime of the Ce3+ in the ground state can be reduced by an IR laser to produce an additional photon.

Milestones: 1) Design readout scheme; 2) Develop signal processing methods; 3) Demonstrate working system.

References:

[1]. L. van Pieterson, S. Soverna, and A. Meijerink, On the Nature of Luminescence of Sr2CeO4, J. Electro-chemical Soc. 147 (12), 4688-4691 (2000).