

Ce-doped lutetium pyrosilicate scintillators LPS and LYPS

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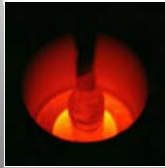
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Abstract – In this paper we present scintillation, optical, and thermoluminescence properties of recently discovered scintillation material, LPS (Lu₂Si₂O₇:Ce) [1,2] and composition with yttrium LYPS ((Lu,Y)₂Si₂O₇:Ce). The latter was first grown at Siemens Medical Solutions Molecular Imaging, and had an yttrium concentration of 50%. Both have the thorveitite structure, with monoclinic symmetry, space group C2/m. XRD measurements confirmed the expected crystal structure in which there is a single crystallographic site for lutetium or yttrium ions, with six oxygen neighbors. The trivalent cerium activator ions are assumed to occupy the cation lattice site. The excited 5d state of Ce³⁺ is split into 2 observable levels with luminescence emission occurring only from the lowest 5d level to the 4f ground state with a Stokes shift of ~ 2250 cm⁻¹. In this paper, we report on the scintillation properties of LPS and LYPS crystals. The difference in scintillation properties observed between samples is discussed. It was based on thermoluminescence data obtained in the temperature range from 30 to 600 K. These data show that the analyzed samples have surprisingly different sets of traps. Crystal growth and cutting issues of LPS and LYPS are also briefly discussed.

Introduction

Cerium doped lutetium pyrosilicate LPS (Lu₂Si₂O₇:Ce) is a new recently discovered inorganic scintillator. The LYPS ((Lu,Y)₂Si₂O₇:Ce) composition with 50 % yttrium was grown for the first time at Siemens Medical Solutions Molecular Imaging. These crystals have the same crystal structure, electronic band structure, electronic energy levels of the Ce activator, and optical properties. However, there are some differences in the scintillation properties, as shown by thermoluminescence measurements. Some of these properties may be changed by means of post-growth annealing.

Experimental Procedures



The Czochralski technique was used to grow cerium-doped LPS and LYPS crystals. The boules were grown from inductively heated iridium crucibles in an atmosphere consisting of a small % of O₂ in bulk N₂, Lu₂O₃, Y₂O₃, SiO₂ and CeO₂, were at least 99.99 % pure.



For light output measurements, we placed the crystal directly onto a Hamamatsu R877 photomultiplier tube. The crystal was covered with a loose fitting Teflon cap. For Excitation a 10 μCi ¹³⁷Cs γ-source was used.



To measure the scintillation decay time the time-correlated single photon technique originated by Bollinger and Thomas was used.



Thermoluminescence glow curves were measured between 30 K and 600 K, using a system with a closed cycled helium compressor, Advance Research Systems model DE202AE. The temperature controller was LakeShore, model 331S

The crystal was fixed to a cold finger in the cryostat with a silver paste that was allowed to dry. It was irradiated with an X-ray generator from Source 1 X-ray, model CMX 003, at a temperature of 30 K for 15 min. The crystal was heated at a constant rate of 0.15 K/s and the thermoluminescence signal was recorded.

Crystal Growth Parameters

Table I. Crystal growth parameters of LPS and LYPS boules

Parameters	B-20	B-22	B-24	C-2
Composition	Lu ₂ Si ₂ O ₇	Lu ₂ Si ₂ O ₇	Lu _{0.5} Y _{0.5} Si ₂ O ₇	Lu _{0.5} Y _{0.5} Si ₂ O ₇
Crucible size	60 mm	125 mm	125 mm	60 mm
Boule diameter	25 mm	70 mm	70 mm	30 mm
Length	75mm	175mm	175mm	75mm
Ce (at%)	0.25	0.25	0.25	0.25
Seed	Iridium pin	LPS	LPS	LPS
Pull rate	1.25 mm/hr	2 mm/hr	2 mm/hr	1 mm/hr
Rotation rate	3 rpm	3 rpm	3 rpm	3 rpm
Cracking comments	Cracked on top	Micro-cracks	Severely cracked	Severely cracked

Results

XRD Measurements

XRD measurements of powdered samples confirmed that both crystals have the expected monoclinic C2/m structure. The refined lattice parameters are shown in Table II.

Table II. Lattice parameters obtained for LPS and LYPS crystals

Lattice parameters	Lu ₂ Si ₂ O ₇	Lu ₂ Si ₂ O ₇
a	6.7664(1) Å	6.8162(1) Å
b	8.8412(2) Å	8.8986(1) Å
c	4.7161(1) Å	4.7187(1) Å
β	101.968(2)°	101.852(1)°
Unit cell volume	276.00(2) Å ³	280.11(1) Å ³

The unit cell volume of LYPS is larger compared to pure LPS, due to the larger ionic radius of Y.

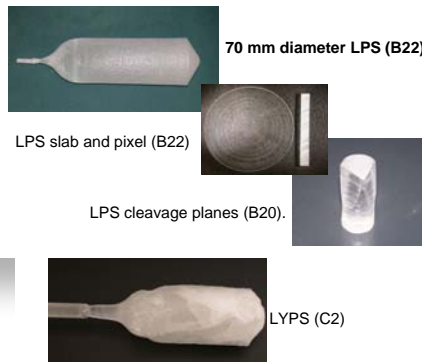
Scintillation Properties

Scintillation light output and decay time measurements for the LPS and LYPS as grown and annealed in air (for 3 hours at 1500 oC)

TABLE III. Comparison of the scintillation light output and decay time measured for LPS and LYPS

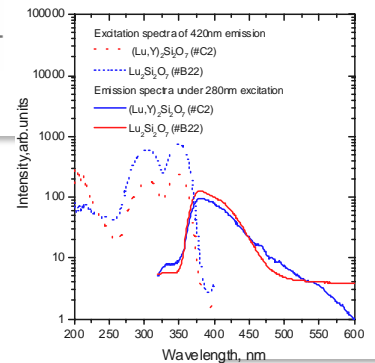
Sample	Boule ID	Atmosphere	Light Output [channel MCA]	Decay Time[ns]
Lu ₂ Si ₂ O ₇	B20	"As grown"	72	37.71
Lu ₂ Si ₂ O ₇	B20	Air	417	40.11
Lu ₂ Si ₂ O ₇	B22	"As grown"	121	38.07
Lu ₂ Si ₂ O ₇	B22	Air	420	39.17
(Lu,Y) ₂ Si ₂ O ₇	C2	"As grown"	125	37.44
(Lu,Y) ₂ Si ₂ O ₇	C2	Air	210	39.9
(Lu,Y) ₂ Si ₂ O ₇	B24	"As grown"	270	40.79
(Lu,Y) ₂ Si ₂ O ₇	B24	Air	287	41.25

Light output of BGO crystal measured in the same geometry is equal to 100 channels MCA.



Optical properties

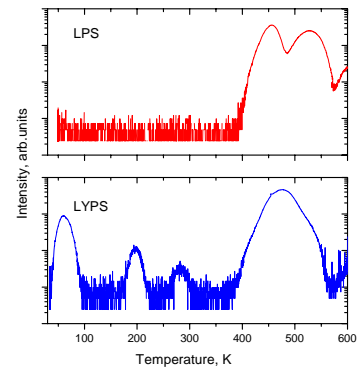
The emission and excitation spectra of cerium emission measured for LPS and LYPS are shown in the figure below. Both materials have very similar optical properties. Excitation at 280 nm (cerium f-d absorption band) produces cerium emission from Ce³⁺5d the lowest level to ²F_{7/2} and ²F_{5/2} manifolds split by the spin-orbit interaction. The two emission bands are centered at 378 and 405 nm. The Stokes shift is ~2250 cm⁻¹.



Thermoluminescence

The thermoluminescence glow curve measured for LYPS shows a greater concentration of shallow traps than LPS does.

The thermoluminescence glow curves measured for LPS and LYPS:



Conclusions

LPS and LYPS crystals were grown via the Czochralski technique. The scintillation, optical and mechanical properties of the materials were studied. The light output of the crystals was relatively low in "as-grown" samples; however, significant improvement in scintillation efficiency was observed after annealing in air. Both compositions have the monoclinic C2/m structure. Cerium ions occupy the same lutetium sites. As a result, the optical properties of LPS and LYPS are identical. However, thermoluminescence data shows a number of shallow traps in the LYPS crystals, which are not detected in pure LPS. These traps may affect the scintillation performance of the crystals. Both compositions have cleavage planes, which make them difficult to cut. Due to striations caused by high viscosity of the melt a large number of scattering centers are observed; the crystals are optically very nonhomogeneous.