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The Scintillation properties of Pr^{3+} doped and Pr^{3+}, Ce^{3+} doubly doped $LaBr_3$

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Pr^{3+} singly doped, and Pr^{3+}、Ce^{3+} doubly doped single crystals, $LaBr_3$:0.25% Pr^{3+}, $LaBr_3$:0.5% Pr^{3+}, $LaBr_3$:2% Pr^{3+}, $LaBr_3$: (4%Pr^{3+}, 2.6%Ce^{3+}) and $LaBr_3$: (8%Pr^{3+}, 2.6%Ce^{3+}), were grown with vertical Bridgman process. The scintillation properties including energy resolution, light output and time profile, the luminescence, and mechanical properties of the single crystals were measured and compared. While Pr^{3+} is doped uniquely, the best energy resolution, largest light output and longest principal decay time are acquired while the concentration of Pr^{3+} is lowest to 0.25%. While Pr^{3+} and Ce^{3+} are doubly doped, the scintillation properties are improved compared with Pr^{3+} singly doped $LaBr_3$ and the scintillator are strengthened compared with the Ce^{3+} singly doped $LaBr_3$.

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Key words: Scintillation, Luminescence, Mechanical properties, $LaBr_3$:Pr^{3+}, $LaBr_3$: (Pr^{3+}, Ce^{3+})

1. Introduction

Pr^{3+} doped $LaBr_3$ is a new scintillator composition that can be used to build gamma ray spectrometers. The $LaBr_3$:1% Pr^{3+} single crystal has an energy resolution of 9% for ^{137}Cs 662 keV gamma ray at room temperature, and has light outputs of ~73000 photons/MeV[1]. The best scintillator now is $LaBr_3$:Ce^{3+} which has a energy resolution of 2.6% for 662 keV gamma ray and has light outputs of ~80000 photons/Mev. It seems that $LaBr_3$:Pr^{3+} is worthless to be researched more. But the luminescence region of Ce^{3+} is near 380 nm which lies on UV region, while Pr^{3+} mainly lies on 400~750 nm of visible light region. Some PMTs may mainly have a light response of visible light region, so the light output region of Pr^{3+} makes $LaBr_3$:Pr^{3+} become a new research interest. What's more, the easily cracking property of $LaBr_3$:Ce^{3+} motivate people to improve the mechanical properties of the scintillator. The solid-solution hardening method that dopes the material with isovalent or aliovalent cations alloying was introduced[2]. So the different concentration of Pr^{3+} doped $LaBr_3$ was grown and measured to ascertain the best concentration for resolution, light output, and time profile, and the Pr^{3+} and Ce^{3+} doubly doped $LaBr_3$ was grown to balance the worse of resolution and better luminescence region, and to test the solid-solution hardening theory compared with the mechanical properties of $LaBr_3$:Ce^{3+} .

2. Experimental procedures

$LaBr_3$:Pr^{3+} crystal has a hexagonal(UCl_3 type) structure with $P6_3/m$ space group, the same with $LaBr_3$:Ce^{3+}. $LaBr_3$ has a density of 5.1 g/cm^3 and melts at 783℃. $PrBr_3$ has a density of 5.3 g/cm^3 and melts at 693℃. The low melting points of these materials allow us to grow the crystals in sealed quartz ampoules by the vertical Bridgman process.

The quartz ampoules were cleaned with water, acetone and ethanol, and then baked in the oven with a temperature of 180℃ for 12 hours. Then the ampoules were transferred to the glove box with a humidy of less than 4%. Anhydrous $LaBr_3$ and $PrBr_3$ polycrystal were loaded into quartz ampoules in the glovebox, then the ampoules were quickly attached to mechanical pump and diffusion pump, evacuated to less than 10^{-3} Pa, and sealed.

The crystals were grown in a two-zone vertical Bridgman furnace (Fig. 1). A stepper motor was used to slowly lower the sealed quartz ampoule at a rate of 1.1 mm/h. The ampoules filled with molten $LaBr_3$:Pr^{3+} moved through a temperature gradient of 30℃/cm at the melting points of the mixtures. After grown, the crystals were cut and polished with oil protected to minimize reaction with moisture in the air, ready for experiments(Fig. 2).

Fig. 1. The single crystal grown furnace using vertical Bridgman method.

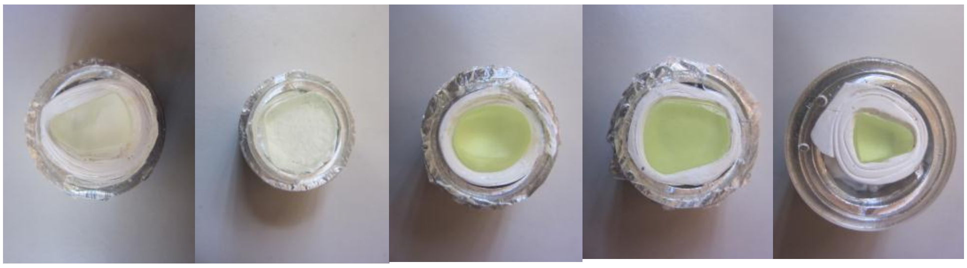

Fig. 2. Crystals ready for scintillation experiments are coverd with Teflon tape and packaged by Al shell and quartz glass: 0.25% Pr^{3+}, 0.5% Pr^{3+}, 2% Pr^{3+} , (8% Pr^{3+}, 2.6% Ce^{3+}), and (4% Pr^{3+}, 2.6% Ce^{3+}) from left to right. The inner diameter of Al shell is 17 mm.

3. Results and discussion

The Hitachi F-4500 FL Spectrophotometer and Hitachi U-2010 Spectrophotometer were used to measure the fluorescence and absorption spectra of single crystals. 454 nm wavelength was used to excite the $LaBr_3$ with different concentration of Pr^{3+} and Ce^{3+} to get the fluorescence information of Pr^{3+} (Fig. 3). Eight fluorescence peaks are acquired due to Pr^{3+} emission: 479 nm, 491 nm, 531 nm, 600 nm, 619 nm, 643 nm, 678 nm and 703 nm. The lower the concentration of Pr^{3+} is, the sharper and clearer every emission peak is. The absorption spectrum of $LaBr_3$:0.5% Pr^{3+} (Fig. 4) was measured. Three absorption valleys peaking at 454 nm, 479 nm and 491 nm exist, which coincide with part of the emission spectrum

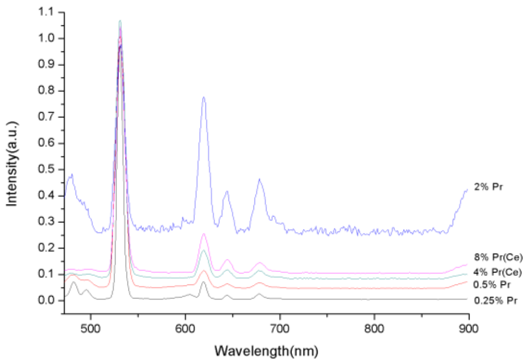

Fig. 3. The emission spectrum of $LaBr_3$: (x% Pr^{3+}, y% Ce^{3+})(x=0.25, y=0; x=0.5, y=0; x=2, y=0; x=4, y=2.6; x=8, y=2.6). The excitation wavelength is 454 nm.

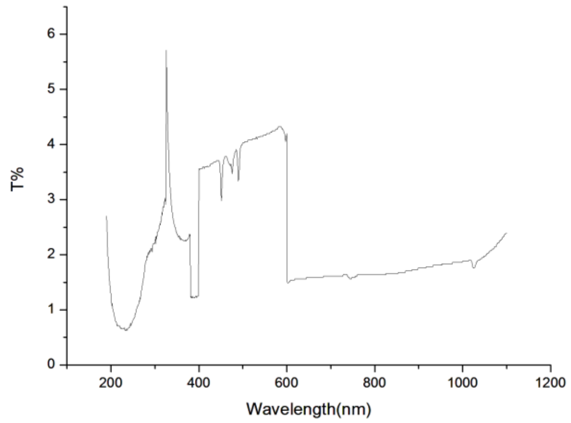

Fig. 4. The absorption spectrum of a 1.90 mm single crystal $LaBr_3$:0.5% Pr^{3+}.

So the photons yielded in the $LaBr_3:Pr^{3+}$ crystal may be reabsorbed by Pr^{3+} while transferring in the crystal before reaching the interface of crystal and photomultiplier. But a longer crystal also has more opportunities to interact with the gamma rays and yield photons. So it's difficult to say better or not using a larger crystal when the scintillation properties are measured. $LaBr_3:Ce^{3+}$ has been considered that the light output and energy resolution are independent with the crystal shape and size[3], but the conclusion can't be applied to $LaBr_3:Pr^{3+}$ crystal simply due to different photon yield and absorption situation. Crystals used in such experiments are usually with a shape of cylinder or cuboid[3], always a cylinder with the same diameter and height, so the light output and energy resolution can be compared precisely excluding other affects. One defect in our scintillation experiments is that the single crystals used weren't with exactly the same shape or size due to the crack during crystal growth. Despite of this, it won't influence the trend of scintillation properties with different Pr^{3+} concentration.

The crystals were coupled to a Hamamatsu XP2020Q PMT when the scintillation properties were measured. The light output of scintillators were measured by comparing their response with a calibrated $LaBr_3$:8% Ce^{3+} crystal under the same test condition. In order to make our interesting spectrum clearer, the spectrum of the calibrated crystal isn't exhibited(Fig. 5 and 6). Fig. 7 is the time profile of three Pr^{3+} singly doped scintillators. The information of light output, energy resolution and principal decay time are listed in Table 1.

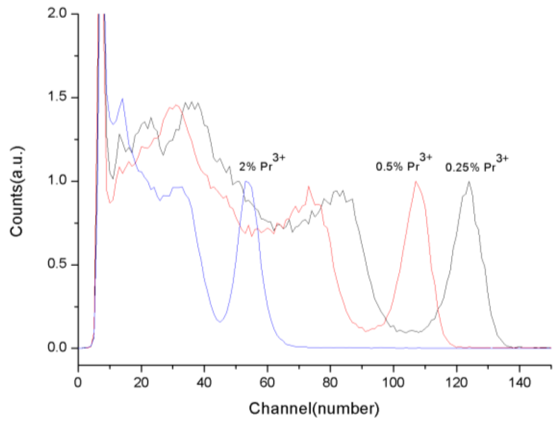

Fig. 5. ^{137}Cs source scintillation pulse height spectra measured with $LaBr_3:Pr^{3+}$.

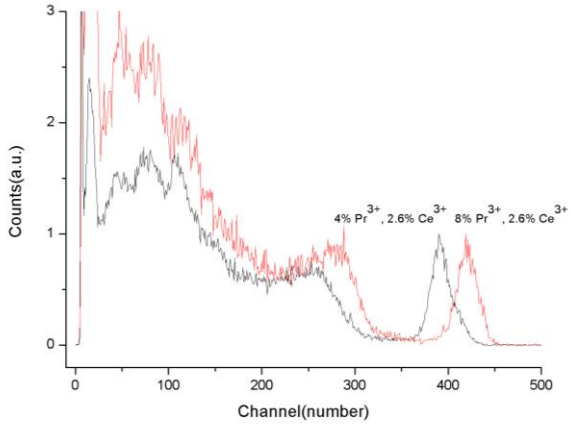

Fig. 6. ^{137}Cs source scintillation pulse height spectra measured with $LaBr_3$: (Pr^{3+},. Ce^{3+})

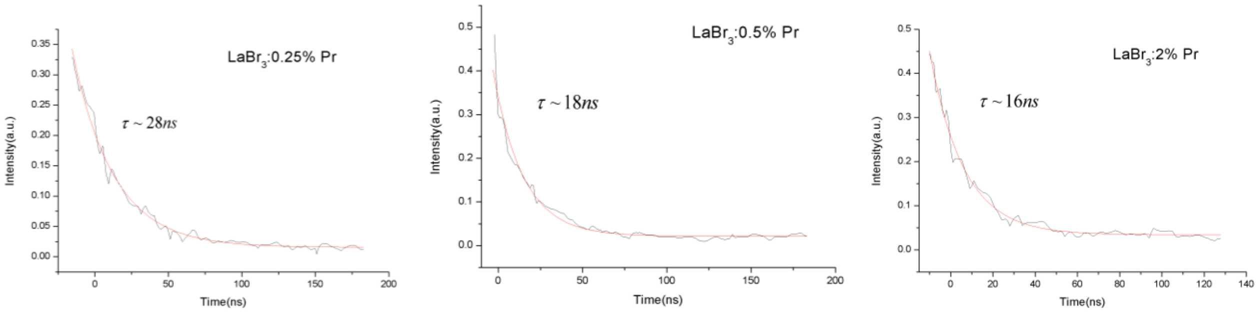

Fig.7. Decay time of $LaBr_3$:x% Pr^{3+}, x=0.25, 0.5 and 2.

Table 1. Scintillation properties of single crystals.

Material	Photoelectric Peak(Number)	Light output (Photons/MeV)	Energy Resolution	Principal Decay Time(ns)
$LaBr_3$:8% Ce	467	80000	2.6%	17
LaBr3:0.25% Pr	124	~21200	8.4%	28
$LaBr_3$:0.5% Pr	107	~18300	8.9%	18
$LaBr_3$:2% Pr	53	~9100	15.3%	16
$LaBr_3$: (4%Pr^{3+},2.6%Ce^{3+})	390	~66800	5.8%	Not measured
$LaBr_3$: (8%Pr^{3+},2.6%Ce^{3+})	419	~71800	5.2%	Not measured

The light outputs of $LaBr_3$:Pr^{3+} decrease while the concentration of Pr^{3+} increases. It is reported that the light output of $LaBr_3$:1% Pr^{3+} and $CeBr_3$:1% Pr^{3+} are approximatively 73000 and 50000 photons/MeV[1], and 16000, 16000, 21000 photons/MeV for pure $PrBr_3$, $PrBr_3$:5%Ce^{3+}, $PrBr_3$:20%Ce^{3+} [4], respectively. The light output increases by 30% while the concentration of Ce^{3+} increases by 15%. Considering the data above and Fig.8[1]. We can conclude that the photons yielded in $CeBr_3$:Pr^{3+} are mainly attributed to Ce^{3+} if the concentration of Ce^{3+} is high enough. Referred to the results we got, the 73000 photons/MeV of $LaBr_3$:1% Pr^{3+} is doubted. The light output of Pr^{3+} and Ce^{3+} doubly doped $LaBr_3$ is another evidence, which just varies 7% (form 66800 to 71800) while the concentration of Pr^{3+} doubled (from 4% to 8%) with the Ce^{3+} concentration unchanged. Another fact is that Pr^{3+} in $LaBr_3$ and $CeBr_3$ is affected by different crystal fields, which surely influence the light emission. The relation of intensity of Pr^{3+} 4f-4f emission in $LaBr_3$[5] compared with 5d-4f emission of Ce^{3+} in $LaBr_3$[6] should be considered further.

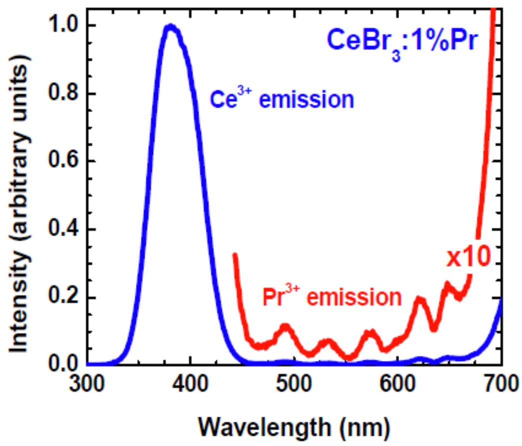

Fig. 8. Emission spectrum of $CeBr_3$:1% Pr^{3+}. Ce^{3+} emission dominates the spectrum around 390 nm. Pr^{3+} emission from 400~800nm is much lower in magnitude than the Ce^{3+} emission[1].

The energy resolution becomes worse (increases from 8.4% to 15.3%) while the Pr^{3+} concentration increases, while the principal decay time decreases from 28 ns to 16 ns.

We evaluated the proportionality of $LaBr_3$:0.25% Pr^{3+} by measuring their responses to gamma ray emissions from 137Cs (662 keV) and ^{152}Eu(121.78, 244.69, 344.28, 1112.0 and 1408.03 keV)(^{152}Eu can emit gamma rays with twelve energies, but not all of them can be see clearly in the spectrum, Fig. 9). The data are normalized with respect to the light output of 662 keV. The nonproportionality is about 6.5% from 120 keV to 1400 keV (Fig. 10).

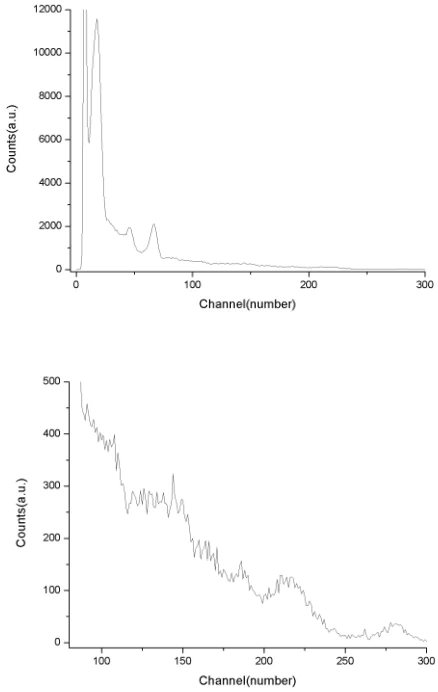

Fig. 9. ^{152}Eu source scintillation pulse height spectra measured with $LaBr_3$:Pr^{3+}. The figure in the right enlarge the ordinate to exhibit the peaks with low intensity more clearly.

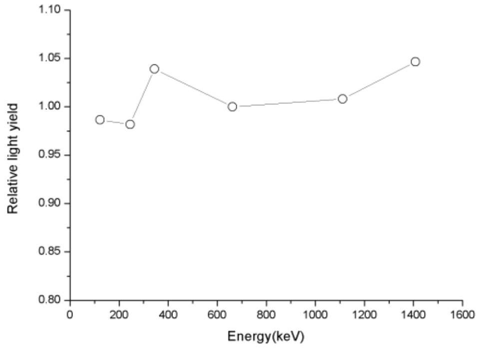

Fig. 10 Proportionality of $LaBr_3$:0.25% Pr^{3+}.

The solid-solution hardening is a potential method for strengthening the Lanthanide Halide scintillators. The isovalent alloying can replace the cation with a like-valence cation of differing ionic radius[2]. We have measured the modulus of elasticity and hardness of $LaBr_3$:Ce^{3+} with nano-indentation method. The results are approximately 30 and 0.6 GPa, respectively[7]. To test the solid-solution hardening theory, the modulus of elasticity and hardness of Pr^{3+} and Ce^{3+} doubly doped $LaBr_3$ were measured, which are approximately 40 and 1.4 GPa, respectively. The Pr^{3+} doping surely strengthens the $LaBr_3$: Ce^{3+} scintillator. What’s also important is that the light output and energy resolution of the doubly doped scintillators aren’t much worse than $LaBr_3$: Ce^{3+}, which are ~70000 and 5%~6%, respectively.

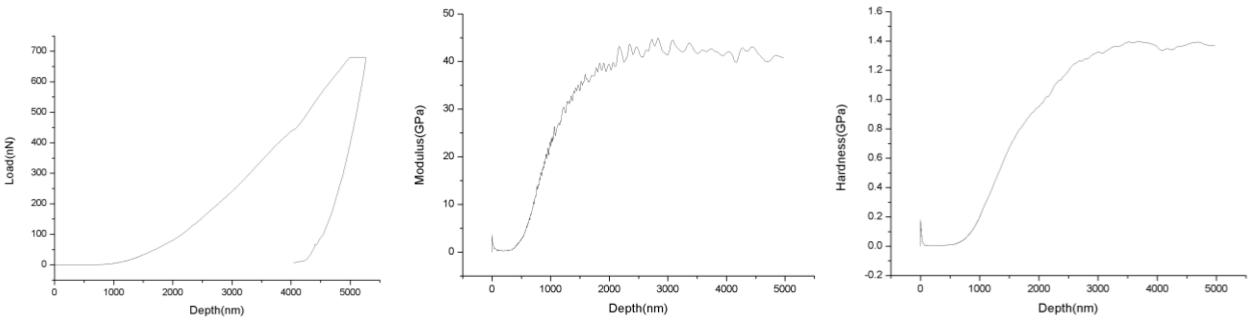

Fig. 11. Trends of load, Young’s modulus and hardness while probe inserting $LaBr_3$: (Pr^{3+}, Ce^{3+}) crystal

4. Conclusion

The scintillation, luminescence, and mechanical properties of Pr^{3+} singly doped, and Pr^{3+}、Ce^{3+} doubly doped single crystals were measured. The Pr^{3+} singly doped $LaBr_3$ exhibits the light output, energy resolution and principal decay time to be below 21000, above 8.4% and below 28 ns, respectively, while the Pr^{3+}、Ce^{3+}

doubly doped $LaBr_3$ exhibits them to be approximately 70000, 5%~6%. Pr^{3+} doped in $LaBr_3$: Ce^{3+} really increases the modulus of elastic and hardness of the scintillator, which may be a clue to improve the easily cracking property.

Acknowledgements

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