Obtaining and functional characteristics of Eu^{2+}-activated scintillation materials on the basis of congruent compounds of alkali and alkaline earth metal chlorides and bromides (ABX_3)

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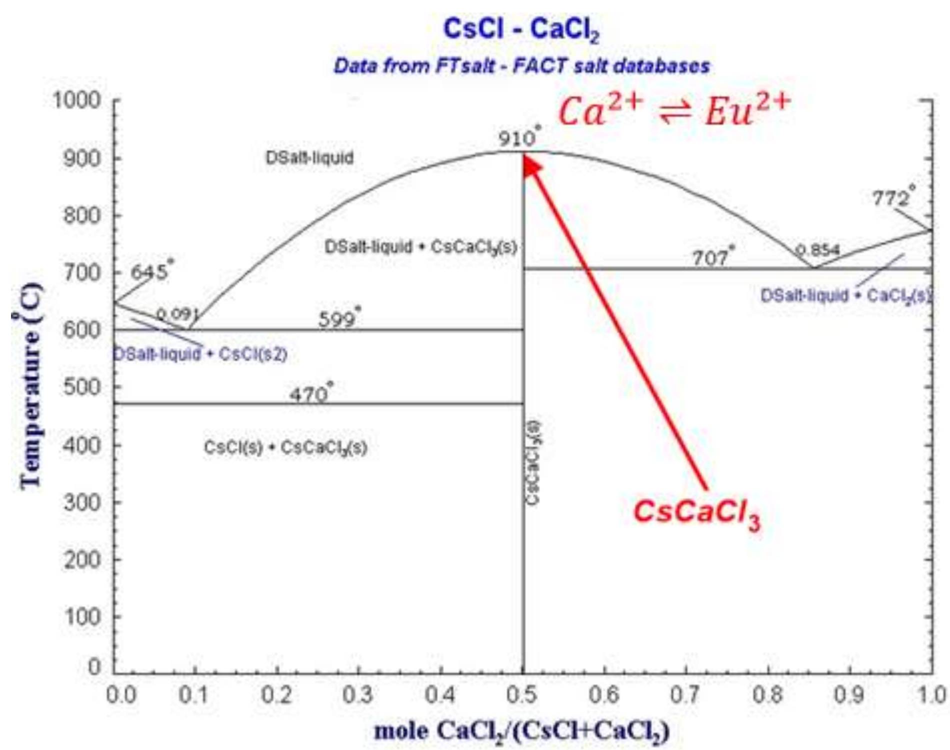
	CaI_2	$CaBr_2$	$CaCl_2$	SrI_2	$SrBr_2$	$SrCl_2$	BaI_2	$BaBr_2$	$BaCl_2$
KX	$KCaI_3$	$KCaBr_3$	$KCaCl_3$	$KI\cdot SrI_2$	$KBr\cdot 2SrBr_2$	$KCl\cdot 2SrCl_2$	$KI\cdot BaI_2$	$2KBr\cdot BaBr_2$	$2KCl\cdot BaCl_2$
RbX	$RbCaI_3$	$RbCaBr_3$	$RbCaCl_3$	$RbI\cdot SrI_2$	$RbBr\cdot SrBr_2$	$RbCl\cdot SrCl_2$	$RbI\cdot 2BaI_2$	$RbBr\cdot BaBr_2$	$RbCl\cdot BaCl_2$
CsX	$CsCaI_3$	$CsCaBr_3$	$CsCaCl_3$	$CsSrI_3$	$CsSrBr_3$	$CsSrCl_3$	$CsI\cdot BaI_2$	$CsBr\cdot BaBr_2$	$CsCl\cdot BaCl_2$

- systems having been studied (literature data)

	$CaBr_2$	**$CaCl_2$**
KX	**$KCaBr_3$**	**$KCaCl_3$**
RbX	**$RbCaBr_3$**	**$RbCaCl_3$**
CsX	**$CsCaBr_3$**	$CsCaCl_3$

The choice of the matrix, example, phase diagram of CsCl – $CaCl_2$ system



Scheme of the charge and activator synthesis and growth furnace

$BCO_3 + HX$

$\downarrow$

$BX_2 \cdot 6H_2O + AX$

$\downarrow$ NH_4X

$AX \cdot BX_2 \cdot NH_4X$

$\downarrow$ t~400 °C

$AX \cdot BX_2$

Eu_2O_3

$\downarrow$ HX, H_2O

$EuX_3 \cdot nH_2O$

$\downarrow$ NH_4X

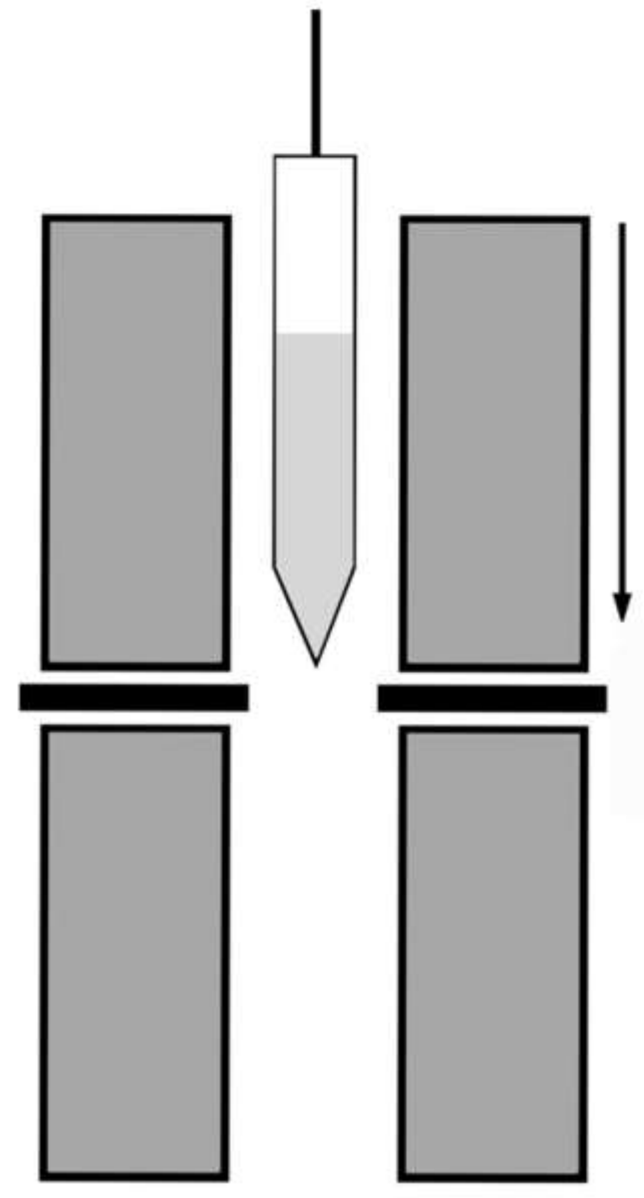
$EuX_3 \cdot mNH_4X \cdot (m-n)\, H_2O$

$\downarrow$ $-NH_4X$, $-H_2O$; t~400 °C

EuX_3

$\downarrow$ $-X_2$; $t_{пл}$

EuX_2



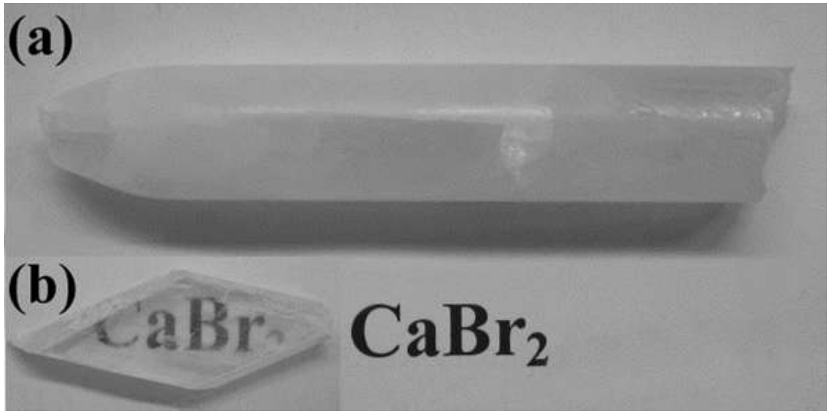
$$(1-y)BX_2 + yEuX_2 + AX = AB_{1-y}Eu_yX_3$$

X=Cl, Br

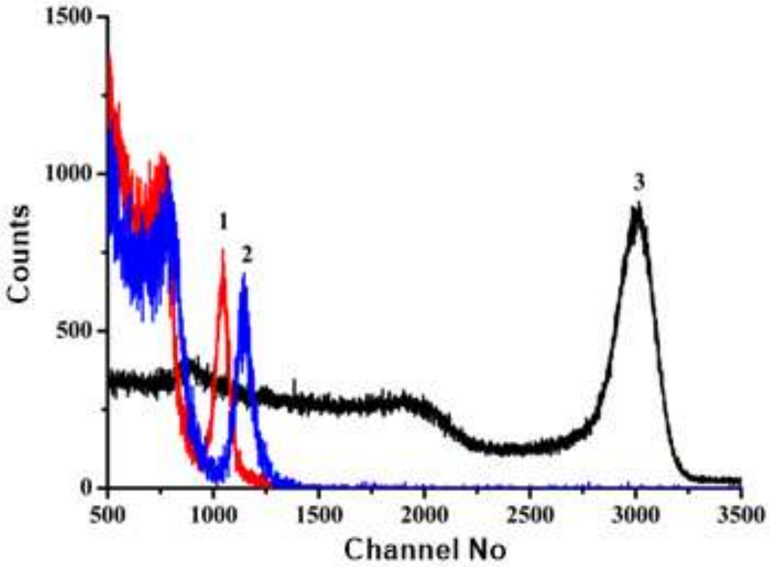
A – alkali metal

B – alkaline earth metal

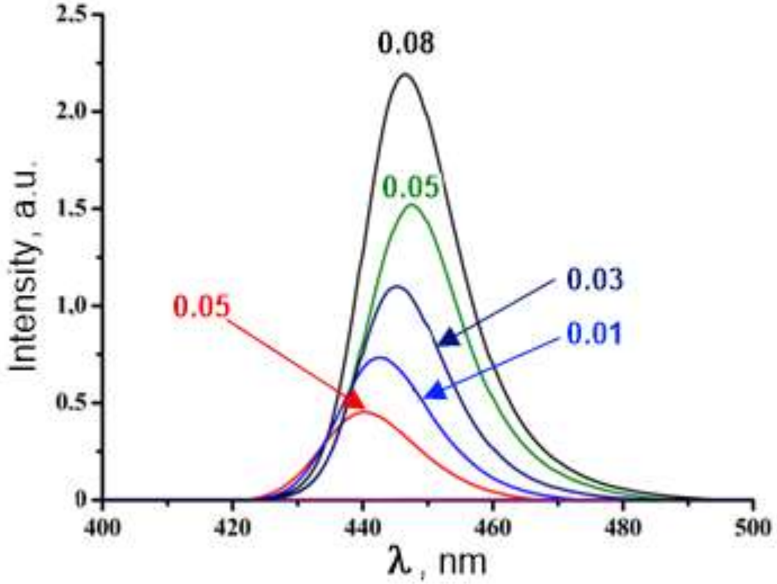
I. *Eu-activated CaX_2-based halides*



$CaBr_2$ crystals



Pulse height spectra of $Ca_{0,95}Eu_{0,05}Br_2$ (1), $Ca_{0.92}Eu_{0.08}Br_2$(2) and NaI:Tl (3) excited by ^{137}Cs.



Radioluminescence spectra of $Ca_{1-y}Eu_yBr_2$ crystals (source γ–^{241}Am)

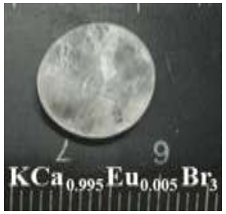
y	L, photon/MeV	R, %	τ, μs
0.005	14000		
0.01	20000		
0.03	30000		1,64
0.05	36000	8.9	2,511
0.08	**39000**	9.1	

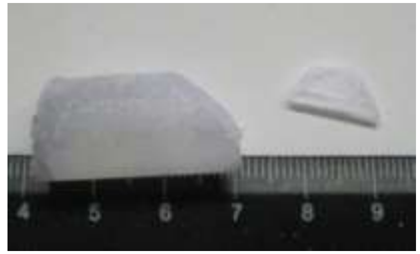
$1\text{-}y CaBr_2 + y EuBr_2$

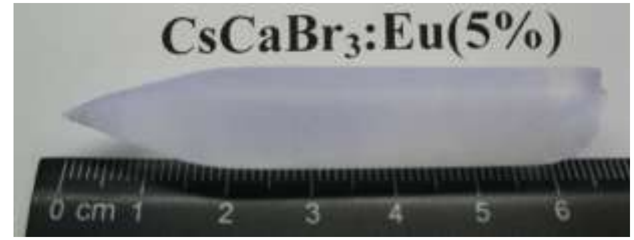
+ KBr → $KCa_{0,995}Eu_{0,005}Br_3$

+ RbBr → $RbCa_{1-y}Eu_yBr_3$

+ CsBr → $CsCa_{1-y}Eu_yBr_3$



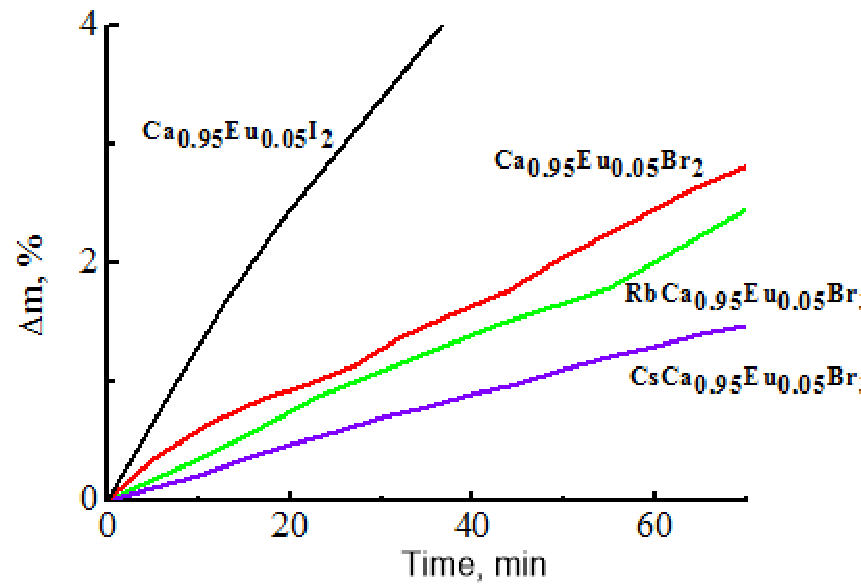




L=10%

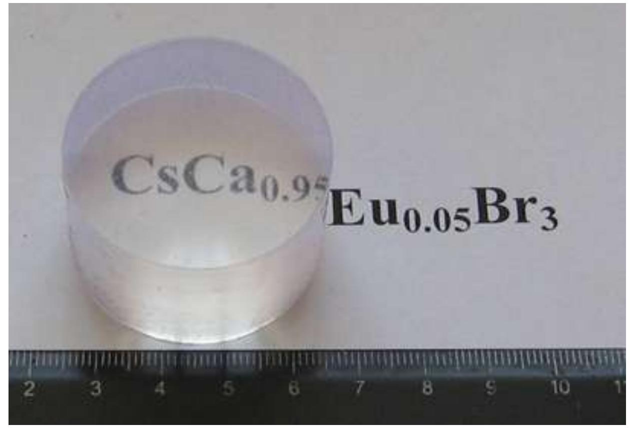
Composition	L, %	R, %	τ, µs
$RbCa_{0.97}Eu_{0.03}Br_3$	35	-	2.70
$RbCa_{0.95}Eu_{0.05}Br_3$	48	12	3.14
$RbCa_{0.92}Eu_{0.08}Br_3$	**77**	**8.2**	3.56
$Ca_{0.92}Eu_{0.08}Br_2$	**55.3**	9.1	-
NaI:Tl	100	5.9	0.23

Composition	L, %	R, %	τ, µs
$CsCa_{0.99}Eu_{0.01}Br_3$	16	-	-
$CsCa_{0.97}Eu_{0.03}Br_3$	24	-	-
$CsCa_{0.95}Eu_{0.05}Br_3$	29	9.9	5.28
$CsCa_{0.92}Eu_{0.08}Br_3$	**34**	9.3	6.1
$Ca_{0.92}Eu_{0.08}Br_2$	55.3	9.1	-

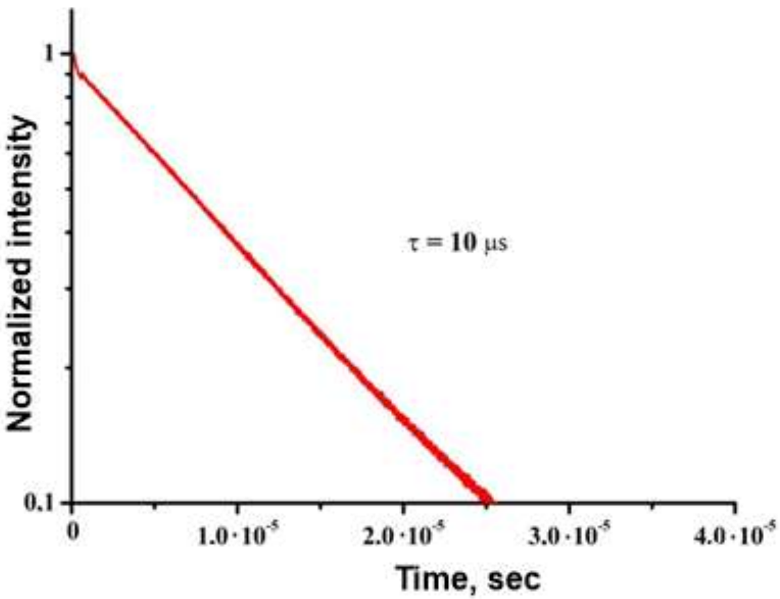


The changes of the masses of sample exposed to the action of wet air, humidity 40 %, *rt*

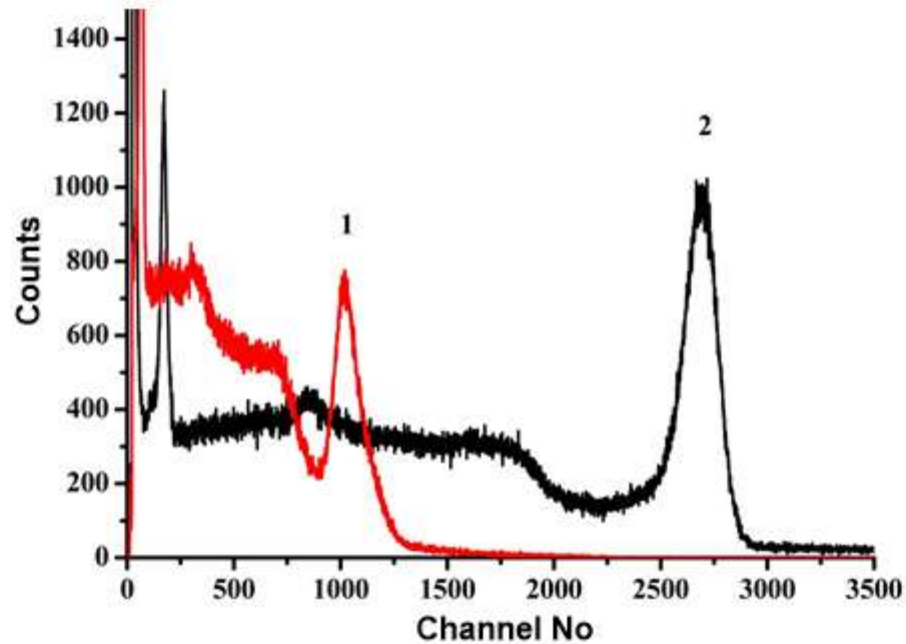
$CsCa_{1-x}Eu_xBr$ crystal



$L_{\varnothing 40\times 40}$=37% ($L_{\varnothing 12\times 2}$=45.2%)
$R_{\varnothing 40\times 40}$=16% ($R_{\varnothing 12\times 2}$=9.9%)



Scintillation time decay of $CsCa_{0,95}Eu_{0,05}Br_3$ crystal ∅40×40, excitation γ-^{137}Cs



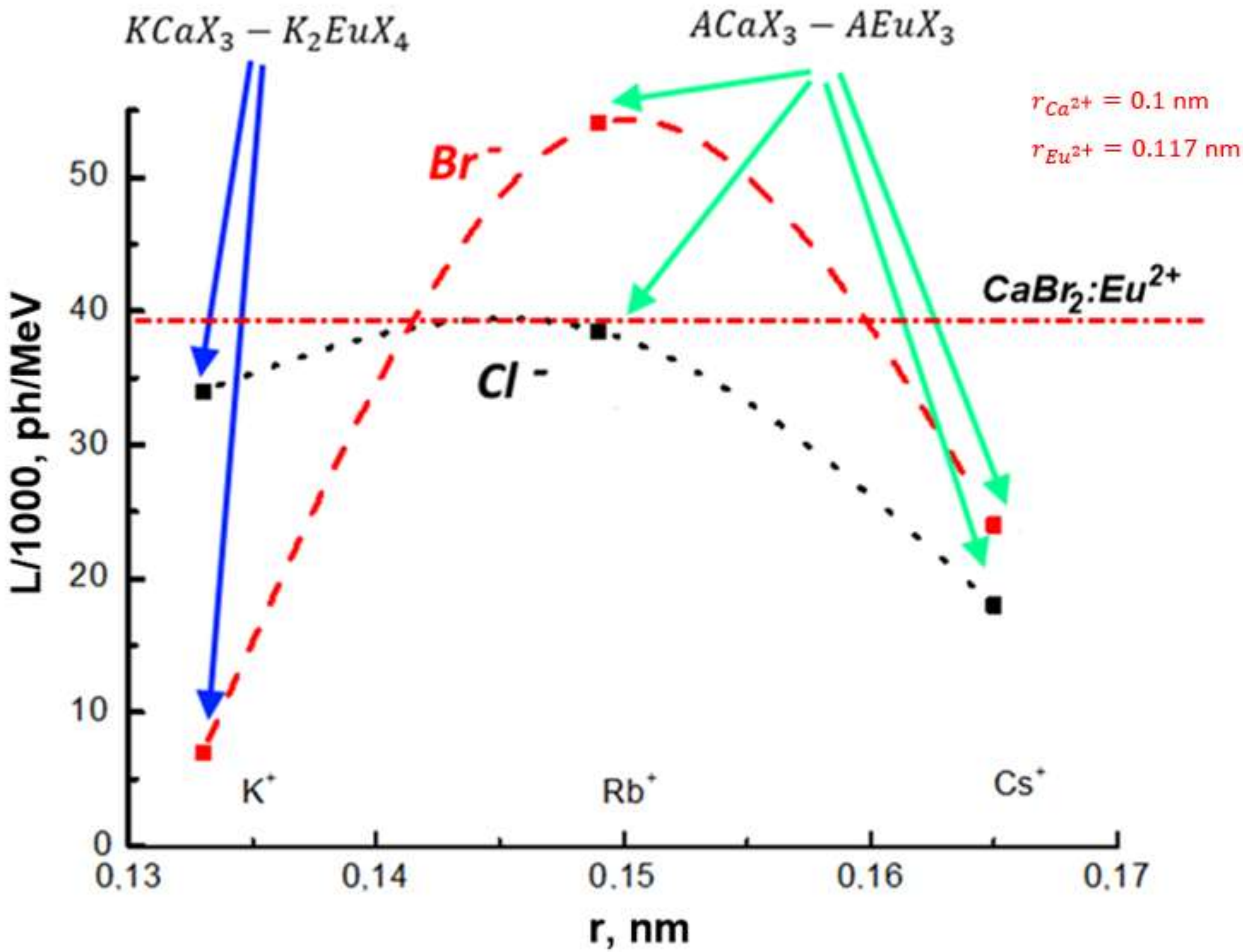
Pulse height spectra of $CsCa_{0,95}Eu_{0,05}Br_3$ ∅40×40 (1) and NaI:Tl (2) excited by ^{137}Cs.

Scintillation properties of $ACa_{1-y}Eu_yX_3$ (X=Cl, Br; A=K, Rb, Cs) crystals

Composition	L	R, %	τ, µs	k
$Ca_{0.92}Eu_{0.08}Br_2$	39000	9.1	-	1.0
$CsCa_{0.92}Eu_{0.08}Br_3$	28000	9.3	6.1	1.1
$RbCa_{0.92}Eu_{0.08}Br_3$	**54000**	8.2	3.56	1.0
$KCa_{0.995}Eu_{0.005}Br_3$	33000	breaks down		
$Ca_{1-y}Eu_yCl_2$	breaks down			
$CsCa_{0.9}Eu_{0.1}Cl_3$ [1]	19000	12	-	-
$RbCa_{0.92}Eu_{0.08}Cl_3$	38500	9	-	1.0
$KCa_{1-y}Eu_yCl_3$	34000	breaks down		

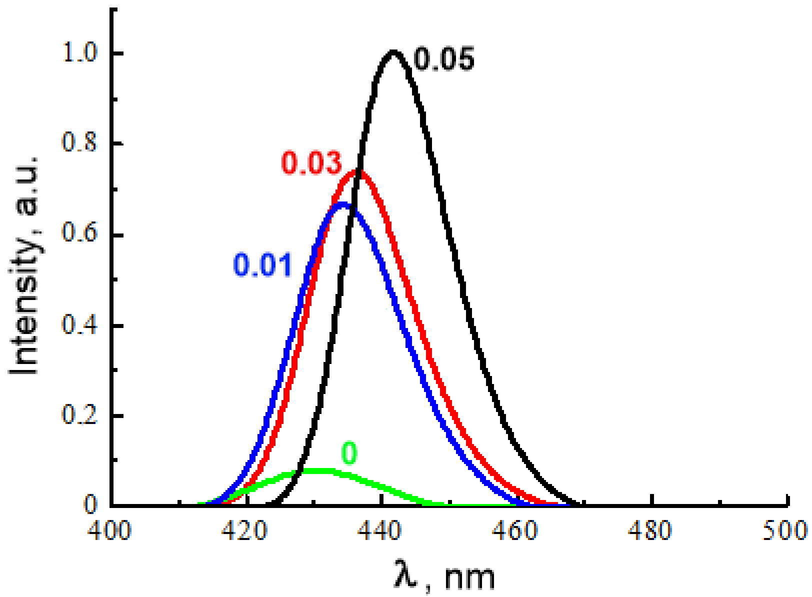
1. Zhuravleva, M., et. al., J.Cryst. Growth. 352(1), 115−119 (2012)

E_g, eV 5.52 4.96 5.45

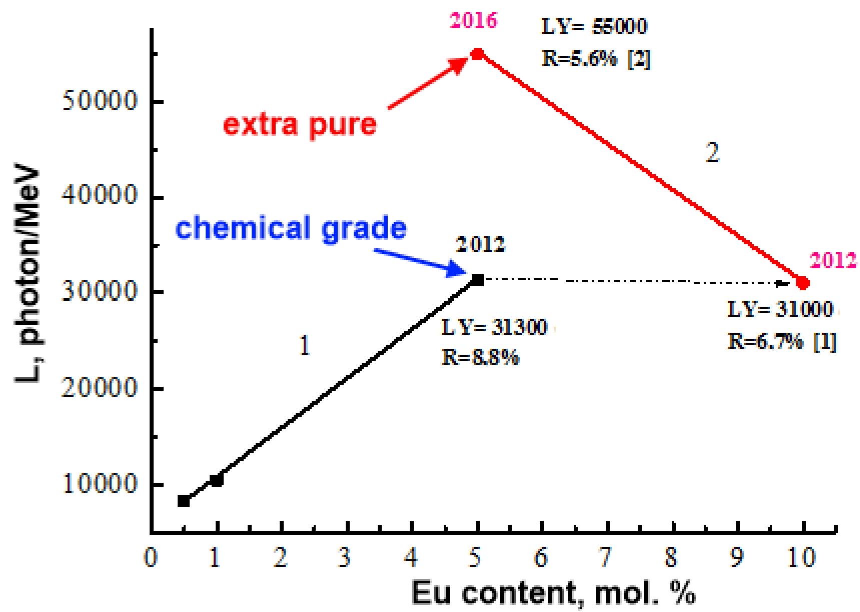


II. Eu^{2+}-activated SrX_2-based materials

$CsSr_{1-y}Eu_yBr_3$



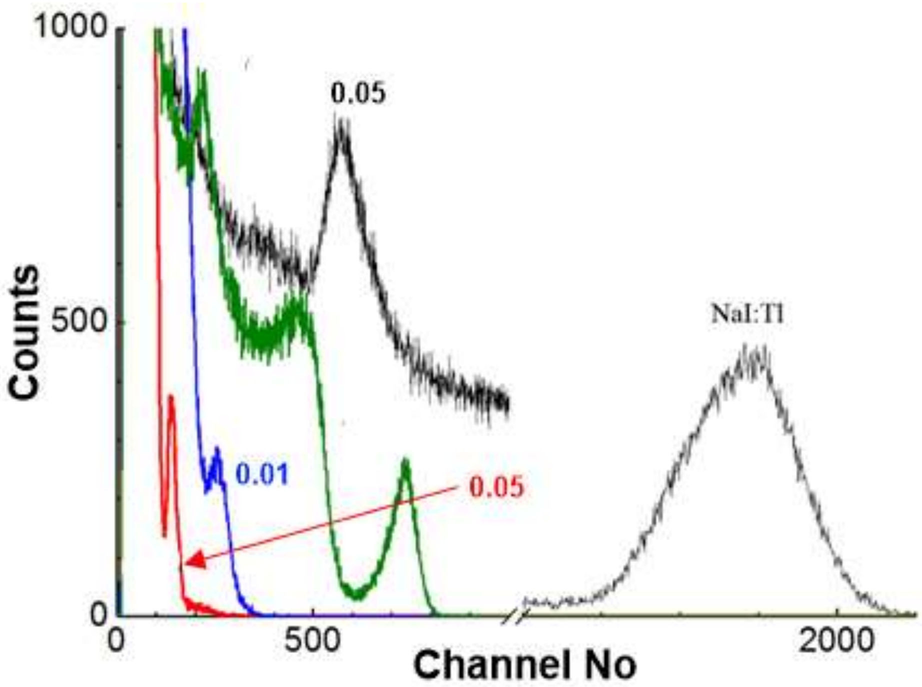
Radioluminescence spectra of $CsSr_{1-y}Eu_yBr_3$ obtained at γ –[241]Am extitation, *rt*.



The dependence of light yield of $CsSr_{1-y}Eu_yBr_3$ scintillator vs. Eu^{2+} concentration (1 – our results, 2 – the data of [1, 2]).

1. Zhuravleva, M., Yang, K. US Patent 2012,0273726 A1.
2. Gokhale, S. S., et. al. J. Cryst. Growth. 452, 89−94 (2016).

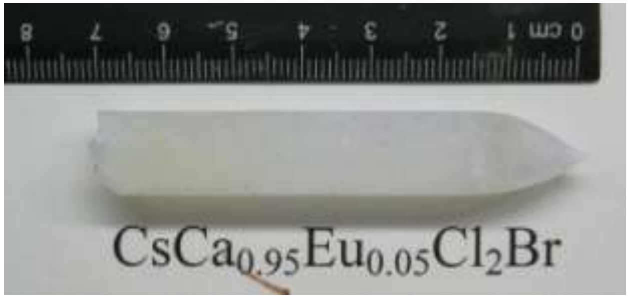
$CsSr_{1-y}Eu_yCl_3$ crystals

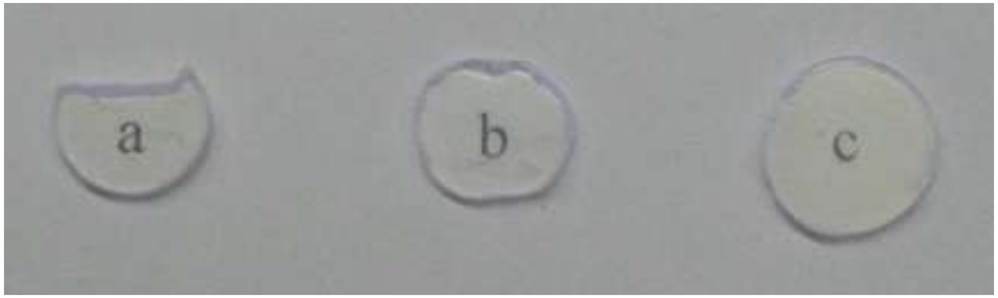


y	L, %	L, ph/MeV	R, %
0.05	8.3		-
0.01	13.5		-
0.05	38.9	**33400**	11.5

Pulse height spectra of $CsSr_{1-y}Eu_yCl_3$ and NaI:Tl crystals, excitation source ^{137}Cs.

III. *Mixed solutions of $CsCaBr_3$-$CsCaCl_3$ composition*

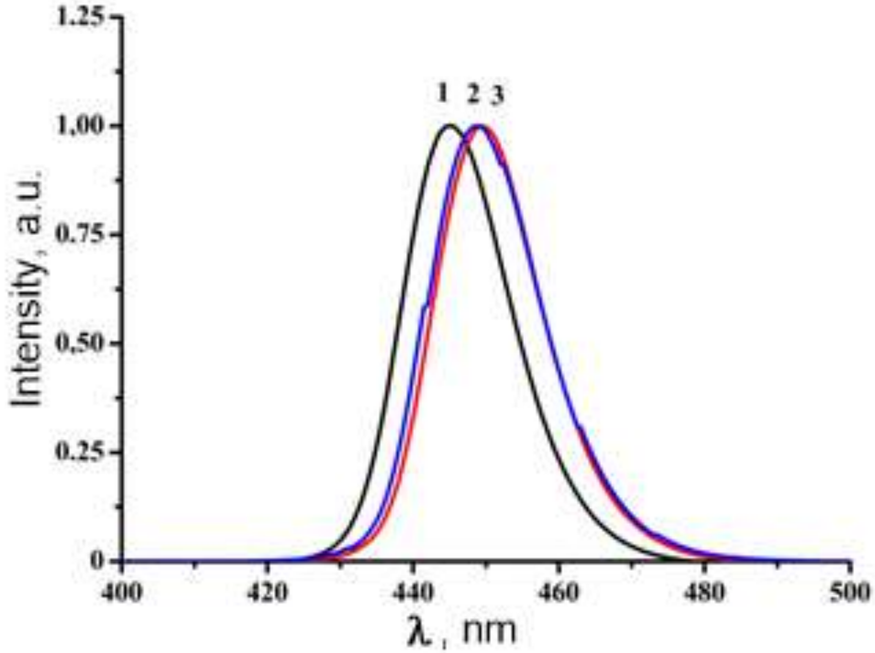


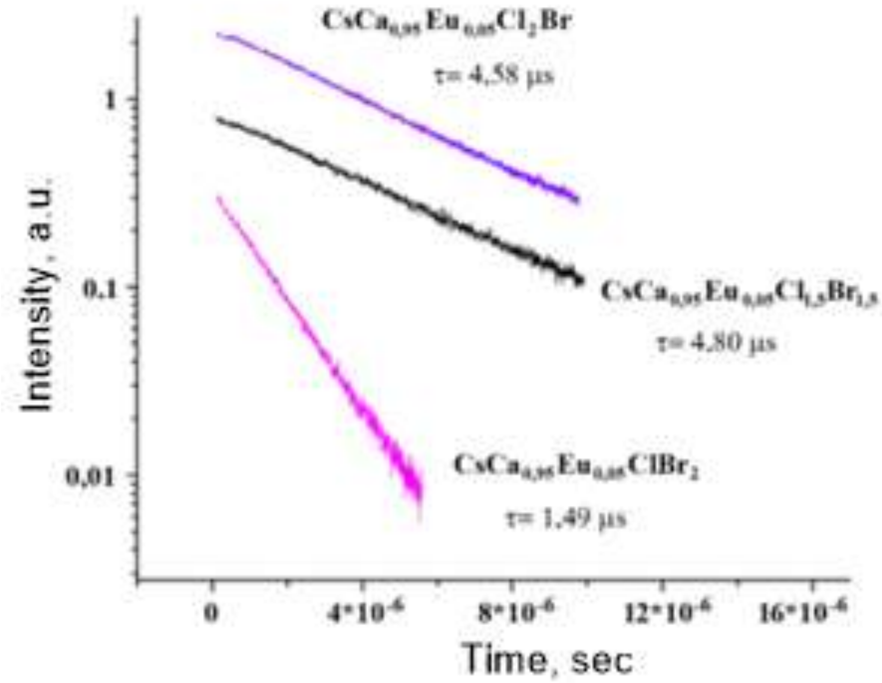


Samples of $CsCa_{0,95}Eu_{0,05}Cl_2Br$, $CsCa_{0,95}Eu_{0,05}Cl_{1,5}Br_{1,5}$ and $CsCa_{0,95}Eu_{0,05}ClBr_2$ composition (from the left to the right

Composition	L, ph/MeV	τ, μs
$CsCa_{0.9}Eu_{0.1}Cl_3$ [1]	18000	5.05
$CsCa_{0.95}Eu_{0.05}Cl_2Br$	23800	4.58
$CsCa_{0.95}Eu_{0.05}Cl_{1.5}Br_{1..5}$	20700	4.80
$CsCa_{0.95}Eu_{0.05}ClBr_2$	**37000**	**1.48**
$CsCa_{0.95}Eu_{0.05}Br_3$	23000	5.28

1. Zhuravleva, M., et. al., J.Cryst. Growth. 352(1), 115−119 (2012)





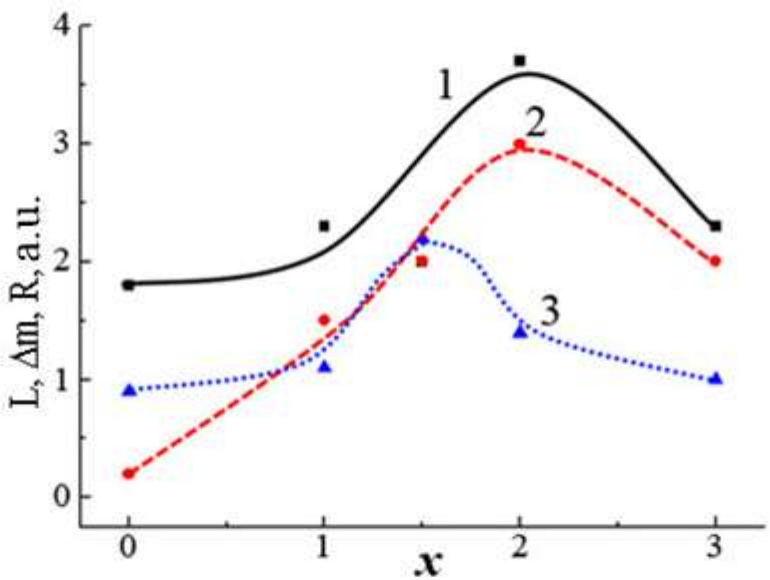
Radioluminescence spectra of $CsCa_{0.95}Eu_{0.05}ClBr_2$ (1), $CsCa_{0.95}Eu_{0.05}Cl_{1.5}Br_{1.5}$ (2) and $CsCa_{0.95}Eu_{0.05}Cl_2Br$ (3) crystals, excited by ^{241}Am.

The scintillation light time profile for $CsCa_{0,95}Eu_{0,05}Cl_2Br$, $CsCa_{0,95}Eu_{0,05}Cl_{1,5}Br_{1,5}$ and $CsCa_{0,95}Eu_{0,05}ClBr_2$ obtained at ^{137}Cs excitation.

The dependence of functional parameters of materials based on Eu^{2+}-activated alkaline earth metal halides form ratio of matrix components

Perfect isomorphism,

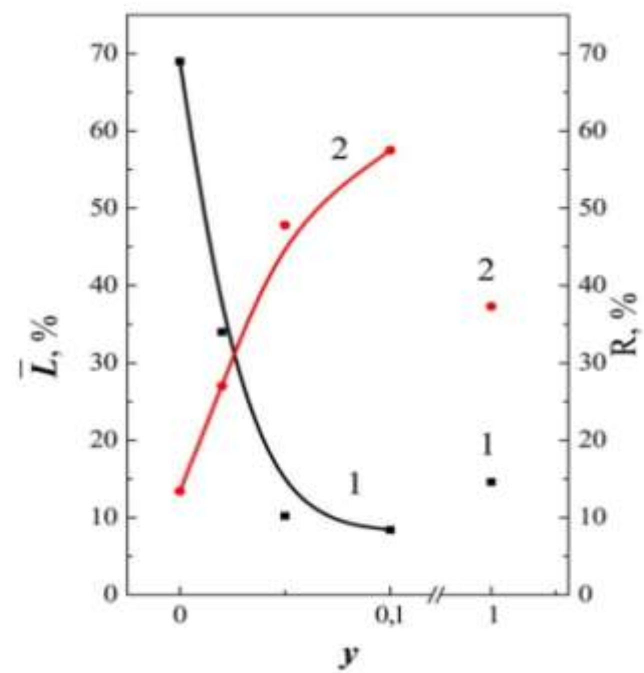
—— =0.08 (Cl→Br)



The dependences of light yield (1, L/10000), changes of crystal mass under contact with wet atmosphere (2) and energy resolution (3, R/10) for $CsCa_{0.95}Eu_{0.05}Cl_{3-x}Br_x$ *vs. x*. Data for *x*=0 are taken from [1]

Limited isomorphism,

—— ≈0.13 (Sr→Ba)

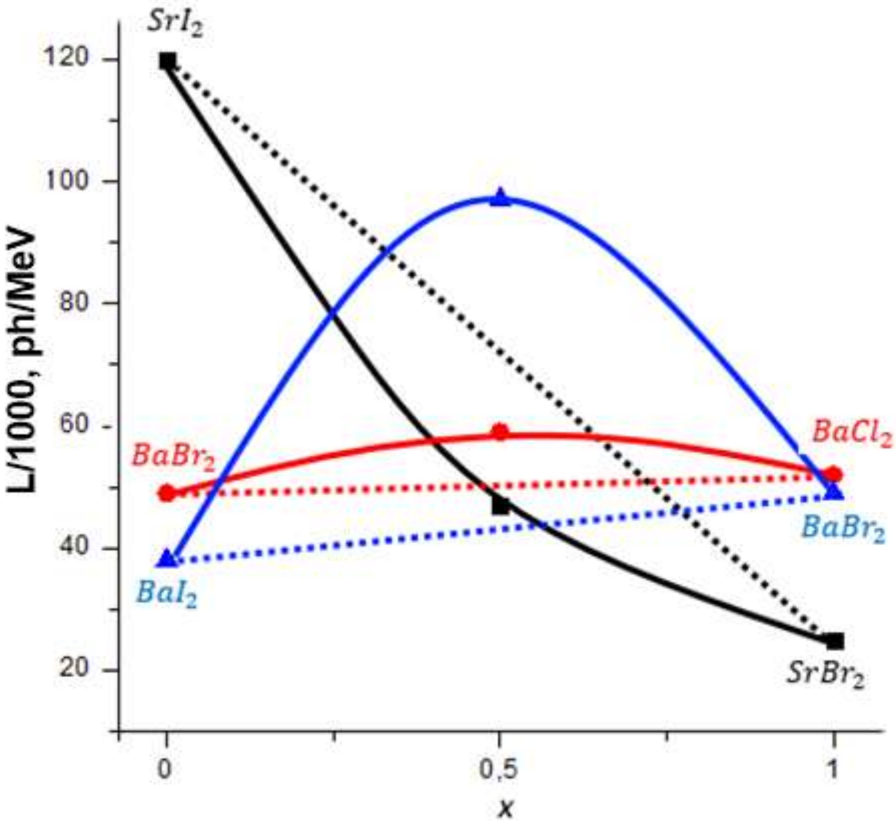


The dependence of light yield (1) and energy resolution (2) for $(Sr_{1-y}Ba_y)_{0,995}Eu_{0,005}I_2$ crystals from *y*

1. Zhuravleva, M., et. al., J.Cryst. Growth. 352(1), 115−119 (2012)

Light yield for the materials based on the matrixes: individual halides and solid solutions

$BX_2:Eu^{2+}$, $BXX':Eu^{2+}$

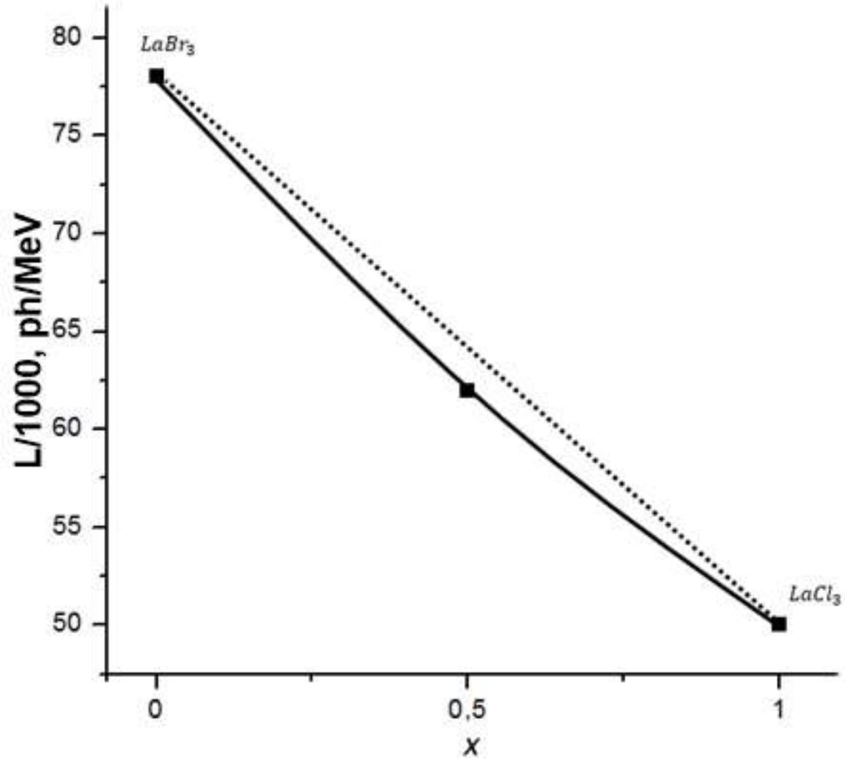


A

mole fraction of B

B

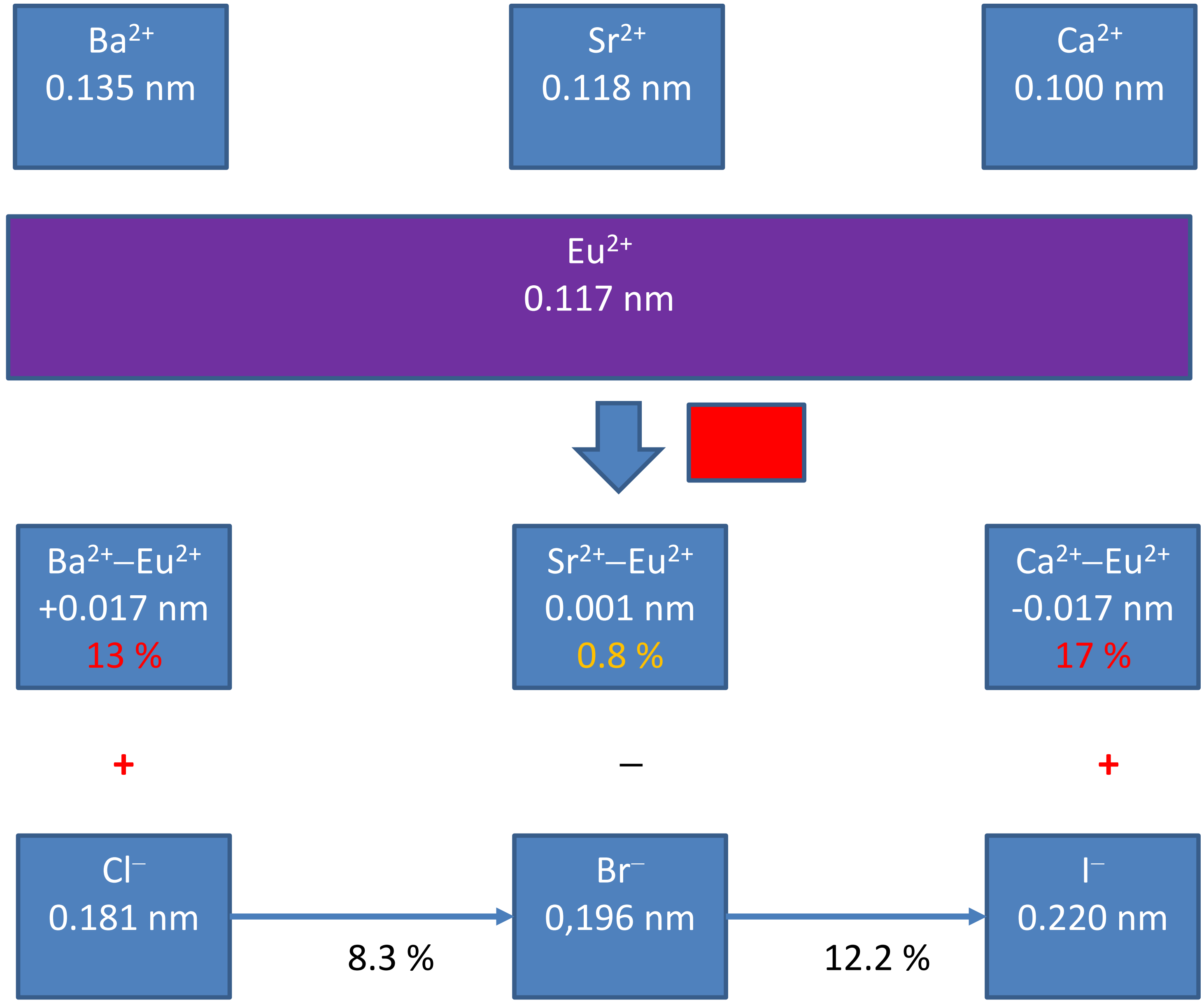
$LaX_3:Ce^{3+}$



A

mole fraction of B

B


Ba²⁺
0.135 nm
Sr²⁺
0.118 nm
Ca²⁺
0.100 nm
Eu²⁺
0.117 nm
Ba²⁺–Eu²⁺
+0.017 nm
13 %
Sr²⁺–Eu²⁺
0.001 nm
0.8 %
Ca²⁺–Eu²⁺
-0.017 nm
17 %
+
–
+
Cl⁻
0.181 nm
Br⁻
0,196 nm
I⁻
0.220 nm
8.3 %
12.2 %