Possible Directions of R&D on the GAGG Crystals

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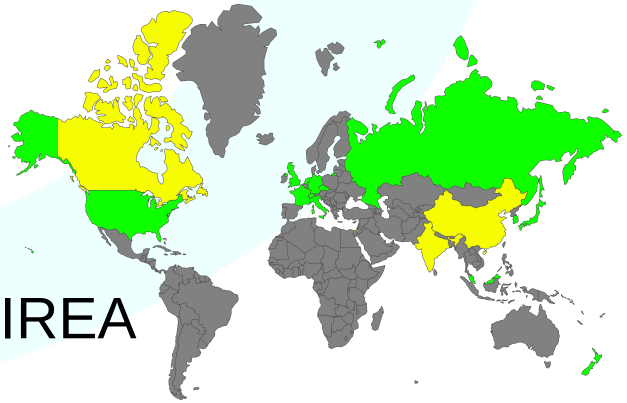
JSC Fomos-Materials

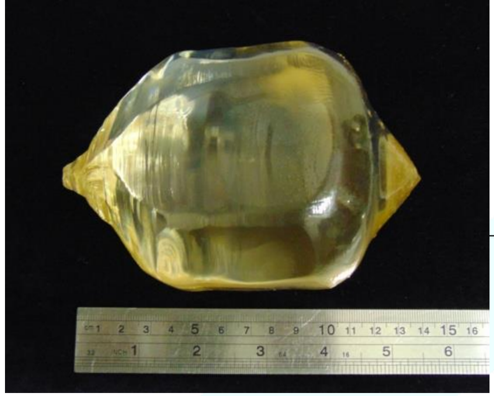
JSC Fomos-Materials

- Founded in 2001
- Main competence is single crystal growing technology
- Company possesses a full production circle that now includes:
  - Initial charge synthesis
  - Crystal growing process **(12 crystal growing Cz pullers)**,
  - Modern and high productivity equipment for crystal processing (orient cutting, drilling, grinding, polishing and electrode deposition)
  - Testing
- High qualified staff, engineers and PhDs
- ISO 9001 certified
- Wide sales geographic:



- Fruitful and mutually beneficial cooperation with institutions

of RAS and Ministry of Education – NRS-KI, IK RAS, NUST MISiS, IREA
- Private companies - RINK, NeoChim etc.



Fomos-Materials

- Company has previous experience in crystal growth of PWO, YAG:Nd, GGG, $LaAlO_3$ and others
- Company manufactures following crystals
  - *Langasite* $La_3Ga_5SiO_{14}$
  - *Langatate* $La_3Ga_{5.5}Ta_{0.5}O_{14}$
  - *Catangasite* $Ca_3TaGa_3Si_2O_{14}$
  - *LN, LT*
  - *Isotopic enriched calcium molybdate* $^{40}Ca^{100}MoO_4$

  and others.
- A wide range of products such as:
  - *SAW wafers for filters & resonators*
  - *Piezoelectric sensitive elements for high temperature sensors*
  - *Scintillation elements for detectors*

The IBS/CUP-JSC Fomos-Materials contract for production of $^{40}Ca^{100}MoO_4$ SEs for AMoRE-Pilot (Dec. 2014 - June 2017)

Isotopical enrichment	*Molybdenum enriched on Mo-100 isotope – no less than 95%*
Isotopical depletion	*Calcium depleted on Ca-48 isotope – less than 0,002%*
Radioactive purity	*No more than 100 micro-Bq/kg for Bi214 (U238 chain)* *No more than 500 micro-Bq/kg for Bi211 (U235 chain),* ***Alpha-activity:*** *No more than 10 mBq/kg for total alpha-activity of U- and Th-chains.*

RESOURSES in Russia

- Production of Mo-100 exists in Russia ***at tenths – hundred kg scale***
- Production of Ca-40 isotope exists in Russia (a stock of enriched on Ca-40 and depleted on Ca-48 material after production Ca-48 isotope
- Up to now JSC Fomos-Materials is a unique company to produce isotopic enriched complex oxide crystals with extra-high pure materials
- JSC Fomos-Materials established technology of SE production, fabricated pilot lot of SEs and have a real possibility of SEs production for big-scale experiment

SE10 Impurity Determination and Isotopic Enrichment

Element	Content, ppb
Th	<0,1
U	<0,1

Isotopic composition	Content, atomic %
^{92}Mo	0,38
^{94}Mo	0,23
^{95}Mo	0,4
^{96}Mo	0,44
^{97}Mo	0,28
^{98}Mo	3,17
^{100}Mo	95,1

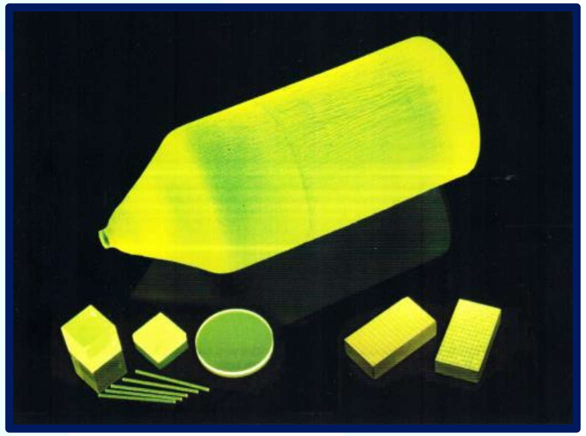
Isotopic composition	Content, atomic %
^{40}Ca	99,949±0,006
^{42}Ca	0,019
^{43}Ca	0,002
^{44}Ca	0,028
^{46}Ca	<0,001
^{48}Ca	0,002

Element	Substance %	Element	Substance %	Element	Substance %	Element	Substance %
Li	<0.0001	Cu	<0.0001	Sn	<0.0001	Yb	<0.0001
Be	<0.0005	Zn	<0.0002	Sb	<0.0001	Lu	<0.0001
B	<0.001	Ga	<0.0001	Te	<0.0002	Hf	<0.0001
Na	<0.002	Ge	<0.0001	I	<0.0005	Ta	<0.0001
Mg	<0.0003	As	<0.0001	Cs	<0.0001	W	0.0007
Al	<0.0003	Se	<0.002	Ba	<0.0001	Re	<0.0001
Si	<0.005	Br	<0.005	La	<0.0001	Os	<0.0001
P	<0.005	Rb	<0.0001	Ce	<0.0001	Ir	<0.0001
K	<0.005	Sr	<0.0001	Pr	<0.0001	Pt	<0.0001
Ca	basement	Y	<0.0001	Nd	<0.0001	Au	<0.0001
Sc	<0.0002	Zr	<0.0001	Sm	<0.0001	Hg	<0.0001
Ti	<0.0004	Nb	<0.0001	Eu	<0.0001	Tl	<0.0001
V	<0.001	Ru	<0.0001	Gd	<0.0001	Pb	<0.0001
Cr	<0.001	Rh	<0.0001	Tb	<0.0001	Bi	<0.0001
Mn	<0.0001	Pd	<0.0001	Dy	<0.0001	Th	<0.0001
Fe	<0.005	Ag	<0.0001	Ho	<0.0001	U	<0.0001
Co	<0.0001	Cd	<0.002	Er	<0.0001		
Ni	<0.0001	In	<0.0001	Tm	<0.0001		

JSC Fomos-Materials can produce extrapure crystals with impurity content lower than 0.1 ppb

New Perspective Crystal for Scintillation Application

Crystal*	Den-city	Melting Point	Hydro-scopicity	Main Scint. Decay Time, ns	LY, Ph/MeV	Energy Res. at 662 keV, %
$Pr:Lu_3Al_5O_{12}$	6.71	1980	No	20 (20-40%)	16000-20000	4.5-6.5
$Ce:Gd_3(Ga,Al)_5O_{12}$	6.63	1850	No	88 (90%)	46000-51000	4.9-5.5
$PbWO_4$	8.28	1160	No	3-6	200	30-40
$CdWO_4$	7.90	1325	No	5000	27000	6.6
$Ce:Lu_2SiO_5$	7.4	2150	No	35	26000	7.9
$Ce:Y_2SiO_5$	4.45	2070	No	39	32000	8.1
$Ce:Gd_2SiO_5$	6.71	1900	No	60	12500	7.8
$Bi_4Ge_3O_{12}$	7.13	1050	No	300	8500	9.0
$Ce:LuAlO_3$	8.34	~1900	No	16-20	11400	9.0
$Ce,Eu:LiCaAlF_6$	4.88	820	No	1670	40000	
$Ce:LaBr_3$	5.30	783	Yes, very high	16(100%)	70000	2.6



Kimura H., et al., Czochralski Growth of $Gd_3(Ga_{1-x}Al_x)_5O_{12}$ Single Crystals, Journal of Crystal Growth 74 (1986) 187—190 187

Kamada, K., et al., Composition Engineering in Cerium-Doped $(Lu,Gd)_3(Ga,Al)_5O_{12}$ Single Crystal Scintillators. Crystal Growth & Design, 2011. 11(10): p. 4484-4490.

*Yoshikawa A., et al., Czochralski Growth and Properties of Scintillating Crystals, Acta Physica Polonica A, 2013., v.124. No.2, p.250-264

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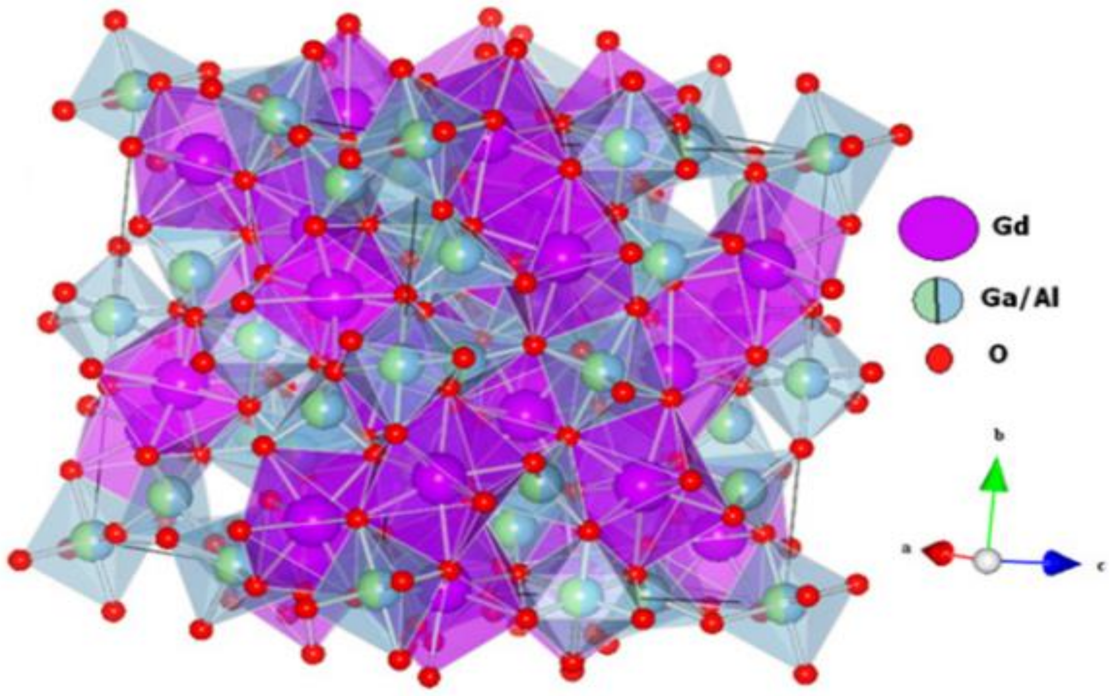
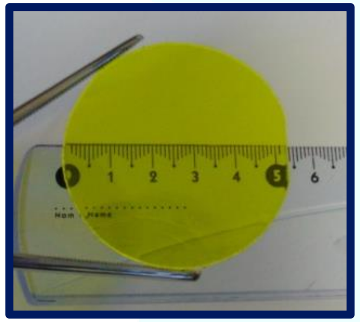
For Wide Commercial Application Need to Decrease or Eliminate Phosphorescence!

$Gd_3Al_2Ga_3O_{12}$ Structure [1]



- Cubic Syngony
- Space Symmetry Group Ia3d

Cross-Section
of the GGAG:Ce Crystal
50 mm in Dia.

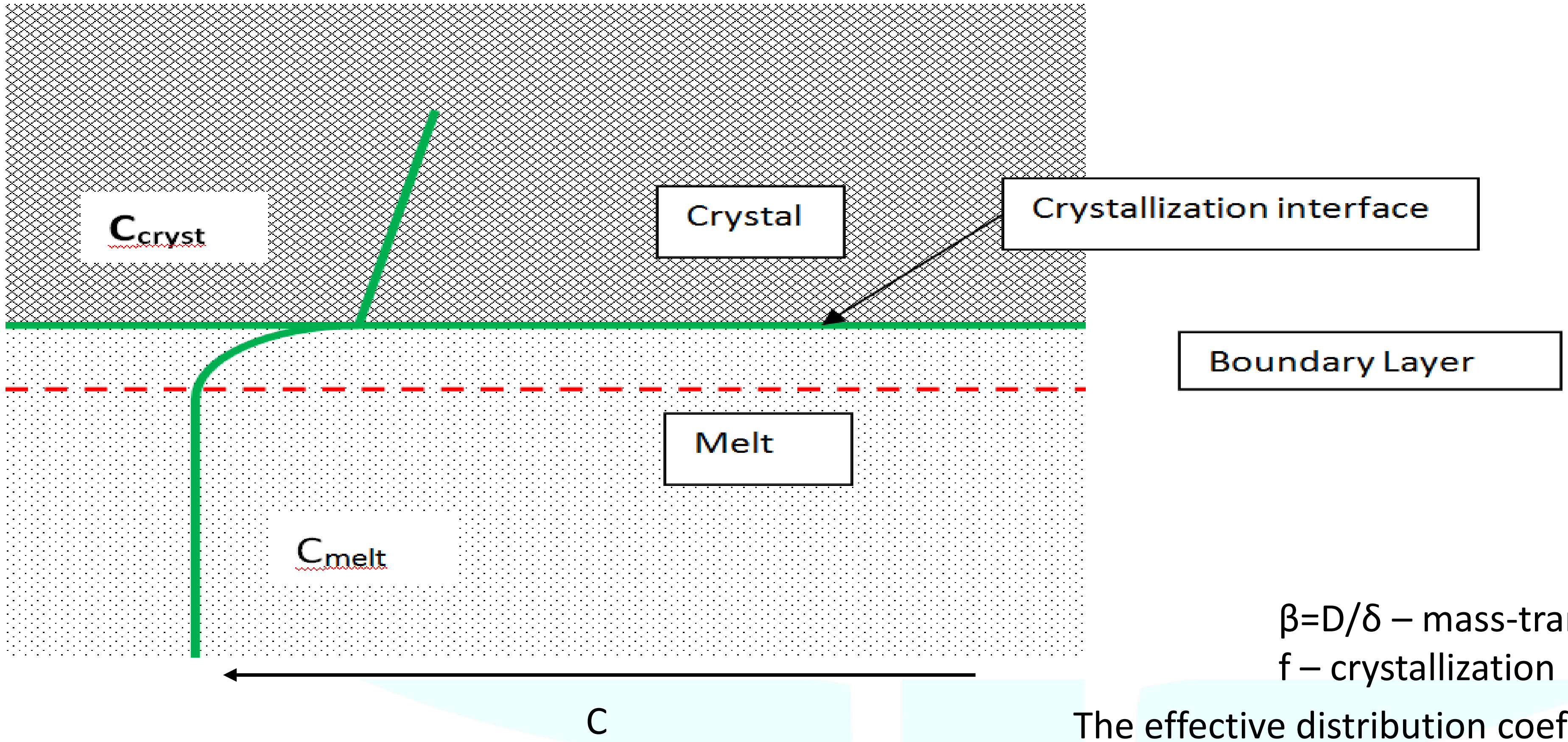


Ion	Gd^{3+}	Al^{3+}	Ga^{3+}	O^{2-}	Ce^{3+}
Position Type- Coordination polyhedron	A – dodecahedron	B – octahedron; C – tetrahedron	B – octahedron; C – tetrahedron	D – vertices of coordination polyhedra	A – dodecahedron

1. Effect of codoping on scintillation and optical properties of a Ce-doped $Gd_3Ga_3Al_2O_{12}$ scintillator / Tyagi M., Meng F., Koschan M., e.a. // Journal of Physics D: Applied Physics. – 2013. – V. 46. – №. 47. – P. 475302.

JSC Fomos-Materials posess know-how
of codoping complex oxide crystals

Impurity Distribution



Equilibrium State

$$k_0 = \frac{C_{cryst}}{C_{melt}}$$

Barton approach:

$$: \frac{k_0}{k_0(1+k)e^{-(f/\beta)}}$$

β=D/δ – mass-transfer coefficient

f – crystallization rate

The effective distribution coefficient of Ce^{3+} ion K_{Ce} is **0.36***

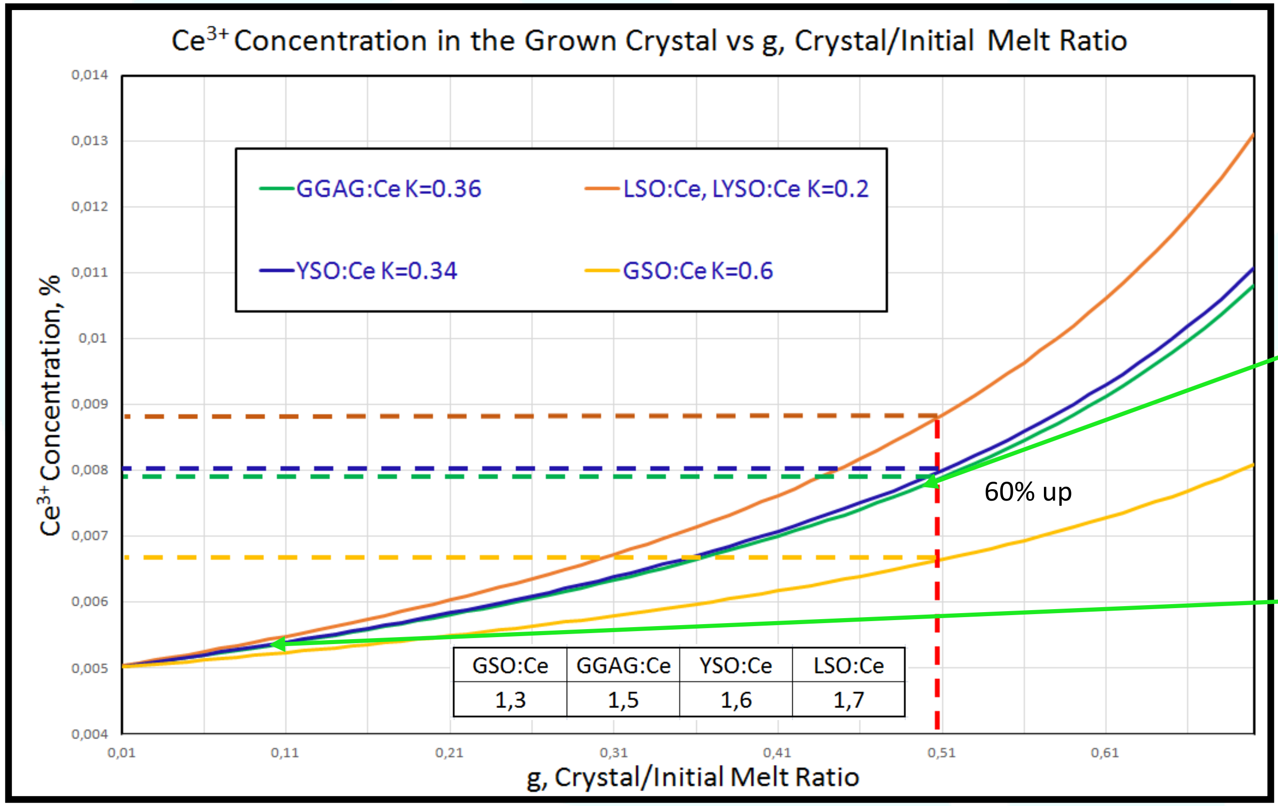
1. *A. Yoshikawaa, V. Chani and M. Nikl, Czochralski Growth and Properties of Scintillating Crystals) Acta Physica Polonica A 124 (2013) No. 2 250-264

JSC Fomos-Materials can optimize a cost of crystal with guarantee of crystal quality and homogeneity

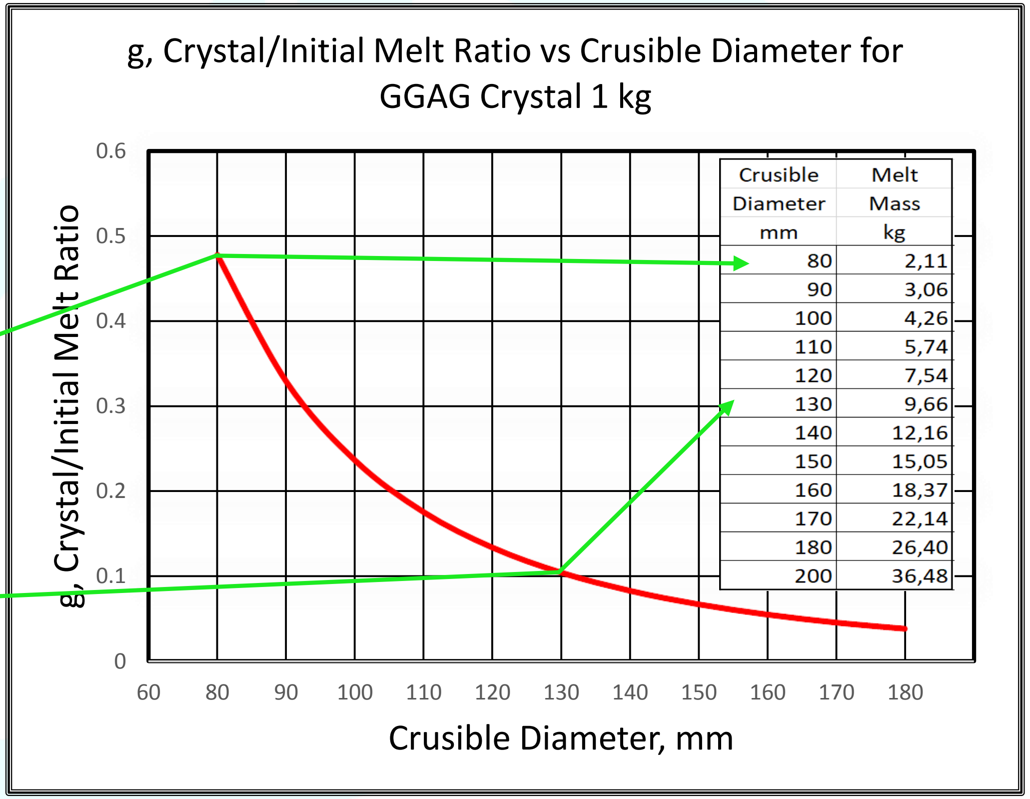
Cerium Distribution in GGAG

$$C_{Ce_{cryst}} = K_{Ce} C_{0_{melt}} (1-g)^{K_{Ce}-1}$$

Pfann Equation for Normal Crystallization Process



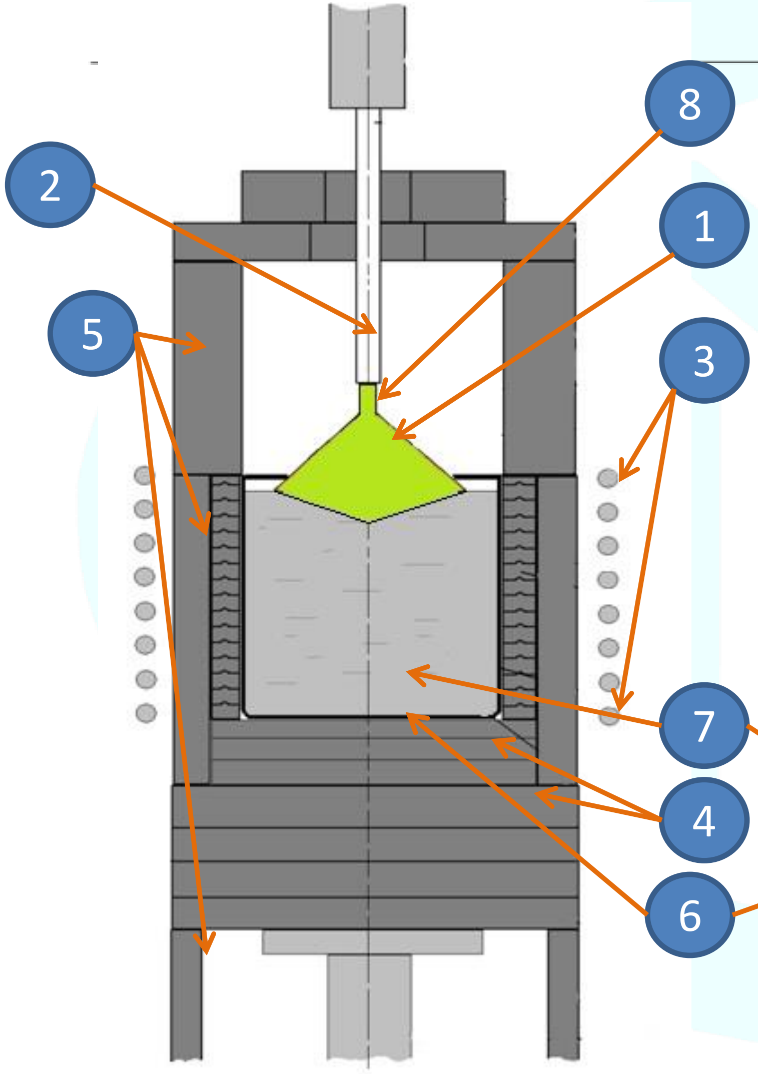
GSO:Ce	GGAG:Ce	YSO:Ce	LSO:Ce
1,3	1,5	1,6	1,7



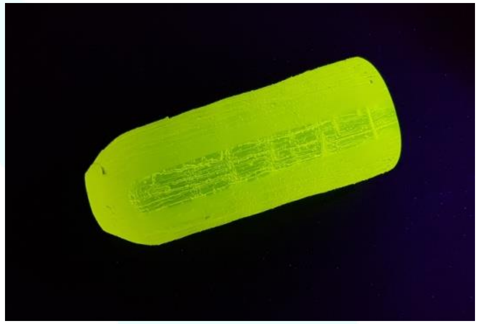
Crusible Diameter mm	Melt Mass kg
80	2,11
90	3,06
100	4,26
110	5,74
120	7,54
130	9,66
140	12,16
150	15,05
160	18,37
170	22,14
180	26,40
200	36,48

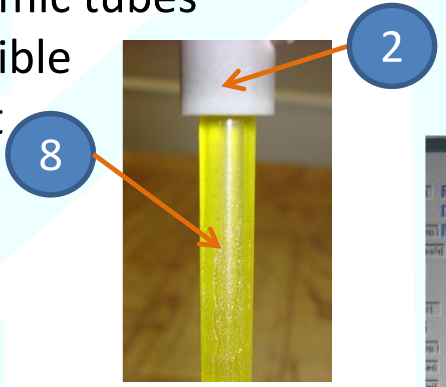
1. L.Qin, H.Li, Sheng Lu, D.Ding, G.Ren, Growth and characteristics of LYSO($Lu_{2(1-x-y)}Y_{2x}SiO_5:Ce_y$) scintillation crystals, J. of Cryst. Growth 281 (2005) 518-524
2. A. Yoshikawaa, V. Chani and M. Nikl, Czochralski Growth and Properties of Scintillating Crystals) Acta Physica Polonica A 124 (2013) No. 2 250-264

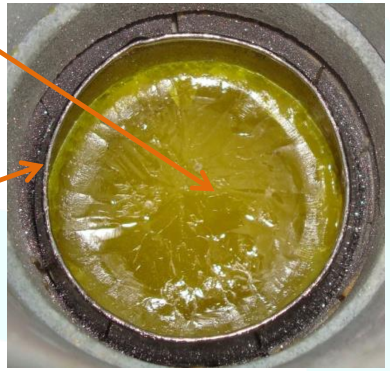
GGAG:Ce Crystal Growth by Czochralski Method

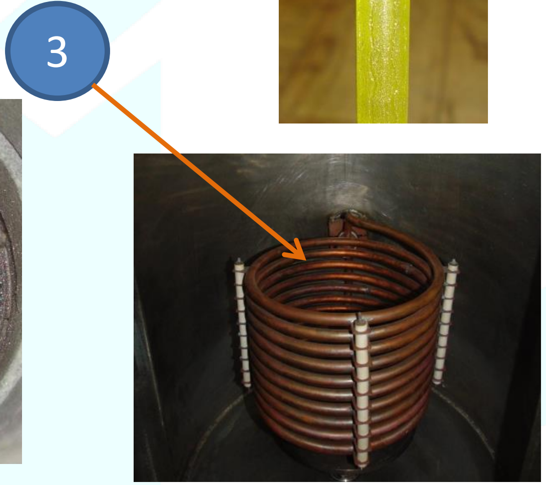


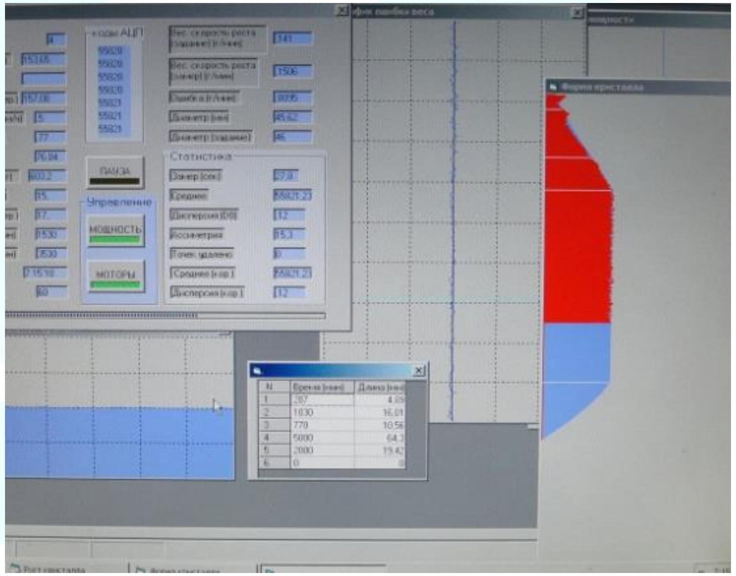
- 1 – growing crystal
- 2 – seed holder
- 3 – induction coil
- 4 – ceramic plates
- 5 – ceramic tubes
- 6 – crucible
- 7 – melt
- 8 - seed









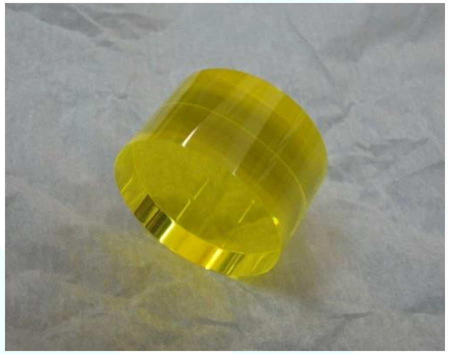


JSC Fomos-Materials made a lot of crystal growth experiments with optically non-active impurities

Already Grown GGAG Crystals

Up to now JSC Fomos-Materials grew GGAG crystals with following compositions:

- GGAG:Ce with different cerium concentrations
- GGAG:Ce with different Ga/Al ratio
- GGAG:Ce with codoping of:
  - Magnesium
  - Calcium
  - Strontium
  - Barium
  - Scandium
  - Zirconium
  - Titanium
- GGAG:Ce with pair and triple codoping of above listed elements

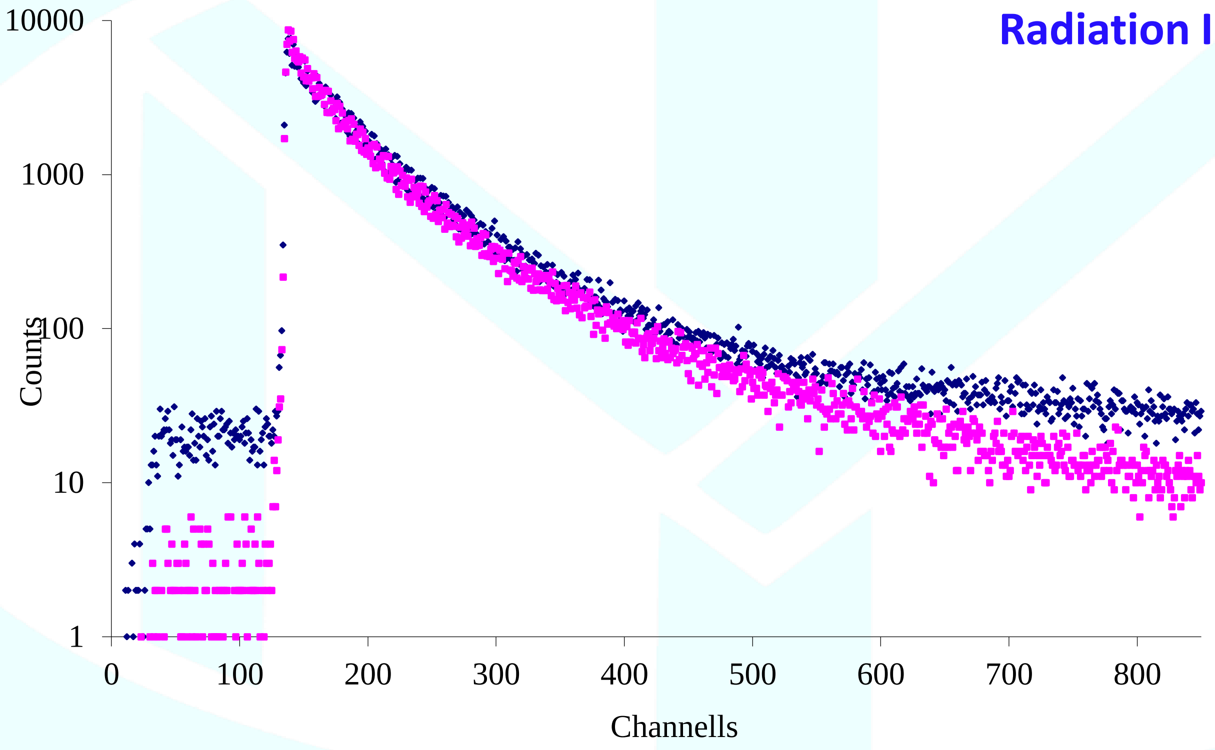


MAGG-MULTIDOPED ALUMINUM GALLIUM GARNET

MAGG is the gadolinium aluminum gallium garnet doped with Ce and pair of codopands is a perfect scintillation material designed to overcome drawbacks of Ce solely doped and Mg or Ca codoped crystals.

Density, g/cm^3	Z_{eff}/photo absorp. coeff., 511 keV,cm^{-1}	Luminescence maximum, nm	Light yield, ph/MeV	Decay kinetics, ns(%)	Energy resolution, %	Time resolution (CTR), ps
6.68-6.63 depending on Al/Ga ratio	51/0.12	520	38000(RT) 46000(-45^{o}C)	30 (25%), 80 (60%), 100-200 ns (15%)	6,2(511keV) At -20^{o}C with SiPM 3,6(1270keV) at -20^{o}C with SiPM	170 (-20 to 20^{o}C)

Scintillation kinetics of GAGG:Ce (dark blue) and MAGG (magenta) samples measured at room temperature



Radiation Instruments and New Components LLC
Minsk, Belarus

Noise before scintillation kinetics characterize level of phosphorescence.
1 channels corresponds to 1 ns

Parameters of kinetics of:
GAGG:Ce: τ1= 32ns(36%),τ2=86ns (56%),τ3=354ns (8%);
MAGG- τ1= 27ns(34%),τ2=73ns (54%),τ3=200ns (11%).

Amplitude spectra of 137Cs source measured with R329 PMT at different temperatures

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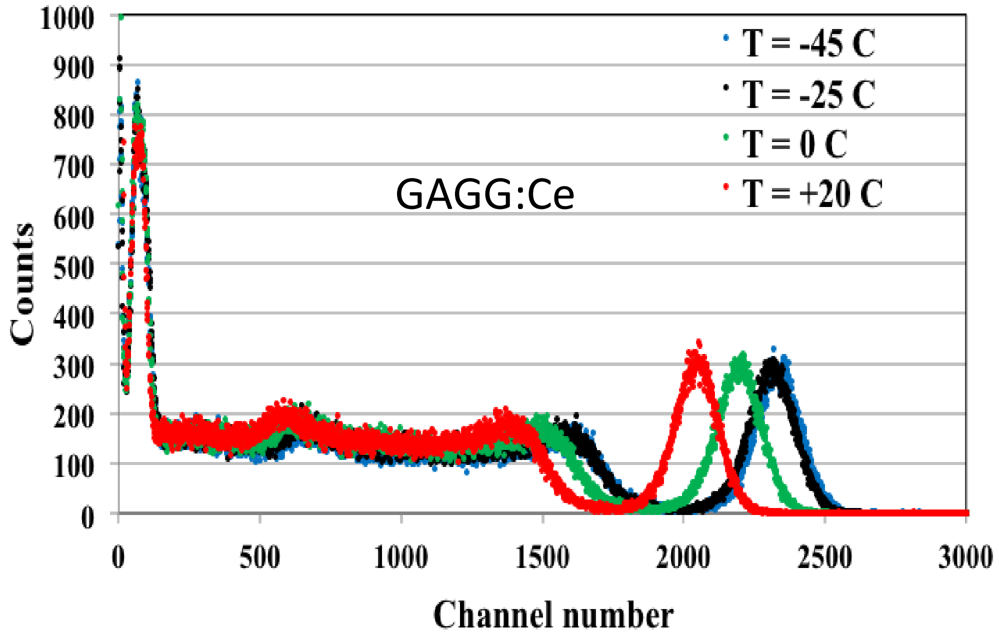
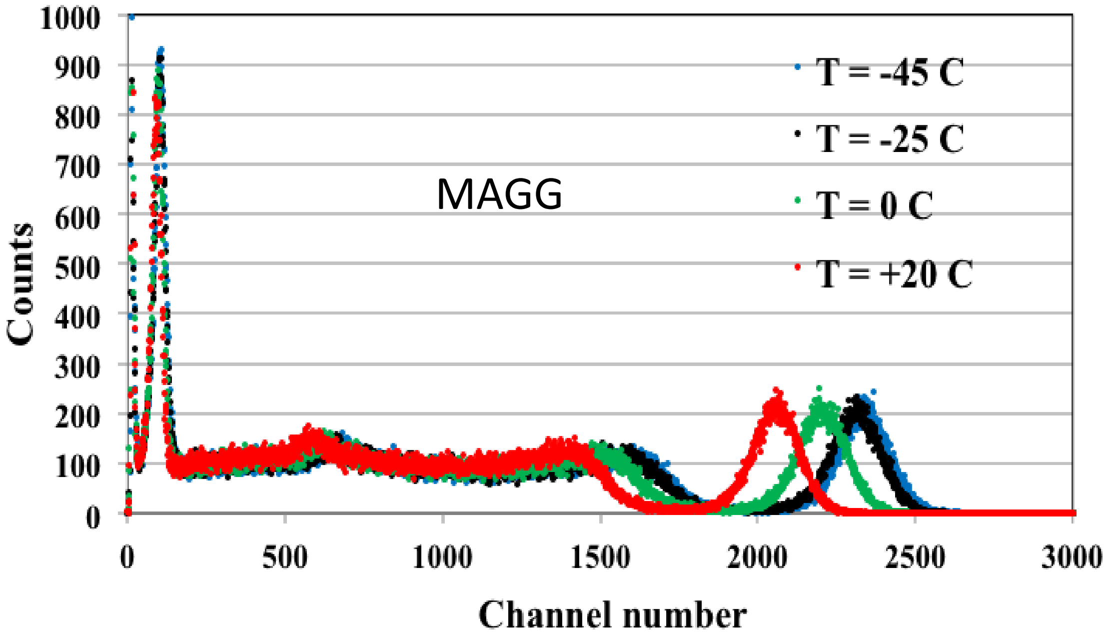
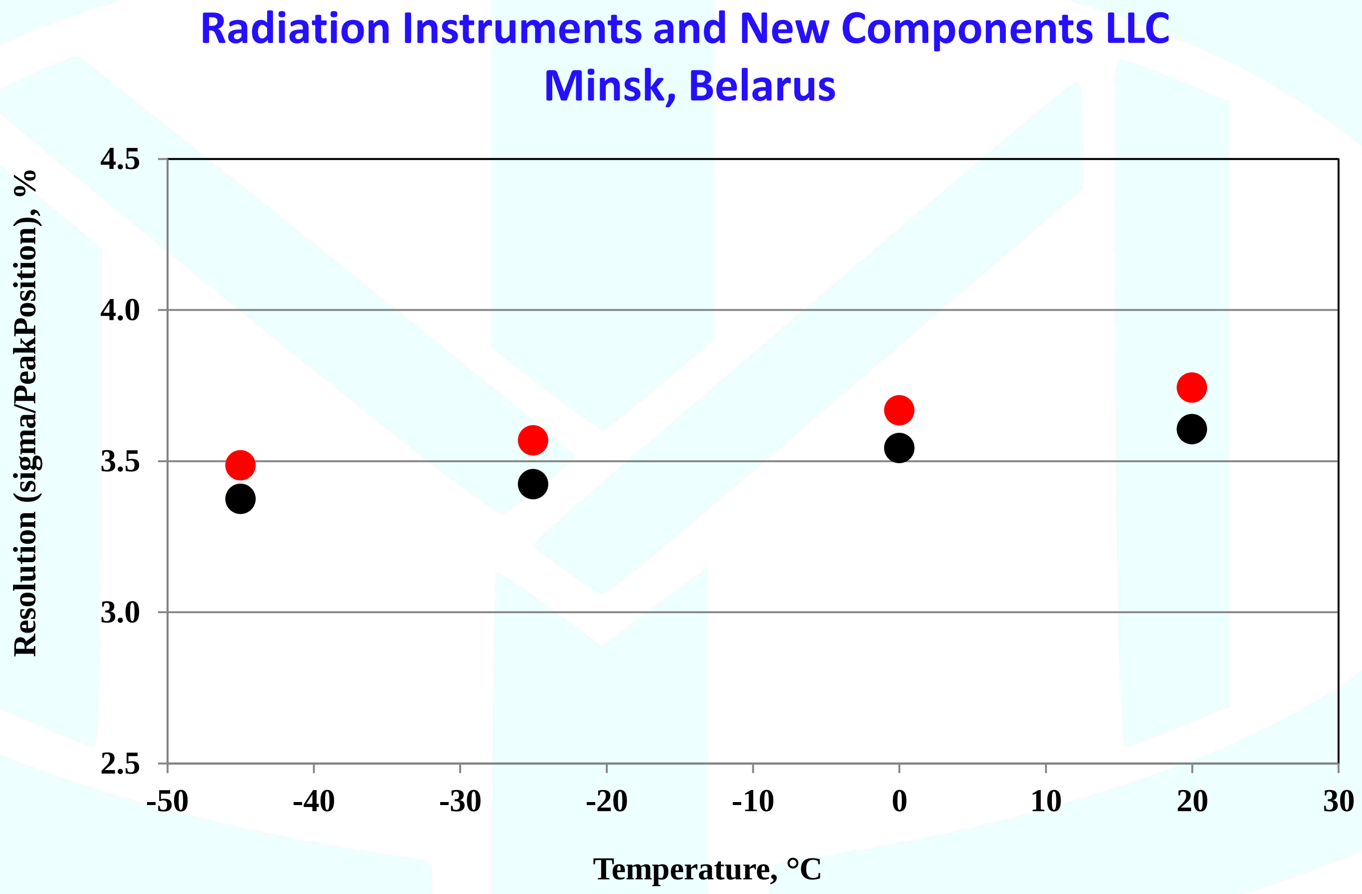
Codoping safe a lightyeld





Change of the energy resolution for a photo-peak with temperature of GAGG:Ce (red dots) and MAGG(black dots)



Gated (measured in different time gates) light output of sample with temperature

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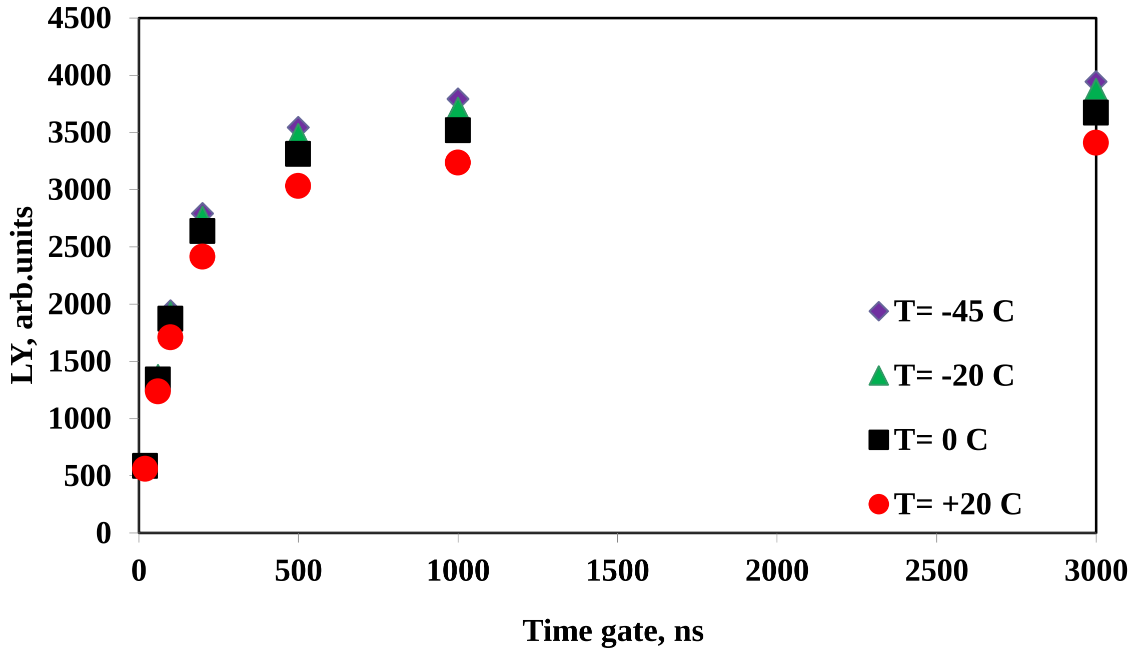
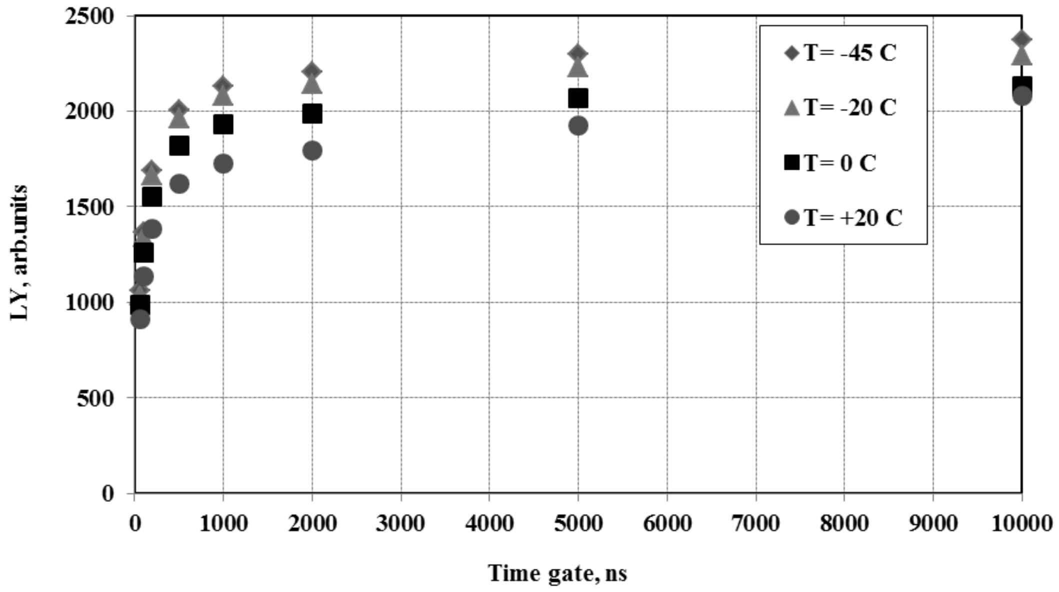


GAGG:Ce



MAGG

Radiation induced absorption spectra of GAGG and MAGG crystals

Radiation Instruments and New Components LLC
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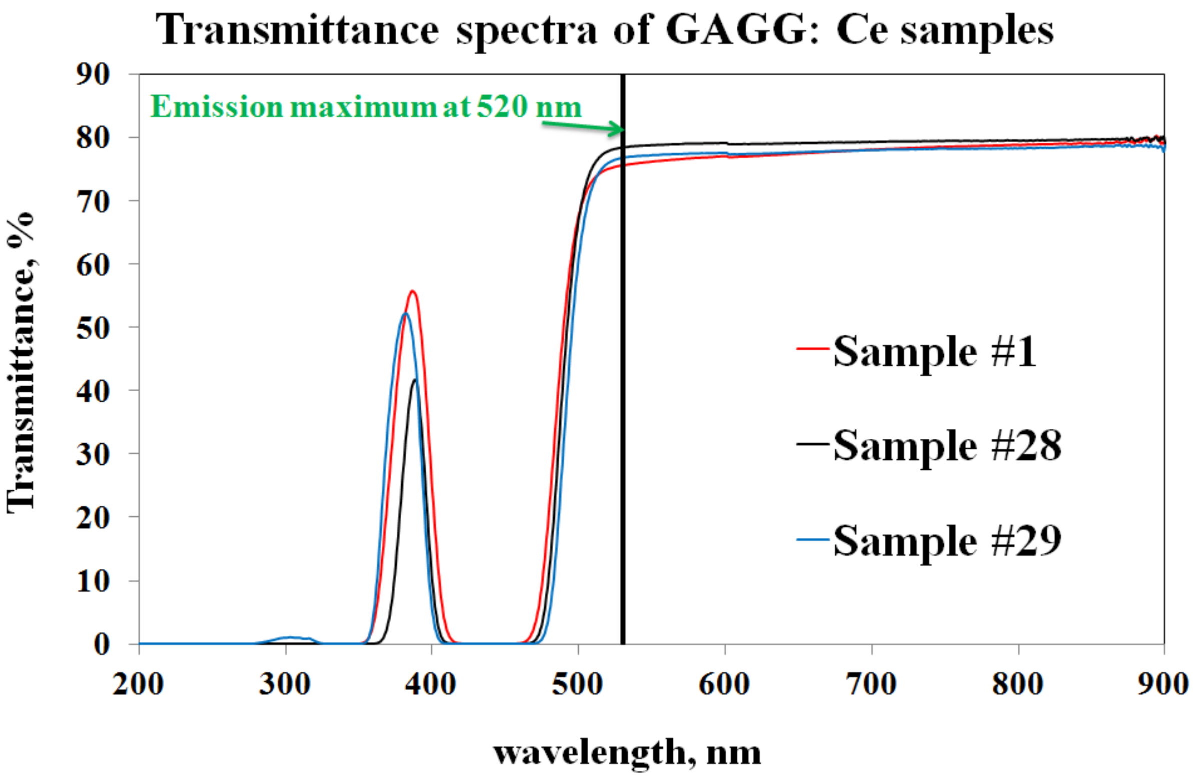
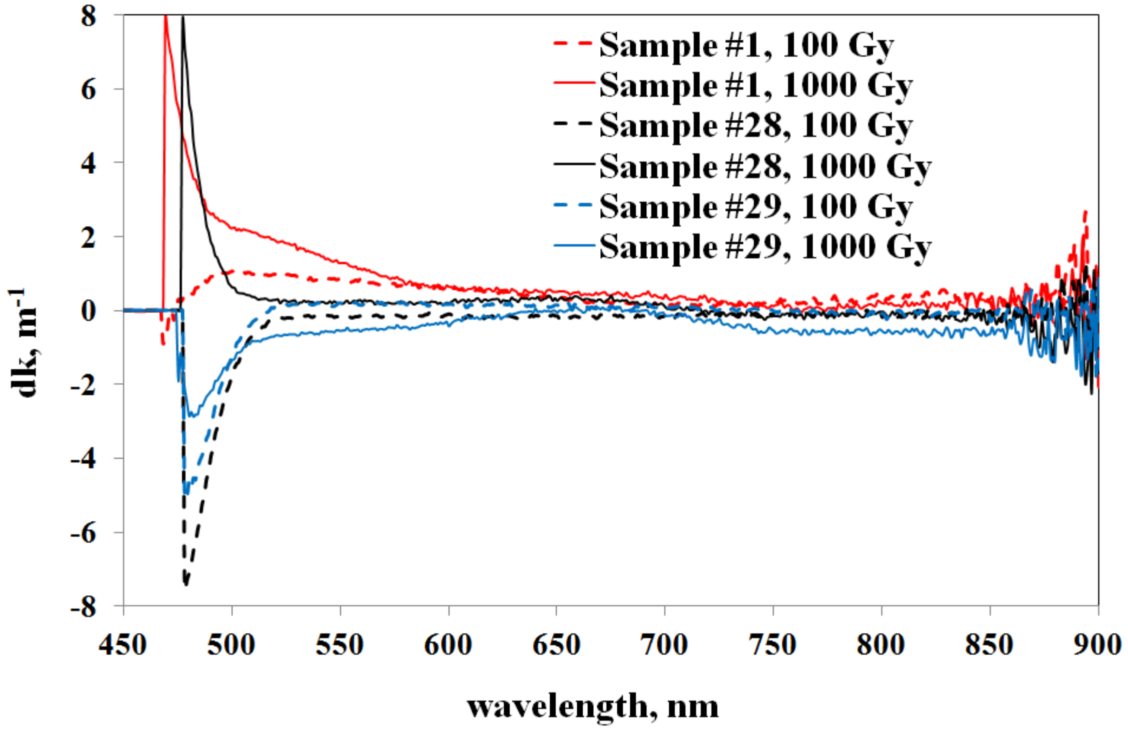


Ce^{3+} absorption bands and location of the Ce^{3+} luminescence realatively to absorption spectra



Radiation induced absorption spectra of GAGG and MAGG crystals obtained at different stages of the technology development (irradiation with 60Co (1,2MeV)

Possible Directions of R&D on the GAGG Crystals

For the 1st Stage

- The quality of the crystal (the energy resolution) and the choice of its methods of control
- Optimization of Ce^{3+} and codopands concentrations (light yield and radiation hardness)
- High temperature heat treatment of the grown crystals (temperature, gas medium, duration etc.)
- Development of technological processes for mechanical treatment of the grown crystals (manufacturing of special form crystal elements)
- Product Specification must be determinate

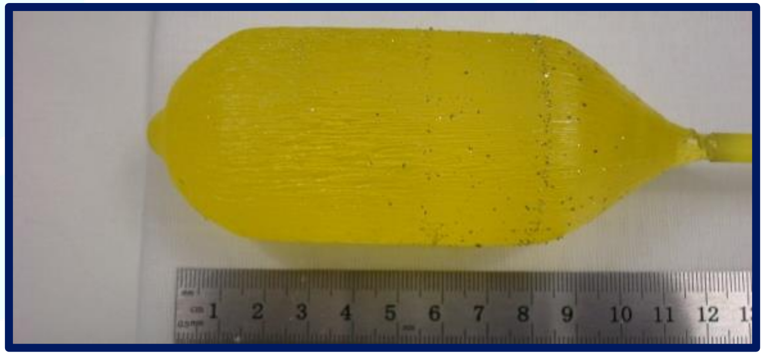
For the 2nd Stage

- Statistical analysis of the developed complex technology –

yield, return and irrecoverable loss of the crystal growth process

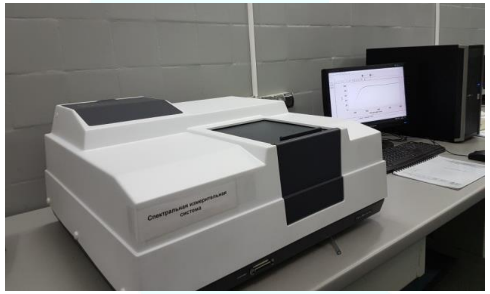
- Economic analysis - initial costs, cost, etc.

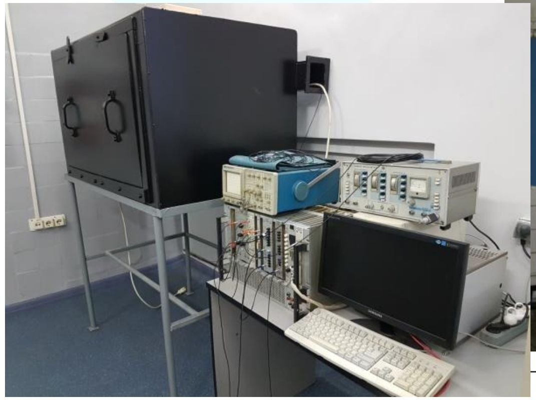
As-grown GGAG:Ce
Crystal 50 mm in dia.



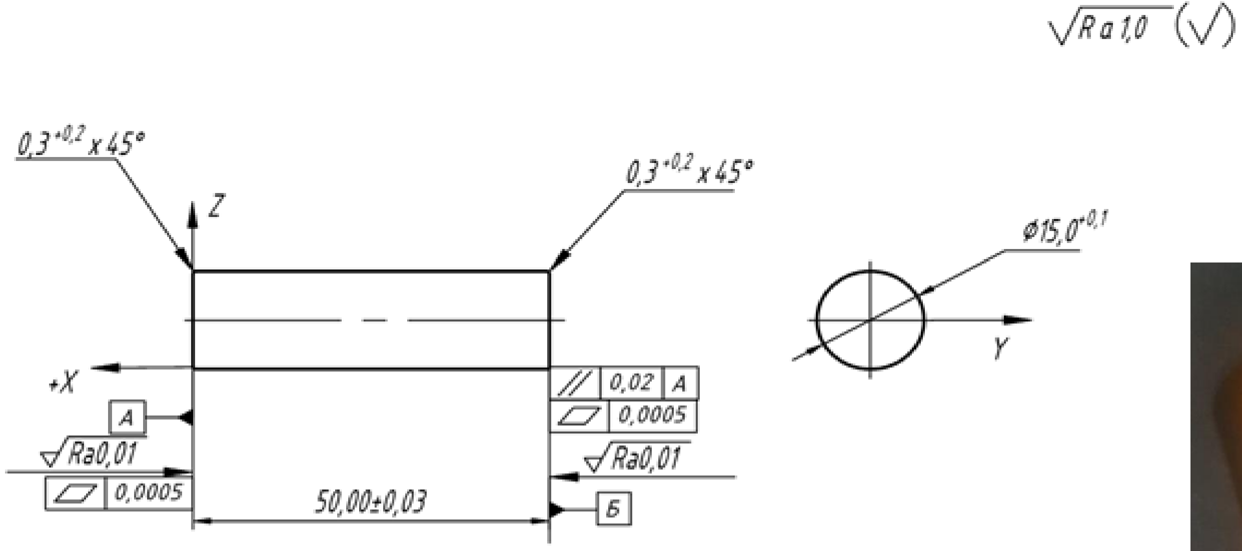
Full Technological Circle

- ***Initial Charge Synthesis***
- ***Crystal Growing***
- ***High Temperature Heat Treatment***
- ***Cutting, Grinding, Drilling, Polishing.***
- ***ISO 9001:2008***

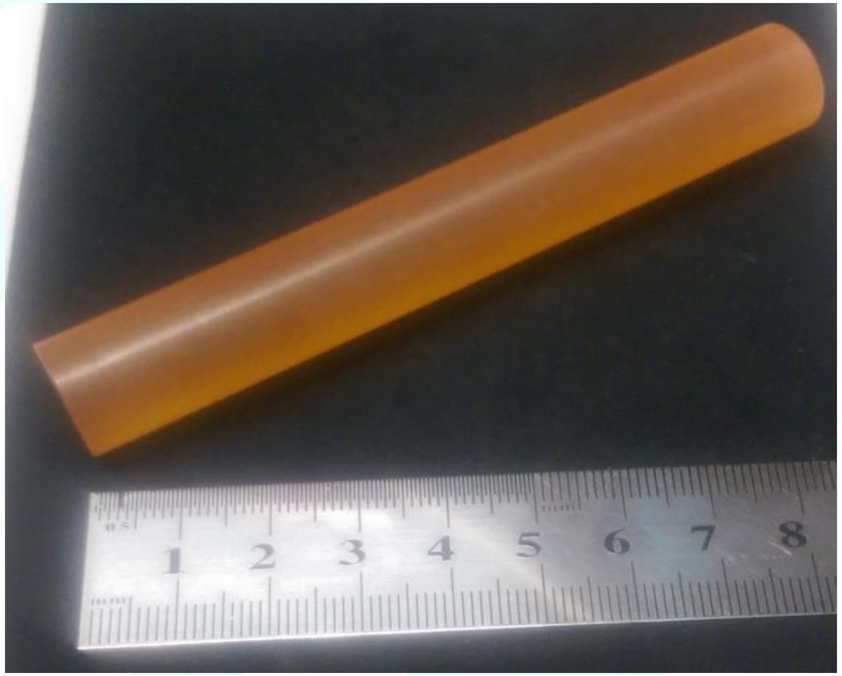




Examples of Optical Elements Production

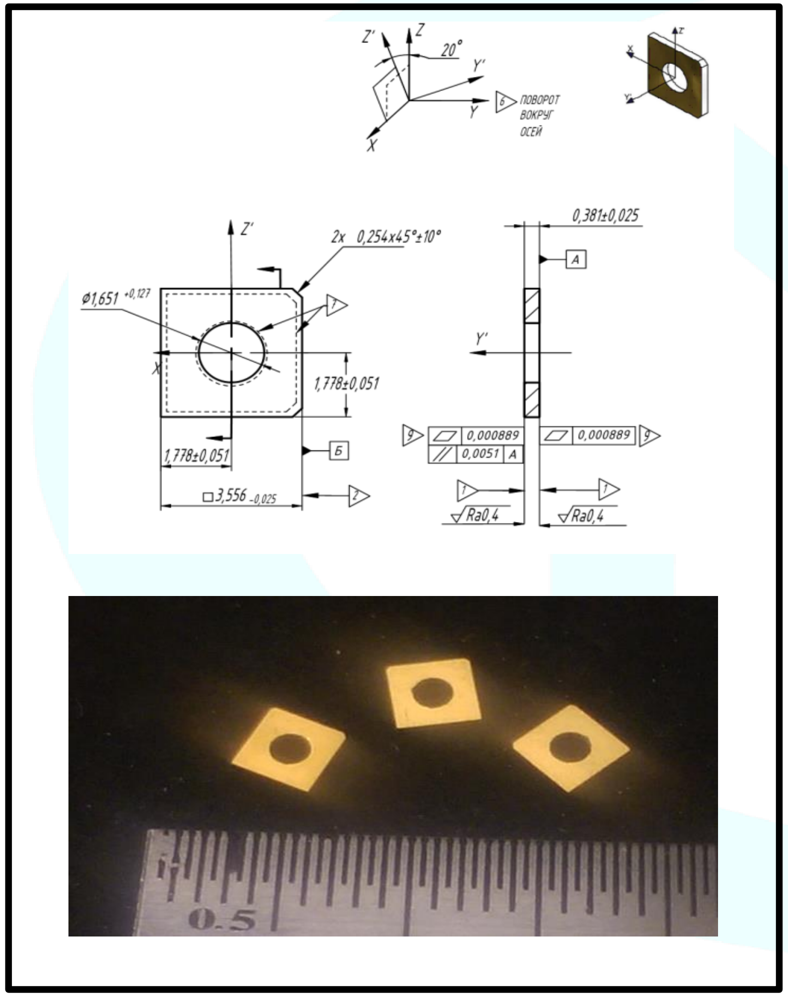


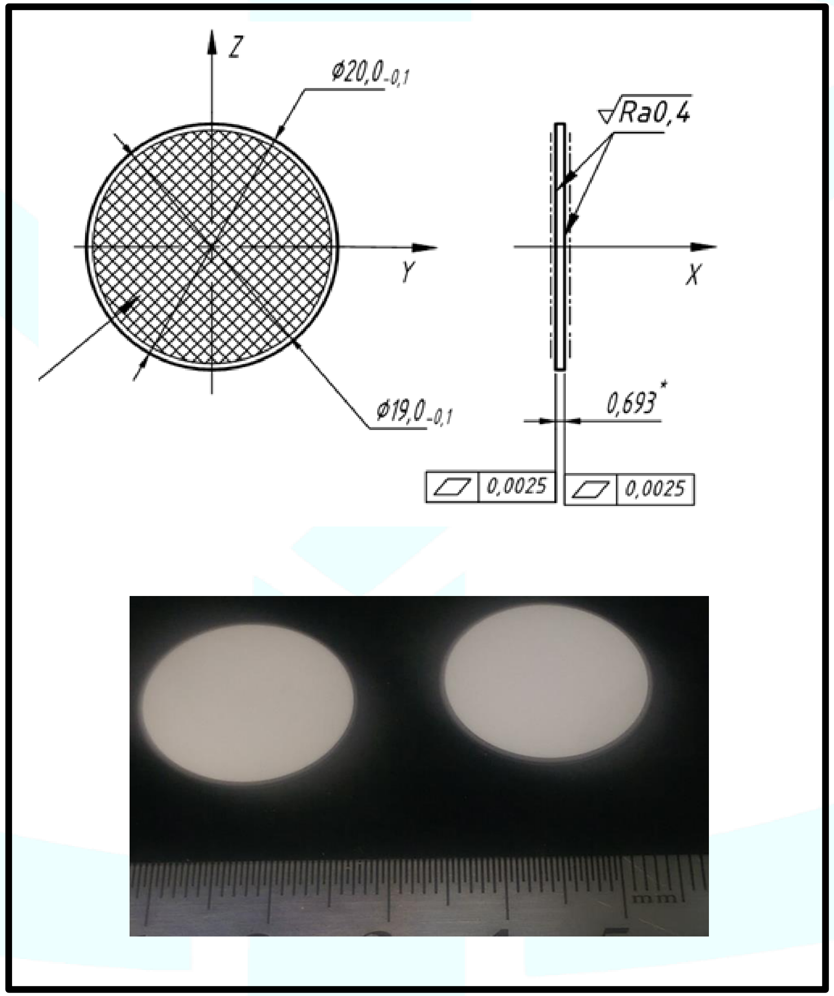
LGS optical element
made for the high voltage
transformer (Pockels effect)

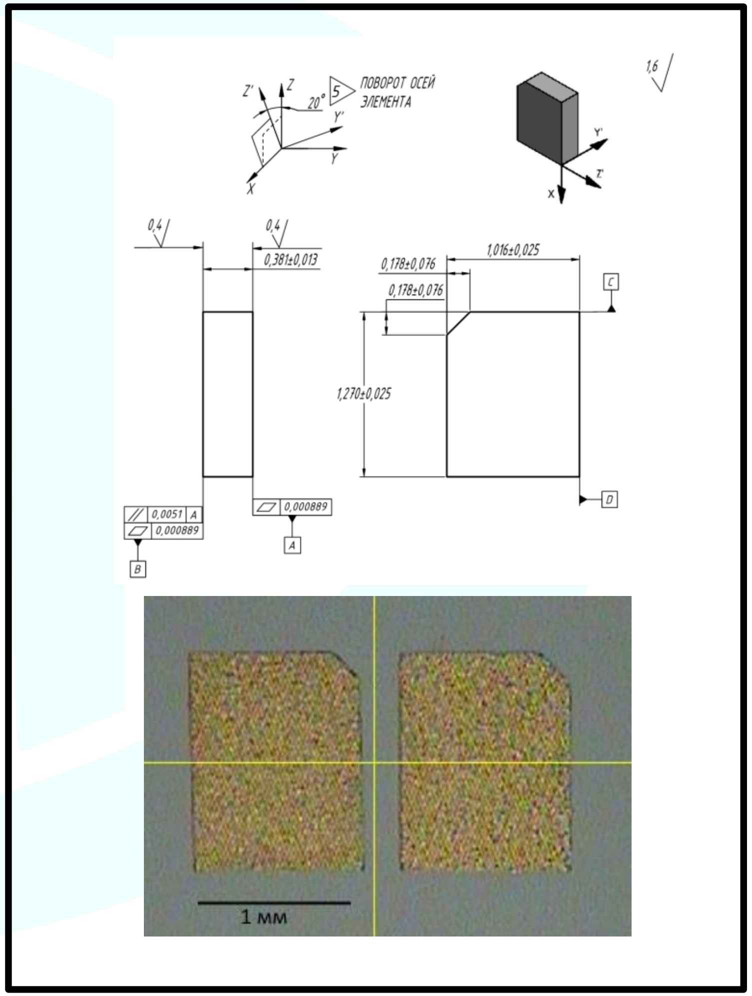


LGS optical element

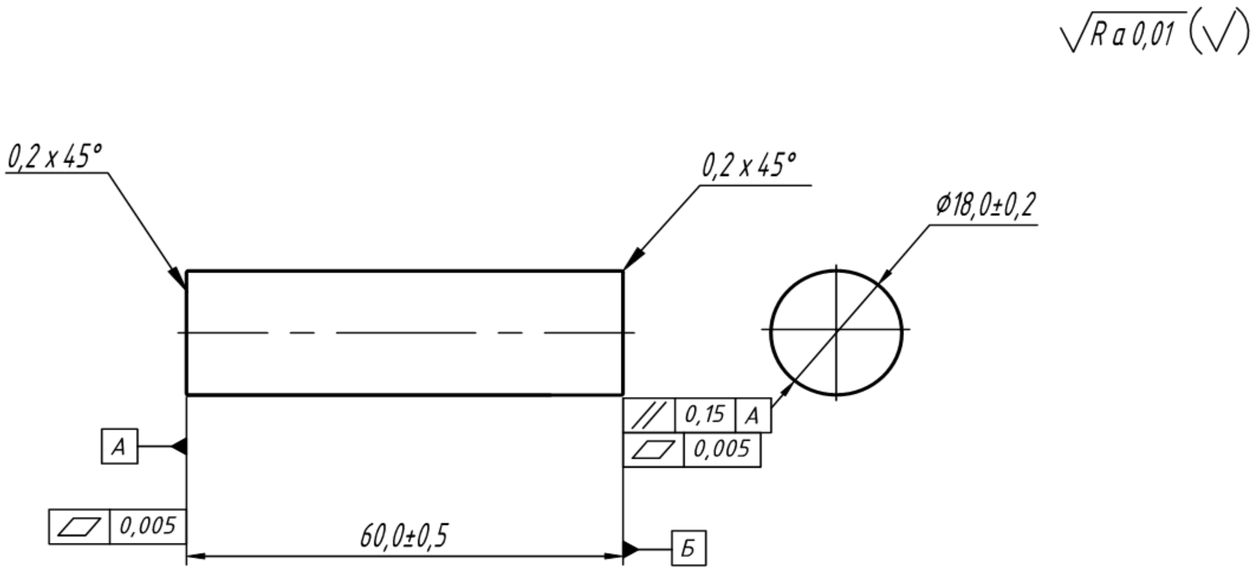
Sensitive elements for HT sensors: pressure and vibration







MAGG Scintillation Elements Ø16x60 mm



THANK YOU FOR YOUR ATTENTION

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