Synthesis of Self-Glowing Crystals doped with Plutonium-238

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Actinide immobilization includes

not only:
development and use of durable advanced materials (ceramic/glass waste forms) before final geological disposal *but also* – advanced materials

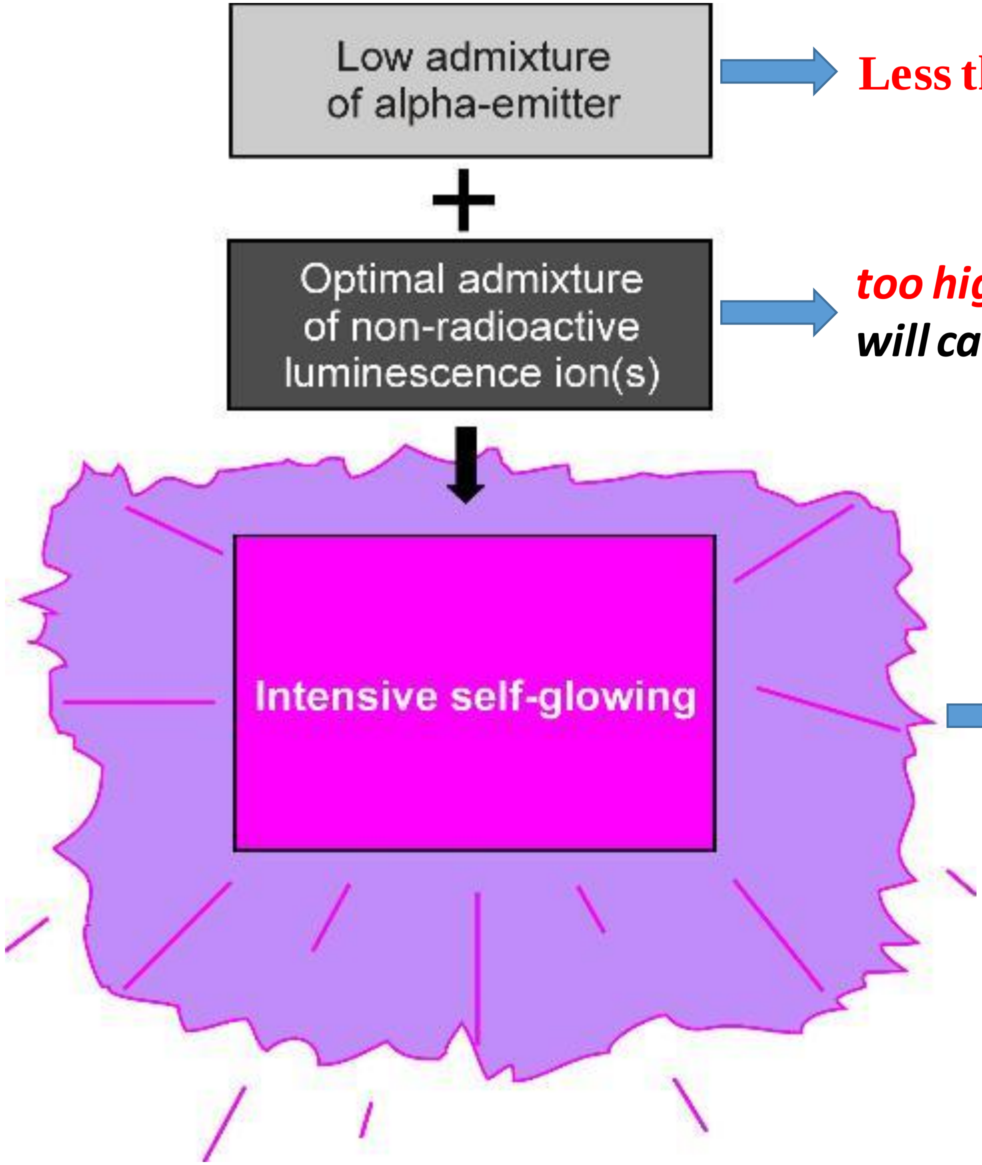
such as:

- inert ceramic nuclear fuel
- durable sources of alpha-irradiation
- self-glowing crystals

In general, radioactive glowing sources developed in the past consist of several separate parts:

1) Non-radioactive crystalline material doped with non-radioactive luminescence ion (for example, ZnS doped with Eu^{3+})
2) Highly radioactive material (for example, $^{238}PuO_2$)
3) Hermetically sealed body(made of steel and transparent glass)

Combination of all three parts in one durable crystal matrix



Less than 0.1 wt.% for ^{238}Pu

too high or too small content of luminescence ion(s) will cause weak self-glowing

optimal ratio between luminescence ion(s) and alpha-emitter(s)

Durable and intensively self-glowing crystals are advanced materials for use in extreme environment for:

- optical couplers
- robotics
- medicine
- other fields

Intensive long-term radio-luminescence might be converted into electric current that allows development of reliable **“nuclear” batteries**.

Such nuclear batteries can potentially be used in aggressive chemical media as well as for applications in space for dozens to hundreds of years.

Why zircon?

- Chemically inert (even at high temp. ~1600°C)

- Resistant to natural self-irradiation or heavy ion irradiation

- Mechanically and geochemically stable which allows to use it for determining isotopic dating of rocks*
- Considered as universal matrix for:
  - ✓ reliable matrix for the final actinide immobilization
  - ✓ safest sources of ionizing radiation and radio-luminescent component of "nuclear" batteries
  - ✓ creating innovative materials

**A.C. McLaren et al. 1994*

Main aims

- To synthesize self-glowing crystals of zircon with impurities:
  - ✓Terbium (Tb^{3+}) and Europium (Eu^{3+}) as luminescence ions

    Tb^{3+} is well known luminescence ion

    but (Tb^{3+} + Eu^{3+}) in a couple may provide much more intensive luminescence

  - ✓Plutonium-238 as a glowing activator

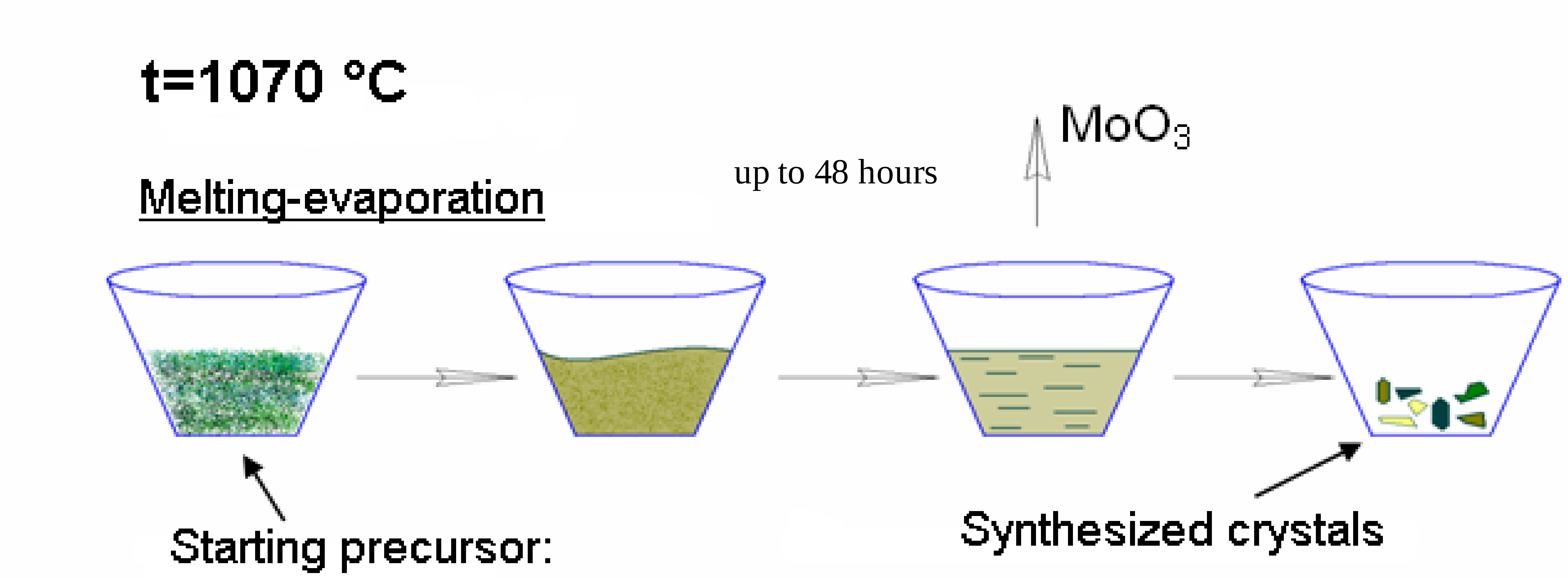
- To achieve intense strong glowing of the developed zircon crystals

- Keep safe working with highly active open sources

Main difficulties

- To find the optimal ratio between luminescence ions and actinide
- Terbium can be in two valence states: (3+) and (4+) and europium: (3+) and (2+). However, only terbium (3+) and europium (3+) are known as effective luminophores => To find the way to stabilize trivalent state
- The content of the radionuclide should be minimal (no more than 0.1 wt. % for plutonium-238)

Synthesis of crystals by flux method 1



MoO_3 (flux)+SiO_2+ZrO_2+PuO_2+Tb_2O_3/Eu2O_3

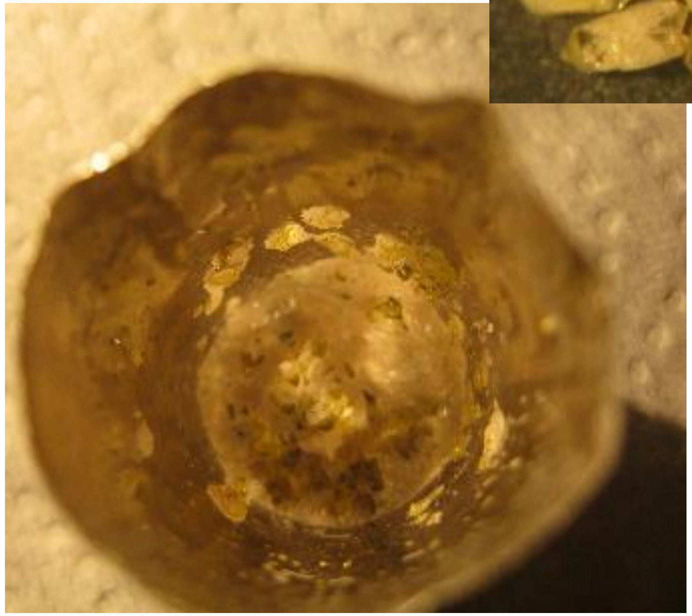
(Zr-phosphate) or $TbPO_4$/$EuPO_4$

Synthesis of crystals by <u>flux method 2</u>

Pt crucible containing starting precursor

Furnace (max.T=1300°C)

Grown zircon crystals at the bottom of Pt crucible



Washing crystals in 25% aqueous solution of NH_4OH and HNO_3

Chemical properties. Valence state.

It is very difficult to incorporate essential amount of Tb^{3+} into zircon crystal structure substituting Zr^{4+}

Also, Tb incorporated into zircon can be in two valence states: (3+) and (4+)

<u>but only trivalent Tb^{3+} are luminescence ions</u>

Admixture of phosphor* may support incorporation of trivalent lanthanides into zircon structure due to charge compensation:

$$\mathbf{(Zr,Tb)(Si,P)O_4}$$

$$\mathbf{Zr^{4+} + Si^{4+} = Tb^{3+} + P^{5+}}$$

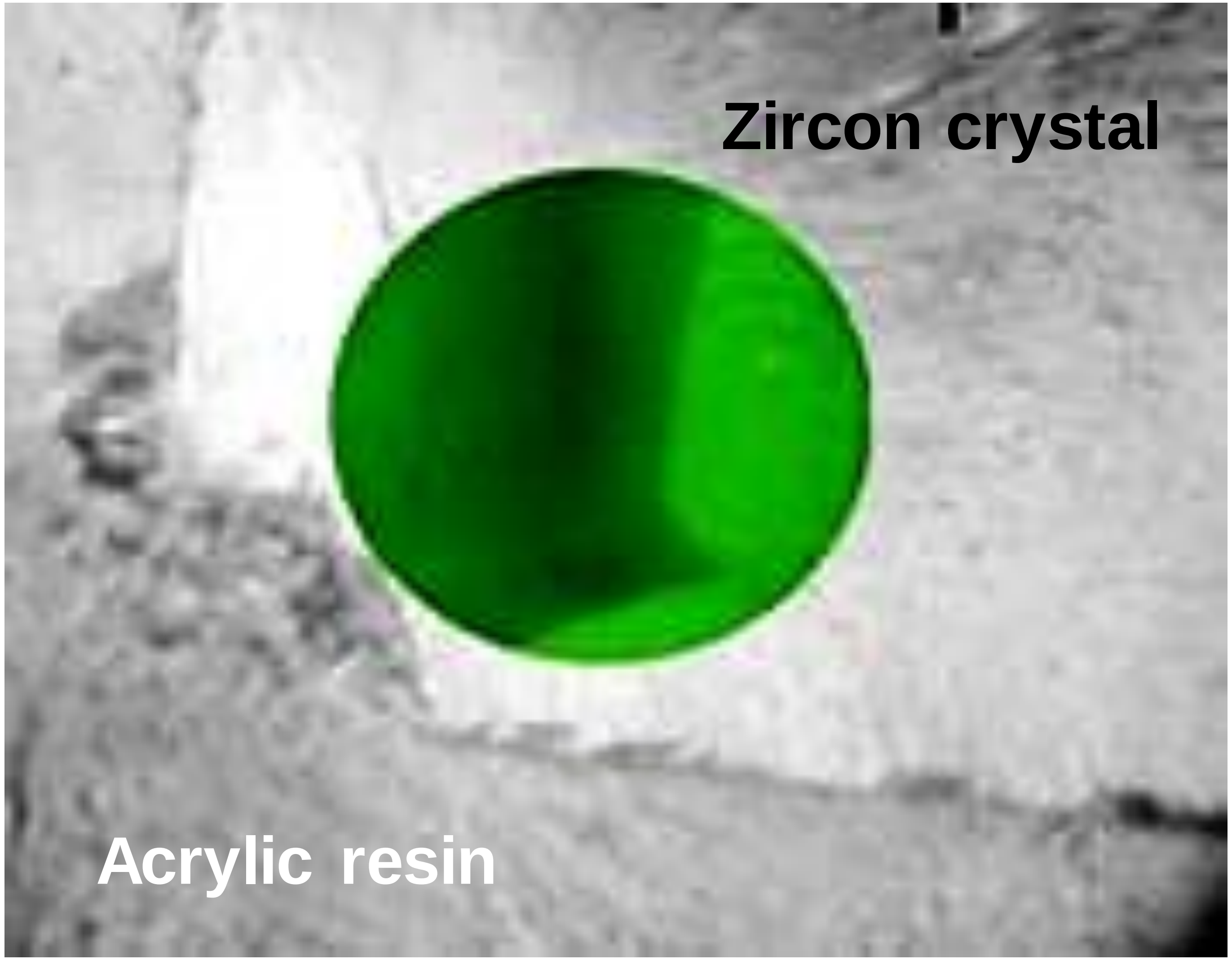
** J.M. Hanchar et al. 2001*

The best luminescence ions as well as their optimal contents are different for different crystalline host phase

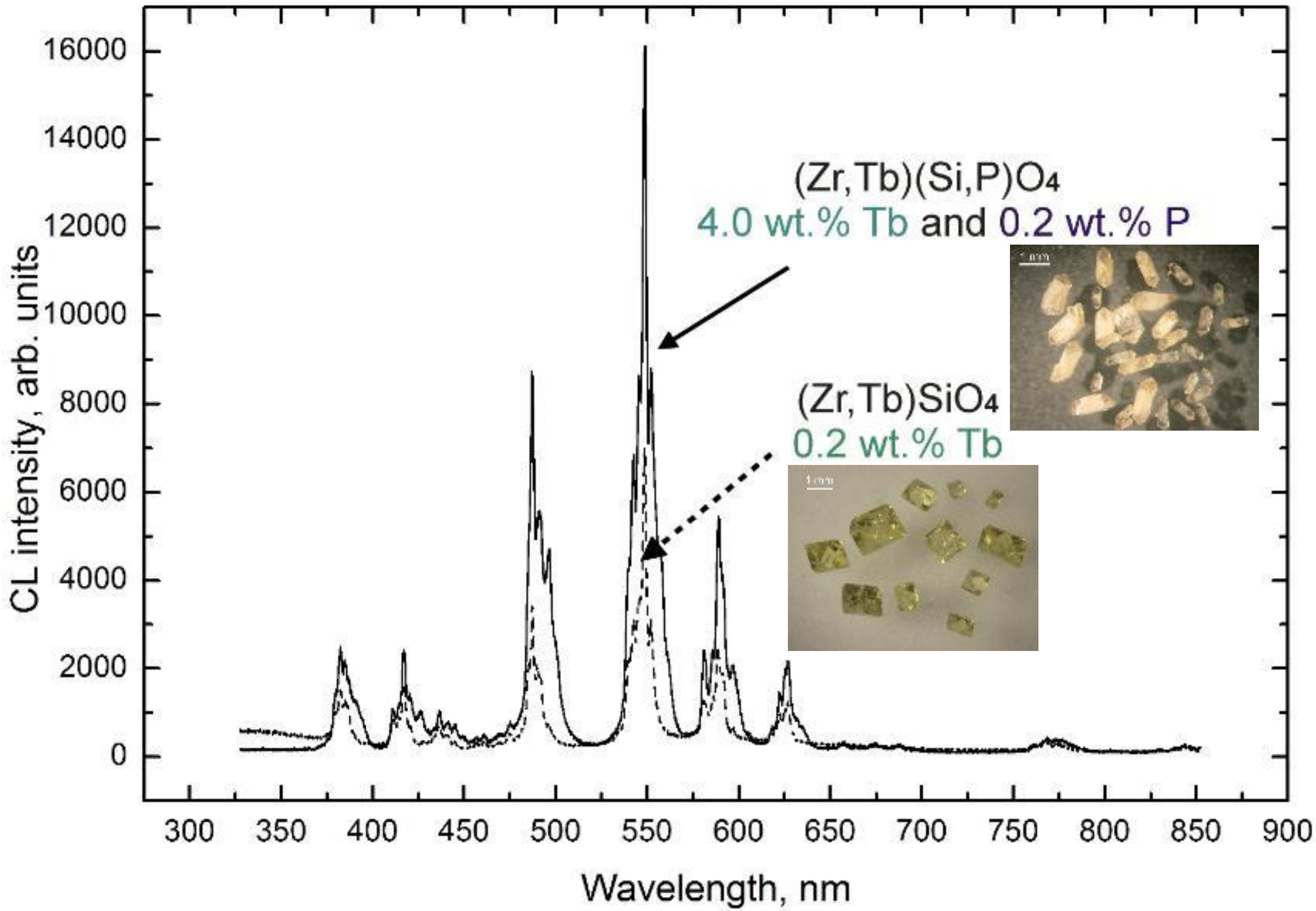
The use of cathodoluminescence spectroscopy may help in identifying optimal content of luminescence ion

Cathodoluminescence image of valence- zoned non-radioactive zircon crystal doped with Tb

(diameter of electron beam 100 μm)



CL-spectra of non-radioactive zircon crystals doped with Tb



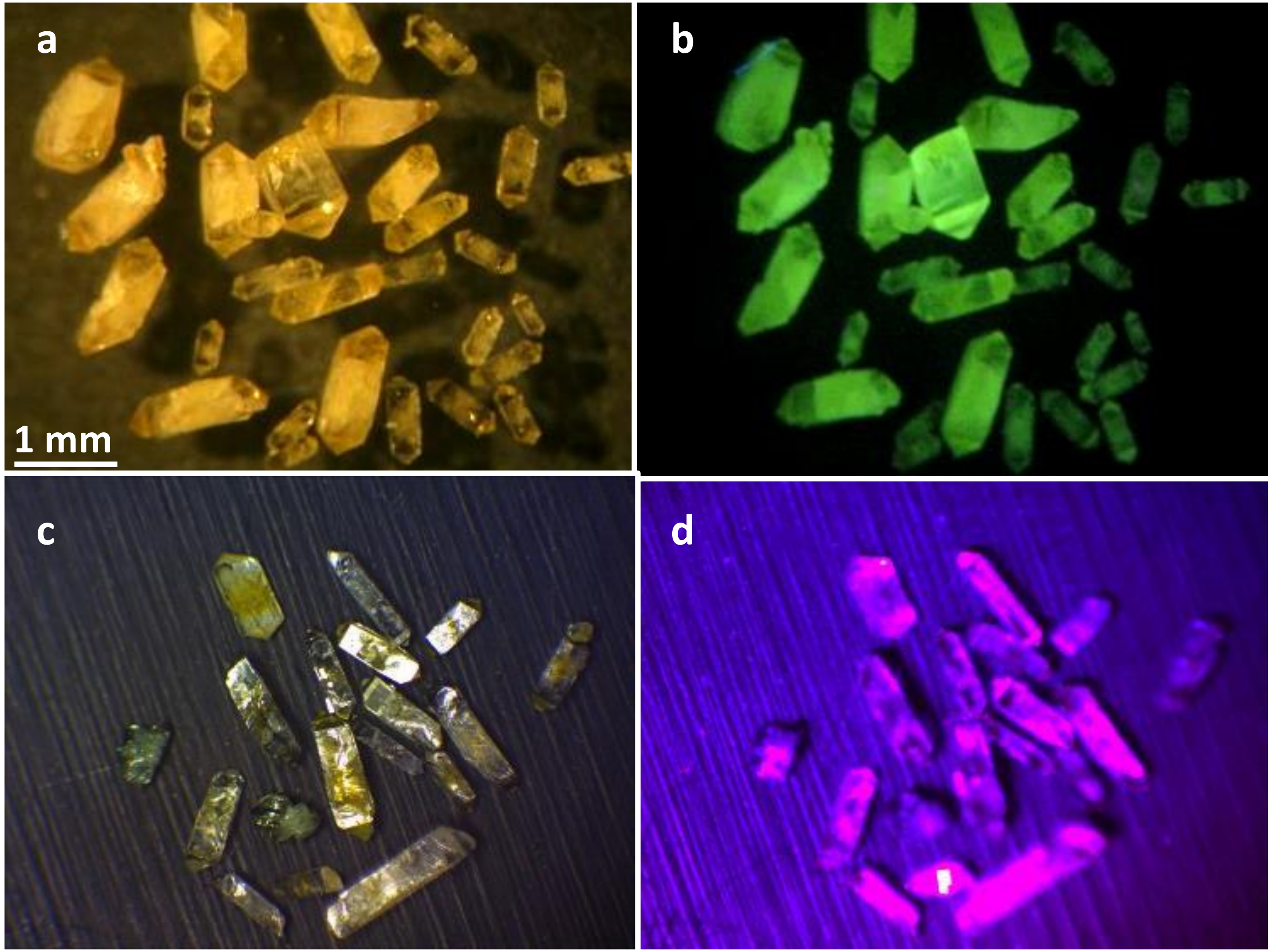
+ monoclinic zirconia as a minor phase

Zircon crystals:

a, c – in normal light; b, d – in the ultraviolet

Intense luminescence!

(Zr, **Tb**)(Si, P)O_4



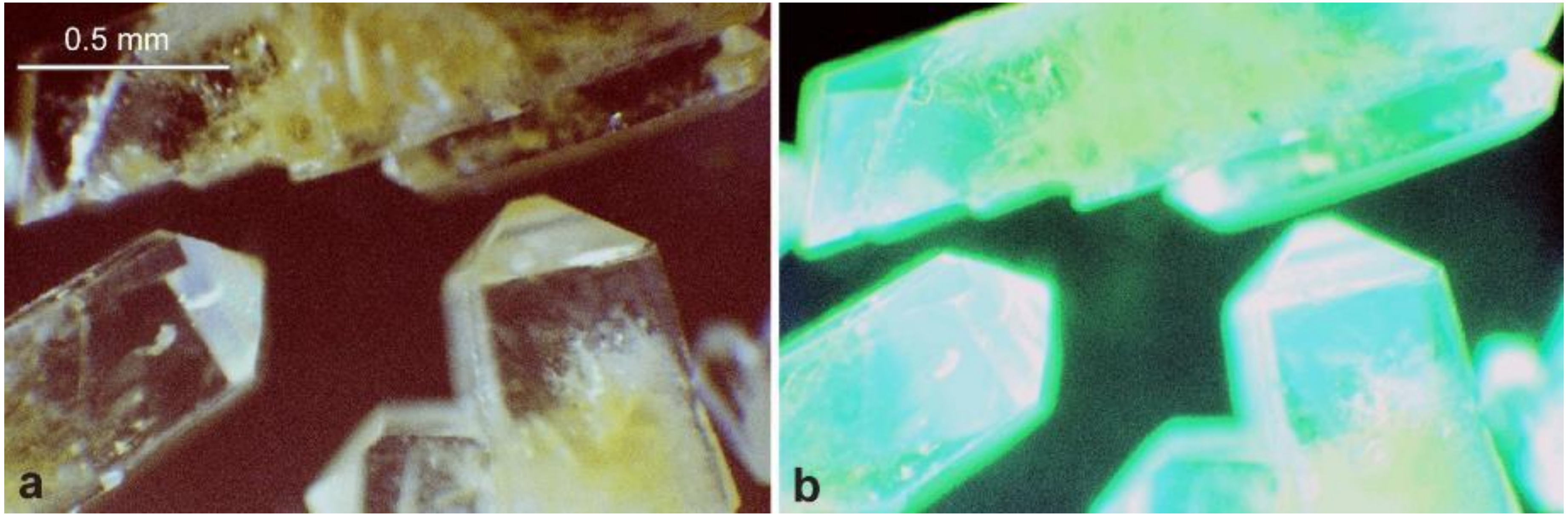
(Zr, **Eu**)(Si, P)O_4

Principal features of zircon crystals observed

Zircon formula	Element content, wt.%				Relative intensity of luminescence or self-glowing
	^{238}Pu	Tb	Eu	P	
$(Zr,Tb)SiO_4$	–	<0.05 0.2	–		very weak
$(Zr,Eu)SiO_4$		–	0.07	–	high
$(Zr,Tb)(Si,P)O_4$		4.0	–	0.2	high
$(Zr,Eu)(Si,P)O_4$		–	0.14	0.2	very high
$(Zr,Tb,Pu)(Si,P)O_4$	0.02	0.2-0.3	–	0.2-0.3	very high
$(Zr,Eu,Pu)(Si,P)O_4$	0.007 0.017 0.02 0.012	–	0.08 0.1 0.1 0.3	0.2-0.3 0.2-0.3 0.2-0.3 0.8	weak weak weak high
$(Zr,Tb,Eu,Pu)(Si,P)O_4$	0.02	<0.1	0.2	0.2-0.3	high

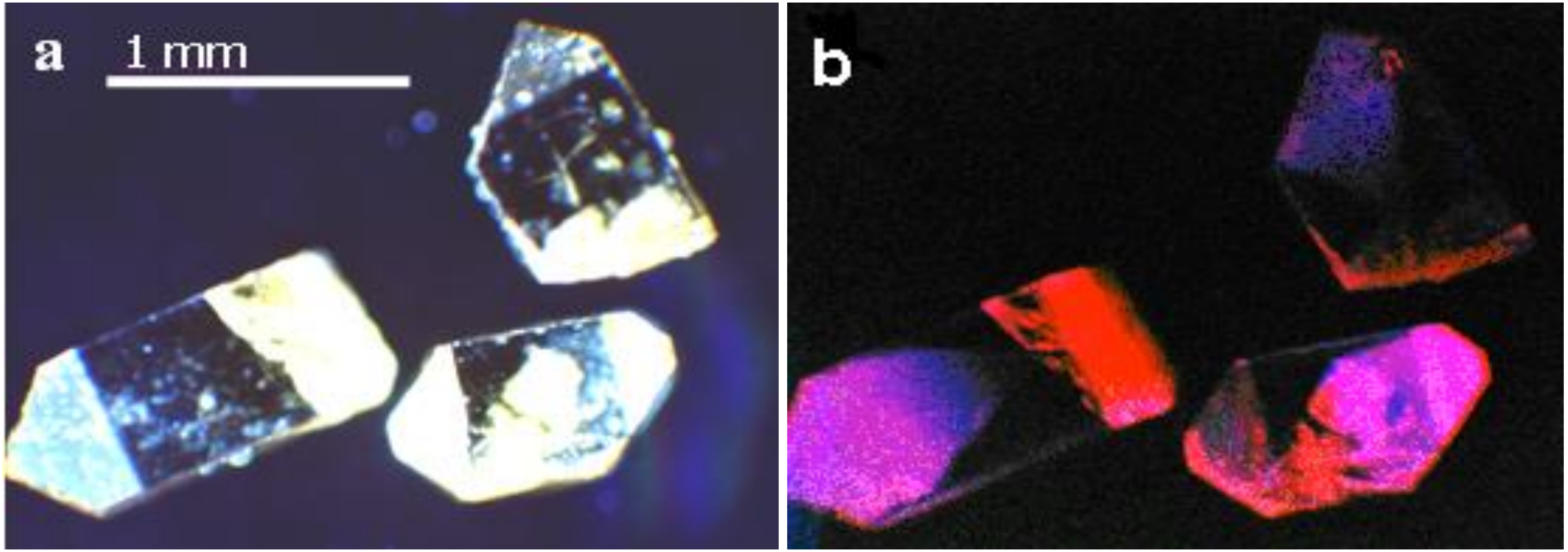
Self-glowing crystals of zircon, (Zr,Pu,Tb)(Si,P)O_4 doped with:

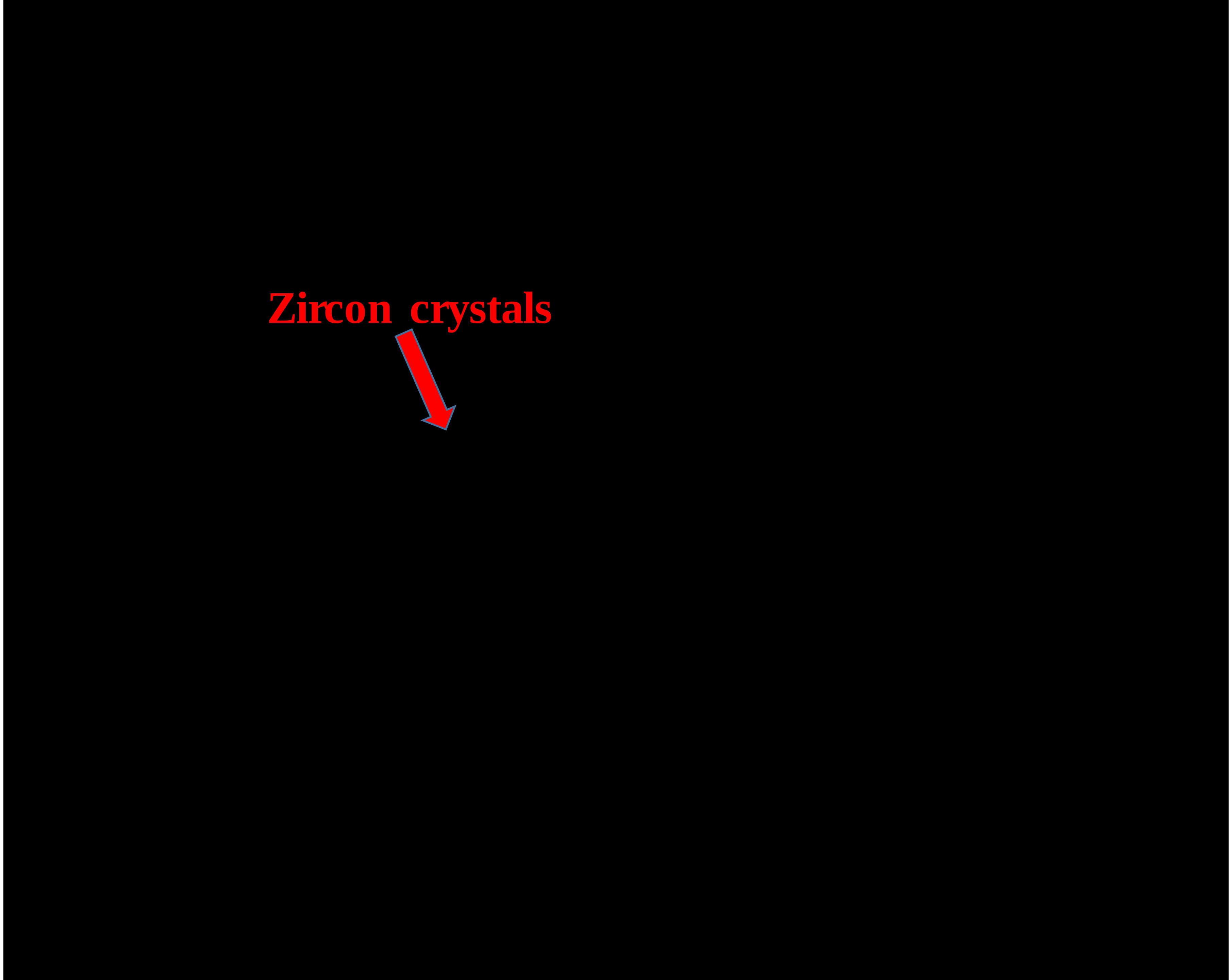
0.02 wt.% ^{238}Pu
0.2-0.3 wt.% Tb
0.2-0.3 wt.% P



Self-glowing crystals of zircon, (Zr,Pu,Eu)(Si,P)O_4 doped with:

0.01 wt.% ^{238}Pu
0.3 wt.% Eu
0.2 wt.% P




Zircon crystals

Conclusions

- Intensively self-glowing crystals of zircon $(Zr,Tb,Eu,Pu)SiO_4$ were successfully obtained. Contents of ^{238}Pu in these crystals did not exceed 0.02 wt.%

- Maximum luminescence intensity is observed at a concentration of Eu in a range 0.1-0.2 wt.% and Tb – 4wt.%

- CL-spectroscopy is an efficient tool that allows identifying optimal content of luminescence ion in non-radioactive crystals. The same content of luminescence ion should be incorporated into radioactive crystals in order to provide highest intensity of self-glowing

- Study of optimal balance between actinide content and amount of non-radioactive luminescence ion(s) should allow obtaining relatively low radioactive crystals with intensive radioluminescence


THANK
YOU!