# $Tm:CaF_2$ nanoceramics: spectroscopic and laser properties


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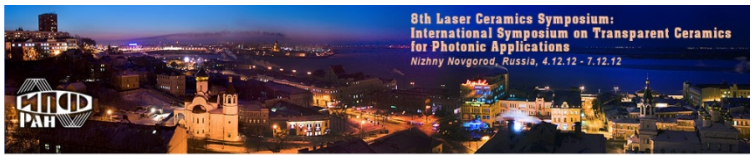


# Motivation

Two-micron laser radiation is widely used :

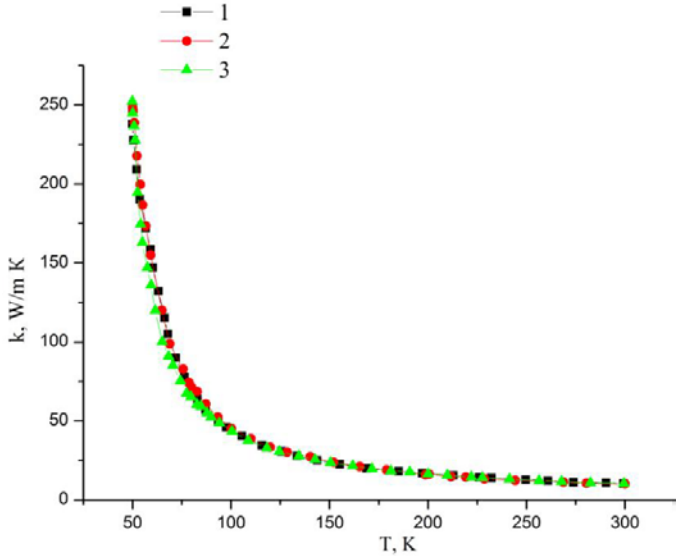
- in medicine
- monitoring of various gases (for example $NO_2$, $CO_2$, $NH_3$) in the atmosphere
- scientific investigations and special engineering

# The objectives

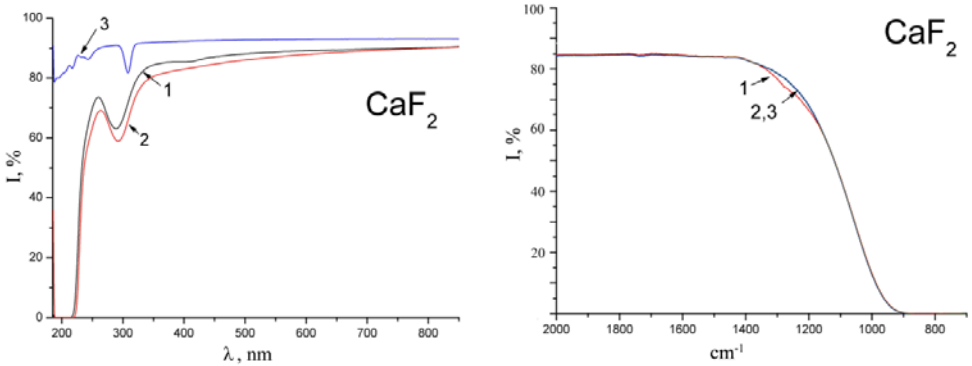
- **Investigation of ceramics microstructure by scanning electron microscopy (SEM) and atomic force microscopy (AFM).**
- **Comparison of absorption and luminescence properties of the ceramics and $CaF_2$:Tm single crystals.**
- **Analysis of lasing properties of the $CaF_2$:Tm ceramics and crystal**

# Literature data

## Ceramics $CaF_2$




Thermal conductivity of $CaF_2$ samples: natural sample from Suranskoe deposit, Urals Mountains (1), single crystal (2) and synthesized optical ceramics (3) [1].




Optical transparency of synthesized $CaF_2$ ceramics (1, 2) and $CaF_2$ single crystal (3) [3].

| | Index of refraction n | |
|---|---|---|
| | 546,07 nm | |
| | $CaF_2$ | $CaF_2$-$SrF_2$-$YbF_3$ |
| Single crystal | 1,4349 ± 0,0002 | 1,4456 ± 0,0002 |
| Ceramics | 1,4348 ± 0,0002 | 1,4458 ± 0,0002 |

Optical properties of synthesized ceramics and single crystals [2].


[1] Popov P A, Dykel'skii K V, Mironov I A, Demidenko V A et al. 2007 Thermal conductivity of $CaF_2$ optical ceramics, Doklady Physics 52, 7

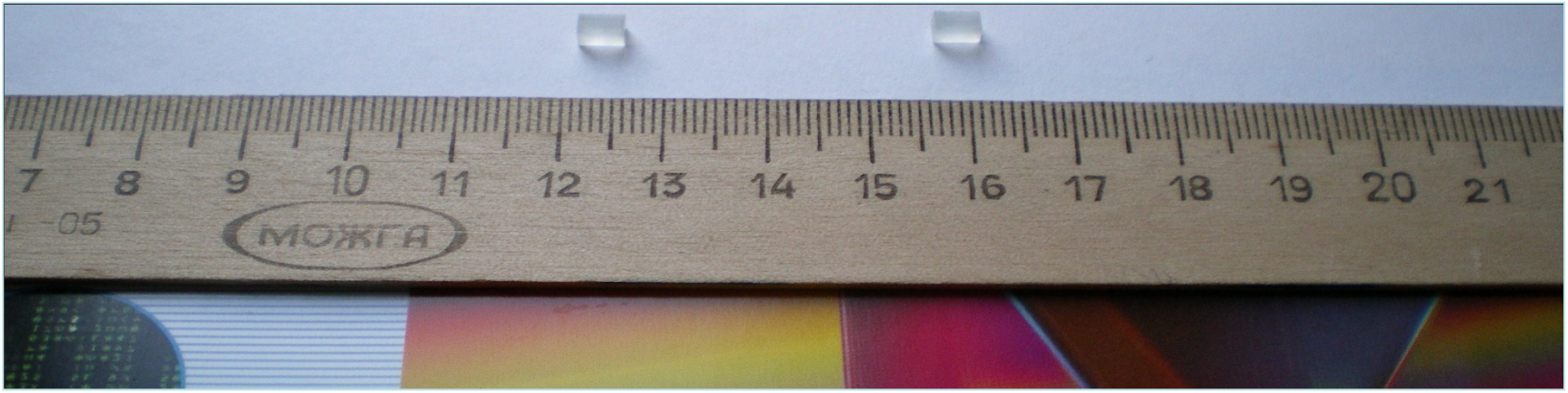
[2] A.A. Lyapin, P.A. Pyabochkina et al. Proceedings of the 8th Russian Conference with elements Youth Scientific School. Saransk, October 5-8, 2009. P.137.

[3] Fedorov P P, Osiko V V, Basiev T T, Orlovskii Yu V, Dykel'skii K V, Mironov I A, 2007 Optical Fluoride and Oxysulphide Ceramics: Preparation and Characterization. In: Developments in Ceramic Materials Research, NOVA

# Optical transparency of $CaF_2$:Tm ceramics

## Ceramics $CaF_2$:Tm

## The active elements of ceramics $CaF_2$:Tm

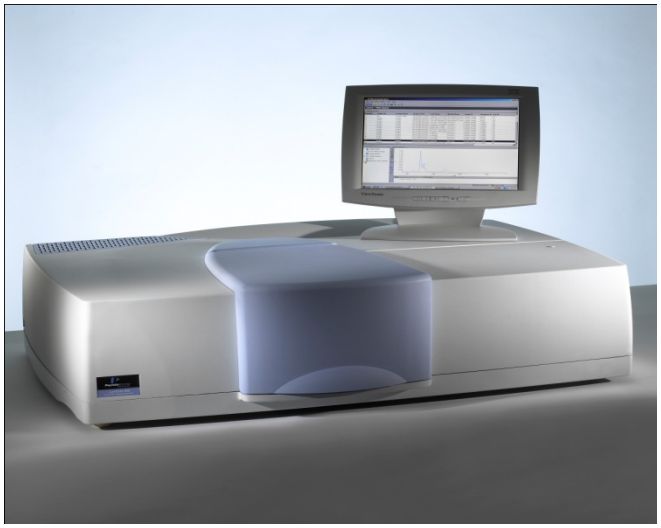



The single crystals and ceramics samples $CaF_2$:Tm were obtained at the Prokhorov General Physics Institute, Russian Academy of Sciences and INCROM Ltd.

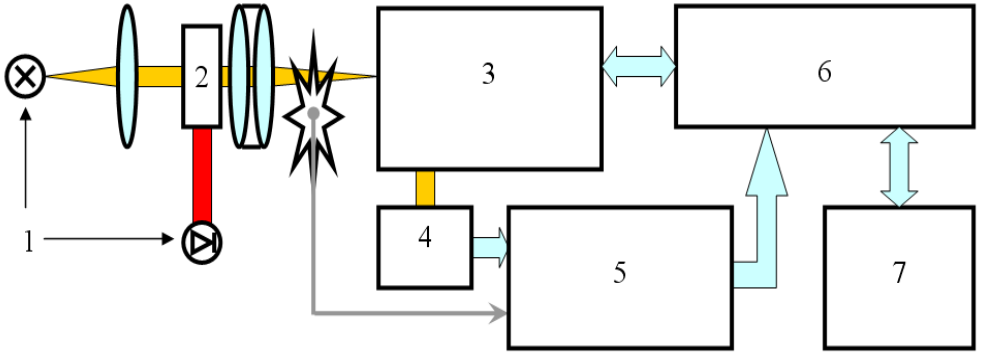
# Experimental setup

SEM Jeol JSM-6490

Solver Pro (NT-MDT)



Perkin Elmer Lambda 950 Spectrophotometer




Scheme for the registration of the luminescence:

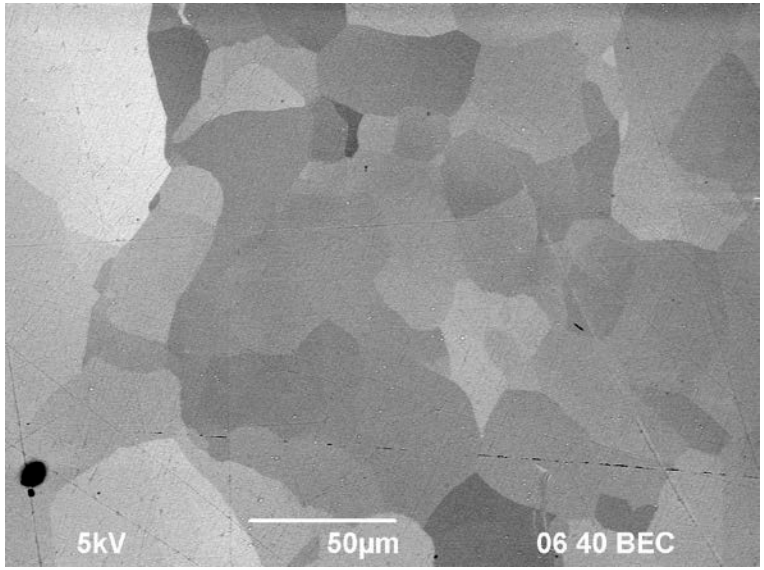
1 - radiation source; 2 - samples;

3 - monochromator; 4 - photodetector;

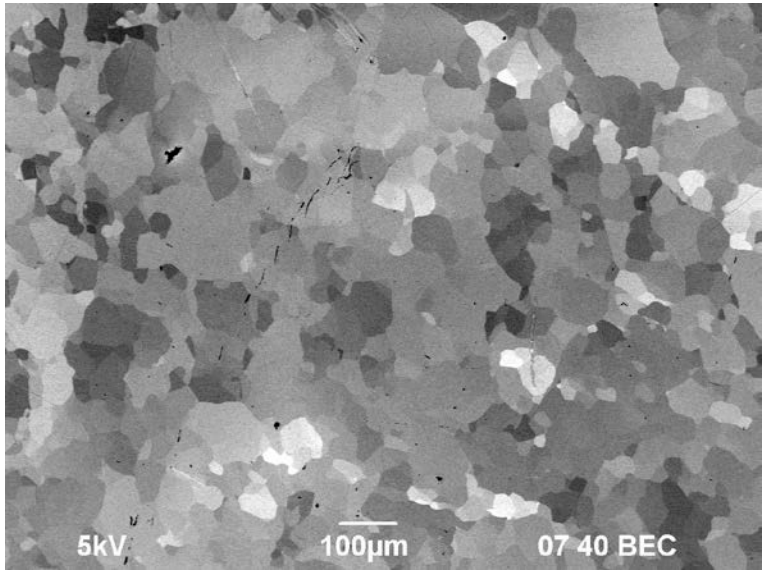
5 - synchronous amplifier SR-810; 6 - control block;

7 – PC

# Microstructure of hot-formed $CaF_2$:Tm ceramic



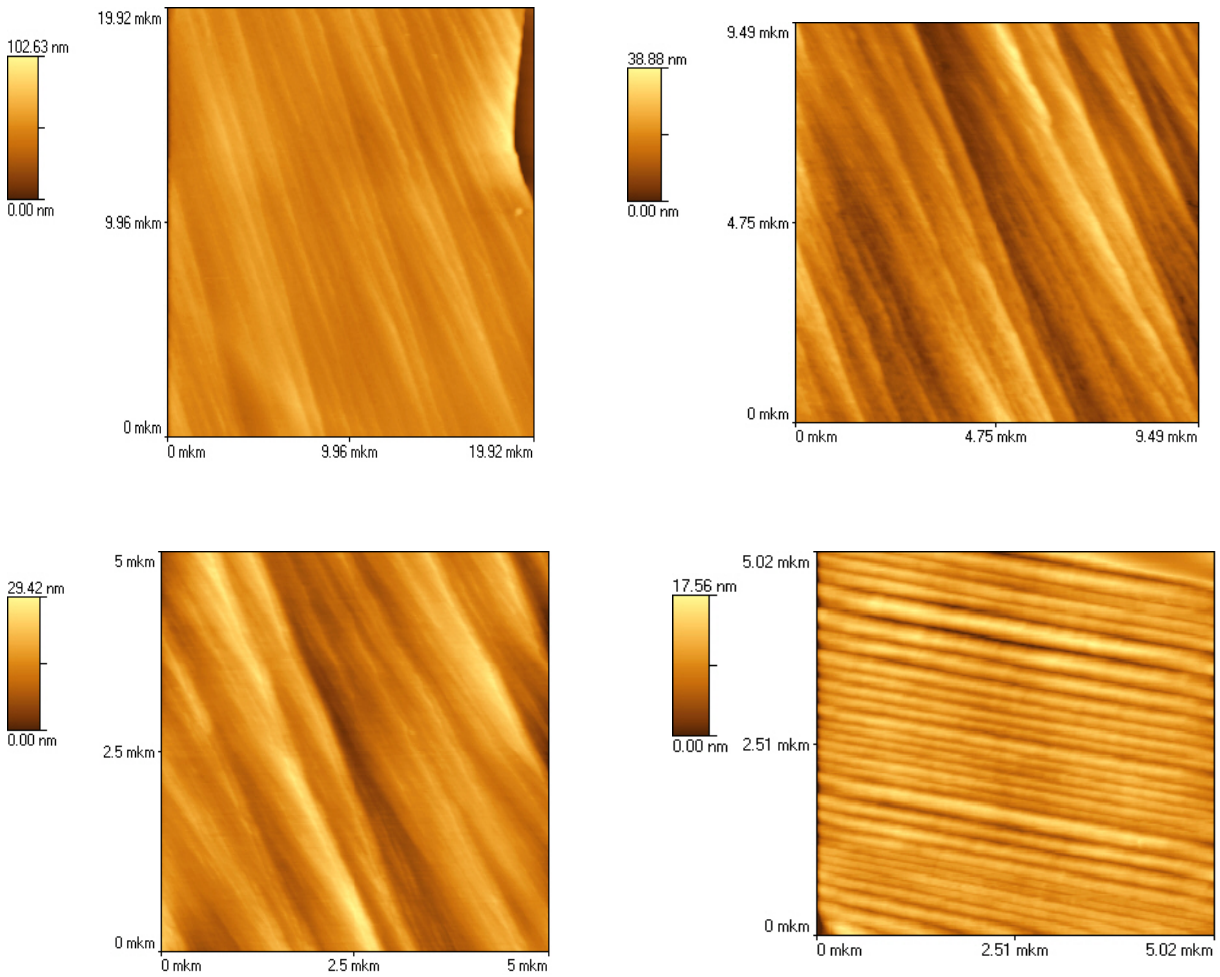

a




b

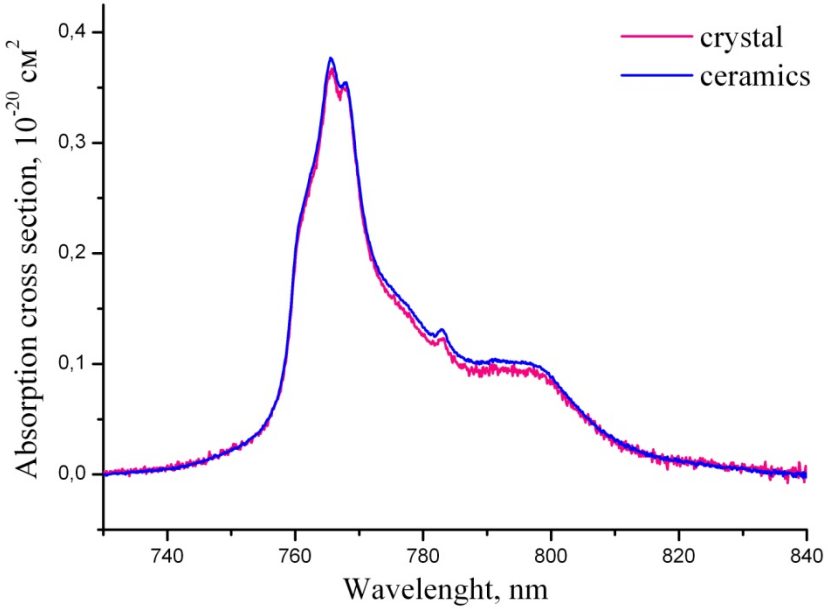
SEM image of hot-formed $CaF_2$:Tm ceramic samples at magnifications of (a) 100 and (b) 50

# Nanostructure of hot-formed $CaF_2$:Tm ceramic

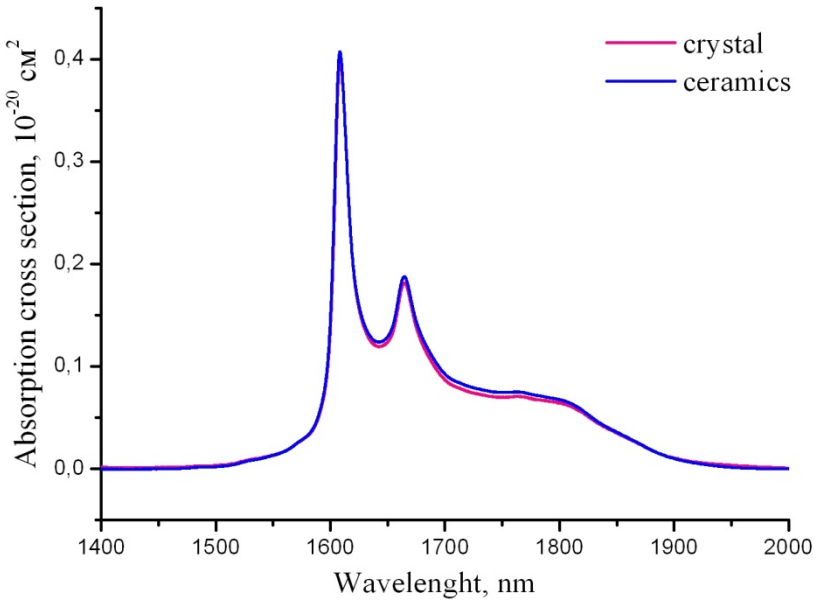



**AFM images of a fracture surface of the $CaF_2$:Tm ceramic at different magnifications.**

# Absorption spectra of the single crystal and ceramics $CaF_2$:Tm



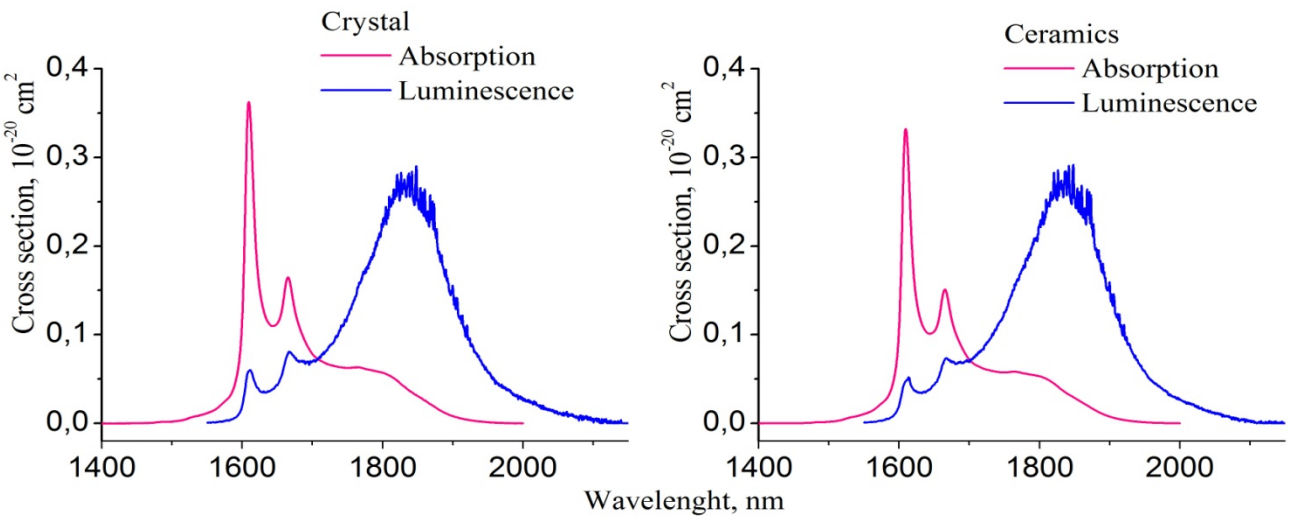

a




b

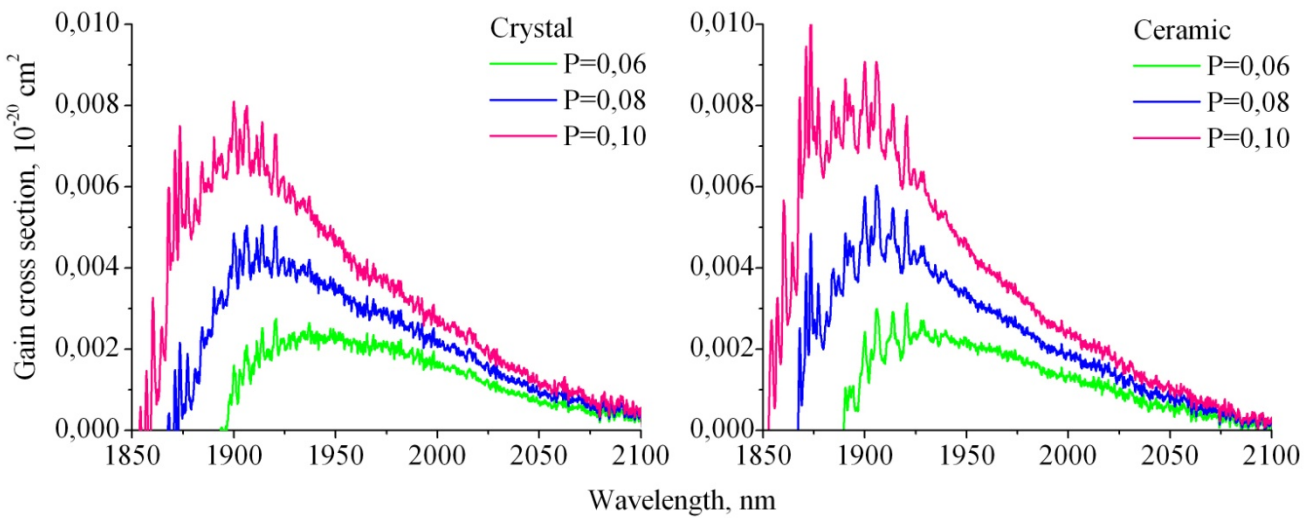
**The absorption spectra of $CaF_2$:Tm (2 mol.% $TmF_3$) single crystal and ceramic samples ((a) $^3H_6 \rightarrow {}^3H_4$, (b) $^3H_6 \rightarrow {}^3F_4$ transitions, T=300 K)**

# Luminescent properties of the single crystal and ceramics $CaF_2$:Tm



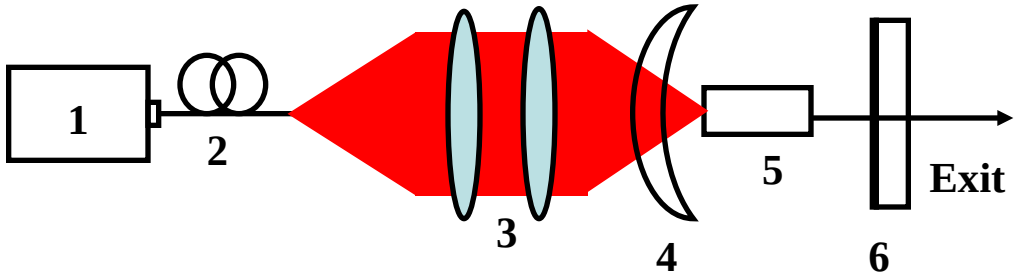

300-K absorption and luminescence spectra of the Tm:$CaF_2$ crystal and ceramics for the $^3H_6 \leftrightarrow {}^3F_4$ transition

$$\sigma_{gain}(\lambda) = P\sigma_{em}(\lambda) - (1-P)\sigma_{abs}(\lambda)$$

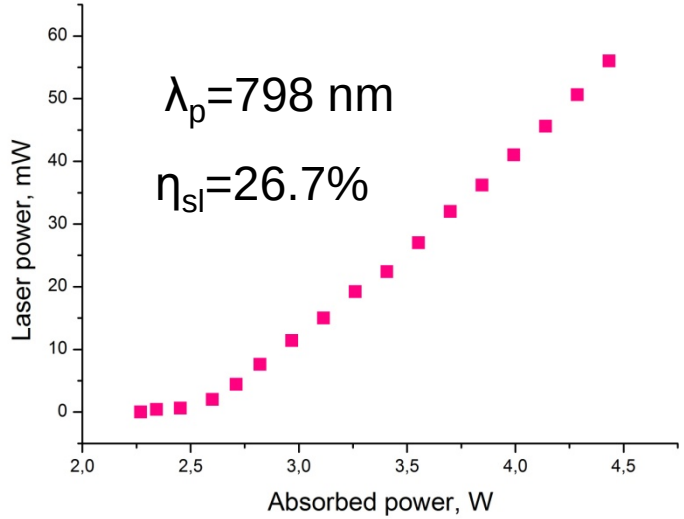



Spectral dependences of the $^3F_4 \rightarrow {}^3H_6$ gain cross section $\sigma_g(\lambda)$ for the Tm:$CaF_2$ crystal and ceramics

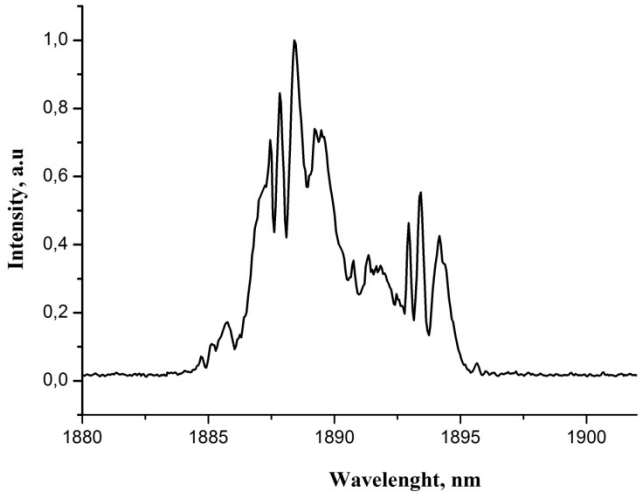
# Lasing properties of the $CaF_2$:Tm crystal




Schematic diagram of the laser experimental setup.
1- pump laser diode, 2-optical fiber, 3-lens (f=19,5 mm),
4-input mirror, 5-Tm:$CaF_2$ sample, 6-output mirror

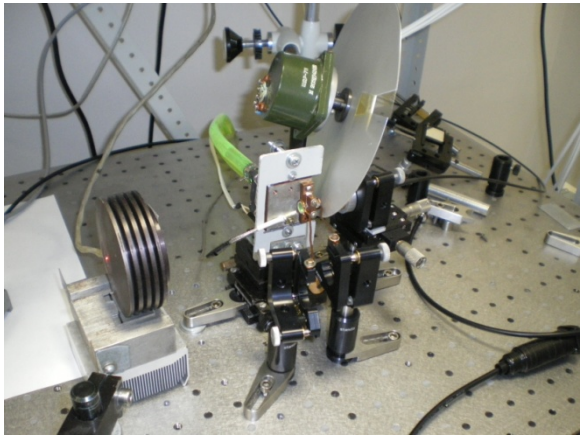


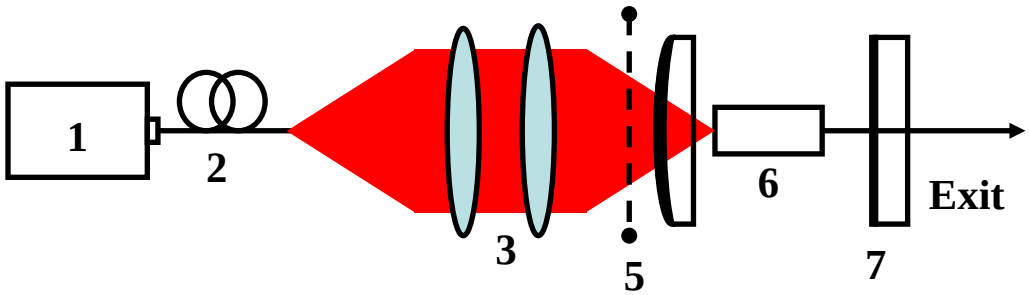

**$CaF_2$:Tm (6 mol.% $TmF_3$) crystal lasing under LD pumping**



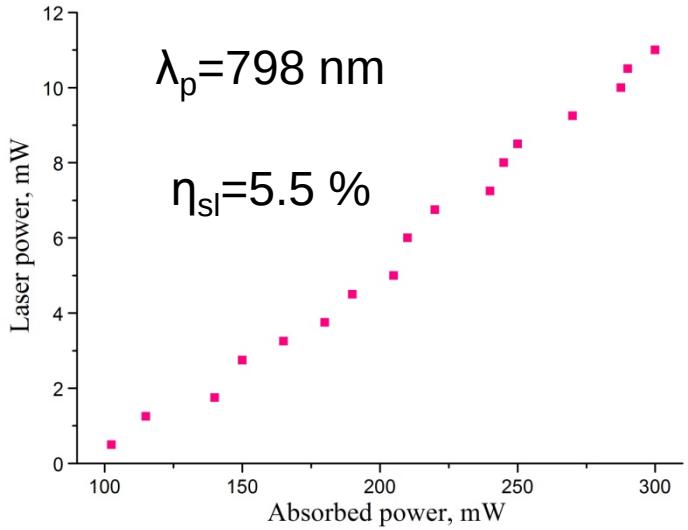

**Oscillation spectrum of $CaF_2$:Tm crystal**

# Lasing properties of the $CaF_2$:Tm ceramics

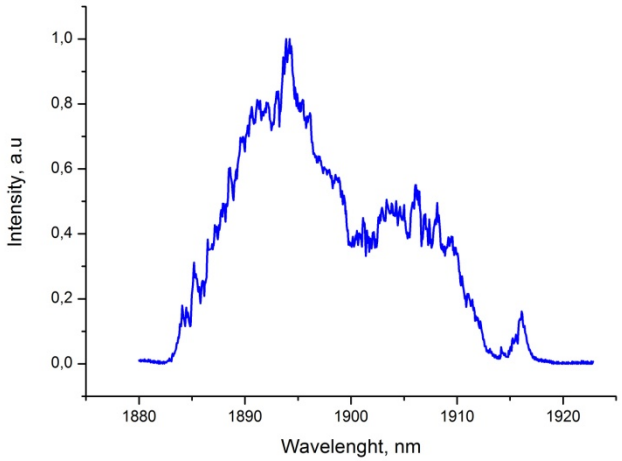





Schematic diagram of the laser experimental setup.
1- pump laser diode, 2-optical fiber, 3-lens (f=19,5 mm), 4- obturator, 5-input mirror, 6-Tm:$CaF_2$ sample, 7-output mirror




**$CaF_2$:Tm (4 mol.% $TmF_3$) ceramics lasing under LD pumping**




**Oscillation spectrum of $CaF_2$:Tm ceramics**

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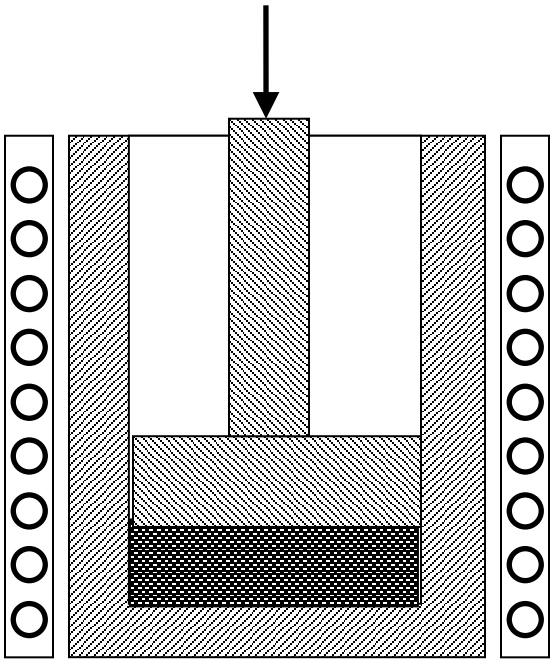
# Conclusion

- **$CaF_2$:Tm fluoride laser ceramics prepared by hot-forming. Analysis of the microstructure of ceramic $CaF_2$:Tm has identified that its grain structure is organized hierarchically. Smallest grains have a size not exceeding 10 microns, the largest up to 100 microns. In AFM images of the $CaF_2$:Tm ceramic, a fine layered structure is well seen. At higher magnifications, the fracture surface is seen to consist of lamellae from 50 to 250 nm thick.**
- **Optical absorption and emission spectra for $CaF_2$:Tm ceramics have been measured and compared to that of single crystal. Almost identical results have been obtained.**
- **For the first time to our knowledge, the laser quality $CaF_2$:Tm fluoride ceramics was prepared and laser oscillations under diode pumping were obtained at 1898 nm.**

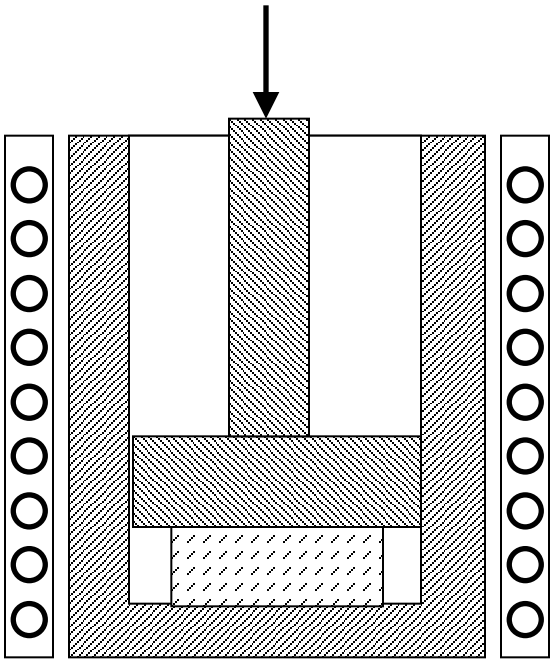
**Thank you for your attention!**

# Development of fluoride nanoceramics

**Nano Powder Hot Pressing**



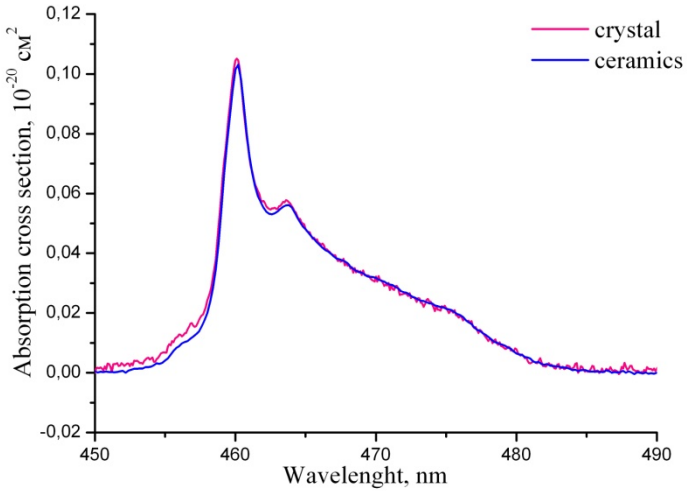
**Hot Deformation of Single Crystals**



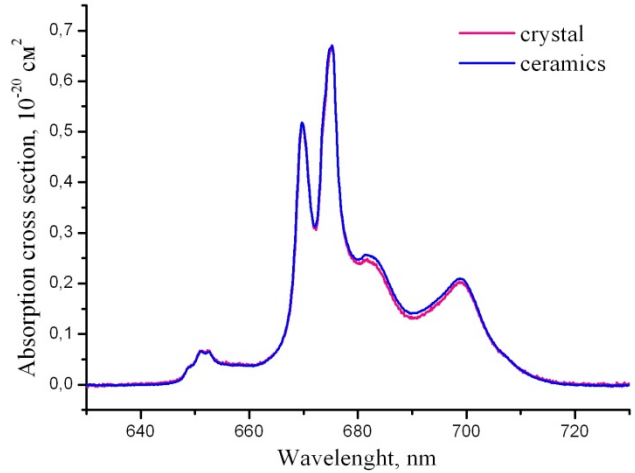
**$T = (0{,}5 \div 0{,}8)\ T_{melt}$ $P \leq 300$ MPa**

**vacuum $10^{-2} \div 10^{-3}$ Torr**

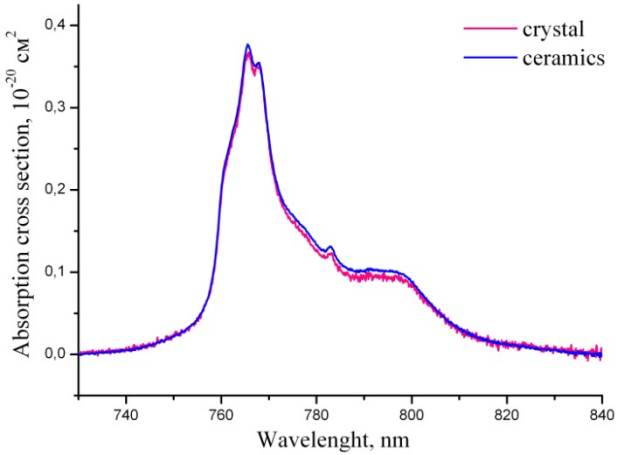
# Absorption spectra of the single crystal and ceramics $CaF_2$:Tm




a



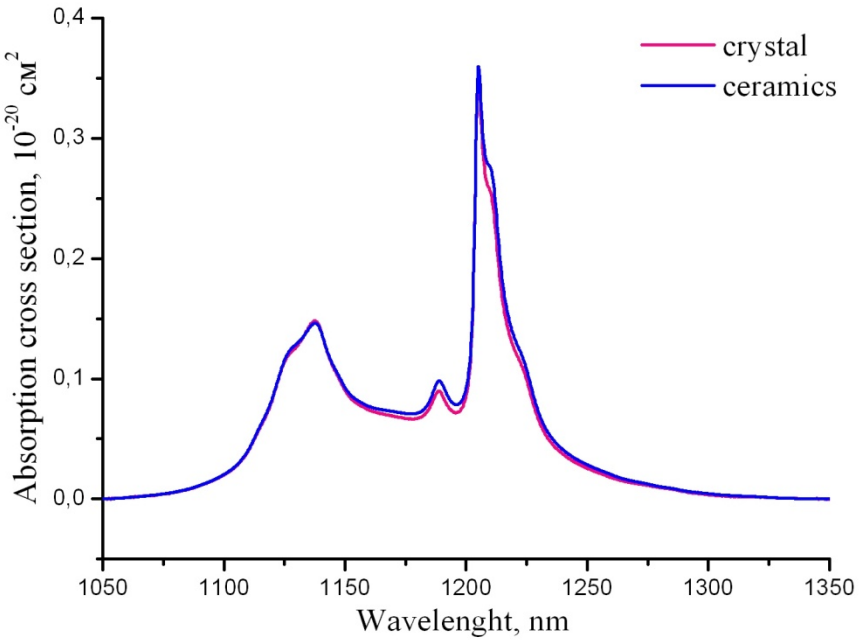

b



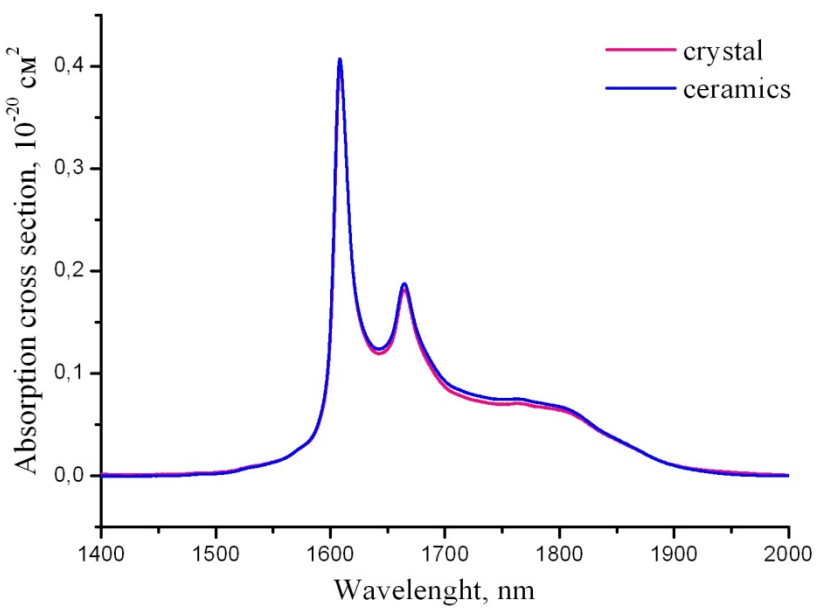

c

**The absorption spectra of $CaF_2$:Tm (4 mol.% TmF3) single crystal and ceramic samples ((a) $^3H_6 \rightarrow {}^1G_4$, (b) $^3H_6 \rightarrow {}^3F_2 + {}^3F_3$, (c) $^3H_6 \rightarrow {}^3H_4$ transitions, T=300 K)**

# Absorption spectra of the single crystal and ceramics $CaF_2$:Tm



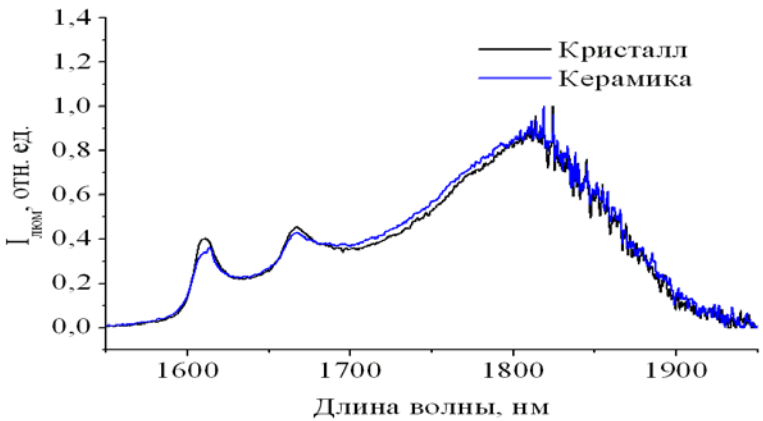

a




b

**The absorption spectra of $CaF_2$:Tm (4 mol.% $TmF_3$) single crystal and ceramic samples ((a) $^3H_6 \rightarrow {}^3H_5$ , (b) $^3H_6 \rightarrow {}^3F_4$ transitions, 300 K)**

# Luminescent properties of single crystal and ceramics $CaF_2$-4 mol. % $TmF_3$

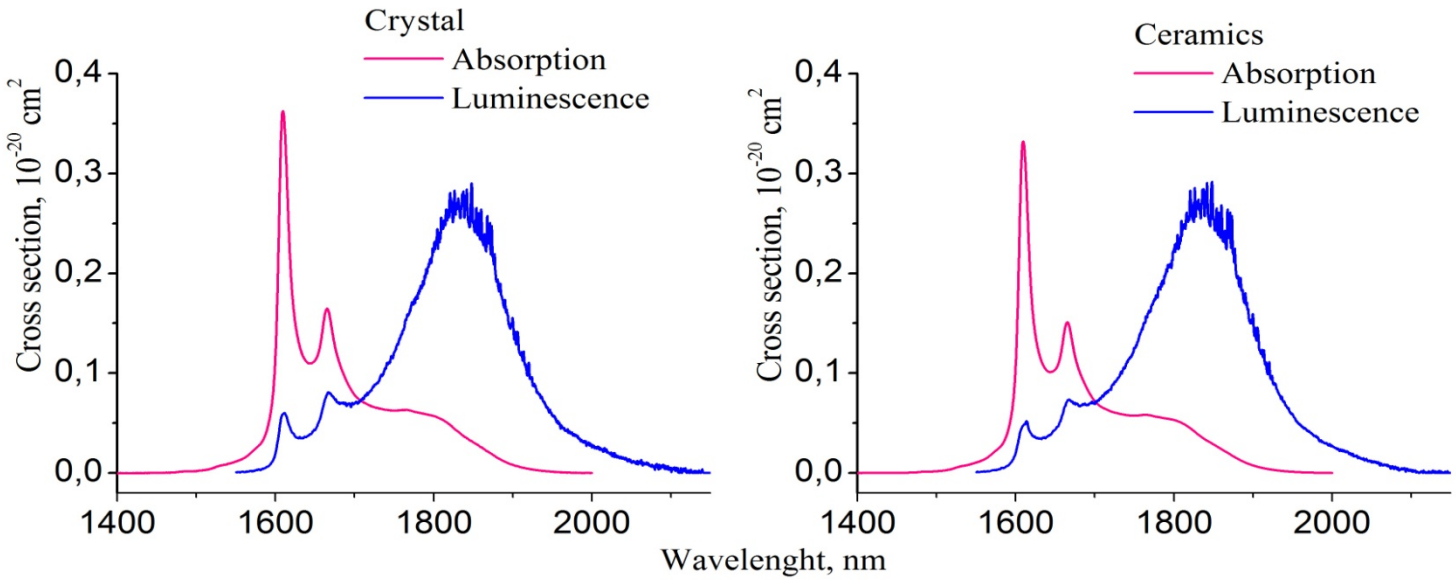



| | $\sigma_{ads}$ (λ=760 нм), см$^2$ | $\sigma_{em}$ (λ=1842 нм), см$^2$ | $\tau_{3F4}$, мс (abs) | $\tau_{3F4}$, мс (exp) |
|---|---|---|---|---|
| $CaF_2$:Tm (кристалл) | 0,33 | 0,28 | 14 | 21 |
| $CaF_2$:Tm (кристалл)* | - | 0,39 | - | 17.4 |
| $CaF_2$:Tm (керамика) | 0,32 | 0,28 | 16 | 23 |

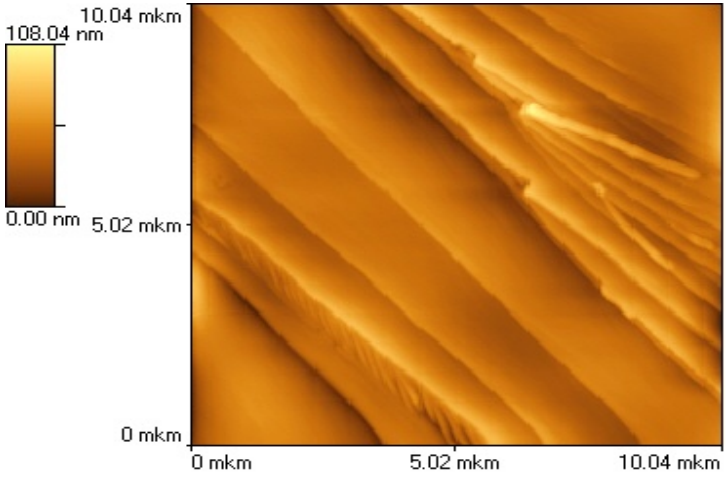
**Fuechtbauer –Ladenburg formula:**

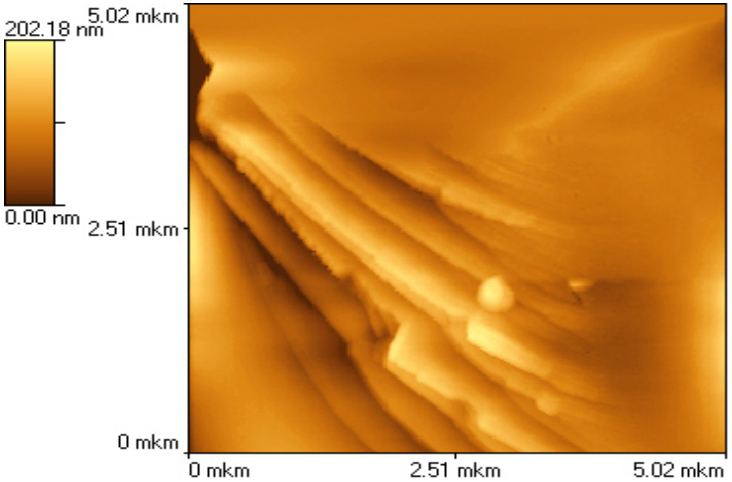
$$\sigma_{em}(\lambda) = \frac{\lambda^5 I(\lambda)}{8\pi c \tau_R n^2 \left[\int I(\lambda)\lambda d\lambda\right]}$$

* P. Camy, J.L. Doulan, S. Renard at. al. //Optics Communications 236 (2004), 395-402

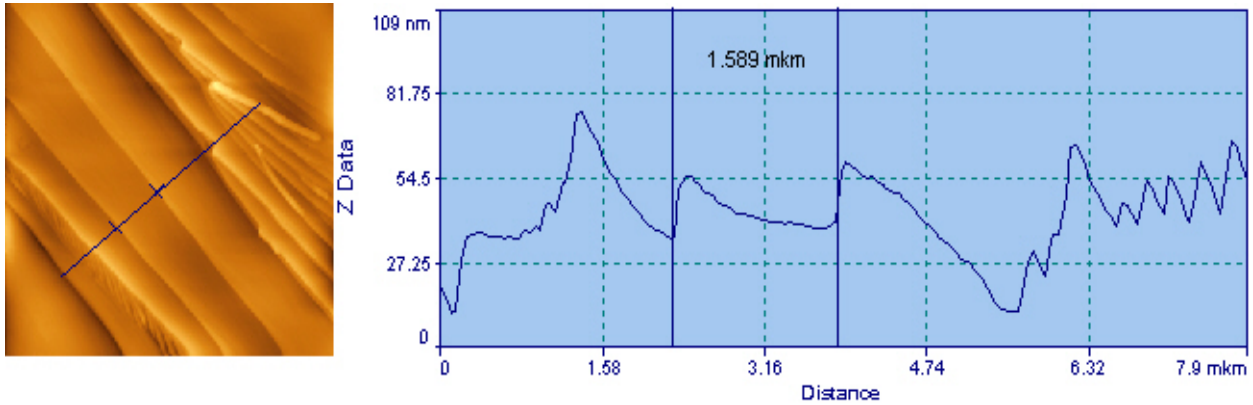


# Структура монокристаллов $CaF_2$:Tm



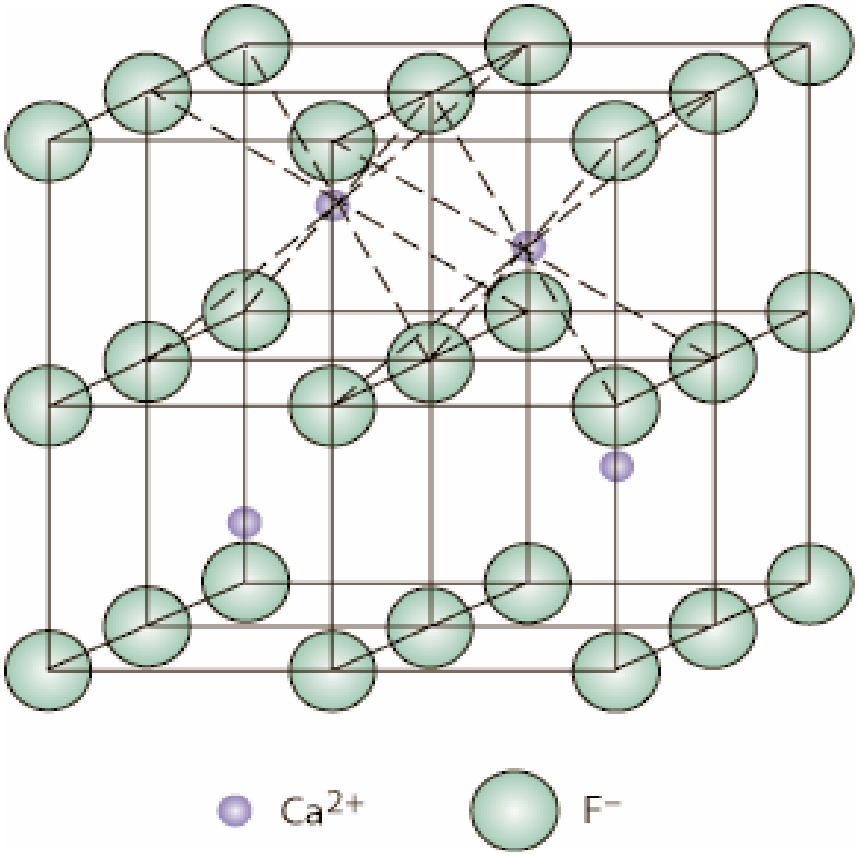




АСМ-изображение скола монокристаллов $CaF_2$-4 мол. % $TmF_3$, с разным увеличением




Средняя высота слоя составляет 10 ÷ 70 нм.

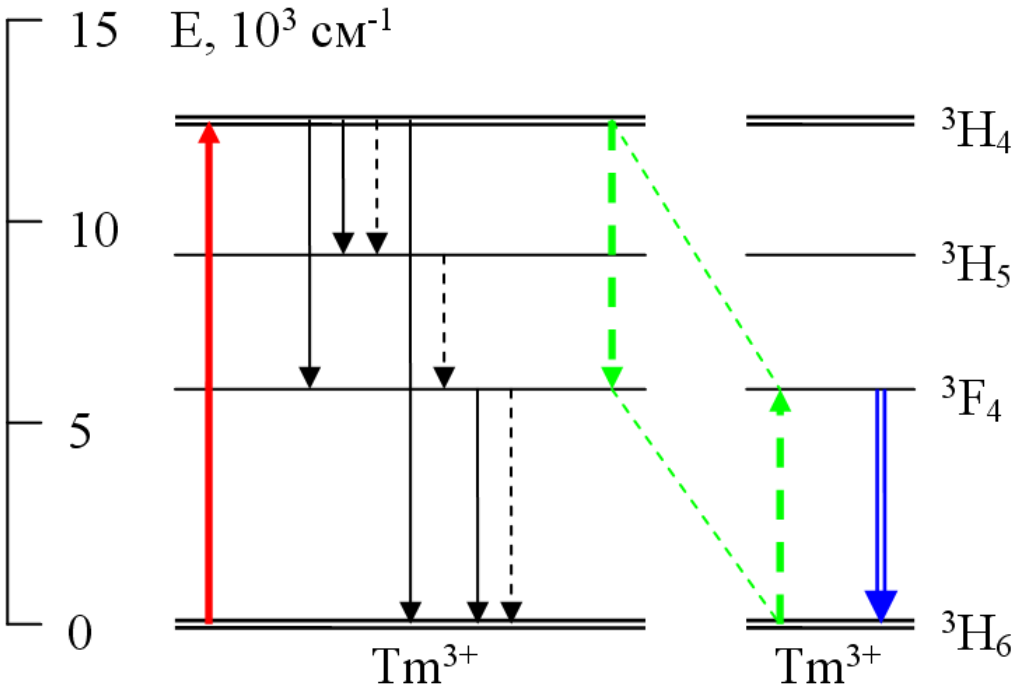
# EXAMPLE OF CRYSTAL STRUCTURE




**Fluorite structure (CaF2)**

http://www.eng.uwo.ca/es021/ES021b_2007/Lecture%20Notes/Chap%2012-13%20SN%20-%20Ceramics.pdf

# Получение 2-мкм генерации на ионах $Tm^{3+}$




Накачка на уровень $^3H_4$

Внутрицентровая релаксация ионов $Tm^{3+}$

Процесс кросс-релаксации ($^3H_4 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^3F_4$)

Генерация на переходе $^3F_4 \rightarrow {}^3H_6$