



Graduate School of Basic Sciences
"Galileo Galilei" – Physics
XVIII cycle PhD course

Crystal Growth and Spectroscopy of Rare Earth Ions Doped Crystals For Quantum Computing Application

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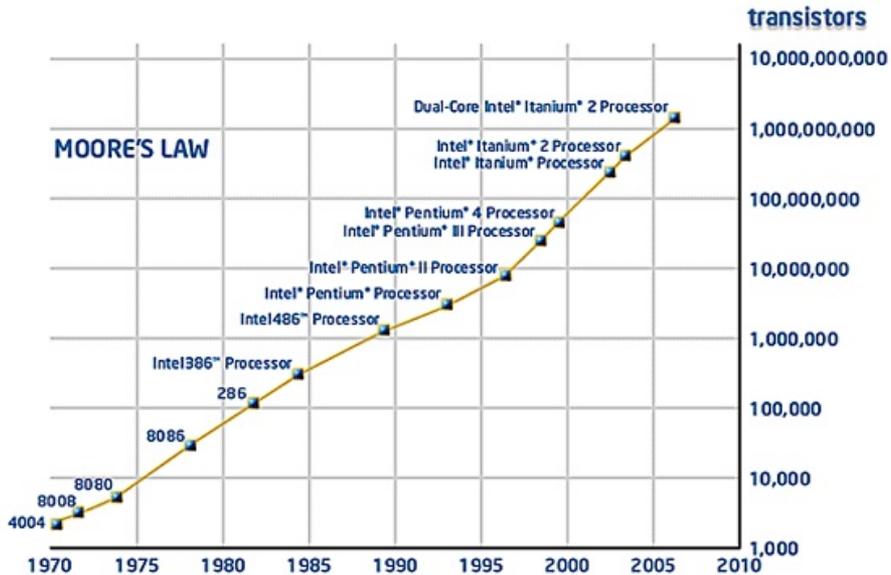
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Prof. A. Di Lieto

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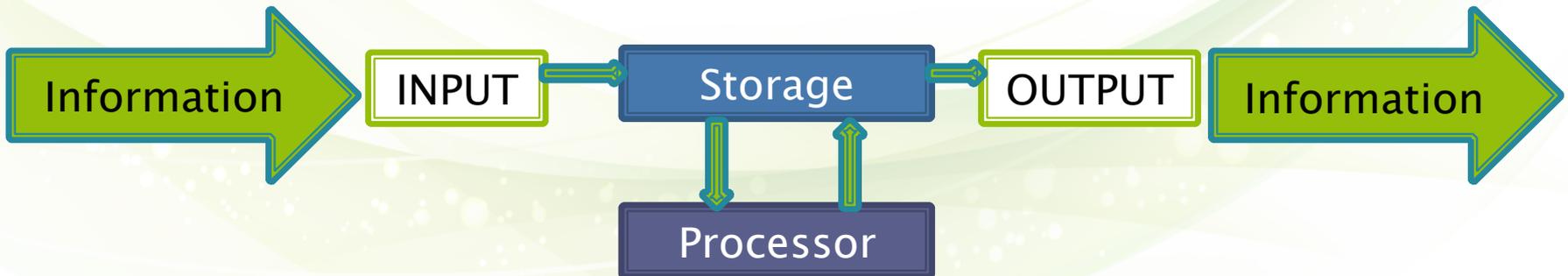
- Background
- Experiment Techniques
- Previous Work
- Future Plan

Background: Classical Computing



Units of Processor:
Electronic valve (1911–1946)
Transistor (1947–1958)
Integrated Circuit (1959–1970)
Large Scale IC (1971–today)

Limit:
Thermal dissipation
Quantum tunneling effect



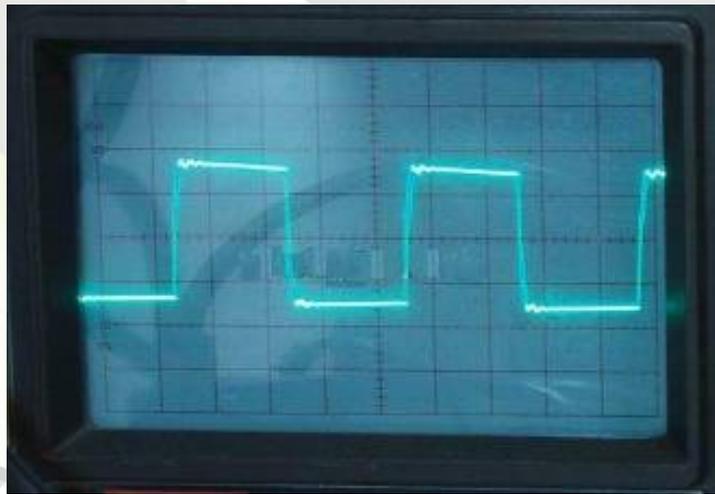
Von Neumann architecture scheme

Background: Quantum Computing

- Classic bits

2 possible voltages
encode one bit

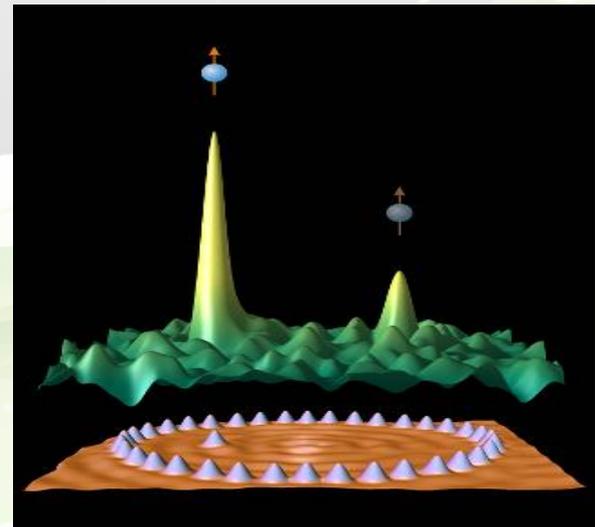
0 or 1



- Quantum bits

2 level system encodes one
bit

$|0\rangle$ or $|1\rangle$ or $a|0\rangle + be^{i\omega t}|1\rangle$



Background: system for quantum computing

Requirement of a system for quantum computing application:

- The system must have well defined qubits that can be stored for a particular length of time.
- There must be a universal set of gates.
- The system can be easily initialized to a particular state.
- The qubit can be read out and the reading process will not destroy the quantum state of the stored information.

Several systems that have been used for quantum computing application.

- Electron spin system
- Nuclear spin system
- Trapped ions system
- Quantum dots
- Optical cavity
- Rare earth doped solids

Background: The Properties of Rare Earth Elements

5	37 ² S _{1/2} Rb Rubidium 85.4678 [Kr]5s 4.1771	38 ¹ S ₀ Sr Strontium 87.62 [Kr]5s ² 5.6949	39 ² D _{3/2} Y Yttrium 88.90585 [Kr]4d5s ² 6.2173	40 ² F ₂ Zr Zirconium 91.224 [Kr]4d ⁴ 5s ² 6.6339	41 ⁶ D _{1/2} Nb Niobium 92.90638 [Kr]4d ⁴ 5s 6.7589	42 ² S ₃ Mo Molybdenum 95.94 [Kr]4d ⁵ 5s 7.0924	43 ⁶ S _{3/2} Tc Technetium (98) [Kr]4d ⁵ 5s ² 7.28	44 ² F ₅ Ru Ruthenium 101.07 [Kr]4d ⁷ 5s 7.3605	45 ⁴ F _{3/2} Rh Rhodium 102.90550 [Kr]4d ⁸ 5s 7.4589	46 ¹ S ₀ Pd Palladium 106.42 [Kr]4d ¹⁰ 8.3369	47 ² S _{1/2} Ag Silver 107.8682 [Kr]4d ¹⁰ 5s 7.5762	48 ¹ S ₀ Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ² 8.9938	49 ² P _{1/2} In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p 7.3439	50 ³ P ₀ Sn Tin 118.710 [Kr]4d ¹⁰ 5s ² 5p ² 7.3439	51 ⁴ S _{3/2} Sb Antimony 121.760 [Kr]4d ¹⁰ 5s ² 5p ³ 8.6084	52 ³ P ₂ Te Tellurium 127.60 [Kr]4d ¹⁰ 5s ² 5p ⁴ 9.0096	53 ² P _{3/2} I Iodine 126.90447 [Kr]4d ¹⁰ 5s ² 5p ⁵ 10.4513	54 ¹ S ₀ Xe Xenon 131.293 [Kr]4d ¹⁰ 5s ² 5p ⁶ 12.1298
6	55 ² S _{1/2} Cs Cesium 132.90545 [Xe]6s 3.8939	56 ¹ S ₀ Ba Barium 137.327 [Xe]6s ² 5.2117	72 ² F ₂ Hf Hafnium 178.49 [Xe]4f ¹⁴ 5d ² 6s ² 6.8251	73 ⁴ F _{3/2} Ta Tantalum 180.9479 [Xe]4f ¹⁴ 5d ³ 6s ² 7.5496	74 ⁴ D ₀ W Tungsten 183.84 [Xe]4f ¹⁴ 5d ⁴ 6s ² 7.8640	75 ⁶ S _{3/2} Re Rhenium 186.207 [Xe]4f ¹⁴ 5d ⁵ 6s ² 7.8335	76 ⁶ D ₄ Os Osmium 190.23 [Xe]4f ¹⁴ 5d ⁶ 6s ² 8.4382	77 ⁴ F _{3/2} Ir Iridium 192.217 [Xe]4f ¹⁴ 5d ⁷ 6s ² 8.9670	78 ³ D ₃ Pt Platinum 195.078 [Xe]4f ¹⁴ 5d ⁹ 6s 8.9588	79 ² S _{1/2} Au Gold 196.96655 9.2255	80 ¹ S ₀ Hg Mercury 200.59 10.4375	81 ² P _{1/2} Tl Thallium 204.3833 [Hg]6p 6.1082	82 ³ P ₀ Pb Lead 207.2 [Hg]6p ² 7.4167	83 ⁴ S _{3/2} Bi Bismuth 208.98038 [Hg]6p ³ 7.2855	84 ³ P ₂ Po Polonium (209) [Hg]6p ⁴ 8.414	85 ² P _{3/2} At Astatine (210) [Hg]6p ⁵	86 ¹ S ₀ Rn Radon (222) [Hg]6p ⁶ 10.7485	
7	87 ² S _{1/2} Fr Francium (223) [Rn]7s 4.0727	88 ¹ S ₀ Ra Radium (226) [Rn]7s ² 5.2784	104 ² F ₂ Rf Rutherfordium (261) [Rn]5f ¹⁴ 6d ² 7s ² 6.0 ?	105 ⁴ F _{3/2} Db Dubnium (262)	106 ⁴ D ₀ Sg Seaborgium (266)	107 ⁶ S _{3/2} Bh Bohrium (264)	108 ⁶ D ₄ Hs Hassium (277)	109 ⁴ F _{3/2} Mt Meitnerium (268)	110 ³ D ₃ Uun Ununnilium (281)	111 ² S _{1/2} Uuu Unununium (272)	112 ¹ S ₀ Uub Ununbium (285)	114 ² P _{1/2} Uuq Ununquadium (289)	116 ⁴ S _{3/2} Uuh Ununhexium (292)					

Atomic Number: 58
Ground-state Level: ¹G₄
Symbol: **Ce**
Name: Cerium
Atomic Weight: 140.116
Ground-state Configuration: [Xe]4f5d6s²
Ionization Energy (eV): 5.5387

57 ² D _{3/2} La Lanthanum 138.9055 [Xe]5d6s ² 5.5769	58 ¹ G ₄ Ce Cerium 140.116 [Xe]4f5d6s ² 5.5387	59 ⁴ F _{3/2} Pr Praseodymium 140.90765 [Xe]4f ³ 6s ² 5.473	60 ⁴ F ₄ Nd Neodymium 144.24 [Xe]4f ⁴ 6s ² 5.5250	61 ⁶ F _{5/2} Pm Promethium (145) [Xe]4f ⁵ 6s ² 5.582	62 ² F ₀ Sm Samarium 150.36 [Xe]4f ⁶ 6s ² 5.6437	63 ⁶ S _{7/2} Eu Europium 151.964 [Xe]4f ⁷ 6s ² 5.6704	64 ⁵ D ₃ Gd Gadolinium 157.25 [Xe]4f ⁷ 5d6s ² 6.1498	65 ⁶ H _{5/2} Tb Terbium 158.92534 [Xe]4f ⁹ 6s ² 5.8638	66 ⁵ F ₅ Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ² 5.9389	67 ⁴ F _{7/2} Ho Holmium 164.93032 [Xe]4f ¹¹ 6s ² 6.0215	68 ³ H ₆ Er Erbium 167.259 [Xe]4f ¹² 6s ² 6.1077	69 ² F _{7/2} Tm Thulium 168.93421 [Xe]4f ¹³ 6s ² 6.1843	70 ¹ S ₀ Yb Ytterbium 173.04 [Xe]4f ¹⁴ 6s ² 6.2542	71 ² D _{3/2} Lu Lutetium 174.967 [Xe]4f ¹⁴ 5d6s ² 5.4259
89 ² D _{3/2} Ac Actinium (227) [Rn]6d7s ² 5.17	90 ² F ₂ Th Thorium 232.0381 [Rn]6d ² 7s ² 6.3067	91 ⁴ K _{11/2} Pa Protactinium 231.03588 [Rn]5f ² 6d7s ² 5.89	92 ⁵ L ₈ U Uranium 238.02891 [Rn]5f ³ 6d7s ² 6.1941	93 ⁶ L _{11/2} Np Neptunium (237) [Rn]5f ⁴ 6d7s ² 6.2657	94 ⁷ F ₀ Pu Plutonium (244) [Rn]5f ⁶ 7s ² 6.0260	95 ⁶ G _{7/2} Am Americium (243) [Rn]5f ⁷ 7s ² 5.9738	96 ⁵ D ₂ Cm Curium (247) [Rn]5f ⁸ 6d7s ² 5.9914	97 ⁶ H _{5/2} Bk Berkelium (247) [Rn]5f ⁹ 7s ² 6.1979	98 ⁵ F ₈ Cf Californium (251) [Rn]5f ¹⁰ 7s ² 6.2817	99 ⁴ F _{15/2} Es Einsteinium (252) [Rn]5f ¹¹ 7s ² 6.42	100 ³ H ₆ Fm Fermium (257) [Rn]5f ¹² 7s ² 6.50	101 ² F _{7/2} Md Mendelevium (258) [Rn]5f ¹³ 7s ² 6.58	102 ¹ S ₀ No Nobelium (259) [Rn]5f ¹⁴ 7s ² 6.65	103 ² P _{1/2} Lr Lawrencium (262) [Rn]5f ¹⁴ 7s ² 7p? 4.9 ?

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4d	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
5p	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
4f		1	3	4	5	6	7	7	9	10	11	2	13	14	14
5d	1	1						1							1

Background: the properties of rare earth elements- energy structures of free ions RE³⁺

Hamiltonian of free rare earth ions:

$$H = T + V_{en} + V_{ee} + V_{so}$$

$$= -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{i<j}^N \frac{e^2}{r_{ij}} + \sum_{i=1}^N \xi(r_i) \mathbf{s}_i$$

The four terms of the formula represent *kinetic energy* (T), *the interaction between electrons and nucleus* (V_{en}), *the interaction between electrons* (V_{ee}) and *spin orbit interaction* (V_{so}).

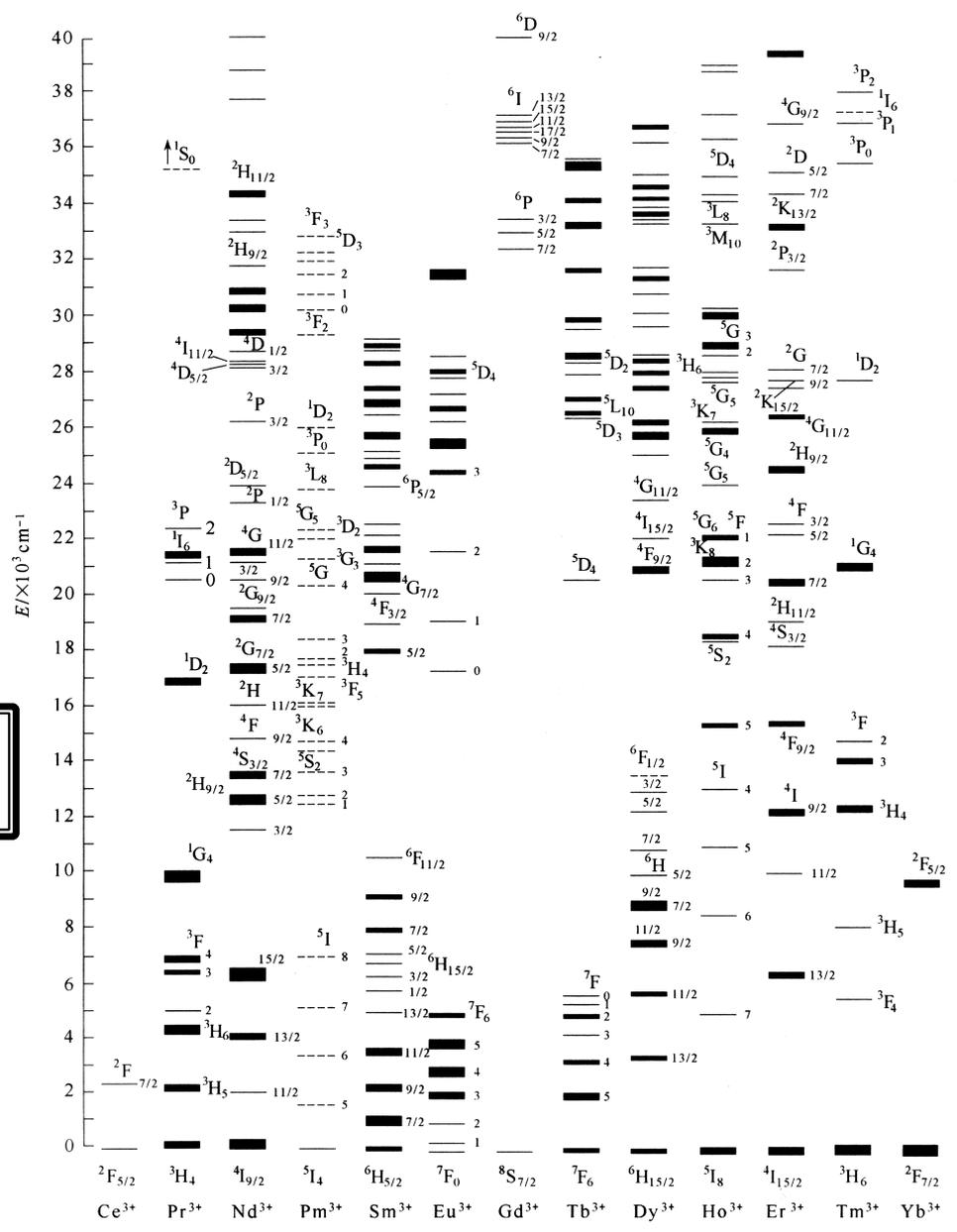
The non spherically symmetric part of (V_{ee}) and (V_{so}).



Split of the degeneracy to $2S+1L_J$

Figure 1. Energy Levels of rare earth ions in LaCl₃ (Dieke Diagram)

Appl. Opt, 675, 2, 1963



Background: Properties of rare earth elements-ions doped in crystals

$$H = H_{FI} + H_{CF} + H_{HF} + H_Q + H_z + H_Z$$

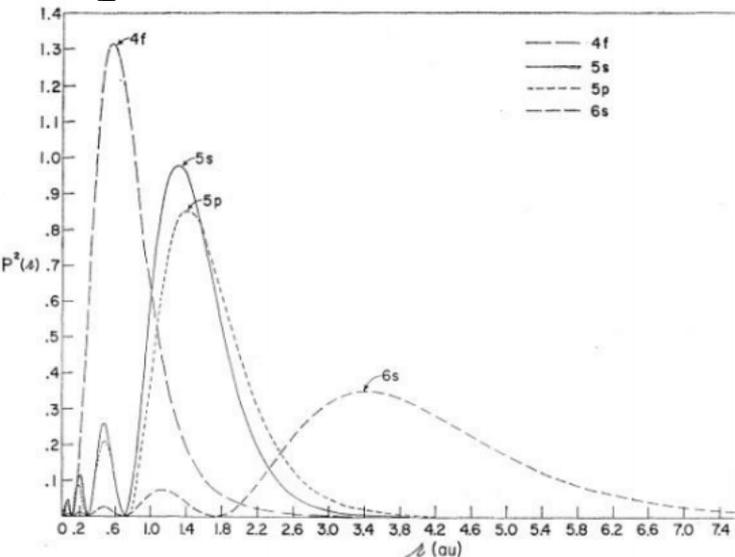
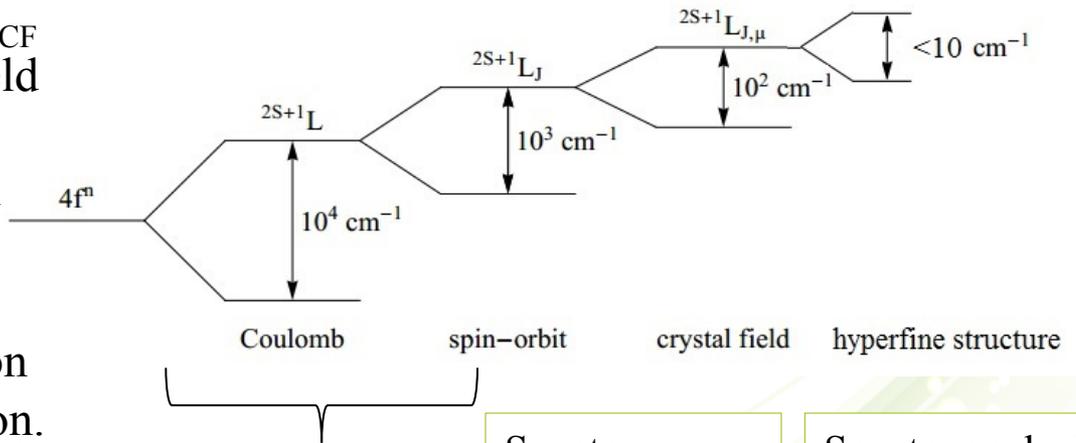
The first two terms H_{FI} and H_{CF} are the free ion and crystal field Hamiltonians.

H_{HF} : the hyperfine interaction

H_Q : the nuclear electric quadrupole interaction

H_z : nuclear Zeeman interaction

H_Z : electric Zeeman interaction.



Spectra measurement at room temperature

Spectra measurement at liquid helium temperature

Spectra analysis with high resolution at liquid temperature with strong magnetic field

Figure 2, the electron density of the 4f, 5s, and 6s orbitals in Gd atom

Background: Energy transfer in rare earth doped crystals

Excited States

- The optical lifetime T_1 .

$$T_{1a} = \frac{1}{\sum_b W_{ab}^R + \sum_b W_{ab}^{NR}}$$

W_{ab}^R the radiative decay rate

W_{ab}^{NR} non-radiative decay rate

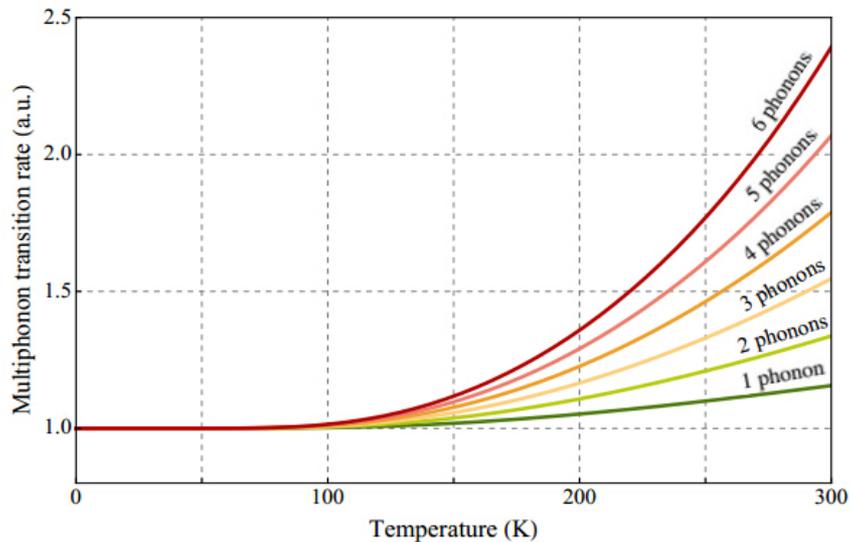


Figure 3. Decay rate via temperature for single and multiphonon relaxation.

Hyperfine structure

- The coherence lifetime T_2 .

$$\Gamma_h = \frac{1}{\pi T_2} = \frac{1}{2\pi T_1} + \Gamma_\phi$$

- Homogeneous bandwidth Γ_h
- Inhomogeneous bandwidth Γ_{ih}

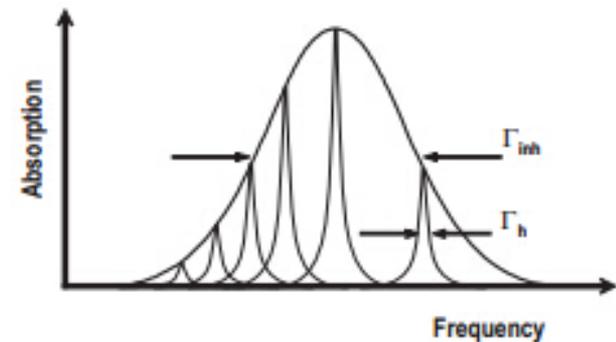


Figure 4. Inhomogeneous linewidth for a resonant optical material and homogeneous linewidth for individual groups of ions.

Background: photon echo techniques for quantum memory application

- Photon echo (two level system):

$$E_{echo}(t) \propto \int E_{write}(\omega) E_{data}(\omega) E_{read}(\omega) e^{i\omega t} d\omega$$

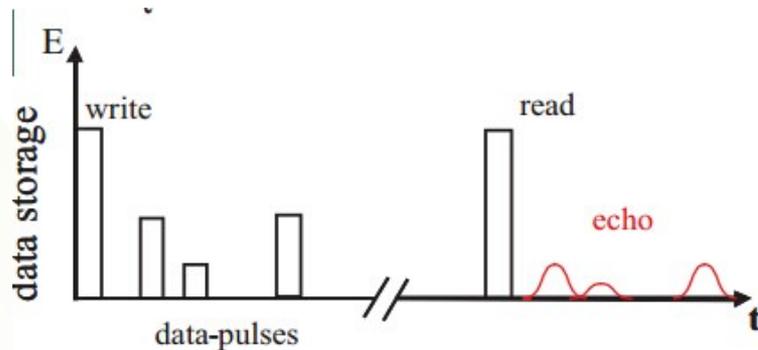
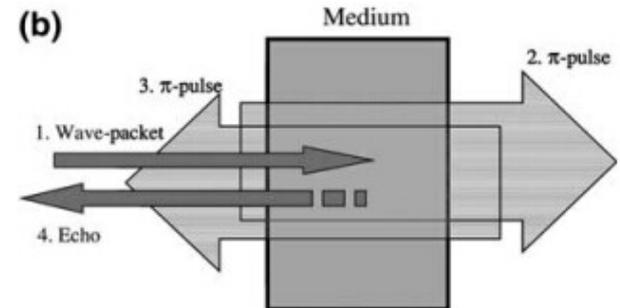
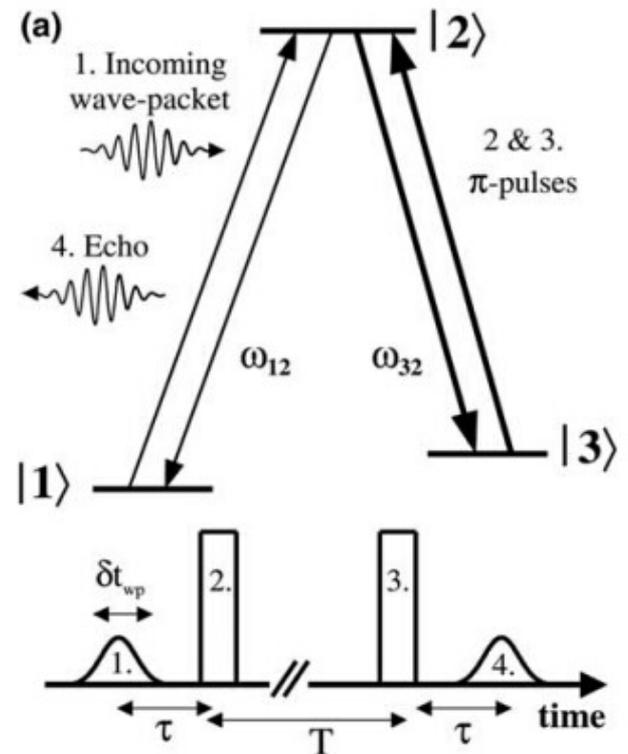


Figure 5. scheme for photon echo data storage.
Optics Communications 247 (2005) 393–403
Laser & Photon. Rev. 4, (2010) 244-267

- Controlled reversible inhomogeneous broadening, CRIB:

Figure 6. the Lambda type energy levels structure used in CRIB.

Optics Communications 247 (2005) 393–403



Experiment Apparatus: crystal growth by Czochralski method

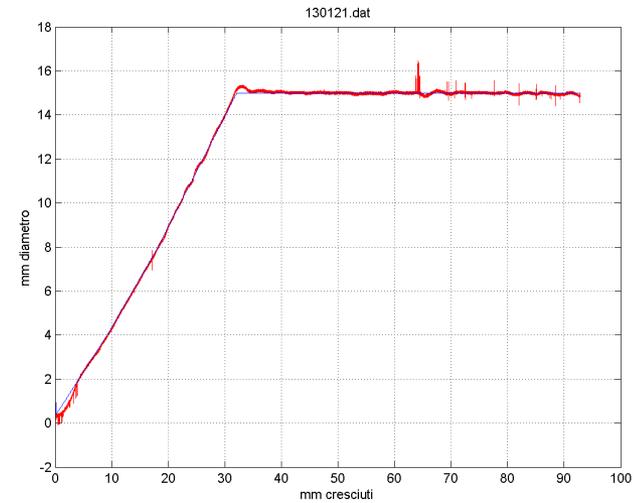
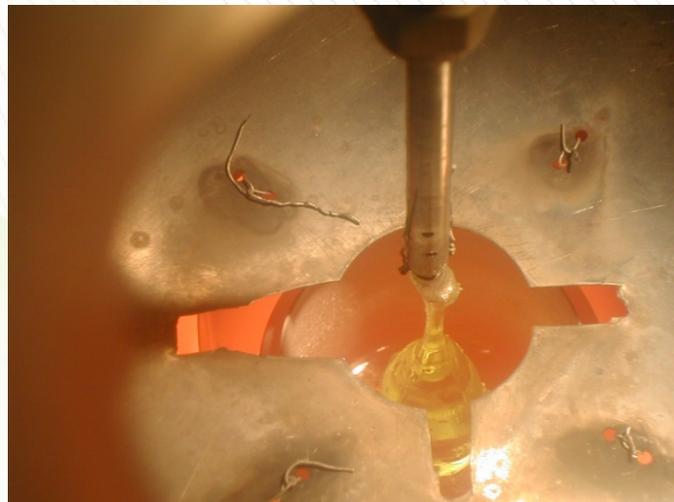
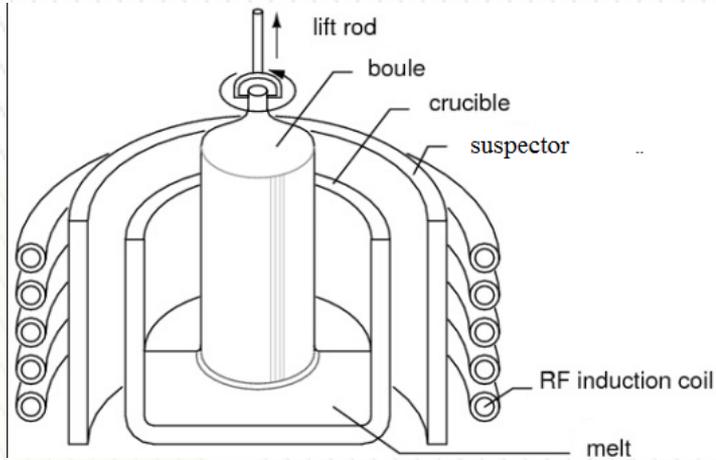


Figure 7. a typical crystal growth process using CZ method. The crystal shown in the picture is Yb^{3+} doped LiYF_4 .

Experiment Apparatus: crystal growth by Micro Pulling Down Method

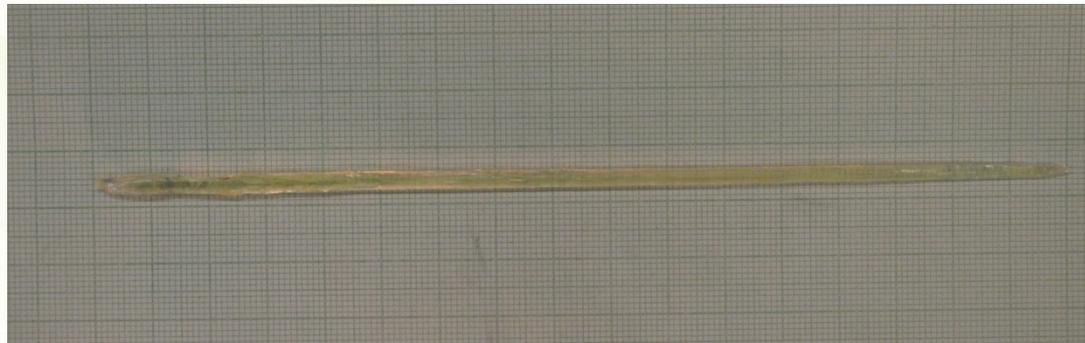
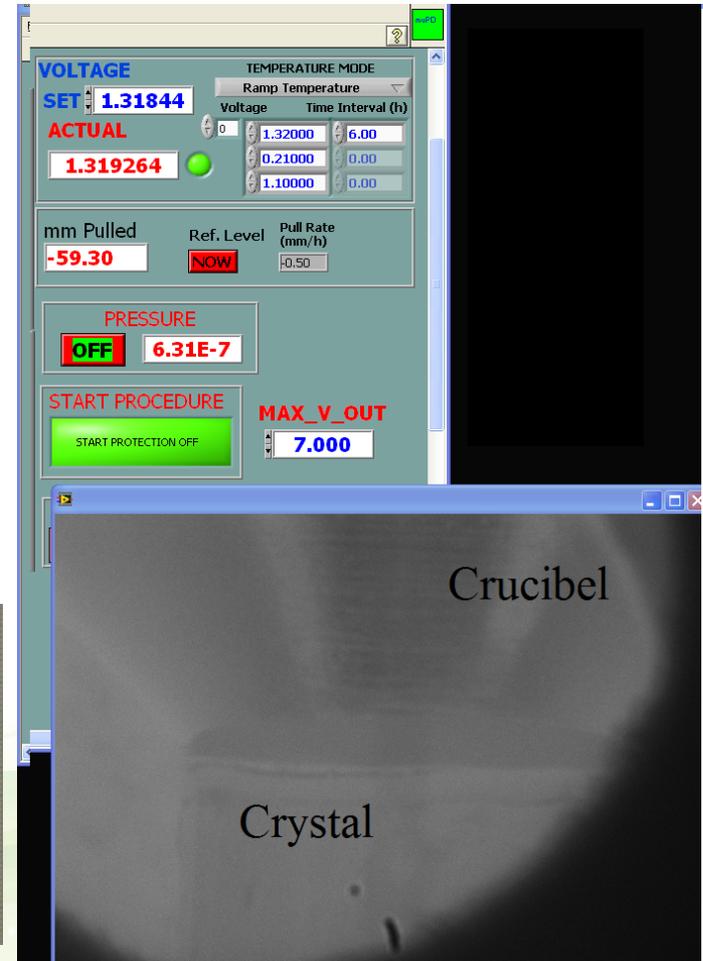
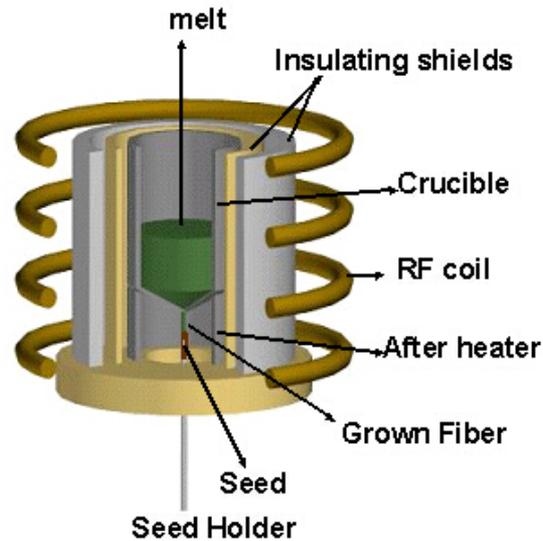


Figure 8. a typical crystal growth process using CZ method. The crystal shown in the picture is Pr^{3+} doped $\text{SrAl}_{12}\text{O}_{19}$.

Experiment Apparatus: spectra measurement

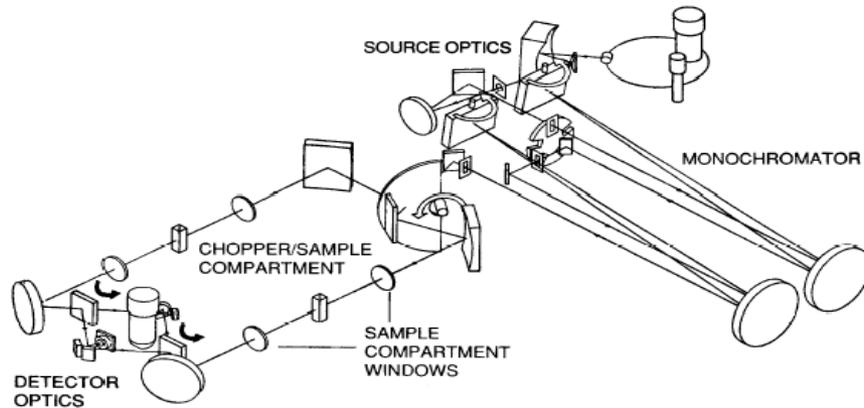


Figure 9. The set up of the VARIAN CARY 500 spectrophotometer.

The absorption spectra can be measured from 180nm to 3200nm. A cryostat can be applied and the temperature of the sample can reach about 10K.

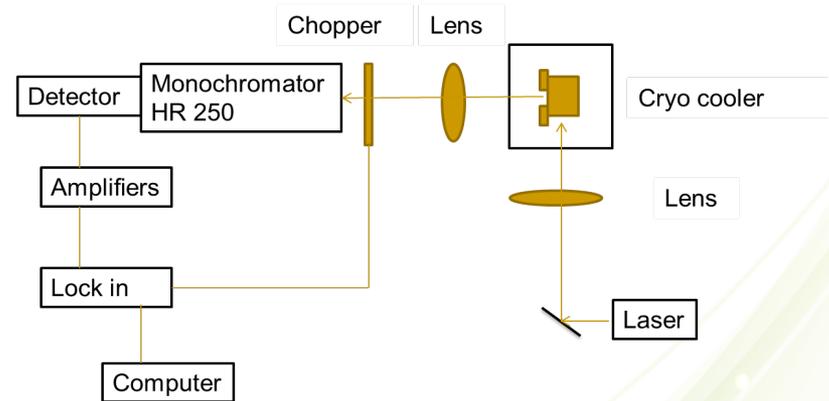
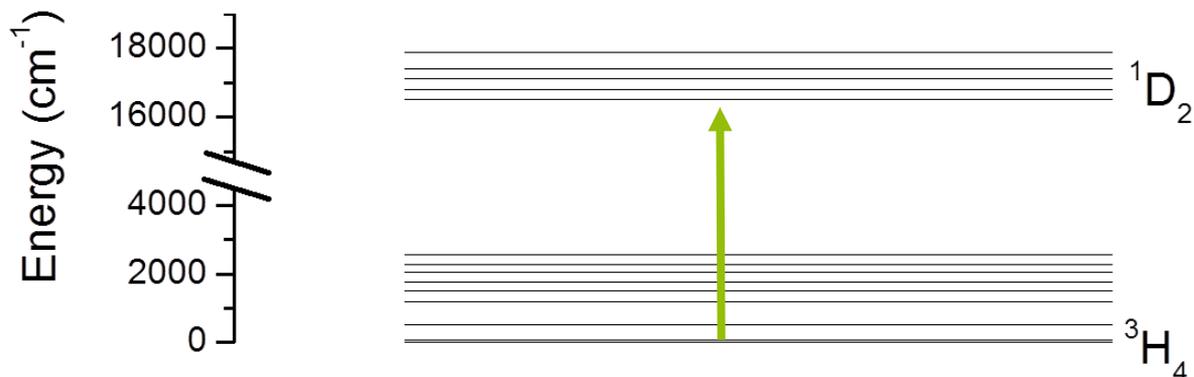


Figure 10, the set-up of fluorescence measurement. The laser here can be diode lasers or cw Ti:Al₂O₃ laser.

A cryostat can also be applied for fluorescence measurement. Various detectors are available covering a spectrum range from UV to IR.

Previous Work: Spectra measurement of Pr³⁺ doped LiYF₄, LiLuF₄ and BaY₂F₈

Zero phonon transition between ³H₄ and ¹D₂ levels of Pr³⁺ ion.



<i>crystal</i>	<i>LiLuF₄:Pr³⁺ 1.25%</i>	<i>LiYF₄:Pr³⁺ 1%</i>	<i>BaY₂F₈:Pr³⁺ 1.25%</i>
<i>growth (melt composition)</i>	<i>congruent (LiF 50%, LuF₃ 50%)</i>	<i>incongruent (LiF 53%, YF₃ 47%)</i>	<i>congruent BaY₂F₈</i>
<i>T_m (°C)</i>	<i>830</i>	<i>850</i>	<i>960</i>
<i>ionic radii (Å)</i>	<i>R_{Lu}=1.12</i>	<i>R_Y=1.16</i>	<i>R_{Gd}=1.12</i>
<i>ionic radius (Å) R_{Pr}=1.27</i>			
<i>k_{eff}</i>	<i>0.1-0.2</i>	<i>0.22</i>	<i>0.3</i>
<i>Pr³⁺ density (10¹⁹ cm⁻³)</i>	<i>18.11</i>	<i>13.85</i>	<i>16.75</i>
<i>Site symmetry Pr³⁺</i>	<i>S₄</i>	<i>S₄</i>	<i>S₂</i>

Previous Work: Spectra measurement of Pr³⁺ doped LiYF₄, LiLuF₄ and BaY₂F₈-room temperature spectra

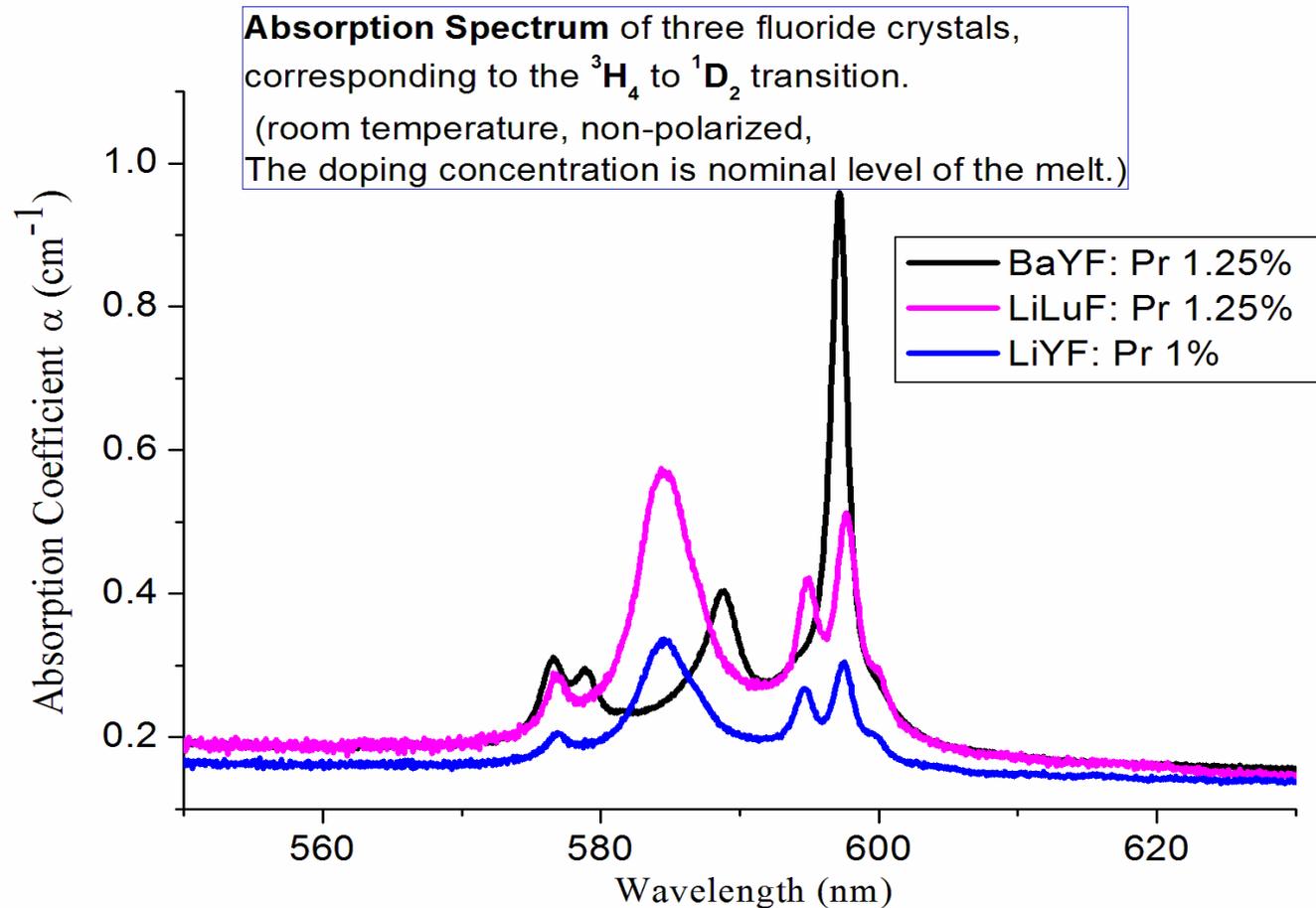


Figure 11, the absorption spectra for these three crystals at room temperature.

Previous Work: Spectra measurement of Pr³⁺ doped BaY₂F₈-low temperature spectra

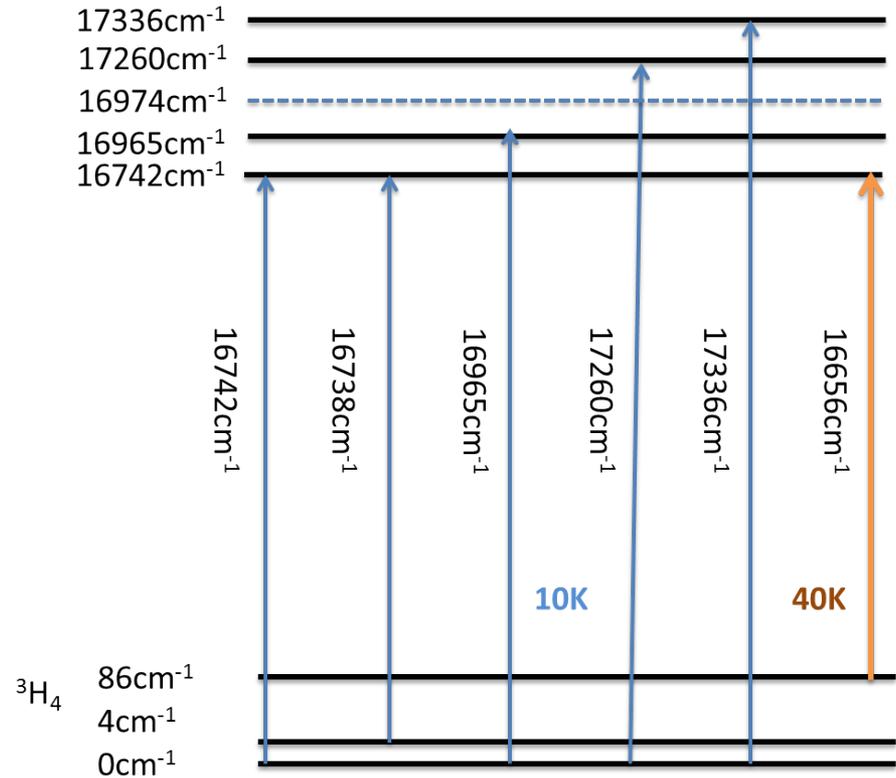
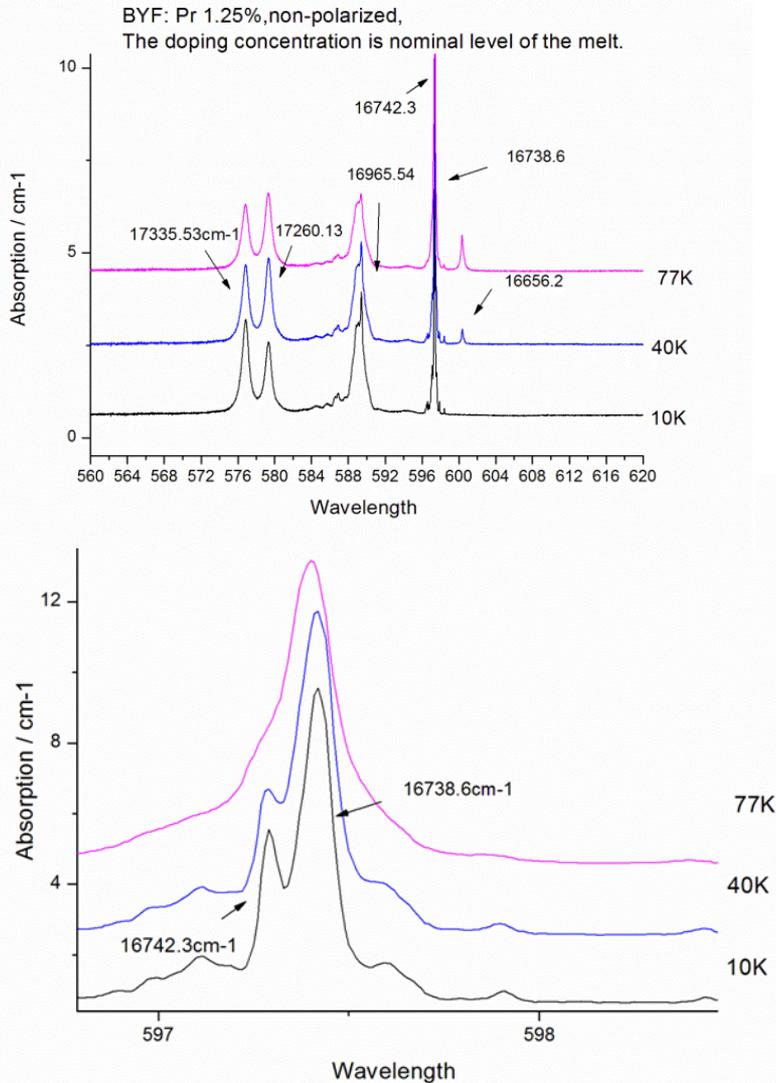


Figure 12, the absorption spectrum of Pr³⁺ doped BaY₂F₈ crystal at low temperature. Analysis of transitions was shown.

Previous Work: Spectra measurement

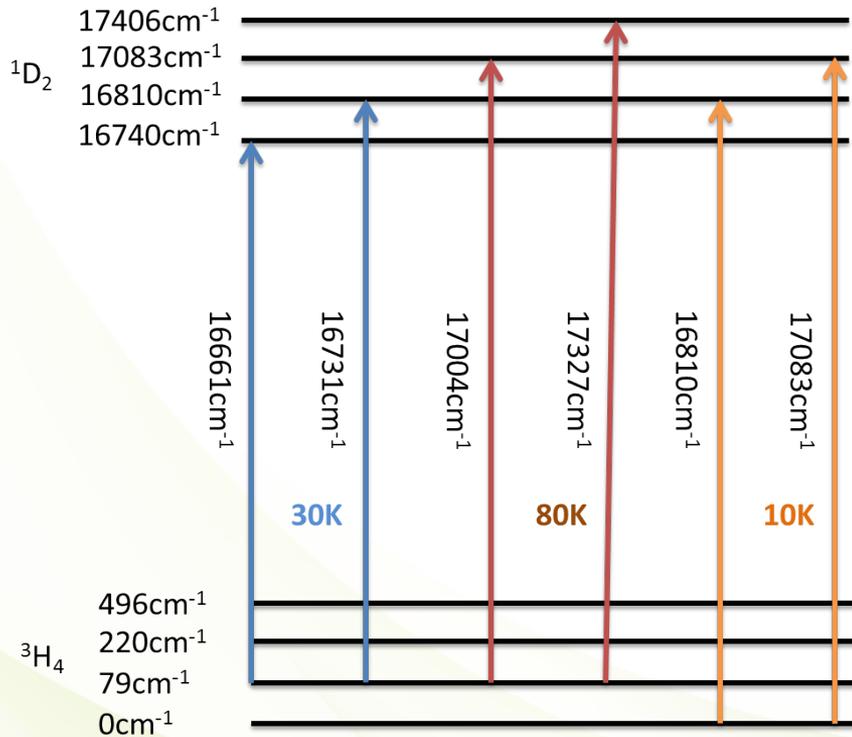
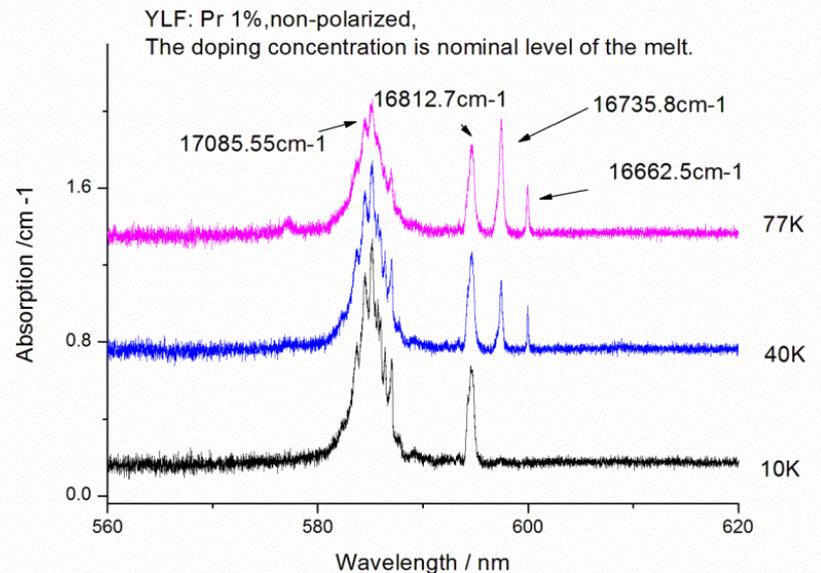
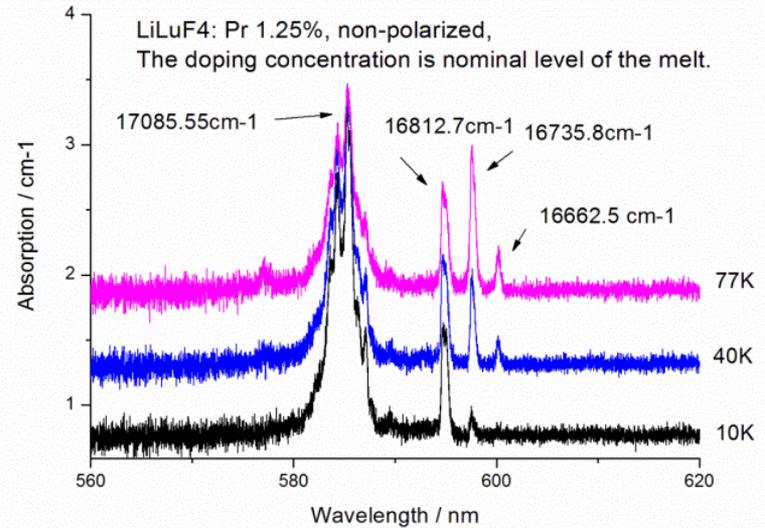


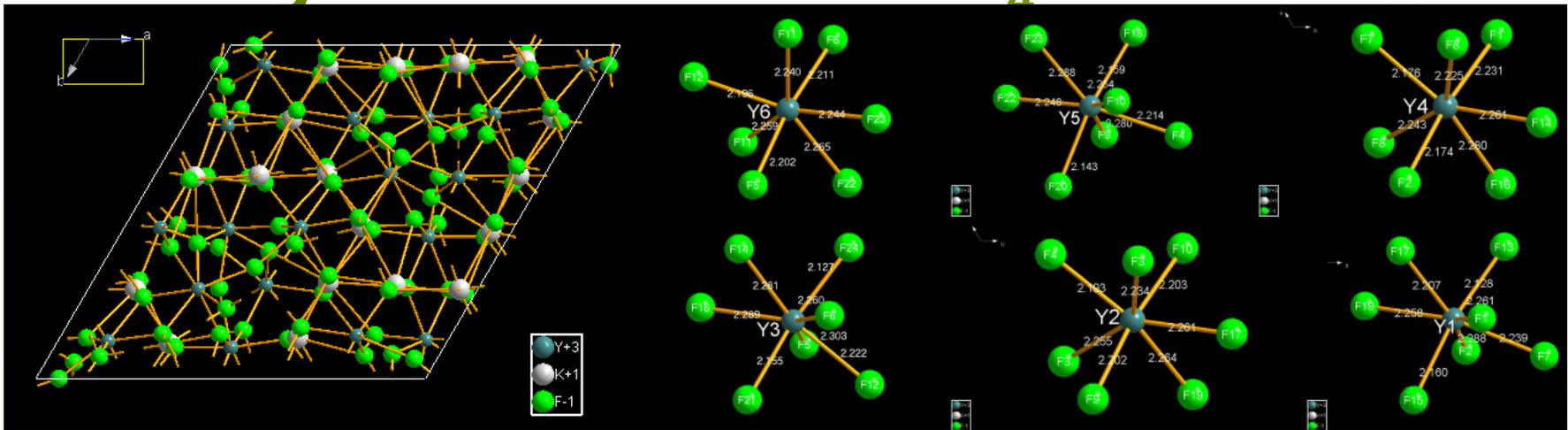
Figure 13, the absorption spectra of Pr^{3+} doped LiYF_4 and LiLuF_4 . Analysis of transitions was shown.



Summary of Spectra measurement of Pr³⁺ doped LiYF₄, LiLuF₄ and BaY₂F₈

- LiYF₄ and LiLuF₄: The zero to zero transition is forbidden by select rule of S₄ symmetry.
- BaY₂F₈: The zero to zero transition is strong. However, there is a transition very close to it that comes from higher crystal field level in the ³H₄ state of Pr³⁺.

4.2 Crystal Growth of $\text{KYF}_4: \text{Er}^{3+0.02\%}$



Parameters of KYF_4	
Crystal lattice Type	Tragonal
Space Group	P_{31}
a	14.06
c	10.10
Z	18
Difference of Y^{3+}	6

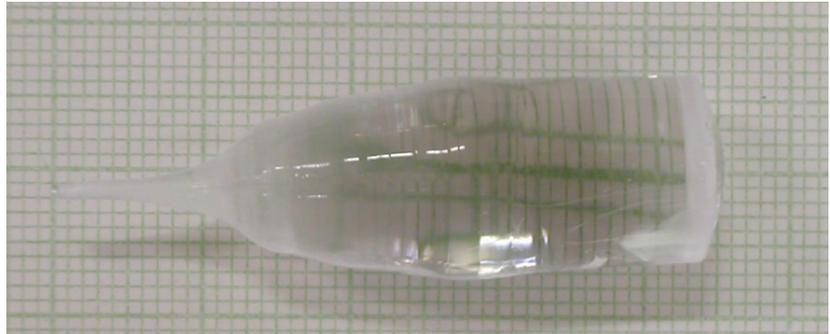
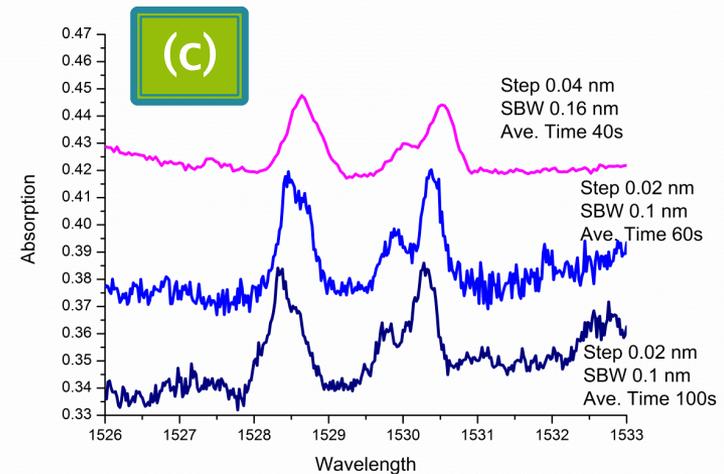
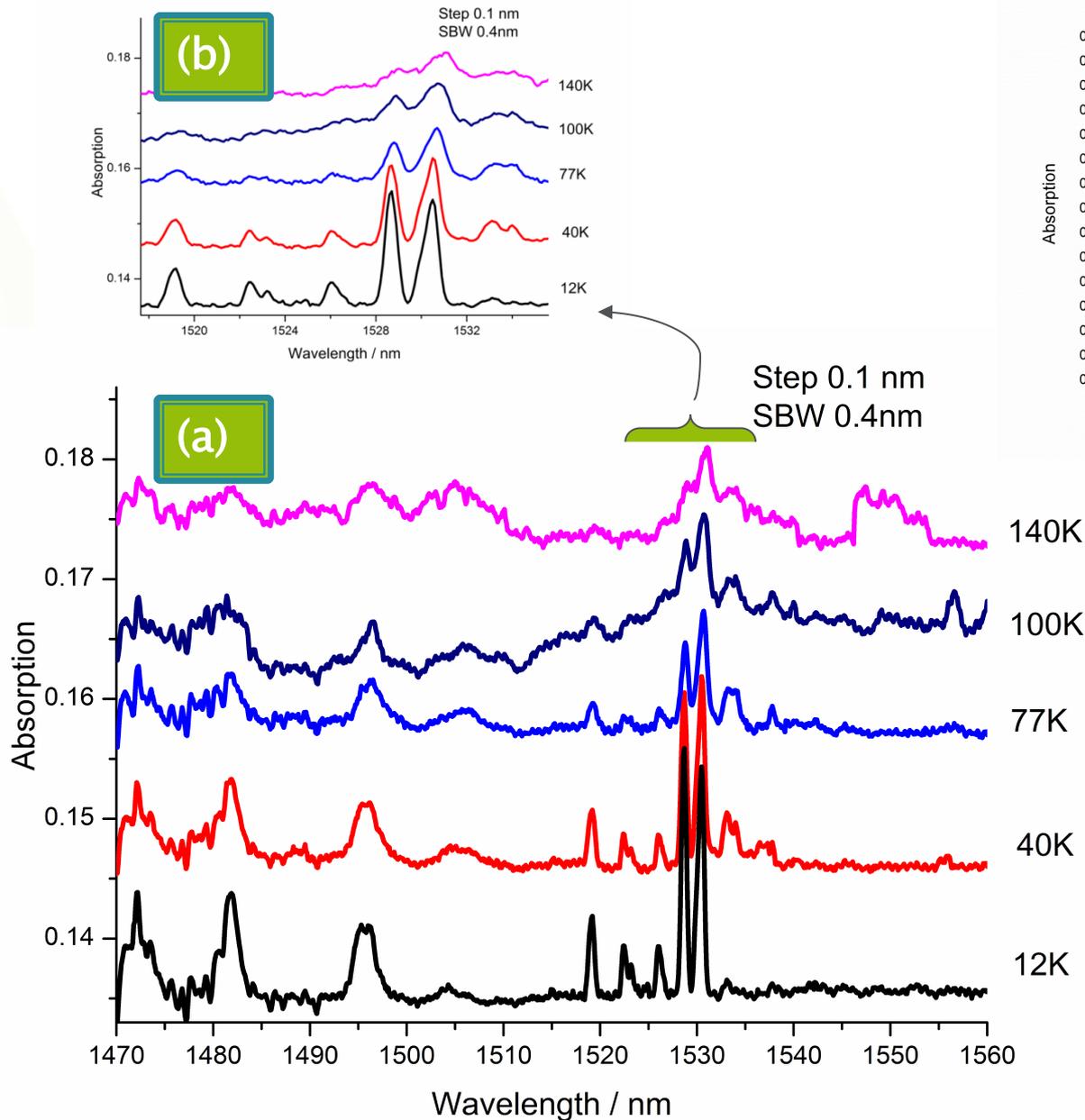


Figure 14, the picture of $\text{KYF}_4: 0.02\% \text{Er}^{3+}$.

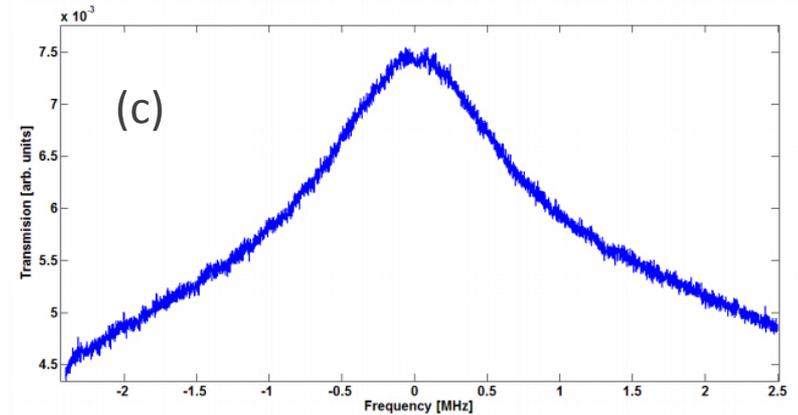
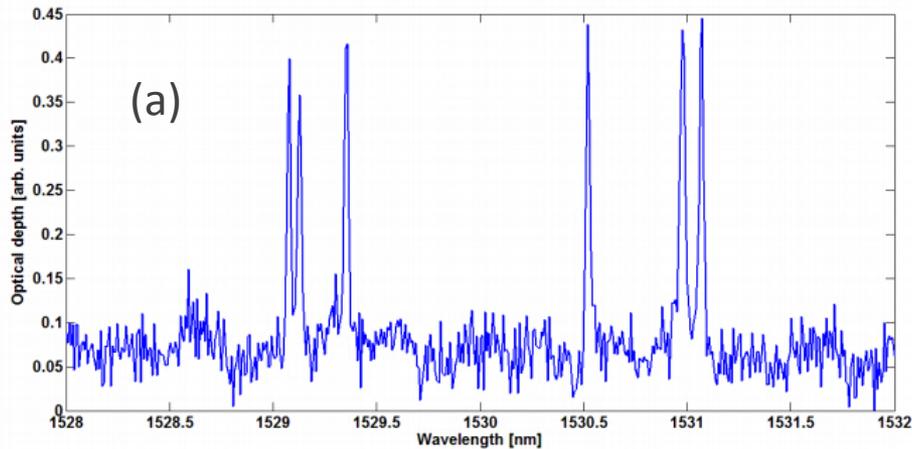
Growth Parameters:
Weight: 12g
Pulling Rate: 0.5mm/h
Temperature: 823-819 °C
Rotation Speed: 5 rpm.
Grown along -a axis.

Absorption Spectrum of Er: KYF₄ 0.02%



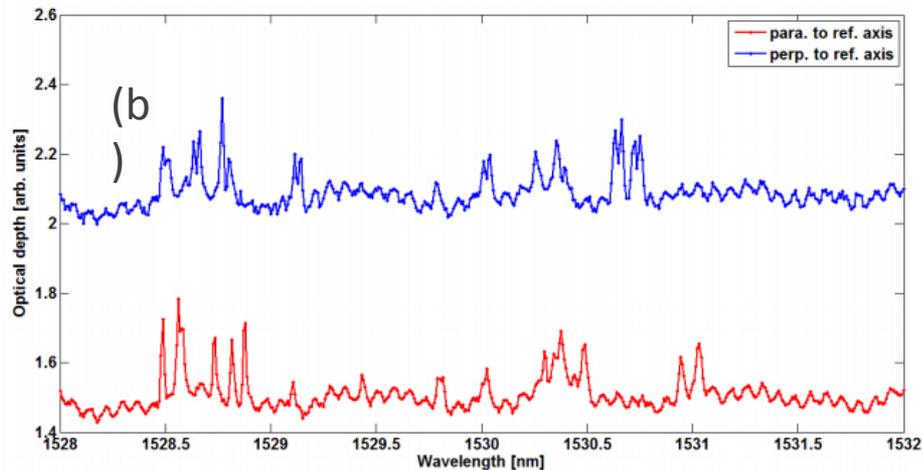
- (a). Absorption Spectrum at the range 1470 nm to 1560 nm at different temperatures.
- (b). Details within the range 1520 nm to 1532 nm.
- (c). Absorption Spectrum from 1528 nm to 1532 nm measured with different SBW settings.

Absorption Spectrum of Er: KYF₄ 0.02% measured with high resolution.



Optical pumping not very efficient, optical depth of the hole about 0,003

Inhomogeneous broadening of 3 GHz for the largest lines



(a). The Absorption of the zero to zero transition at 2K.

(b). The absorption of the zero to zero transition at 2K with 3T 's magnetic field.

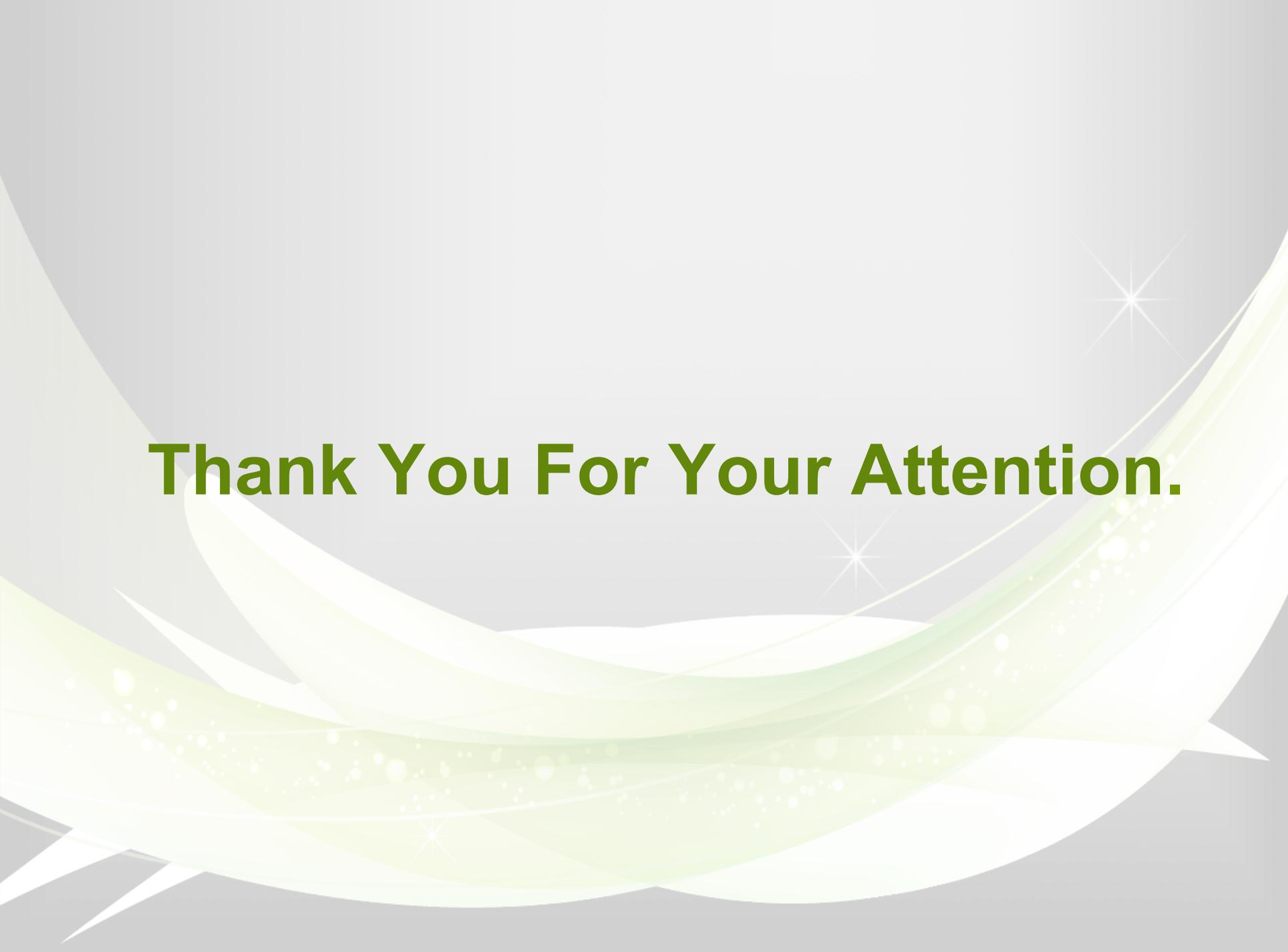
(c). The result of the spectrum hole burning at one of the zero to zero transition.

Summary of the experiments with Er: KYF₄ 0.02%

- Crystals with high quality were grown.
- The wavelength of zero phonon transition was measured.
- High resolution spectra analysis implied that there are six separated zero phonon transitions.

Future Plan

- ▶ Investigate some more coherent measurement on the sample of Er^{3+} doped KYF_4 to learn the prospect of this crystal in quantum information application.
- ▶ Grow some other fluoride crystals (OR oxide) (KYF_4 or LiCaAlF_6 or YAG) using CZ method or Micro Pulling Down method and investigate the spectra of these crystals.
- ▶ Spectra measurement will be carried on the new crystals. Absorption and fluorescence spectra will help us to detect the 0 to 0 transitions. Photon echo measurement will tell the coherence time of particular state.



Thank You For Your Attention.