Electrochemical behaviors of Sm and Yb cations in LiCl-KCl melt investigated by electrochemical, UV-Vis absorption, and laser induced luminescence spectroscopic methods

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Outline

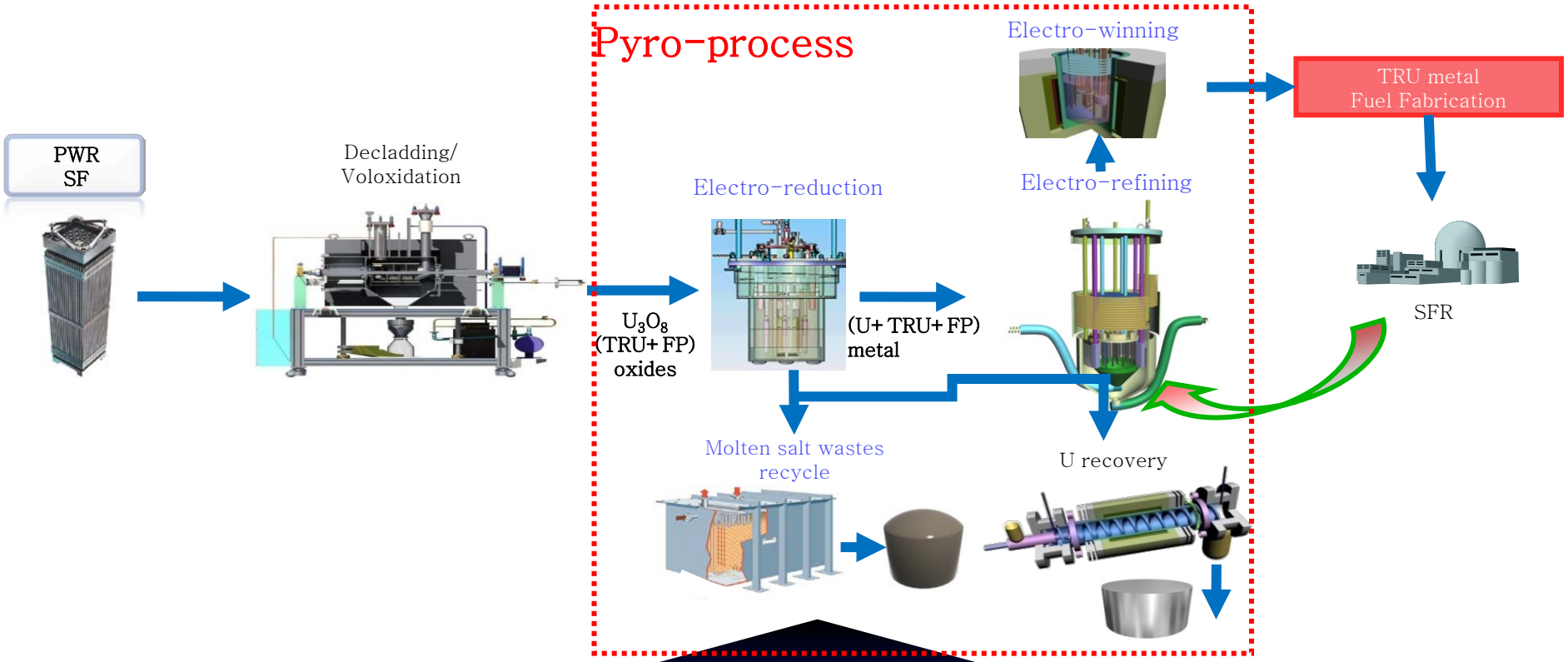
1. Introduction
   - Background
   - Electrochemical and Spectroscopic methods

2. Apparatus and Experimental

3. Results
   - Electrochemical and RDE studies of LN ions in LiCl-KCl melt
   - UV-Vis absorption spectroscopic studies of LN ions in LiCl-KCl melt integrated with electrochemistry
   - Laser induced luminescence spectroscopic studies of LN ions in LiCl-KCl melt

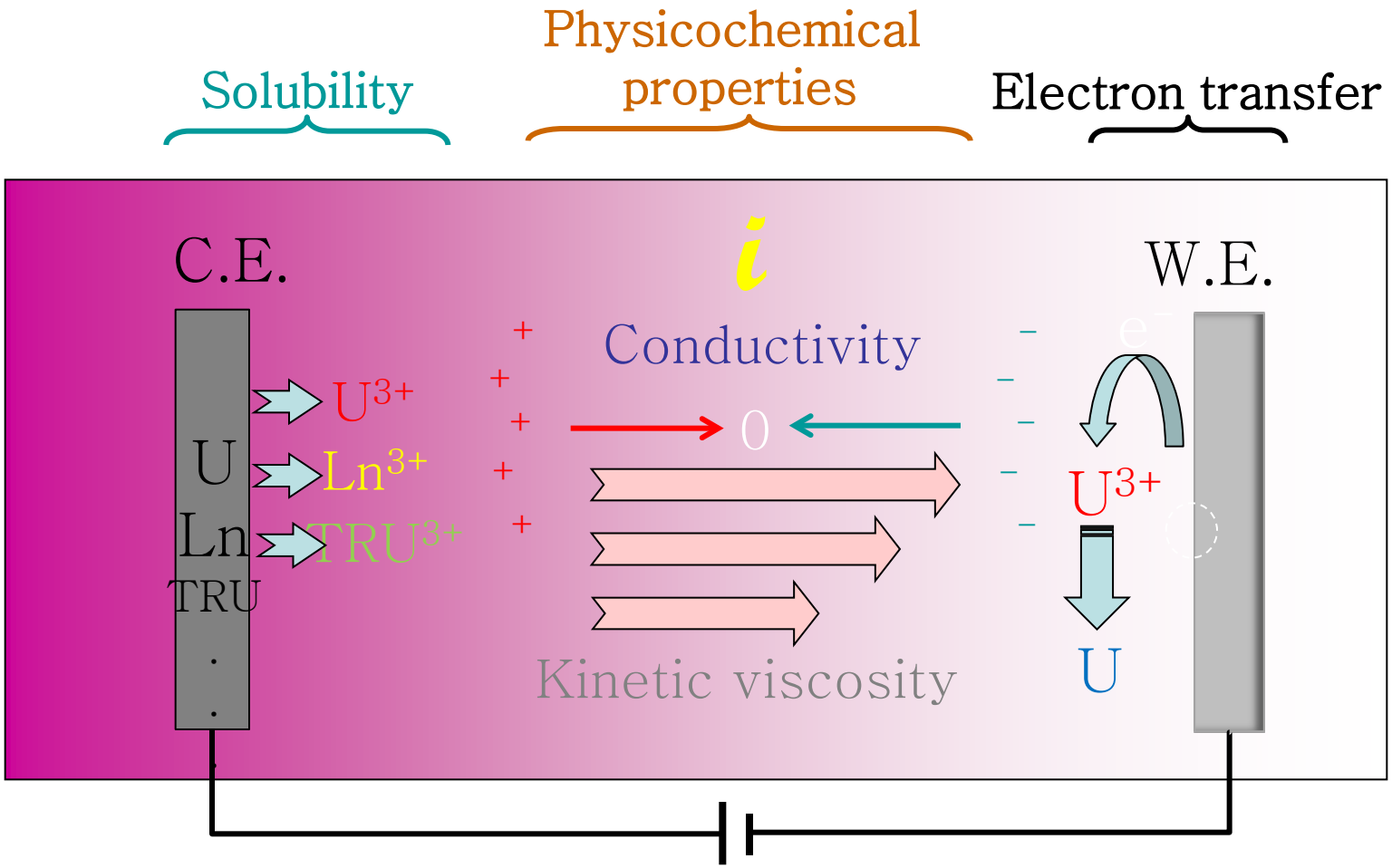
4. Conclusion

Introduction (Pyro-chemical process)

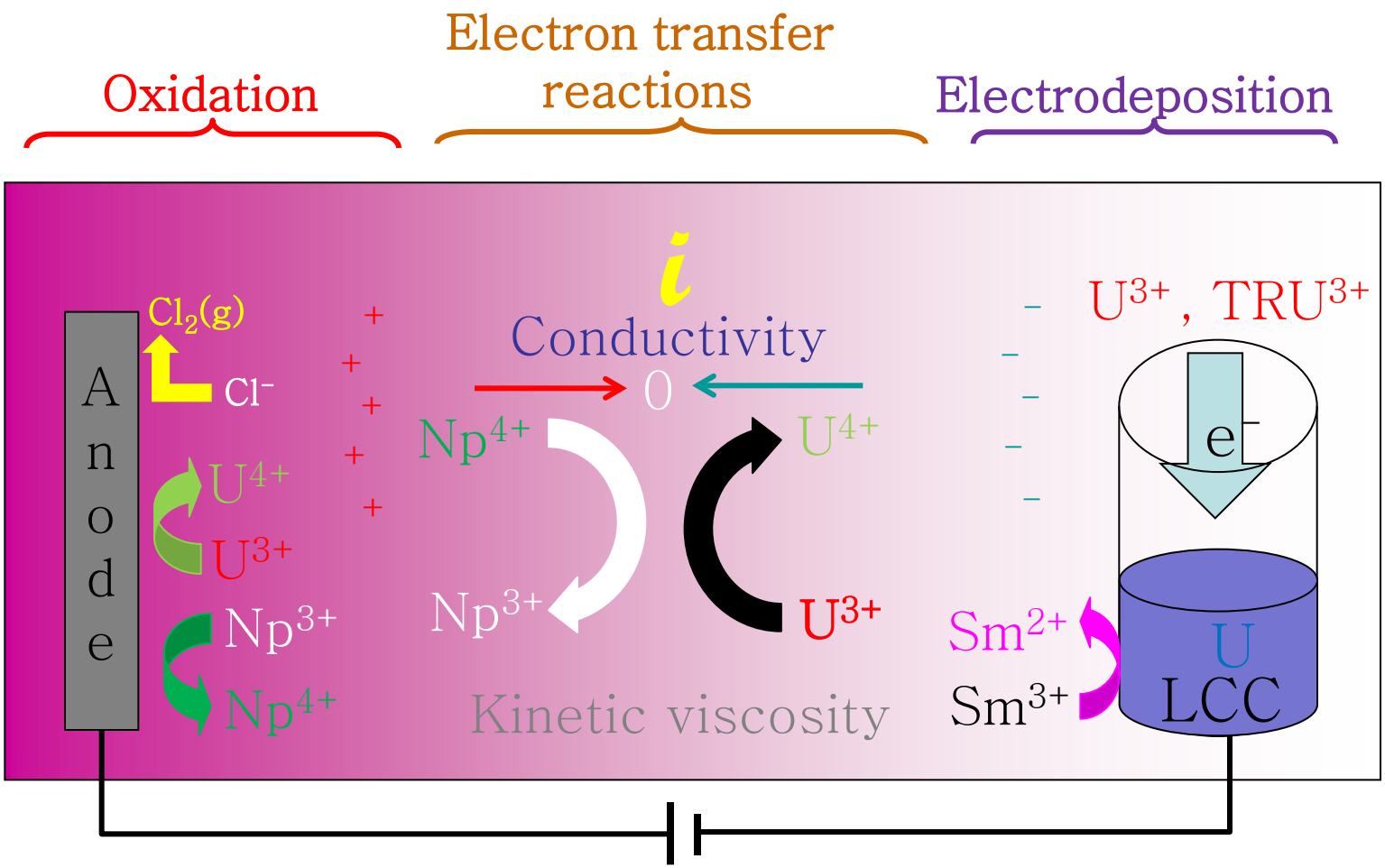


- **Necessity of on-line monitoring technique for actinides and lanthanides in LiCl-KCl molten salt at high temp. for pyro-chemical process in Korea.**
- **Application of spectroscopic analysis (UV-Vis absorption, TRLFS, Electrochemical method and etc.) for in-situ monitoring.**
- **Electrochemical behaviors of ANs and LNs in pyro-chemical process.**

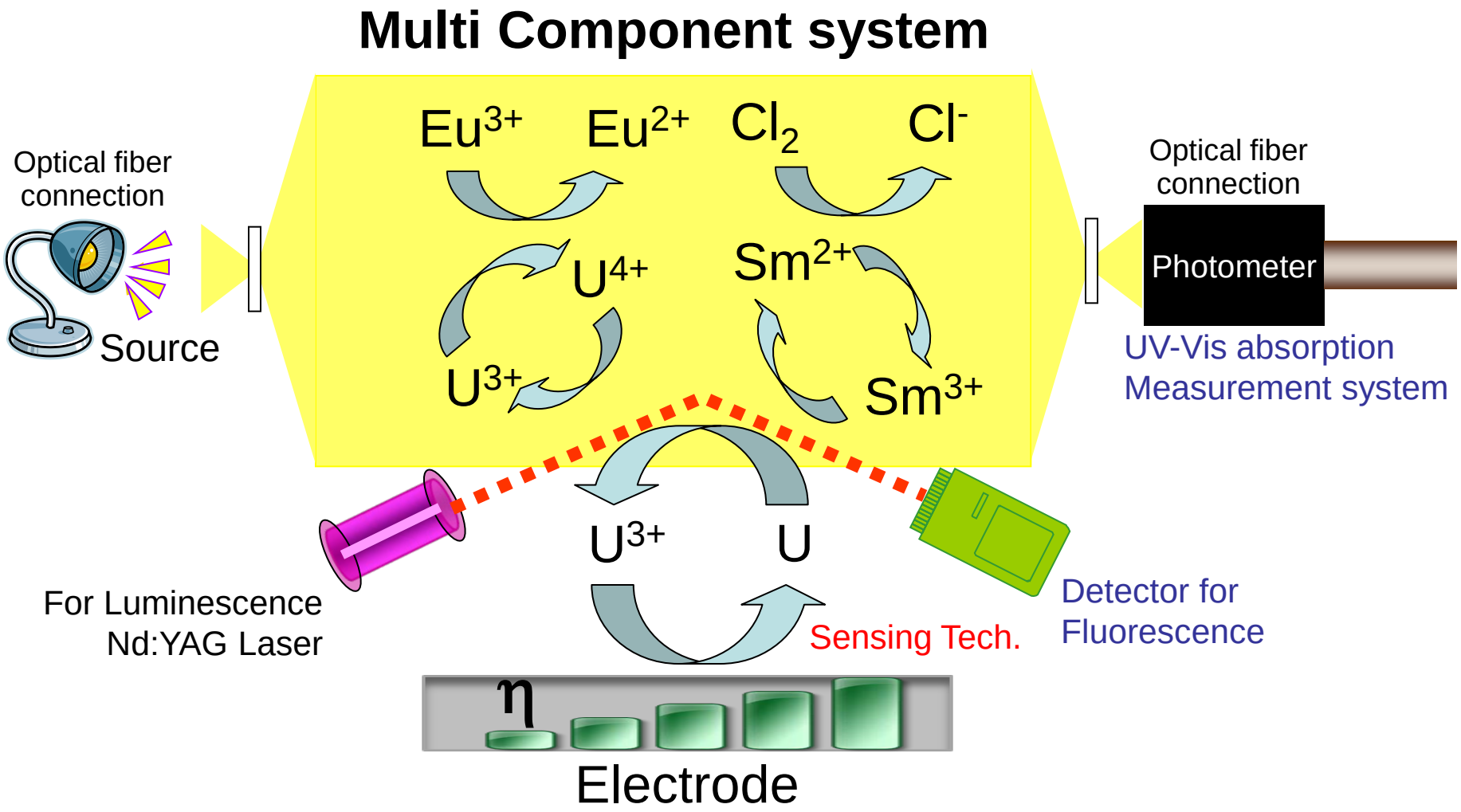
Electro-refining process



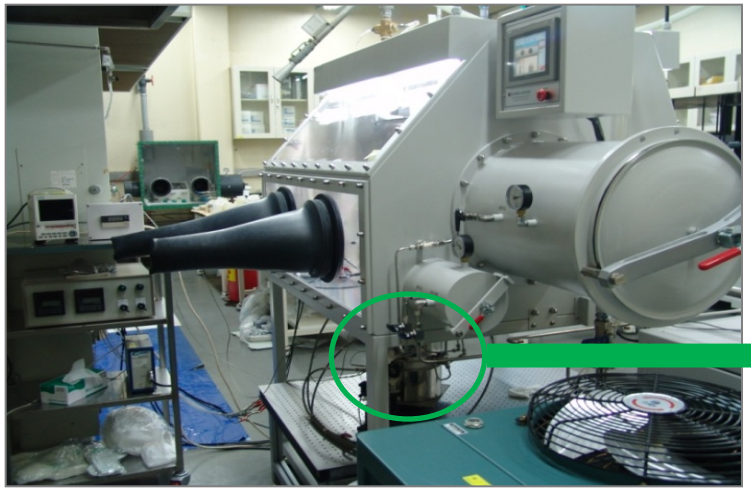
Electro-winning process



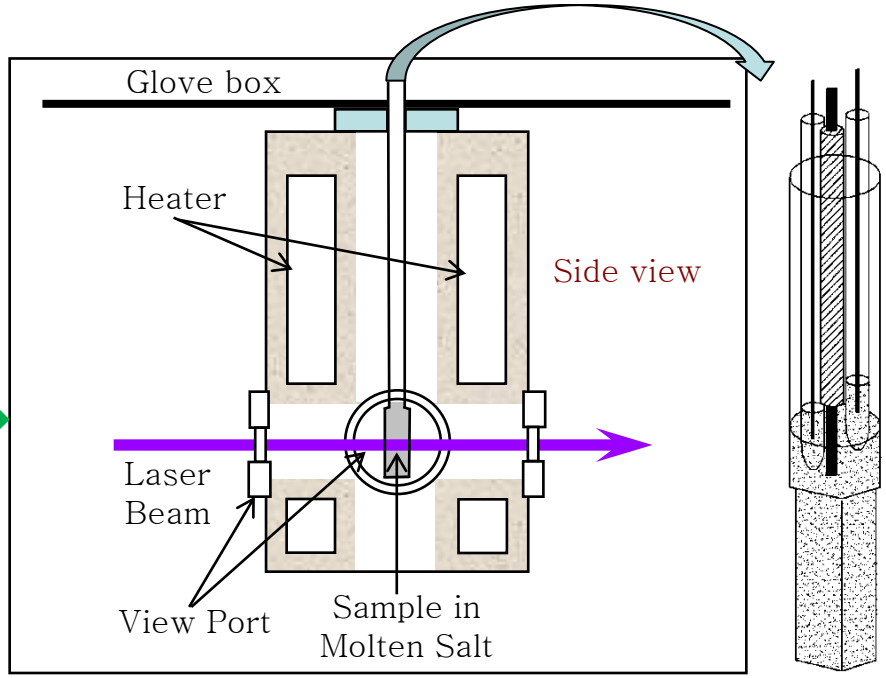
Spectro-electrochemical study

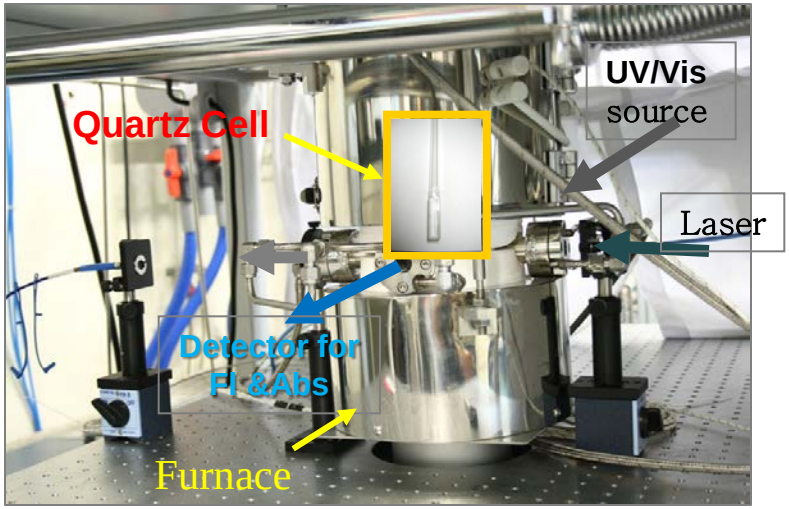


Experimental (Glove Box and Furnace system)

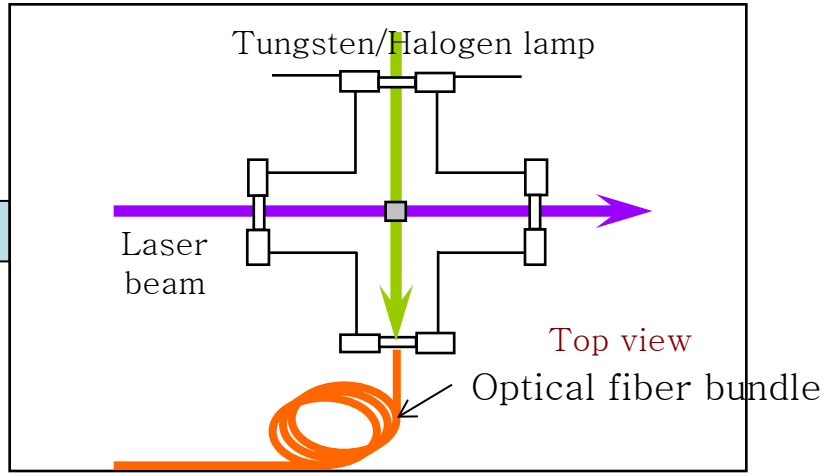


H_2O, O_2 < 1 ppm

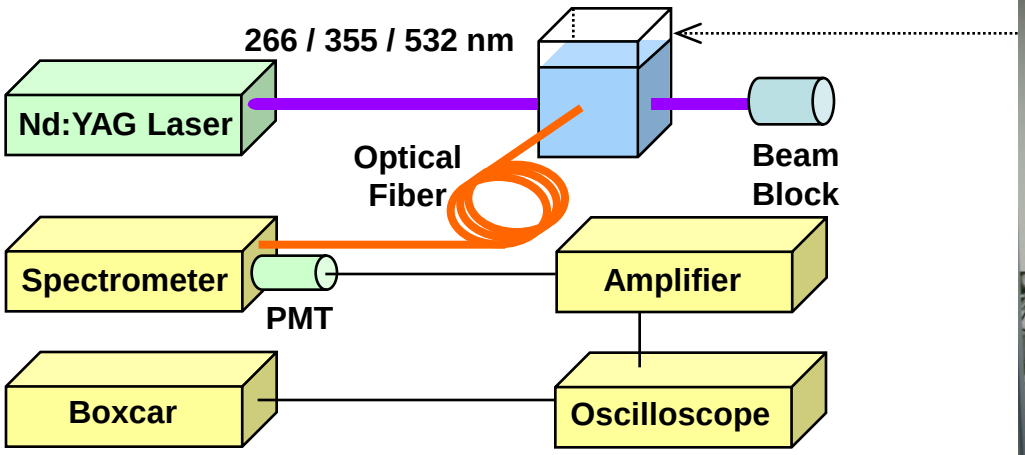




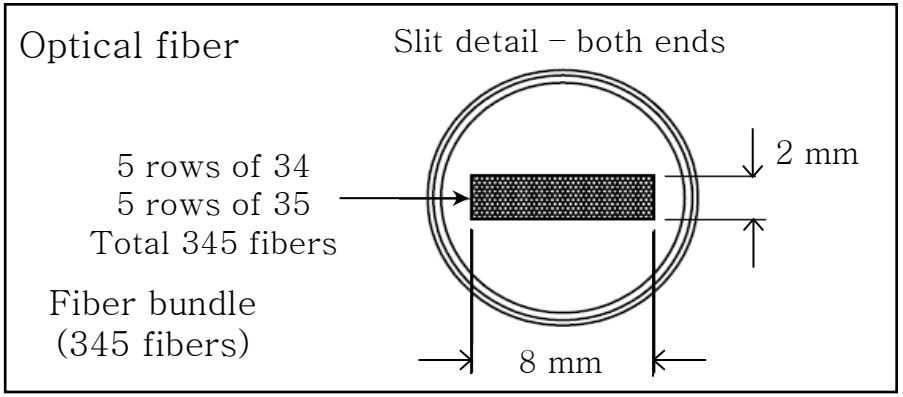
Simultaneous Meas. of Ab. and FL

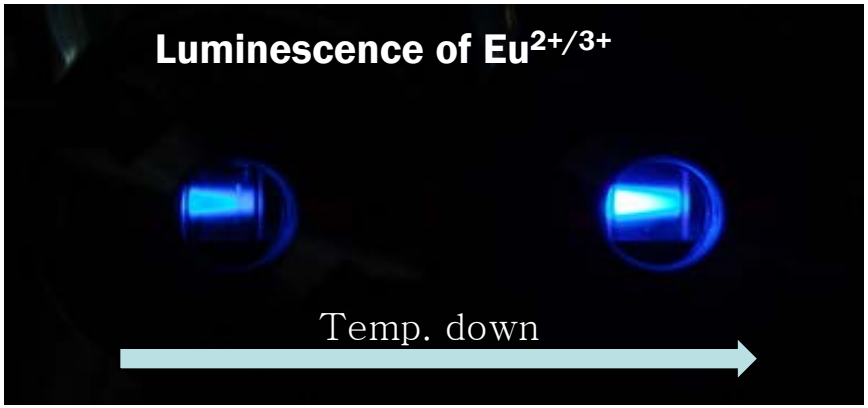


Experimental (Luminescence measurement)



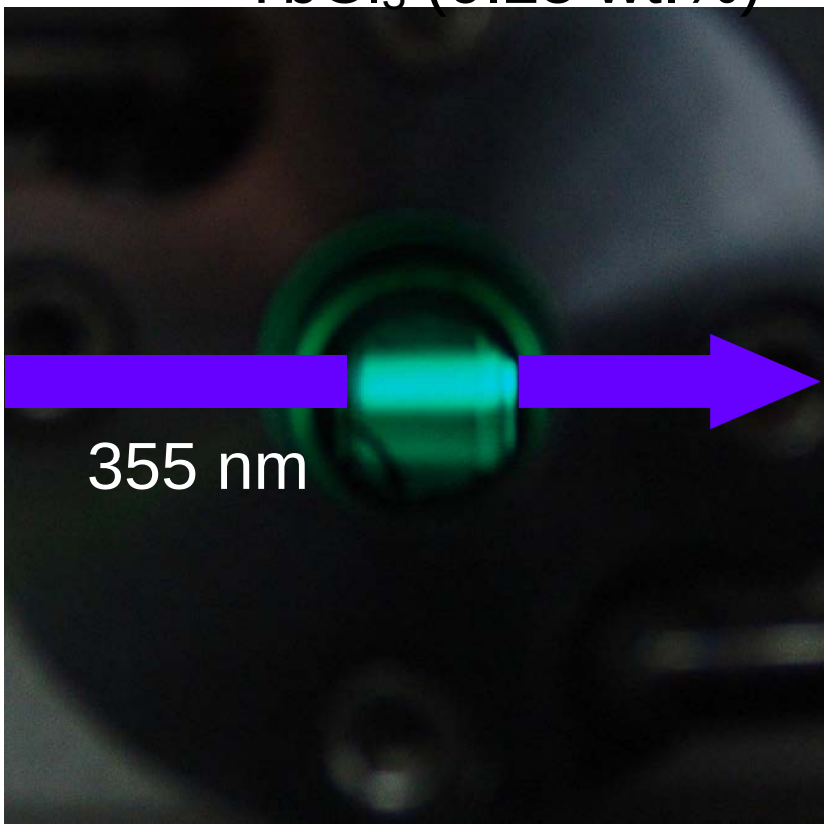
- **PMT-Photon Counter, PMT-Gated Integrator**



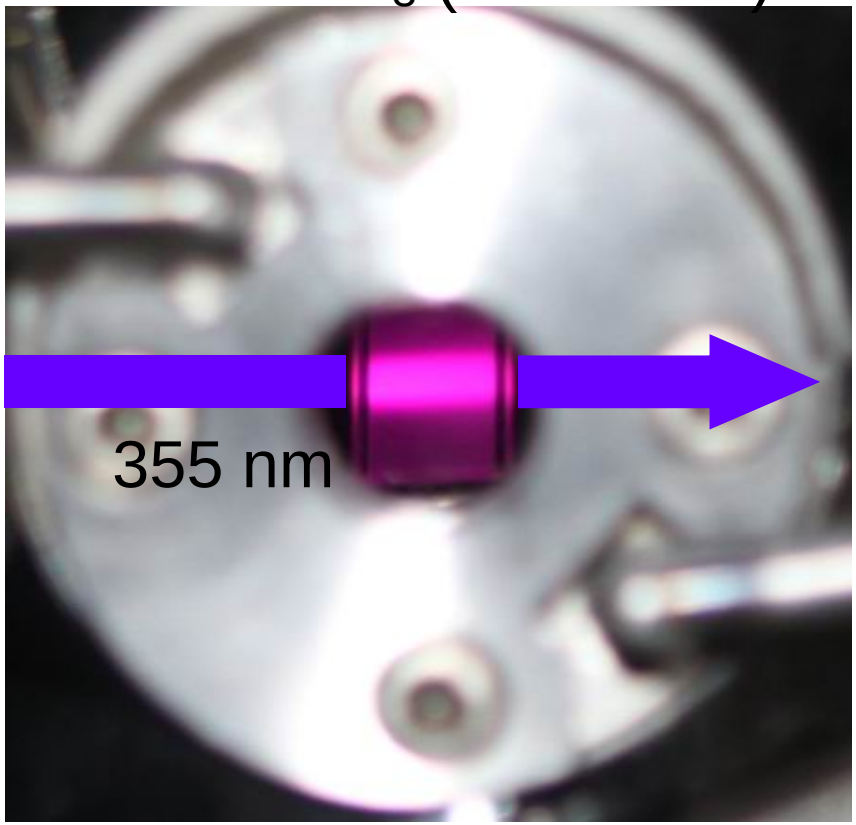


Luminescences of Tb^{3+} and Nd^{3+}

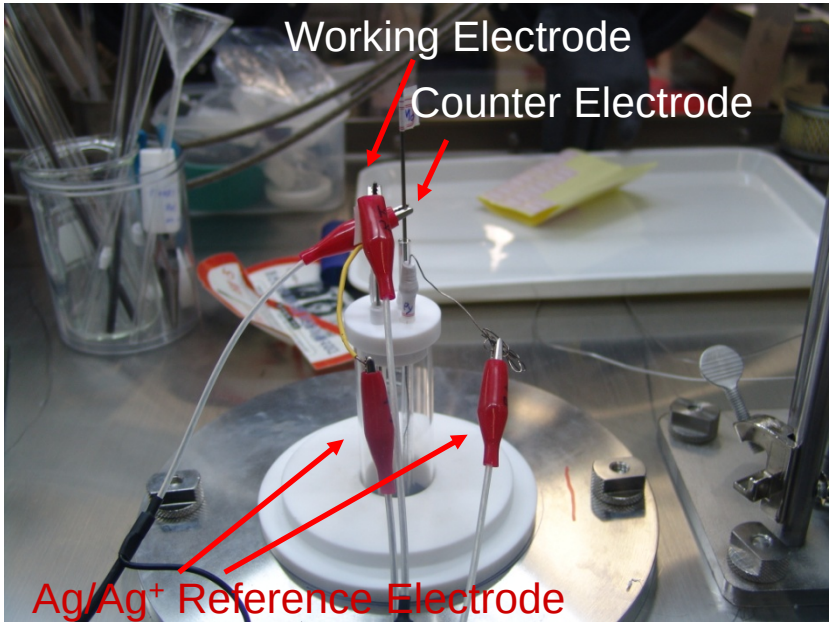
$TbCl_3$ (0.25 wt.%)



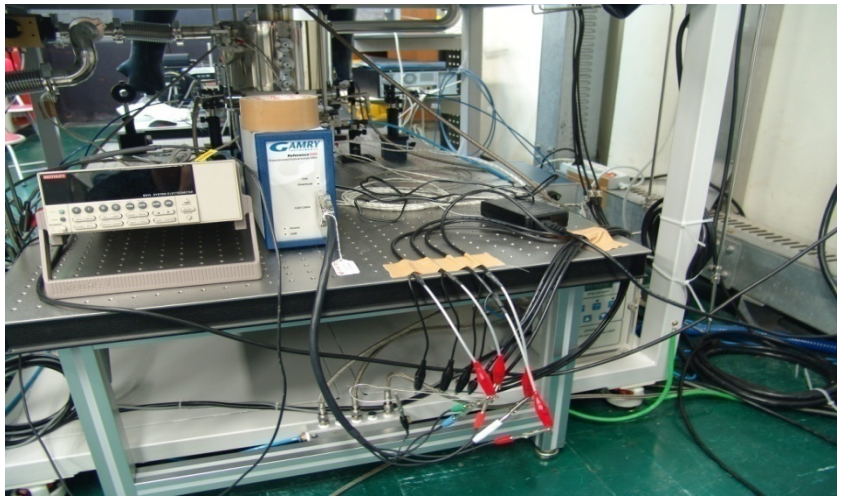
$NdCl_3$ (0.25 wt.%)



Electrochemical Measurement in Molten Salts



GAMRY Reference 600 Potentiostat/Gavanostat/ZRA

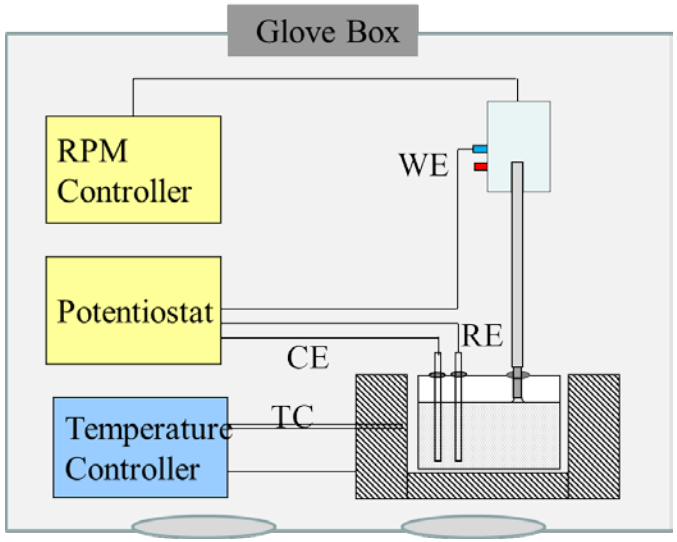


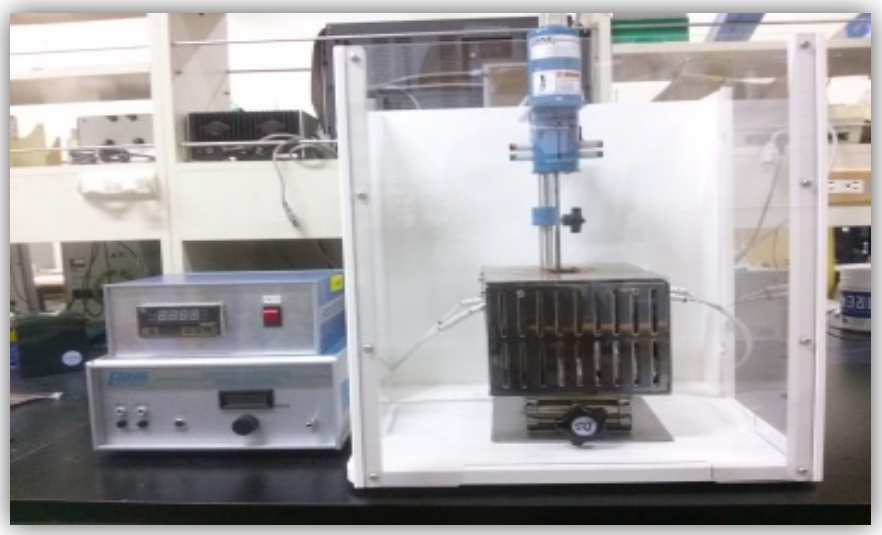
Autolab Potentiostat/Gavanostat

- **WE : Tungsten or GC**
- **CE : GC**

  pyrex tube (Ag|Ag+ in molten salt)
- **RE : pyrex tube (Ag|Ag^+ in molten salt)**

Rotating disk electrode system in Molten Salts





Levich Equation

$$i_L = 0.62\, nF\, A D_0^{2/3} \omega^{1/2} \nu^{-1/6} C_0$$

Tafel Plot

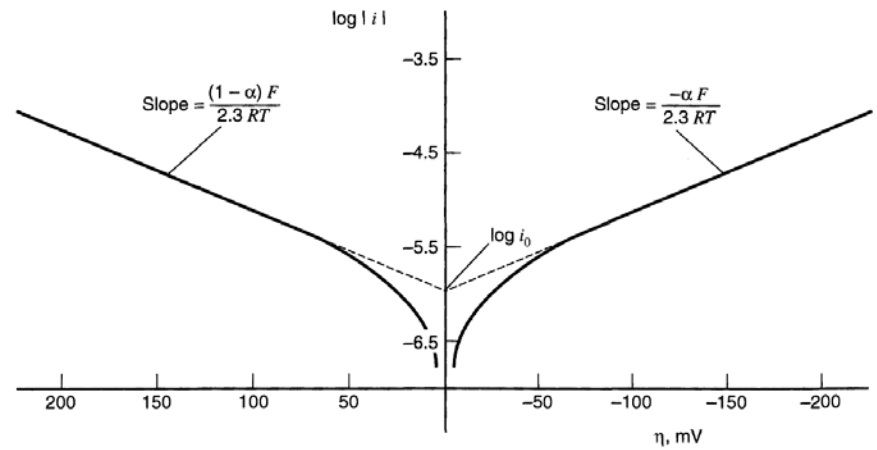
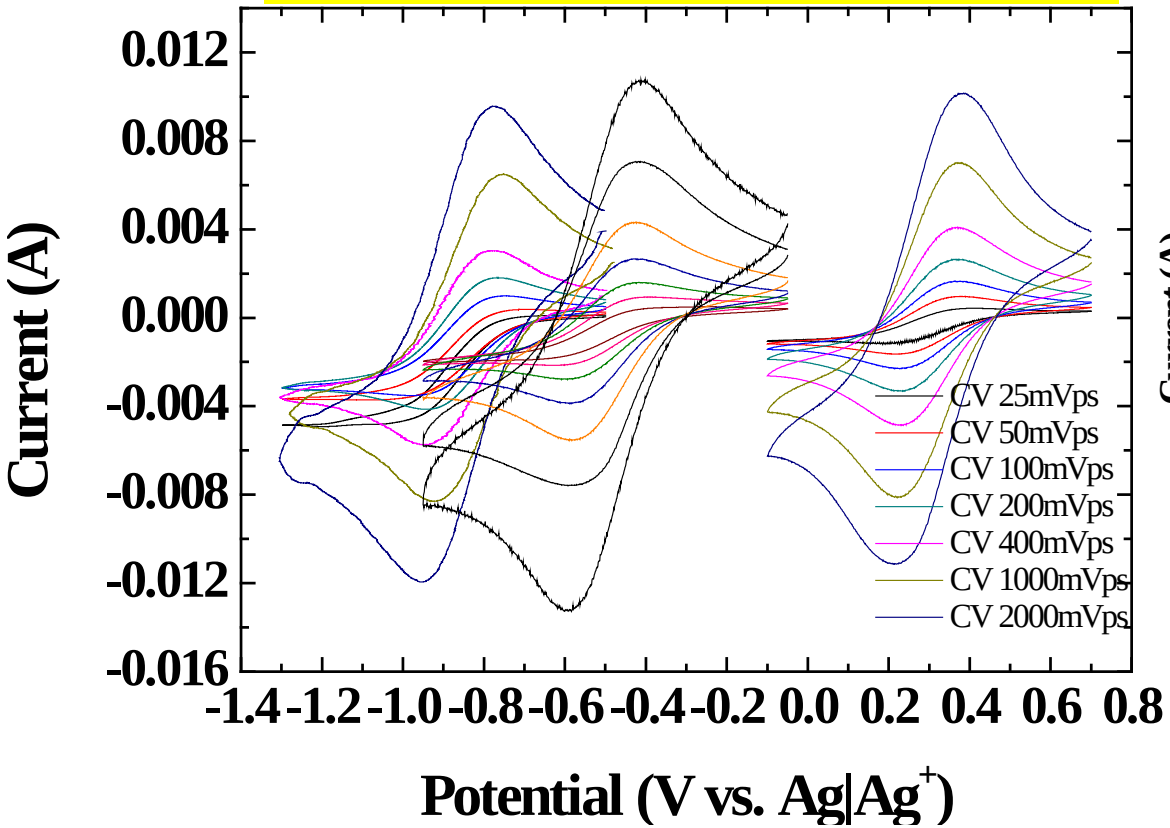
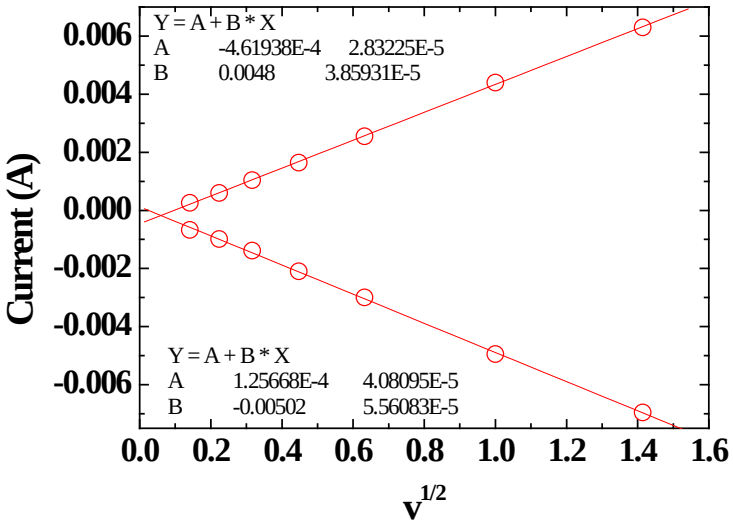


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftarrows R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm^2.

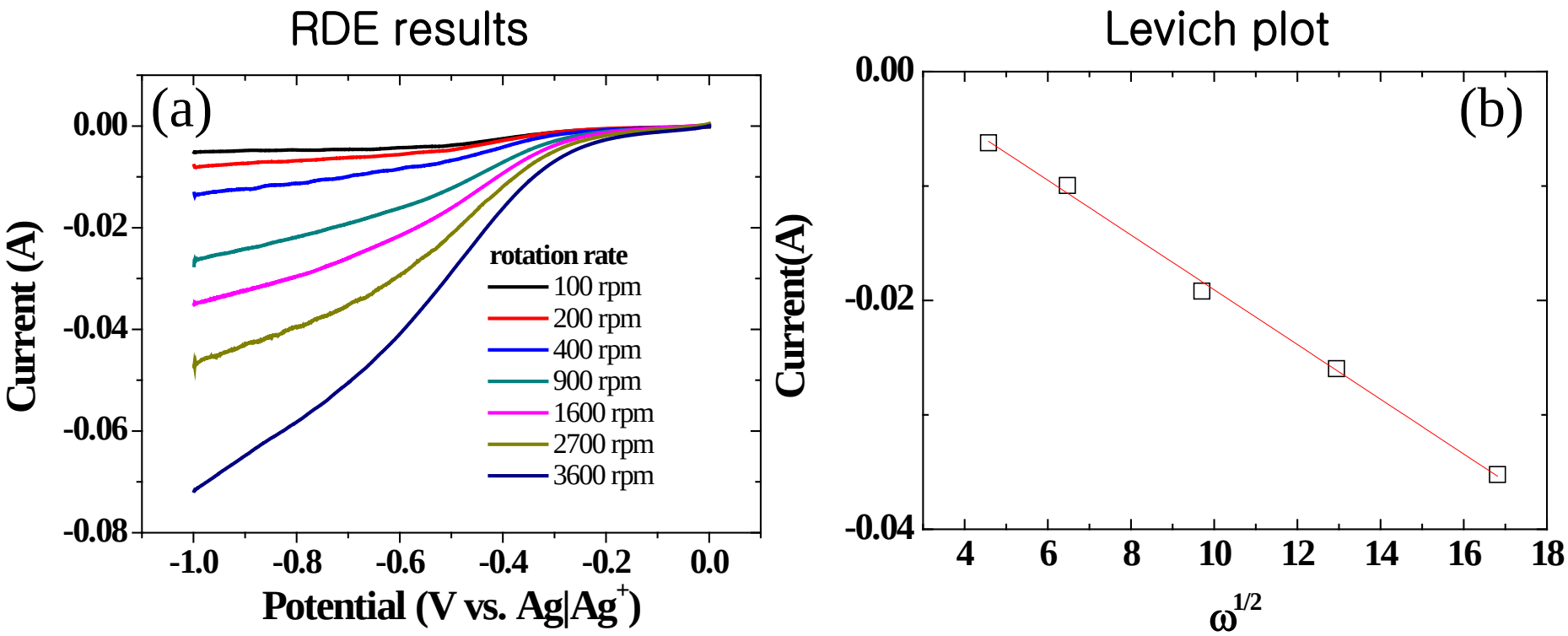
Scan rate dependences of CV

$Sm^{2+/3+}$, $Yb^{2+/3+}$, $Eu^{2+/3+}$





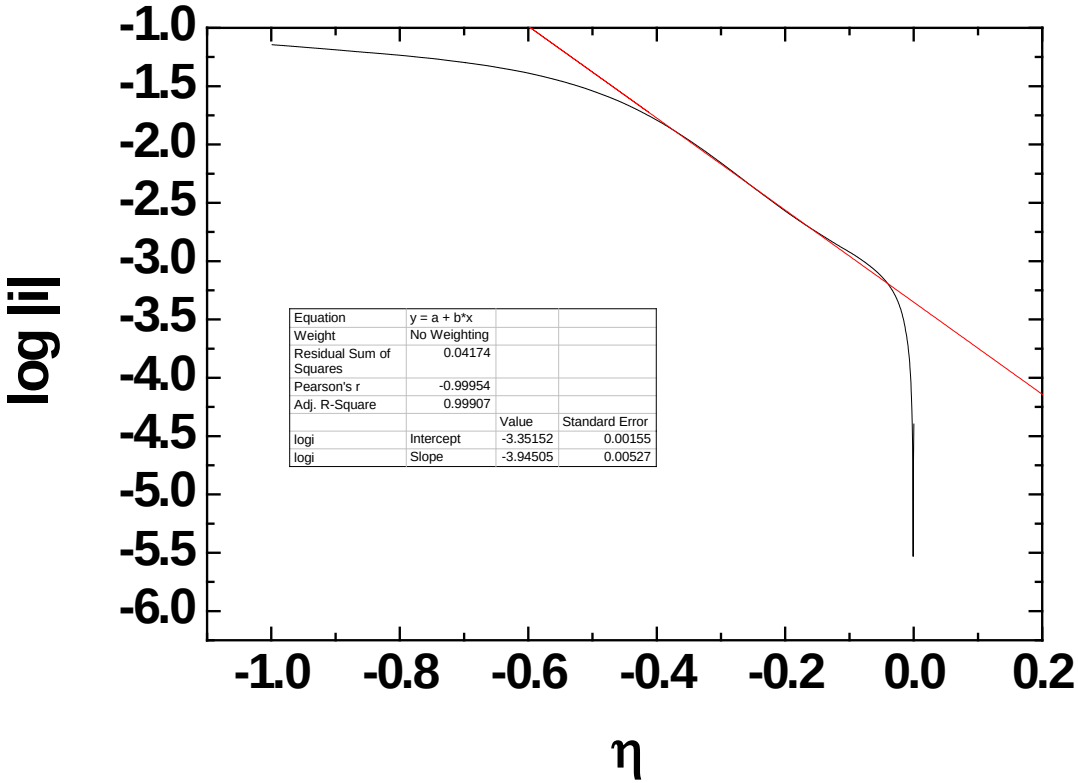
Results : RDE results of $YbCl_3$



$$i_L = 0.62 nFAD_0^{2/3} \omega^{1/2} \nu^{-1/6} C_0$$

D_0=3.60E-05 cm^2 s^{-1}

Results : Tafel Plot for $YbCl_3$



	Value	Standard Error
Intercept	−3.35152	0.00155
Slope	−3.94505	0.00527

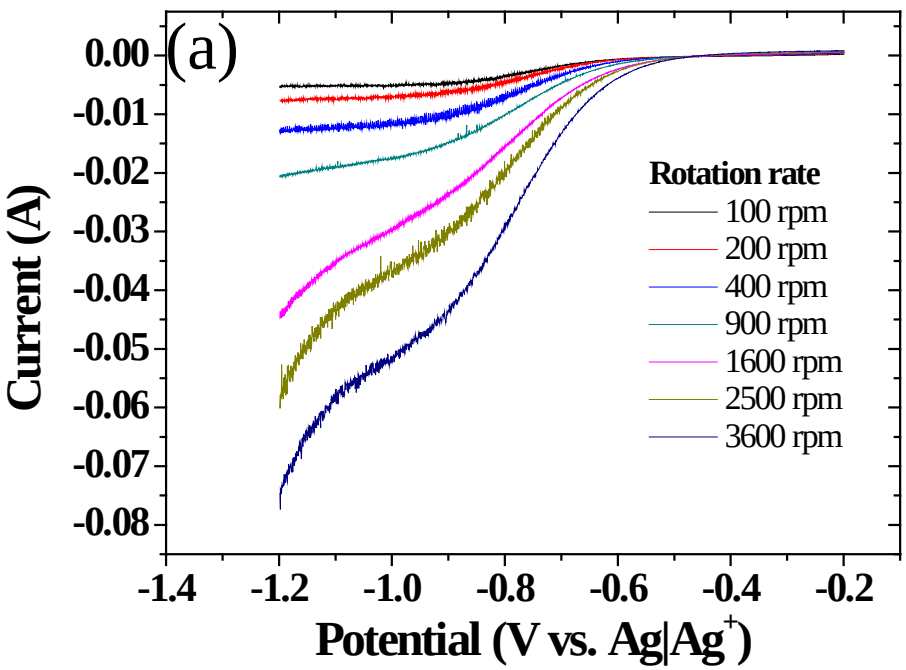
Slope = $-\alpha F/2.3RT$

$\alpha = 0.60$

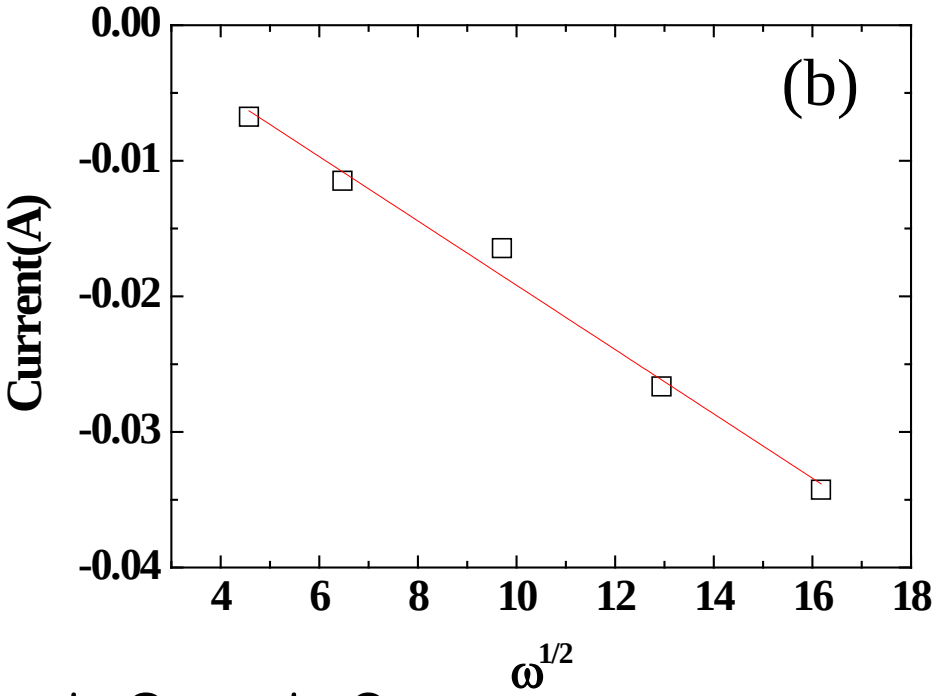
$i_0 = 1.59\ E{-3}\ A/cm^2$

Results : RDE results of $SmCl_3$

RDE results



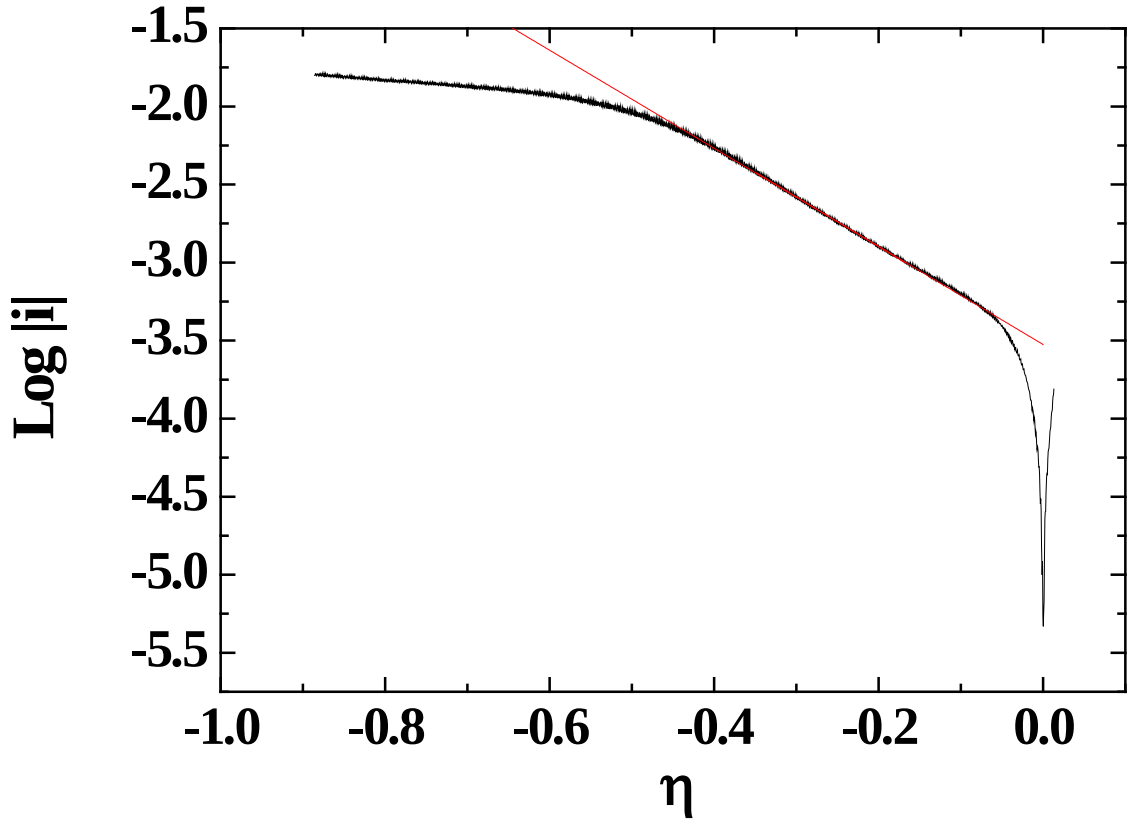
Levich plot



$$i_L = 0.62 nFAD_0^{2/3} \omega^{1/2} \nu^{-1/6} C_0$$

D_0=3.02E-05 cm^2 s^{-1}

Results : Tafel Plot for $SmCl_3$



	Value	Standard Error
Intercept	−3.53544	0.00246
Slope	−3.18667	0.00933

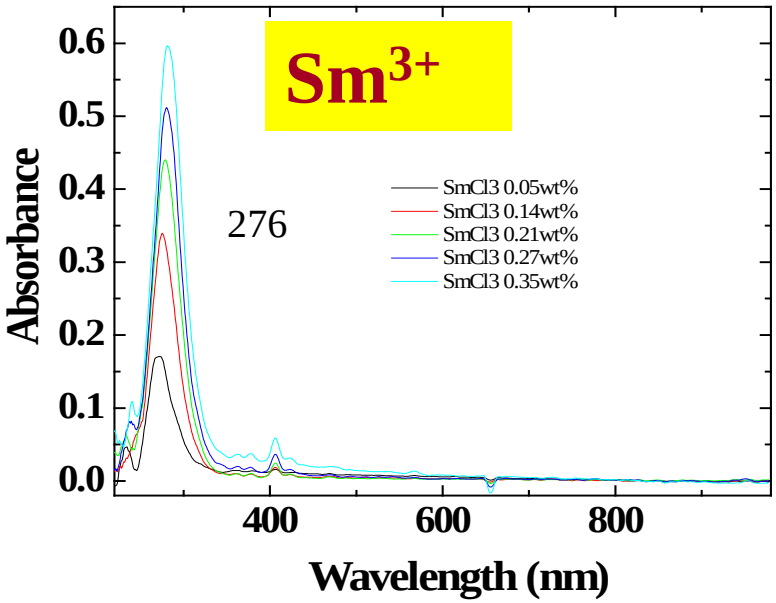
Slope = $-\alpha F/2.3RT$

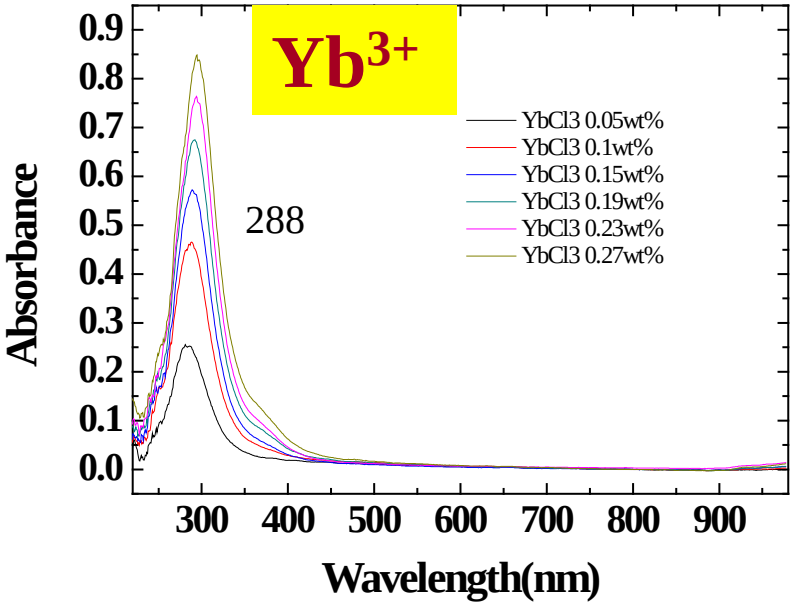
$\alpha = 0.49$

$i_0 = 1.03\ E{-3}\ A/cm^2$

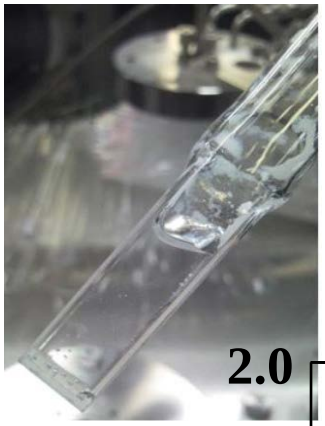
Results : UV-Vis Absorption spectra of LNs

Concentration dependence of spectra

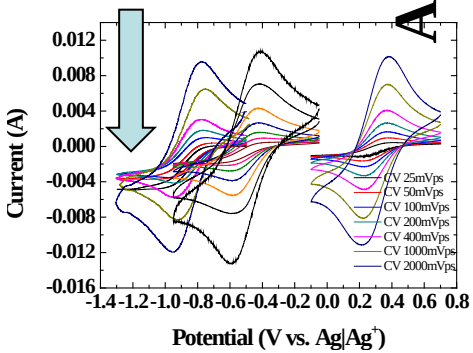


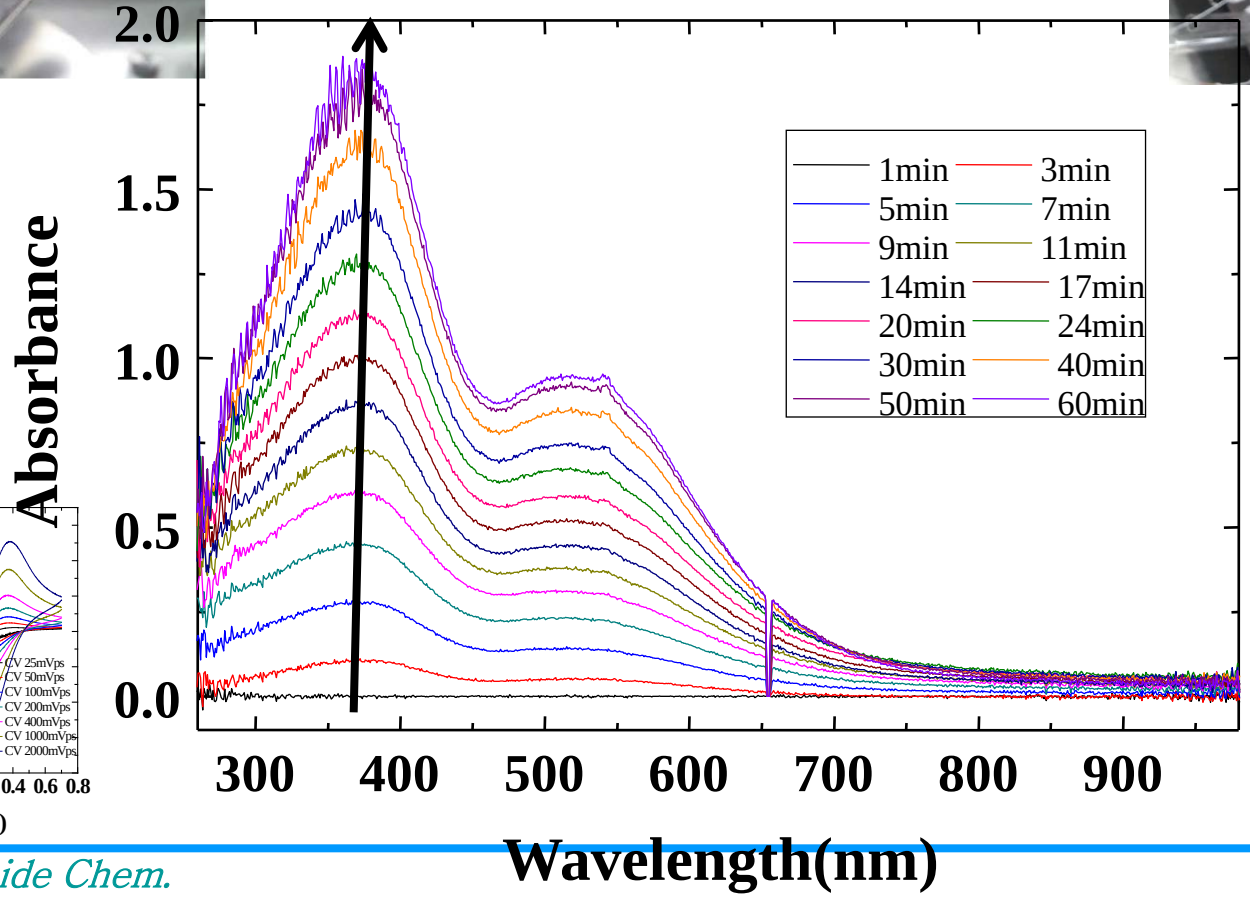


Results : Potential dependence(-1.2V) of Sm^{3+}



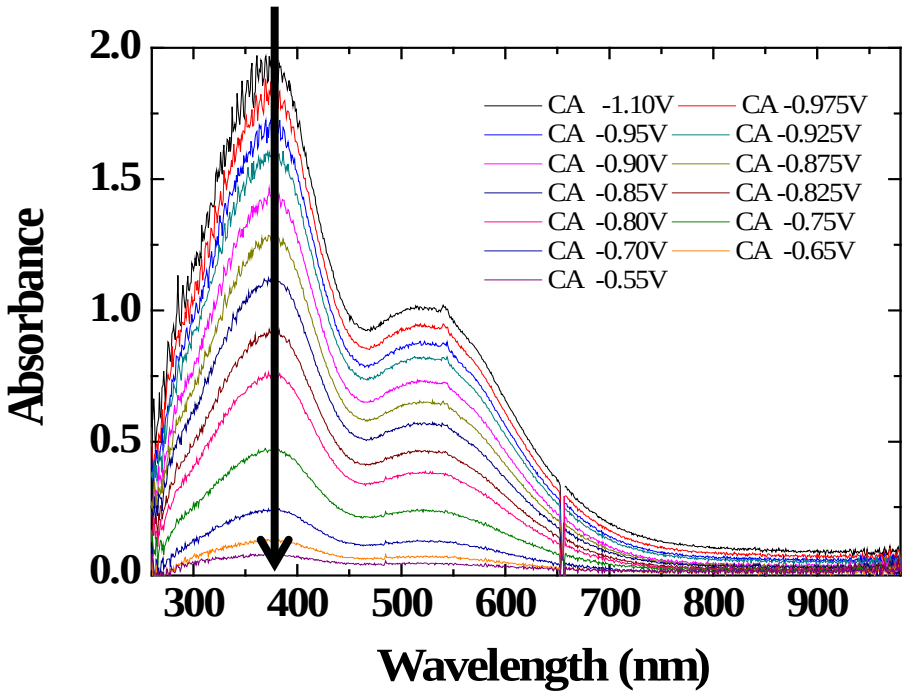
$$Sm^{3+} + e^- \rightarrow Sm^{2+}$$

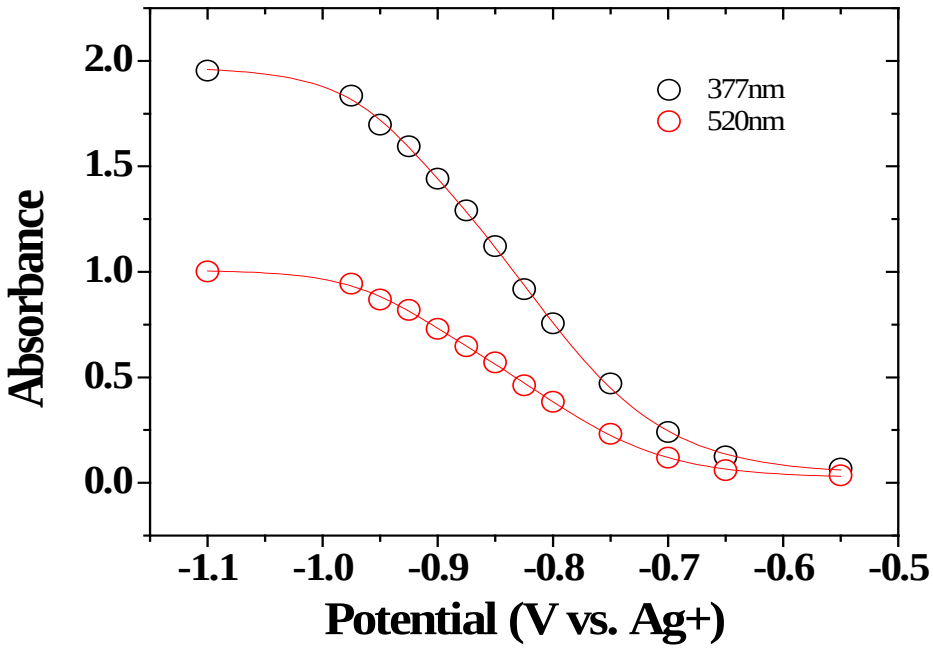




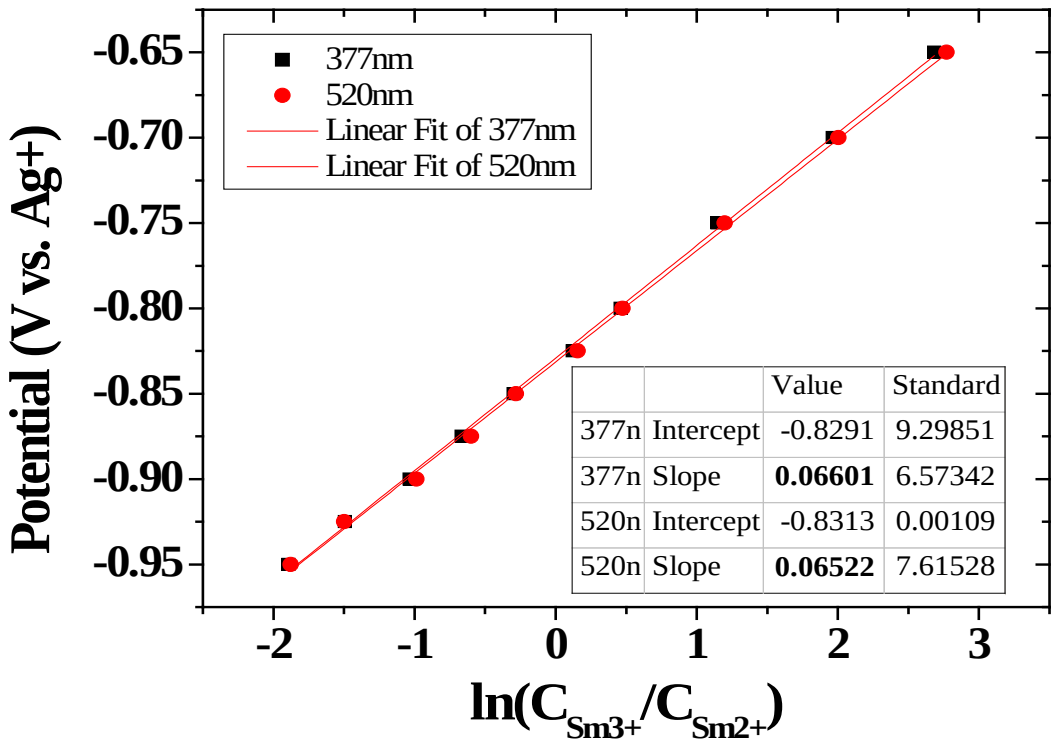
Results : Potential dependence of Sm^{3+}

$$Sm^{3+} + e^- \leftarrow Sm^{2+}$$





Results : Formal Potential of Sm^{3+}



		Value	Standard
377n	Intercept	-0.8291	9.29851
377n	Slope	**0.06601**	6.57342
520n	Intercept	-0.8313	0.00109
520n	Slope	**0.06522**	7.61528

$$E = E^{0'} + \frac{RT}{nF}\ln\left(\frac{[O]}{[R]}\right)$$

$$\frac{RT}{nF} : Slope(ideal = 0.061)$$

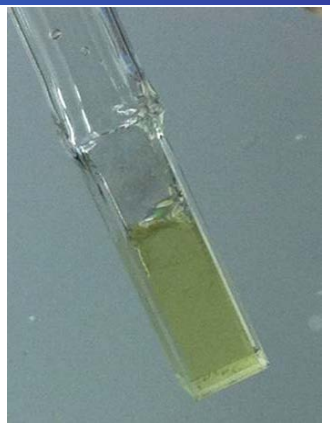
$$\rightarrow \boxed{n = 1}$$

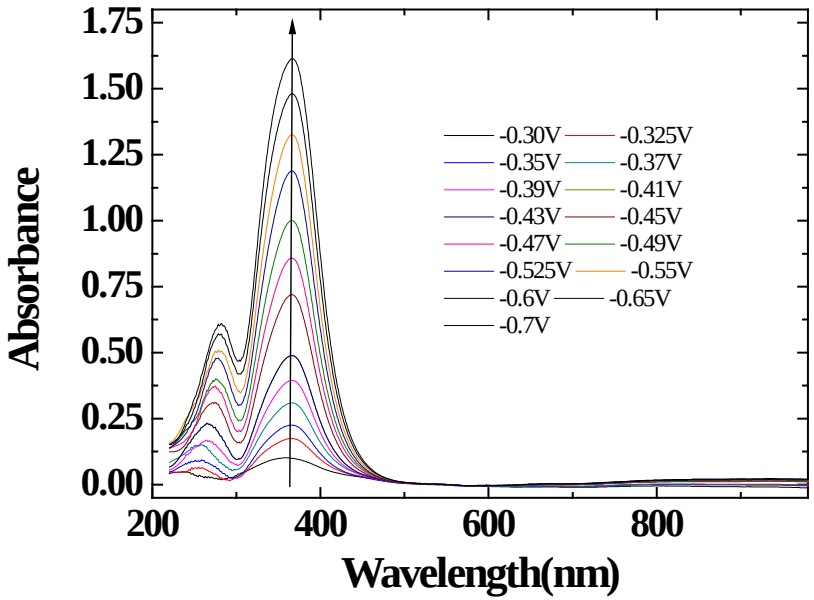
$$E^{0'}(\text{intercept}) = -0.83V$$

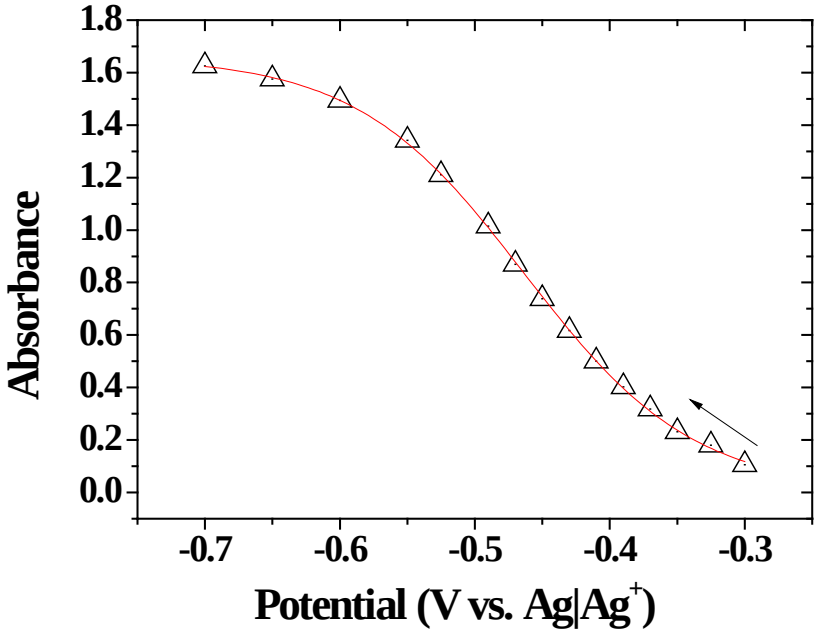
	Formal potential (V vs. Ag|Ag+)
$Sm^{2+/3+}$	-0.83

Results : Potential dependence of Yb^{3+}

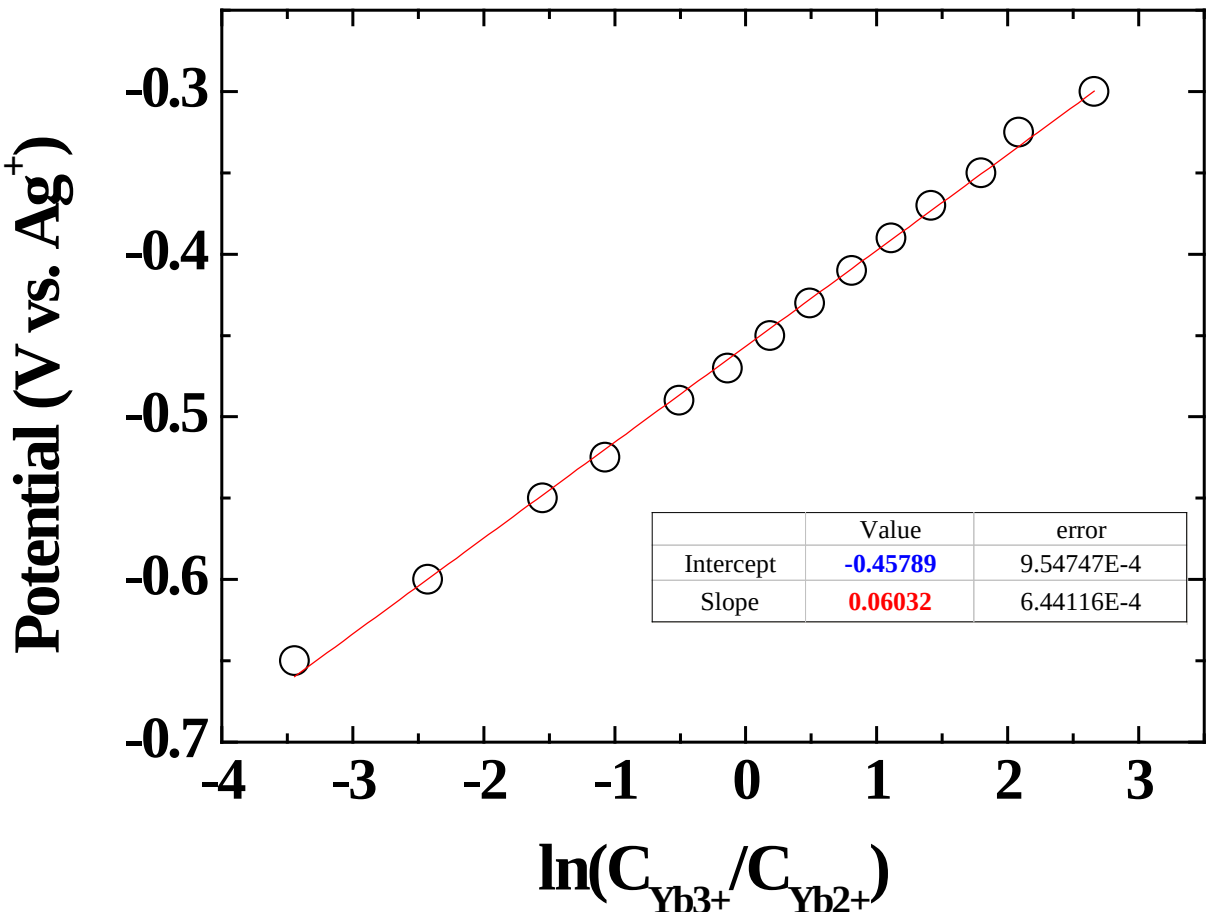
$$Yb^{3+} + e^{-} \rightarrow Yb^{2+}$$







Results : Formal Potential of $Yb^{2+/3+}$



$$E = E^{0'} + \frac{RT}{nF}\ln\left(\frac{[O]}{[R]}\right)$$

$$\frac{RT}{nF} : Slope(ideal = 0.061)$$

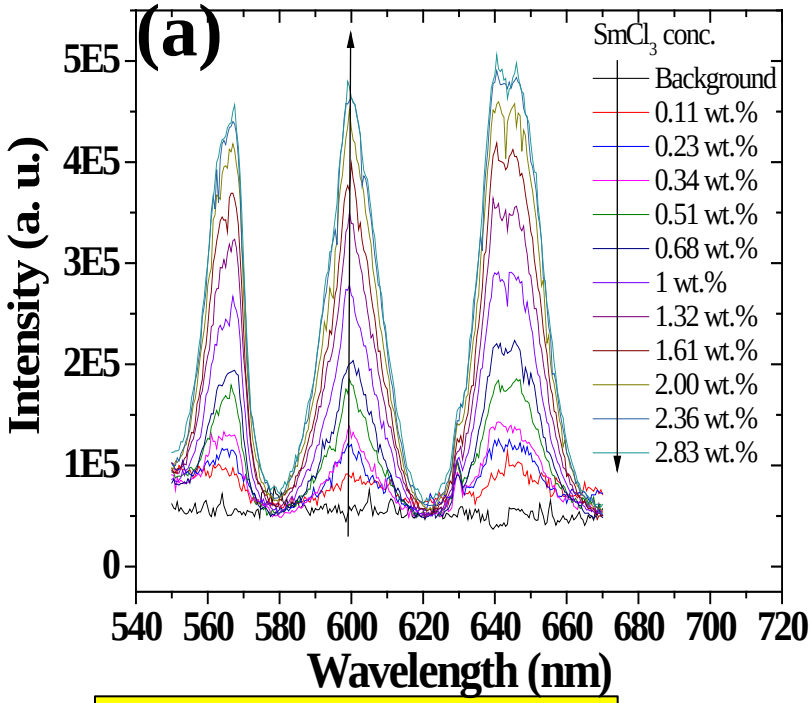
$$\rightarrow \; n = 1$$

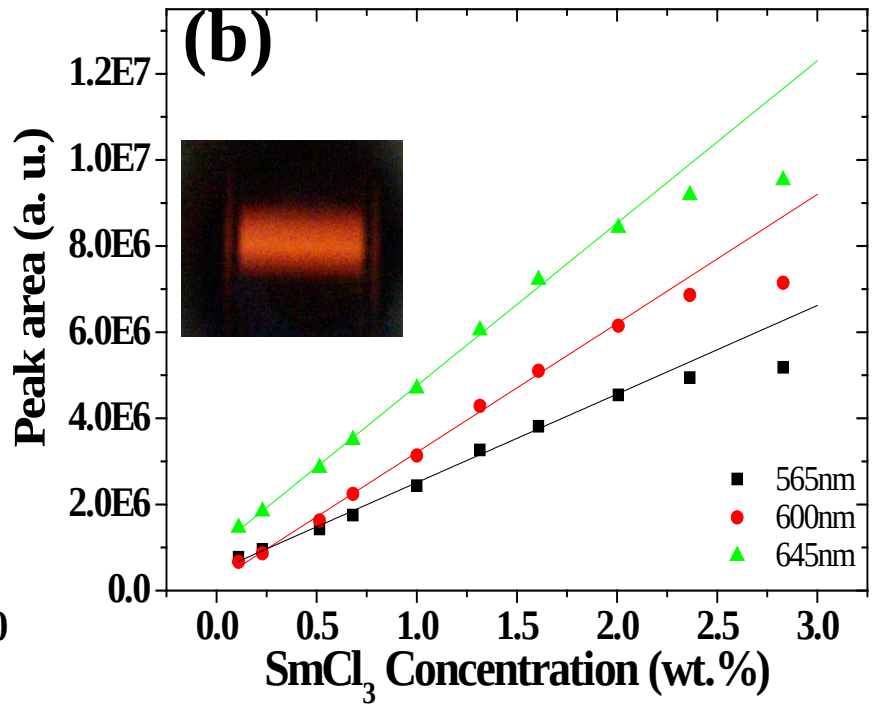
$$E^{0'}(\text{intercept}) = -0.458V$$

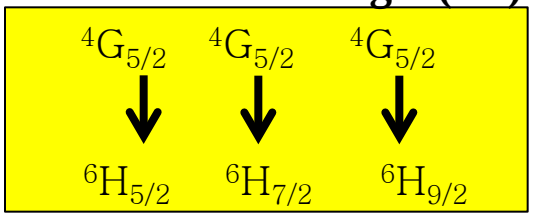
	Formal potential (V vs. Ag|Ag+)
$Sm^{2+/3+}$	-0.83
$Yb^{2+/3+}$	-0.458

Results: Laser induced luminescence spectra

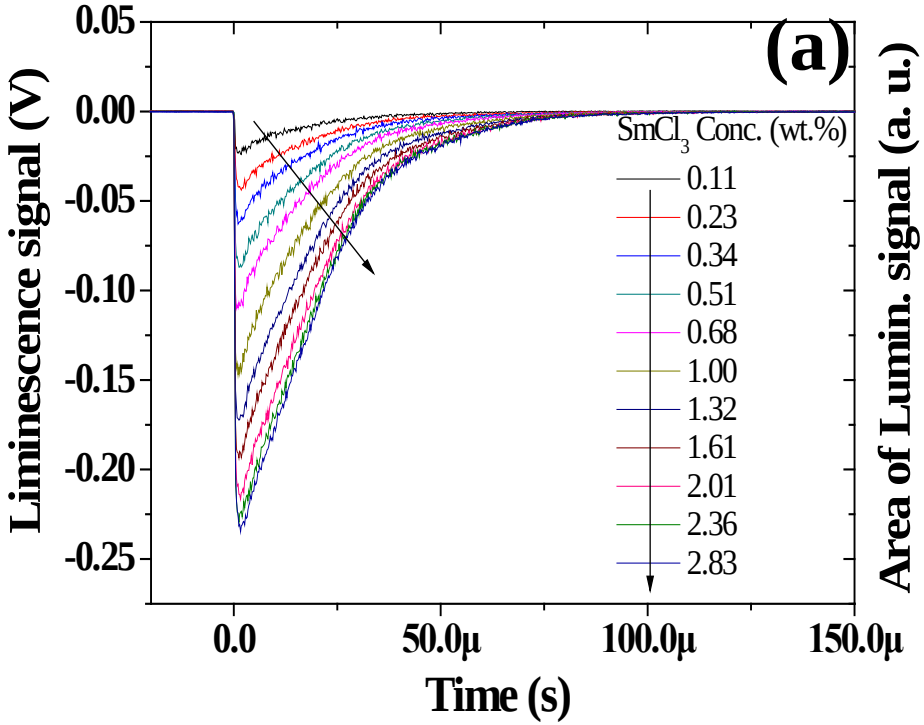
Concentration dependence of Sm^{3+}

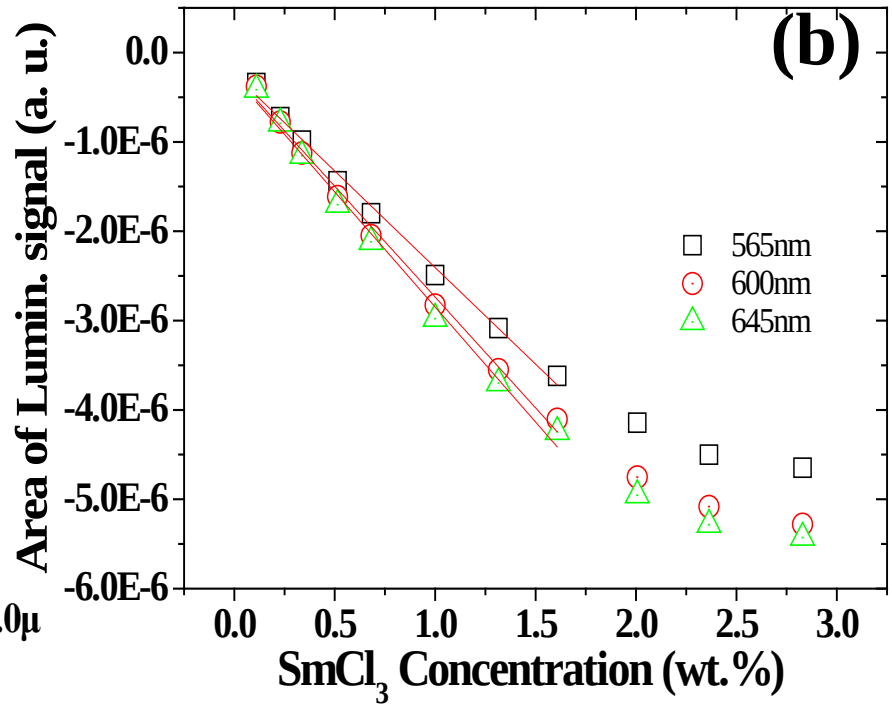






Concentration dependence of Sm^{3+}





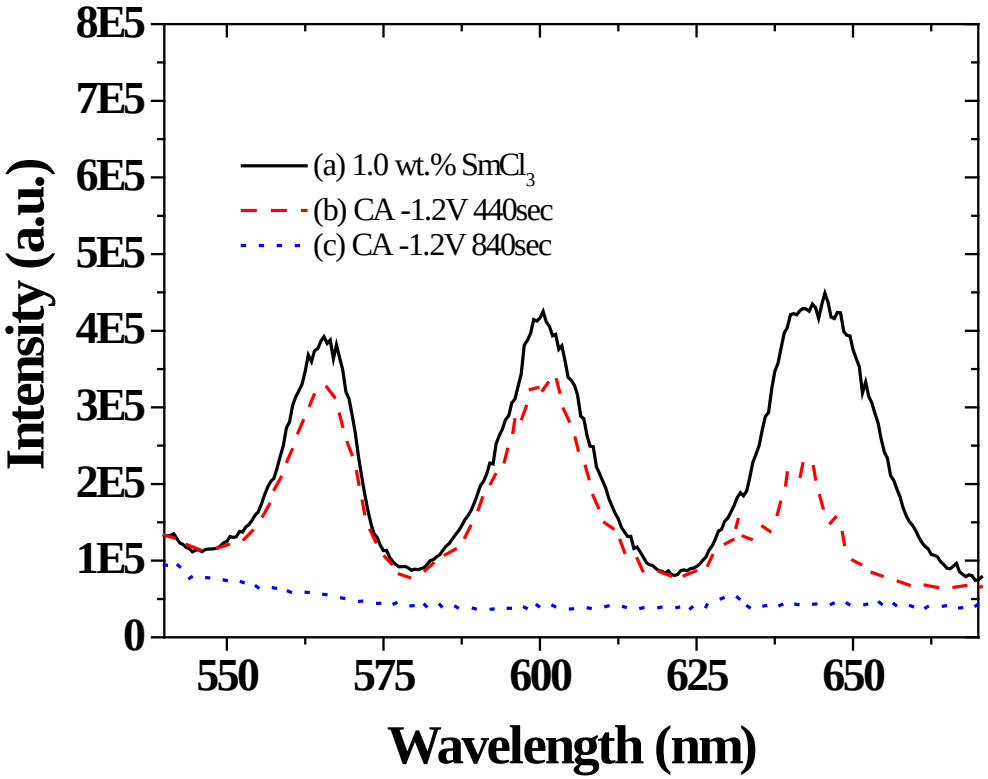
$$I = I_0 + A_1 \exp(-t/\tau_1)$$

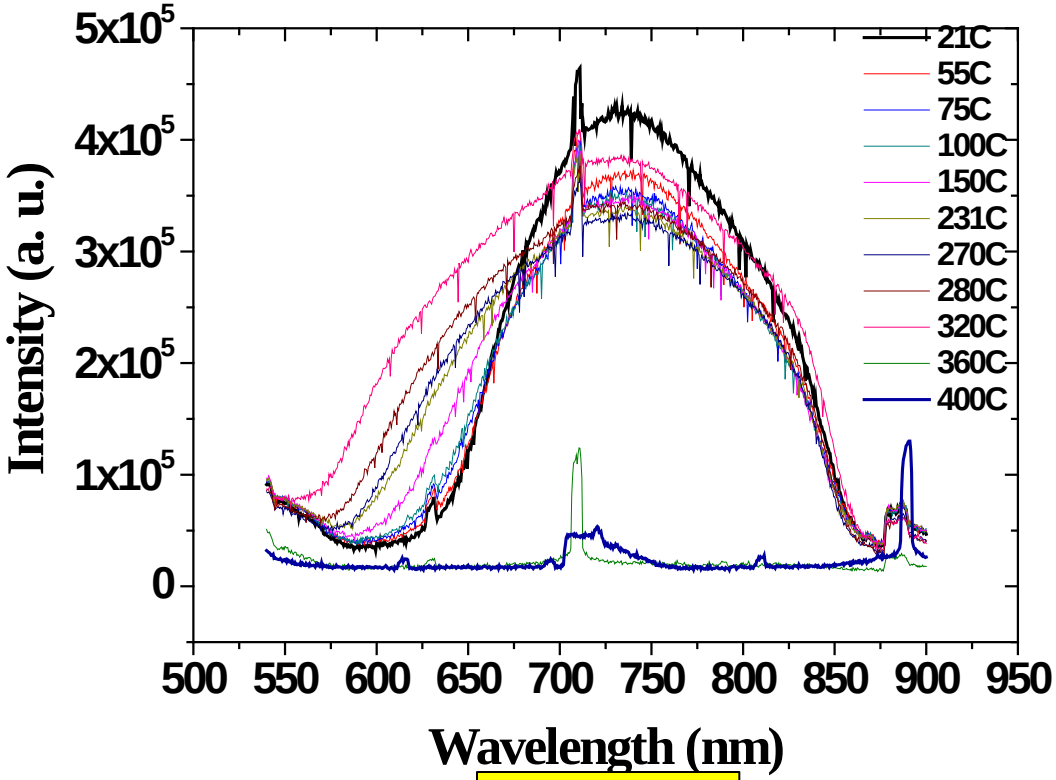
I: Luminescence intensity, A_1: constant, τ_1: life time

Wavelength (nm)	Life time (μs)
565	18.76
600	18.92
645	19.56

Results: Laser induced luminescence spectra

Potential dependence of Sm luminescence





$^5D_0$ $^5D_1$

↓

$^7H_{J,\ J=0\sim6}$

Conclusions

- **Spectro-electrochemical techniques have been employed to investigate the behaviors of LN ions in LiCl-KCl melt.**
- **Electrochemical results showed that the electrochemical reactions of LN ions are limited by the diffusion rate of each ion in LiCl-KCl melt. The diffusion coefficients, electron transfer coefficients, and exchange current densities were measured from RDE results.**
- **Formal potentials of LN ions were measured using electrochemical as well as spectro-electrochemical techniques. It was found that the electrochemical behavior of LN ions in LiCl-KCl melt obeys Nernst equation.**
- **It was also shown that the intensity of laser induced luminescence is proportional to the concentration of the trivalent cation in the melt.**

Thank you for your attention

Acknowledgment

This work was supported under the mid- and long-term nuclear research and development program of the Korean Ministry of Education, Science and Technology.