

Optical Cooling: Material Synthesis, SEM & XRD Analysis, & Fluorescence Thermometry

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Abstract

Optical cooling is the process in which the sequential absorption of two or more photons leads to the emission of light at a shorter average wavelength than the excitation wavelength. This produces a net loss of heat energy in the material. This process allows solid-state refrigeration in a robust and predictable package, without the need for moving parts or refrigerant products - revolutionizing many areas of science such as micro-processing or space-equipment design, where size and vibration is an issue. However, the materials that promote this effect and their respective growth procedures are not well defined. It is known that trivalent ytterbium, Yb^{3+} , successfully fluoresces when doped into crystalline substances. Rigorous synthesis methods are sought after to allow for consistent reproduction of Yb^{3+} doped materials.

Objectives

- Define growth techniques (hydrothermal, co-precipitation, solution) for Yb:YAG, Yb:YLiF, and certain morphologies of CaCO_3 .
- Test growths using x-ray diffraction and scanning-electron microscopy.
- Measure the ratio of Yb^{3+} fluorescence in YAG for two different transitions.
- Characterize the response of Yb:YAG to up-conversion processes.

Growth Methods

Yb:YAG Co-Precipitation Procedure

Titrant: 300mL *HPLC* + 23.7g $(\text{NH}_4)\text{HCO}_3$

Titrand: 250mL *HPLC* + 14.22g $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 0.754g $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ + 23.44g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

1. Titrant solution is titrated into titrand solution at $8\frac{\text{mL}}{\text{min}}$ while stirring.
2. Centrifuge natant solution off, rinse with H_2O twice, then Ethanol.
3. Dry in vacuum and on hotplate, then in furnace at 300°C for 3 hours.
4. Split into two equal amounts, add 10% LiCO_3 to one batch.
5. Grind in mortar and pestle until fine powder is formed.
6. Filter through $25\mu\text{m}$ mesh. Crystallize at 1300°C for 12 hours.
7. Repeat crystallization with additional LiCO_3 and precursor YAG powder.

Yb:YLiF Hydrothermal Procedure

Solution A: 7.04mL of 0.1M $\text{Y}(\text{NO}_3)_3$ 0.8mL of 0.5M $\text{Yb}(\text{NO}_3)_3$ 1.17g *EDTA* in 5mL H_2O Combine above chemicals on hotplate at 70°C while stirring.

Solution B: 0.21g *LiF* 0.68g NH_4HF_2 Combine above chemicals with 7mL H_2O on hotplate at 70°C while stirring.

1. Mix A and B together while stirring. Transfer to Teflon-lined autoclave.
2. Heat at 220°C for 72 hours.
3. Wash resulting black powder thoroughly with *Ethanol* and *DI-H}_2\text{O}.*
4. Calcine in furnace at 300°C for 5 hours.

Eu:CaCO₃ Solution Procedure

Combine: $\text{CaCl}_2 \rightarrow 5\text{mL of } 0.1\text{M} + \text{MgSO}_4 \rightarrow 1.5\text{mL of } 0.1\text{M} + \text{RE} : (\text{NO}_3)_3 \rightarrow 0.1\text{mL of } 0.5\text{M} + \text{NaCl} \rightarrow 0.1\text{mL of } 0.5\text{M} + \text{K}_2\text{CO}_3 \rightarrow 0.5\text{mL of } 0.1\text{M}$

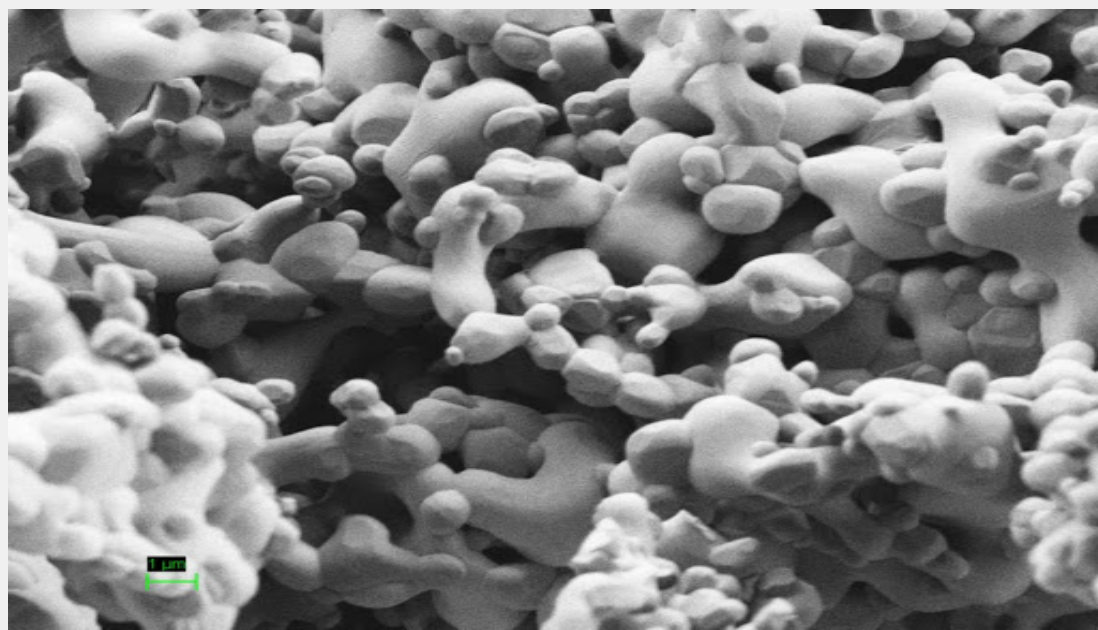
1. Strongly agitate the solution for 5-10 minutes, until minimum turbidity.
2. Centrifuge off natant solution. Rinse and centrifuge twice with *DI-H}_2\text{O}* and *Ethanol*.
3. Dry in furnace at 300°C for 30 minutes.

Scanning Electron Microscopy

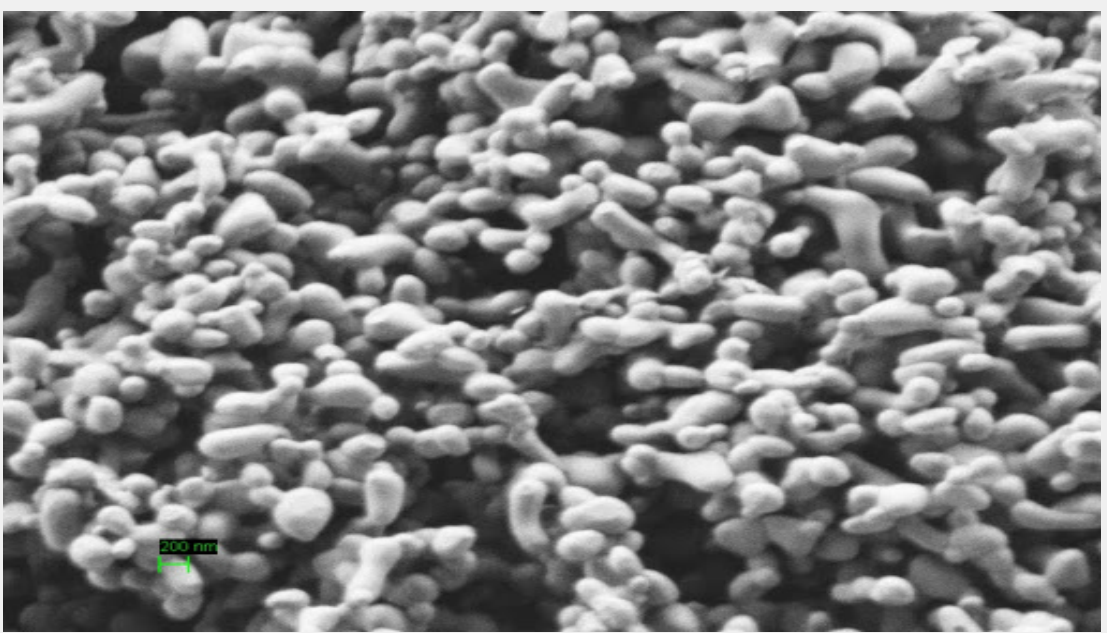
Yb:YAG



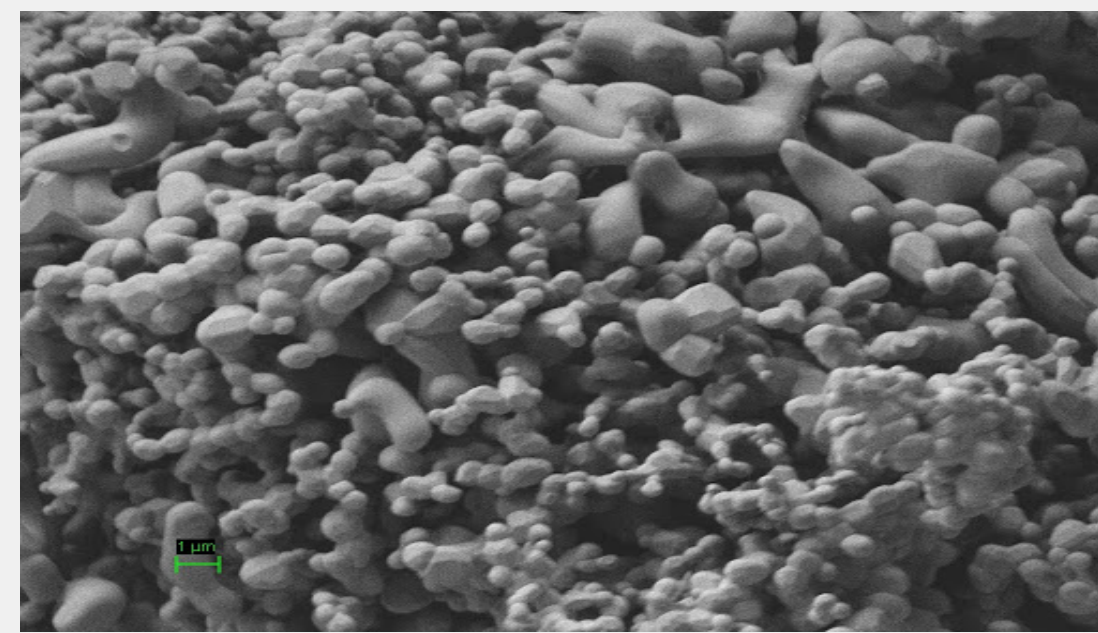
(a) 49310x magnification of Yb:YAG.



(b) 15720x magnification of Yb:YAG + LiCO_3 .



(c) 48800x magnification of Yb:YAG + precursor.

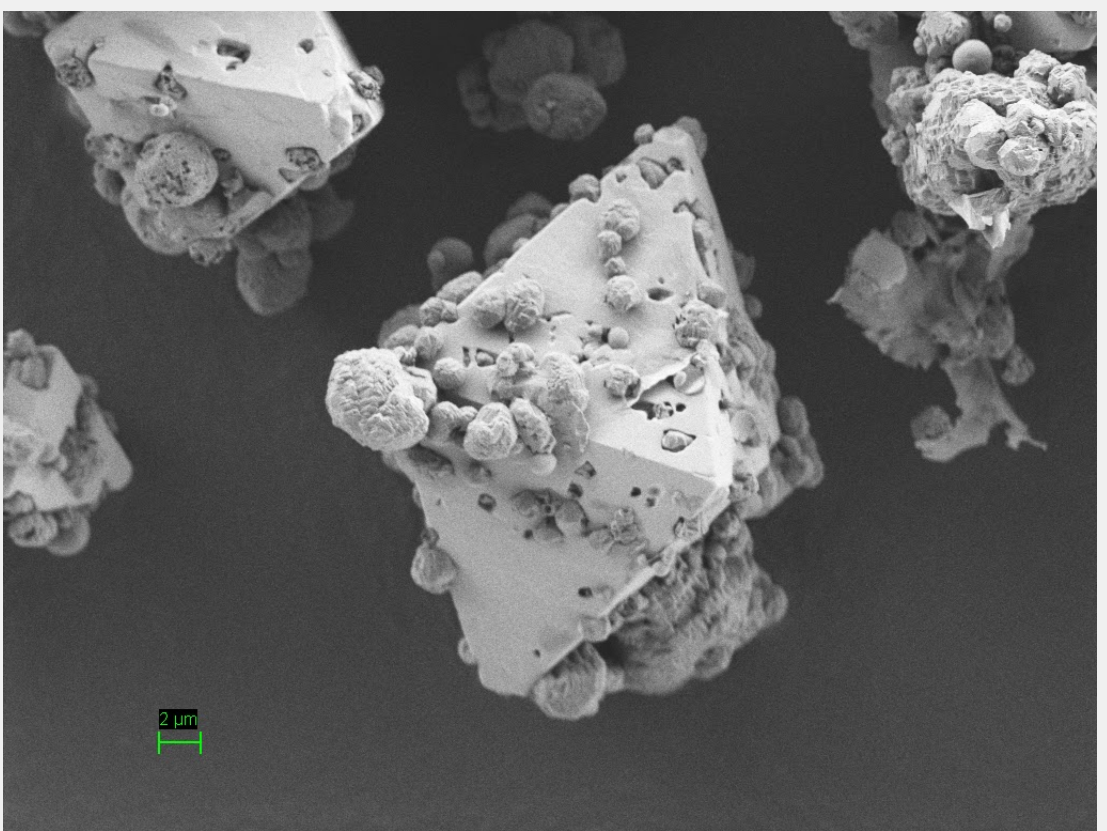


(d) 14840x magnification of Yb:YAG + LiCO_3 + precursor.

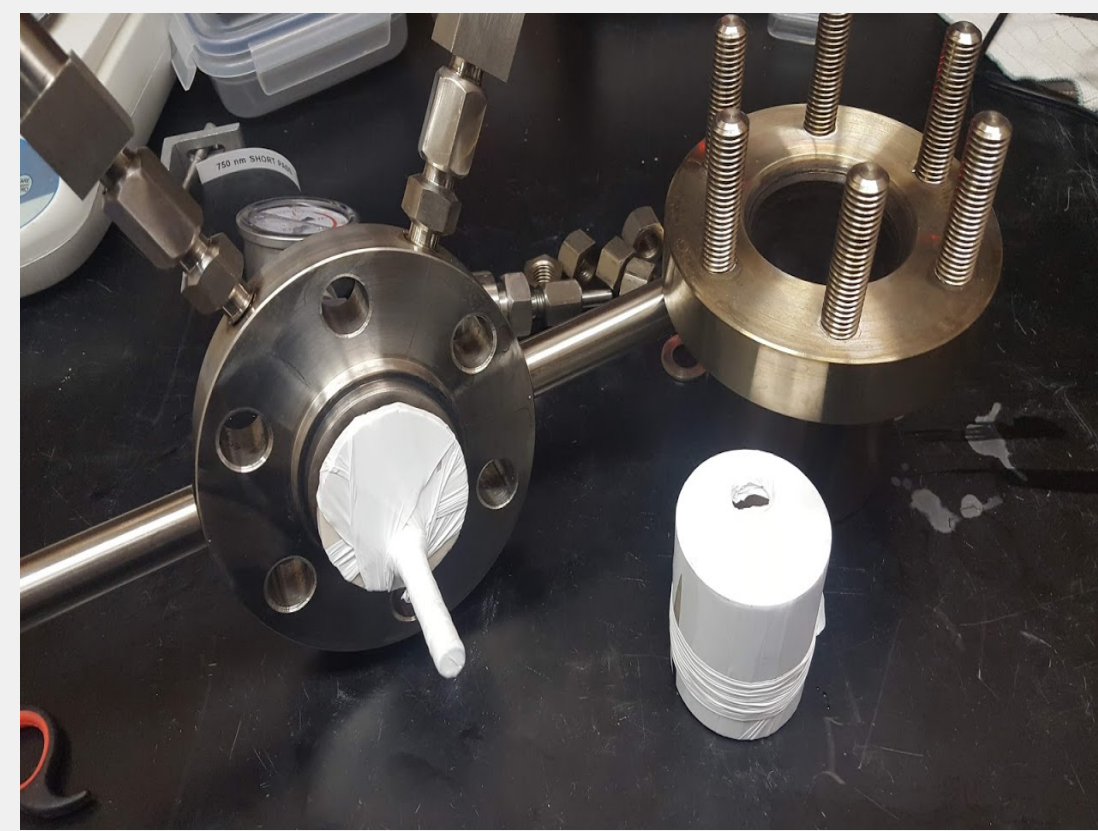
Figure: Yb:YAG Co-Precipitation Growths.

- Subfigure (a): Conglomerates of small crystals.
- Subfigure (b): Larger crystals. No change in separation.
- Subfigure (c): Increase in separation.
- Subfigure (d): Largest crystals with best levels of separation.

Yb:YLiF



(a) 7240x magnification of Yb:YLiF.

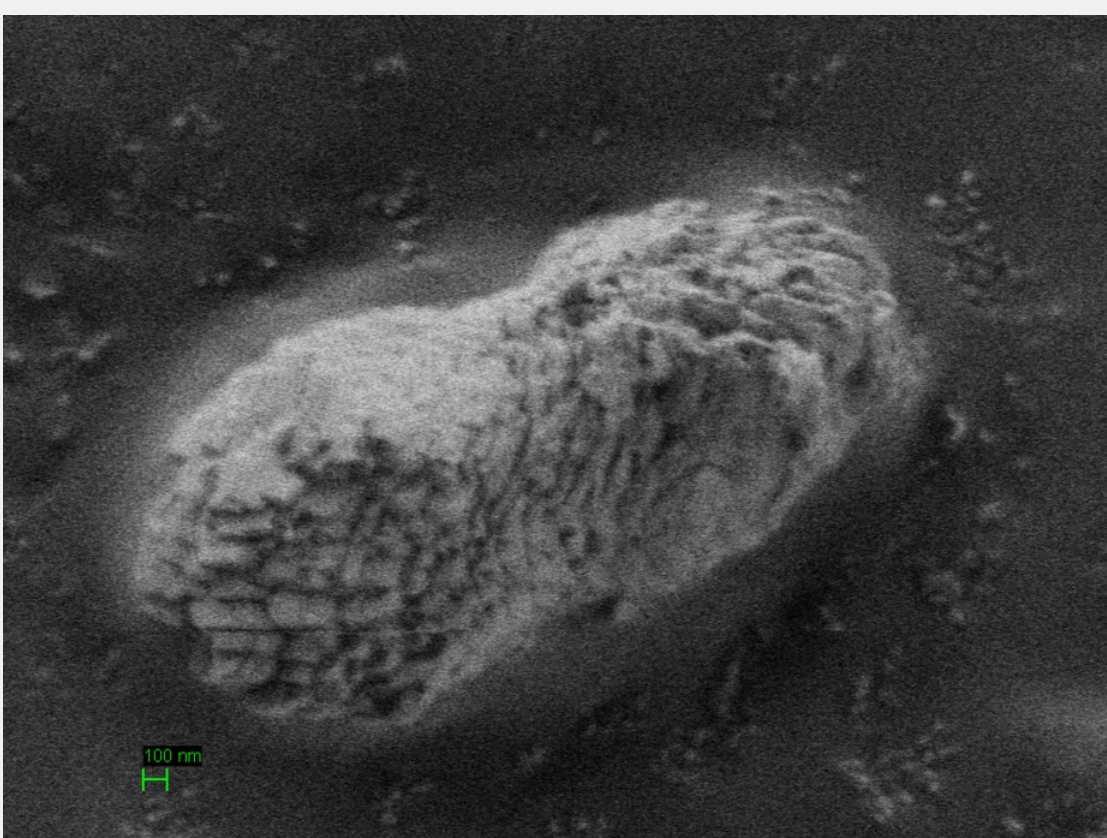


(b) Hydrothermal Growth System.

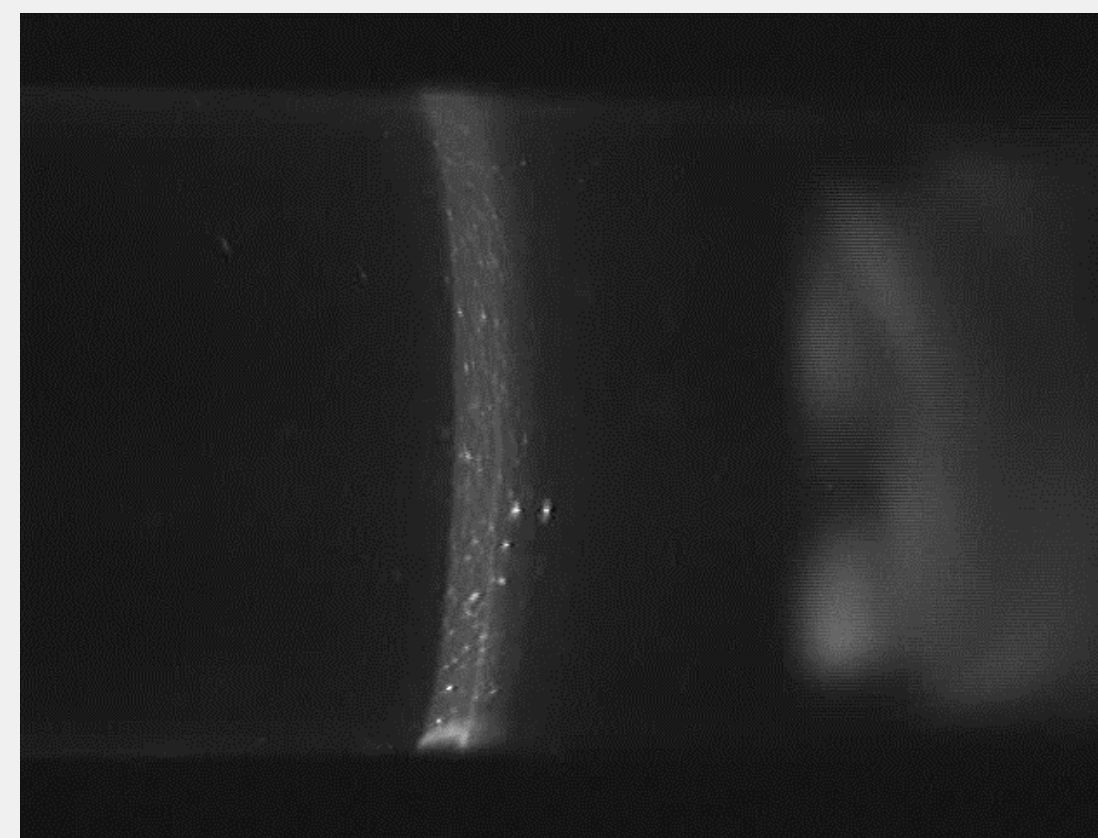
Figure: Yb:YLiF Growth and Hydrothermal System.

The YLiF single crystals grew to significant size and were almost always independent of one another. Organic contaminants are a product of the deterioration of teflon at 260°C .

Eu:CaCO₃



(a) 80820x magnification Eu:CaCO₃.



(b) Eu:CaCO₃ (in isopropanol) exposed to 405nm laser, recorded on CCD Camera with Red-Pass-Filter. 590nm fluorescence detected.

Figure: Eu:CaCO₃ Solution Growths and Fluorescence

The CaCO₃ growths were not single spherules, and thus were not of the vaterite polymorph. However, the CaCO₃ was successfully doped with europium.

Eu:CaCO₃ X-Ray Diffraction

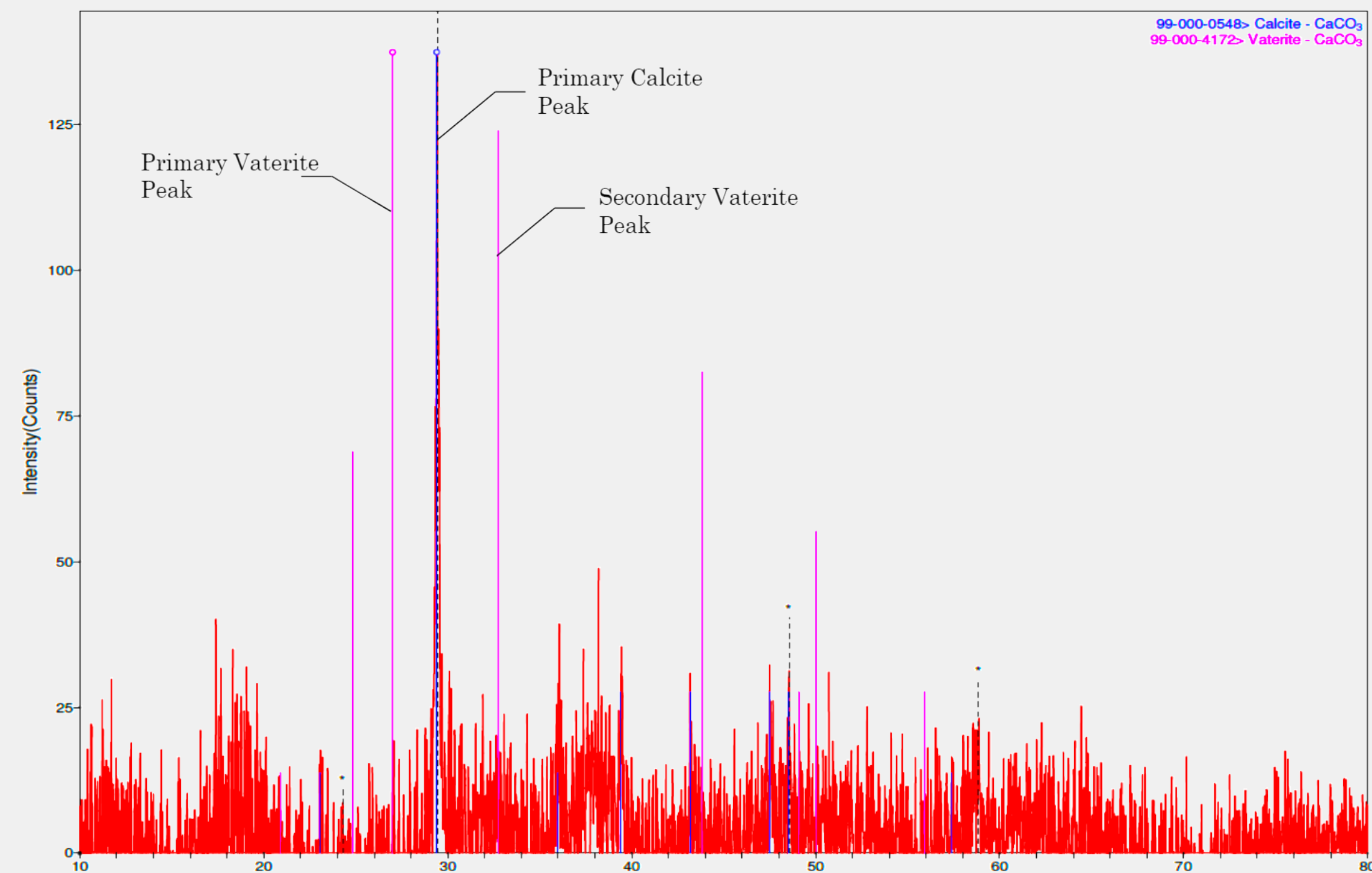
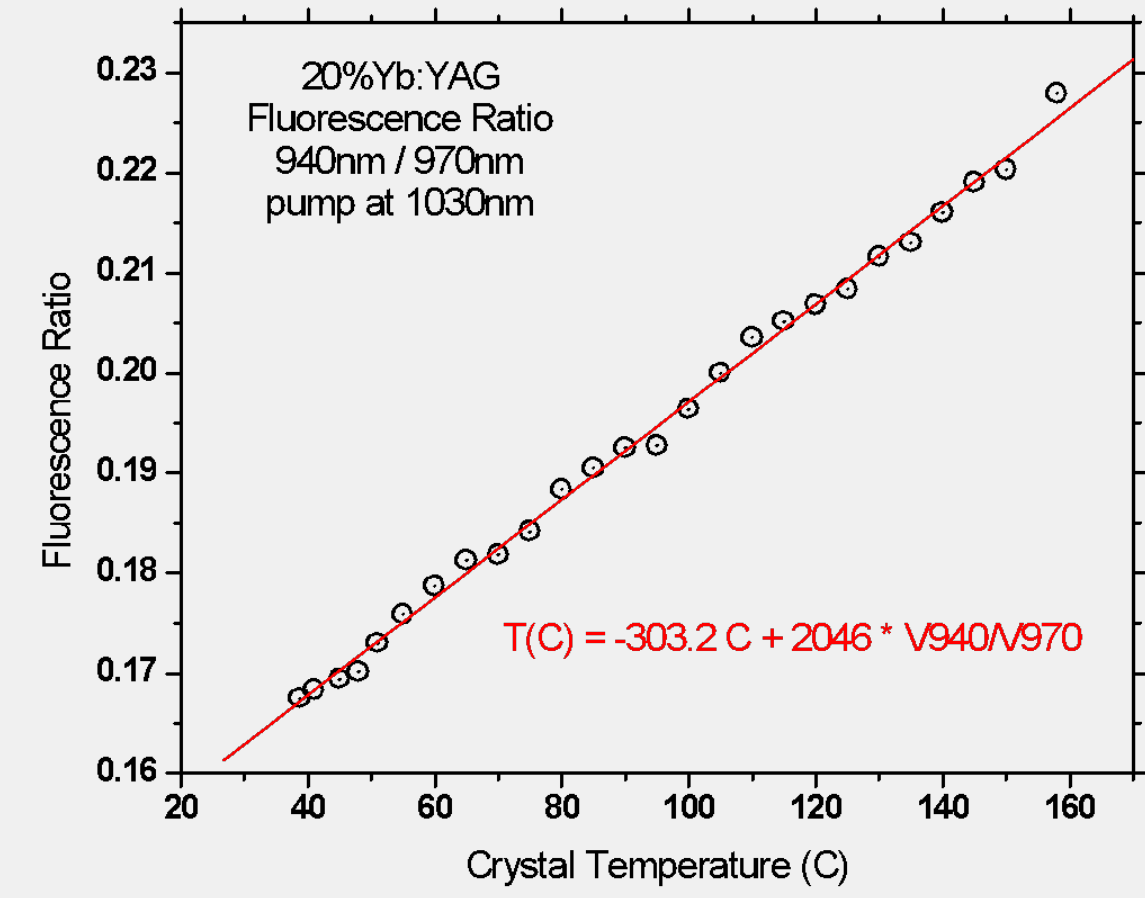


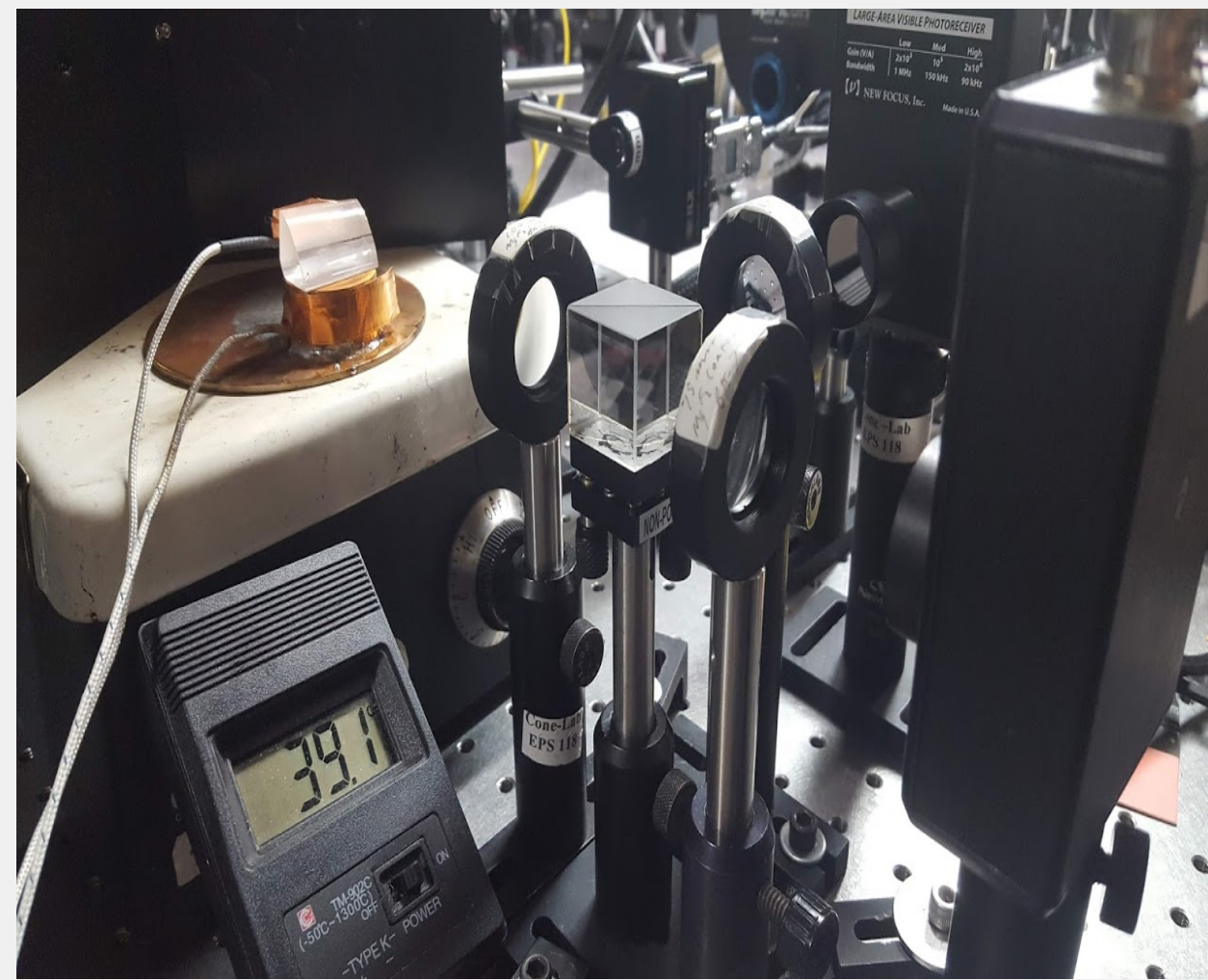
Figure: Eu:CaCO₃ XRD showing calcite morphology peak.

Eu:CaCO₃ XRD spectra aligned with calcite spectra. The metastable vaterite changed to calcite at some point during the growth procedure.

Yb:YAG Fluorescence Thermometry



(a) Response of Yb:YAG to up-conversion processes is characterized as linear at high temperatures (293K to 443K)



(b) Yb:YAG Fluorescence Thermometry Setup.

Figure: Yb:YAG Fluorescence Thermometry and Setup.

20% Yb:YAG crystal was mounted and the assembly was heated by a hotplate. Crystal temperature and fluorescence levels were recorded as the temperature of the assembly increased. The correlation was very strongly linear and of high resolution, allowing for the detection of temperature changes of a few degrees.

Conclusions

- The ratio of Yb^{3+} fluorescence for two different transitions, pumping at the 1030nm cooling transition and utilizing 10nm bandpass filters centered at 940nm and 970nm, was shown to behave linearly in a temperature range of 293K to 443K.
- The crystalline structure of the YLiF was nominal, however organic contaminants appeared to cling to the surface of the individual crystals.
- RE:Calcite, as opposed to RE:Vaterite, was grown. This morphology change can be attributed to the *DI-H}_2\text{O}* wash, which changes the metastable vaterite polymorph into the more stable calcite morphology.

Acknowledgements

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