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Synthesis and evaluation of ultra-pure, rare-earth doped glass for laser refrigeration

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ABSTRACT

Significant progress has been made in synthesizing and characterizing ultra-pure, rare-earth doped ZIBLAN (ZrF_4-InF_3-BaF_2-LaF_3-AlF_3-NaF) glass capable of laser refrigeration. The glass was produced from fluorides which were individually purified and subsequently treated with hydrofluoric gas at elevated temperatures to remove impurities before glass formation. Several Yb^{3+}-doped samples were studied with varying degrees of purity and composition with successive iterations producing an improved material. We have developed a non-invasive, spectroscopic technique, two band differential luminescence thermometry (TBDLT), to evaluate the intrinsic quality of the ytterbium doped ZIBLAN used for laser cooling experiments. TBDLT measures local temperature changes within an illuminated volume resulting solely from changes in the relative thermal population of the excited state levels. This TBDLT technique utilizes two commercially available band pass filters to select and integrate the "difference regions" of interest in the luminescence spectra. The goal is to determine the minimum temperature to which the ytterbium sample can cool on the local scale, un-phased by surface heating. This temperature where heating and cooling are exactly balanced is the zero crossing temperature (ZCT) and can be used as a measure for the presence of impurities and the overall quality of the laser cooling material. Overall, favorable results were obtained from 1% Yb^{3+}-doped glass, indicating our glasses are desirable for laser refrigeration.

Keywords: optical refrigeration, laser cooling, ZBLAN, fluoride glass, rare-earth, fluoride purification, solvent extraction, luminescence thermometry.

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1. INTRODUCTION

Our goal is to provide effective and relatively expedient feedback for our glass fabrication facilities, in order to determine whether our purification techniques have been successful in increasing the laser induced cooling capabilities of the material. An excellent introduction to laser refrigeration has been covered elsewhere [ref].

In our facilities, we synthesize rare-earth doped fluorozirconate glasses beginning with high purity starting materials to produce the fluorides constituting the glass. These glass components must be processed in a clean room environment and further purified in order to have the possibility of ever reaching laser cooling at cryogenic temps. This further purification is necessary as we will need to reduce the impurities in even the current record holding ZBLAN glass by a factor of 20-30 times to reach the target < 100 ppb impurity levels needed [ref]. However, even ZBLAN of this impurity is no longer commercially available. We therefore must synthesize our own ZBLAN. In our context, an impurity is any species in the material that lowers the external quantum yield of the rare-earth dopant. The primary quenching mechanism is by non-radiative energy transfer from the rare-earth ion to transition metal impurities such as Cu^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}. Impurities with high-energy vibrational modes (for example, OH^- and H_2O) can also quench the excited state of the rare-earth ion via multi-phonon relaxation. Additionally, impurities can also directly absorb at the pump wavelength causing heating in the form of background absorption. A great number of successful cooling cycles (each extracting only a few kT of heat) are required to compensate for each non-radiative heating event. Thus, is it imperative to reduce these impurities to extremely low levels.

The figure of merit for sample quality comparison we have chosen is the zero crossing temperature (ZCT), that is, the minimum temperature at which the sample can sustain laser-induced cooling. The experiment we have developed,

TBDLT, allows relatively rapid characterization of our samples yielding the ZCT for the material in question. This technique builds on a previous version of DLT also developed at Los Alamos National Laboratory. This technique, which relied heavily on an Ocean Optics spectrometer (providing poor efficiency), and the implementation and analysis was overly complex. In our past attempts to identify ideal coolers, bulk cooling experiments were employed which illuminate the sample with an intense pump beam and the magnitude of the cooling or heating observed using a thermal camera. While it has its own merit, the bulk cooling experiments [ref] are still highly sensitive to preparation of the surfaces of the glass. Photothermal deflection has also been used in the past [ref]. However, it involves some subjective interpretations and is not robust because the photothermal deflection profiles depend on the exact alignment of the pump and probe beams and can be easily be misinterpreted, especially at low temperatures where the signal is weak.

This manuscript will begin with a brief overview of the material synthesis process used to fabricate the Yb^{3+}-doped glasses. The Methodology section describes the figure of merit used for sample quality comparison as well as a description of the method used to obtain this quantity. This is followed by the Experimental section where a detailed description of the TBDLT setup is described. The Data Analysis section then follows to describe how we extrapolate our figure of merit from our experimental data. The Results and Discussion describe the results from testing our materials synthesized with the TBDLT experiment. A final summary is given in the final Conclusions section.

2. MATERIAL SYNTHESIS

Significant progress has been made in synthesizing and characterizing ultra-pure, defect-free, rare-earth doped ZIBLAN (**ZrF_4-InF_3-BaF_2-LaF_3-AlF_3-NaF**) glass capable of laser refrigeration.

The glass was produced from fluorides which were individually purified via solvent extraction (SE) in order to remove transition metal impurities. The fluorides were subsequently treated with hydrofluoric gas at elevated temperatures to remove hydroxyl ions and traces of water impurities before glass formation. Our approach for producing ultra-pure ZBLAN differs from previously available, commercial ZBLAN. Often, these samples were "purified" after fluoride synthesis by flowing CF_4, NF_3, SF_6, Cl_2, CCl_4, or O_2 gases over the melt. This is not acceptable for laser cooler as these gases can and do re-contaminate the final glass product with unwanted. Our method utilizes a distinctly different approach where we begin with the most pure compound for a given metal ion and further purify the compound as our first purification step. The purity remains intact throughout the glass fabrication as all further steps are performed in a clean environment. The details of these purification techniques are beyond the scope of this manuscript and are described elsewhere [ref??].

The glass stoichiometry has been redefined (relative to the customary ZBLAN stoichiometry) to include a significant amount of oxidizer, InF_3, to counteract the considerable reduction of ZrF_4 – the primary component in our glass. The melting procedure has been greatly refined and extended to longer time periods to avoid crystallites of LaF_3 and YbF_3, as well as undissolved fluorides and microbubbles in our final product. We have also adopted new polishing techniques which drastically improve the quality of the polish, and hence, the potential amount of bulk cooling. Here, we use a combination of aluminum oxide particles of varying diameters suspended in mixtures of various water-free glycols.

Several samples were prepared as described here and are summarized in TableXX below. Over the course of approximately six weeks, a new sample can be produced, then evaluated using the characterization tools described in sectionX.

Sample name	%Yb	composition	melt time	Notes
H262a	1	?ZBLAN	?	Fluorides were procured from commercially available sources – not produced or purified in-house.
I052a	1	?	?	First attempt at SE. Visible "scattering center" from crystallites and undissolved fluorides.
I158a	1	?	?	Second attempt at SE.
I267a	1	?	?	Third attempt at SE. Visually impeccable sample with no obvious defects.
I276a	2	?	?	2% version of I267a

3. METHODOLOGY

3.1 Material evaluation – Zero crossing temperature as a figure of merit

We have selected the zero crossing temperature (ZCT) as the figure of merit for our sample quality comparison. One goal of the laser-cooling effort is to develop ytterbium-doped ZBLAN that can cool efficiently at low temperatures. With this aim in mind, we employ this particular diagnostic that measures the minimum temperature at which the material can exhibit localized cooling. As the ambient temperature is lowered, the cooling efficiency decreases and reaches a critical temperature where laser cooling and residual heating from impurities are exactly balanced. This zero crossing temperature can be used as a measure for the presence of impurities and of the overall quality of a laser cooling material.

Another metric which might be considered for sample comparison are the absolute change in temperature of the bulk material (i.e. the magnitude of heating or cooling) at a given sample temperature. Simply looking at the change in temperature leaves us vulnerable to the effects of reabsorption, which is difficult to decouple from our bulk cooling measurements. Additionally, the time at which the sample reaches steady state is somewhat subjective and hence, so too is the absolute magnitude of cooling or heating. The zero crossing wavelength, that is, the pump wavelength in which the sample goes from heating to cooling, could also be a valid metric for sample quality. However, this experiment would require a largely tunable pump source and the ability to hold the absorbed power constant at each wavelength.

3.2 Material evaluation – TBDLT to measure ZCT

In order to deduce the ZCT, we have employed a non-contact, spectroscopic technique, TBDLT. This technique relies on the temperature dependence of the fluorescence of our rare-earth ion.

Unlike the case of semiconductors, for which a similar DLT experiment has been developed [ref], the change in the spectral intensity of rare-earths is solely due to the relative thermal population in the excited state – dictated by the Boltzmann distribution. For rare-earth-doped materials, such as ZBLAN:Yb^{3+}, the 4f electrons are well shielded from their surroundings, thus the energy (and hence the peak fluorescence wavelength) does not shift by an experimentally observably amount. This is not the case for semiconductors, which also have a shift in the transition energy in addition to the change in thermal population taking place upon temperature change. *Thus, the only observable temperature induced change in the rare-earth spectra arises from broadening of the homogeneous component of the line widths of the 12 potential ytterbium emission transitions as the temperature increases [ref 20,21].* FIX THIS. This broadening becomes significantly more evident when then difference of two spectra, or two portions of the same spectra are observed. However, selection of these "difference regions" must be chosen... MORE HERE.

In order to deduce the laser induced temperature change at a fixed sample temperature, we begin by selection regions of the fluorescence spectra in which the intensity changes uniformly. For example, we can select 4 distinct regions as depicted in Fig.X in which an increase in temperature corresponds with an increased intensity in that "band". The "transition regions" are omitted as the intensity near these points does not change at that particular wavelength. We omit enough of the regions surrounding these transition points to allow regions with distinct uniform temperature change. This step greatly decreases the noise in the final result. In order to deduce our difference, we subtract regions with opposite signs. Thus, candidate regions for difference subtraction would be either A-D or A-B or even (A-D) + (B-C) for example. However, given our method of selecting these regions, we have chosen A-D as our difference to deduce temperature change. This selection is done with a set of commercially available band pass filters with transmission as shown overlapped with our fluorescence spectra in FigX. In our experiment, we need not include the B and C bands given that they are very narrow with respect to available interference filters and would hence not add much information. Obviously then, for our TBDLT method, we would require at least two bands, and more makes it experimentally complicated. Also, it is necessary to have at least two bands for comparison so that the difference can be normalized to the total fluorescence to eliminate changes in absorbed power due to pump power fluctuation.

In theory, a technique such as described here can be applied to any material which exhibits temperature dependent luminescence. The experiment we develop must be independent of surface preparation, reabsorption effects, and power fluctuations to allow comparison of different samples.

4. EXPERIMENT

The sample is cooled to a set temperature in a cryostat. The laser then irradiates the material and DLT determines whether it cools or heats. By taking measurements of the laser-induced temperature change at temperatures above and below the ZCT, we can accurately find the zero crossing temperature by interpolation. A sample with lower impurity concentrations will have a lower ZCT, enabling us to use the ZCT as a metric for the quality of a glass sample.

The sample is excited with a diode pumped Yb:YAG laser (Nanolase, DP12011-T01), equipped with a birefringent filter tunable between 1010-1050 nm producing ~3W of pump power at 1021nm. This wavelength was chosen such that we have sufficient emission for the entire temperature range yet maintain a high cooling efficiency.

The experiment, as shown in FigX, uses a sequence consisting of the pump laser being on for several seconds during which the sample heats or cools, followed by the pump laser being off for several seconds during which the sample equilibrates back to the ambient temperature. A function generator controls the data acquisition by triggering a shutter at 5 second intervals. This cycled pump method reduces the effects of long term temperature drifts, and also decouples temperature changes occurring inside the illuminated sample volume from those occurring due to poor surface preparation.

The sample is placed on the cold finger of an open cycle Helitran cryostat and maintained at a chosen temperature between 300 – 100K using liquid nitrogen. Importantly, it is necessary to monitor the actual sample temperature, not simply the cryostat set point which differs significantly from the sample itself. To accomplish this without adding a heat load to the sample (which would inevitably distort the cooling data), we have used a Lakeshore silicon diode (DT-421) having a mere 1.5 mm diameter adhered to the surface of the sample.

The fluorescence is collected during each 5 second pump interval by two 2" collection lenses which collimate (f = 60 mm) and guide the fluorescence (f = 100 mm) into a 600 um multimode fiber. This collected fluorescence at a given temperature is directed to a collimator, followed by a 50/50 non-polarizing beam splitter which splits the light into two "channels". Channel A is equipped with the "band A" filter with transmission spectra as shown in FigX, and similarly for Channel D. Both channels are also equipped with collimators which refocus the selected luminescence onto 600 um multimode fibers.

The fluorescence from each collimator is independently routed to an InGaAs balanced pair of photodetectors.
The Thorlabs PDB145C photodetectors consist of two photodiodes with well matched responsivity. This device converts the integrated luminescence from each channel to a voltage. An ultra-low noise, high-speed transimpedance amplifier generates an output voltage proportional to the difference between the photocurrents in the 2 photodiodes, i.e. the two optical input signals. This is yet another reason we use the difference between channels A and D, in order to take advantage of the very high electrical gain offered by the balanced detector in the (A-D) output. The two signal monitor outputs allow observation of the input power levels and can be used as independent power meters for each channel. The A and D monitor outputs are used to normalize the A-D signal as described later in the Data Analysis section of this manuscript. Each of these three detector outputs are independently and simultaneously read by a multi-channel data acquisition (DAQ) board (USB-1616FS, Measurement Computing) that provides 16-bit resolution at an acquisition rate of 36 KHz. In theory, this would allow a time resolution of 0.03 ms for the resulting TBDLT transients. A USB line connects the DAQ to a computer where the data is captured and analyzed real-time by a LabView application.

The data collected from each 5 second shutter/pump exposure is averaged many times to improve signal to noise. Depending on the amount of signal available, this can be anywhere between 10 minutes to 2 hours. Such measurements can be performed at different sample temperatures inside a cryostat. As the ambient temperature is lowered, the cooling efficiency decreases and reaches a critical temperature where laser cooling and residual heating are exactly balanced. This zero-crossing temperature can be used as a measure for the presence of impurities and of the overall quality of a laser-cooling material.

Thus, we have successfully developed a technique to collect fluorescence from a localized volume, independent of how well the surfaces of the sample were prepared. We can use this technique to compare our samples fabricated in-house in our quest to build an efficient laser cooler.

5. DATA ANALYSIS

In order to account for power fluctuations allowing comparison of transients from different experiments quantitatively, we must normalize the amplified (A-D) signal resulting from our experiment by (A+D) – the total fluorescence, which is proportional to the absorbed power.

At each temperature a transient spanning the 5 second beam exposure time is recorded. Each transient is fitted with a single exponential function, $y = Ae^{-x/t} + y_o$. We use the derivative of the fitted function, $dy/dt = -A/t$, (not actual temperature or (A-D)/(A+D) change alone) as the final evaluation parameter. We use this initial slope as a measure of the potential for the sample cooling where a larger slope would represent more heating or cooling than a shallower slope would. The sign of the slope indicates the difference between heating and cooling and the ZCT is characterized by the change in sign of our d [(A-D)/(A+D)] / dT parameter. Unlike using the magnitude of heating or cooling, this initial slope method uses much of the available dataset instead simply using the initial and final data points. This method reduces the noise in our final result. Also, simply using the magnitude of the heating or cooling would leave the measurement somewhat open to interpretation as one would need to properly judge when the sample temperature had reached steady state. This is not a reasonable approach given the small, finite size of our cooling samples.

However, there is one remaining question that must be addressed when using the initial slope of the transients to deduce the ZCT. How much of this initial slope would one use? In order to answer this question, we can look at the initial slopes, -A/t from various increments of the transients at different temperatures. We can compare the magnitude of the errors resulting from this analysis to determine approximately how much of the initial slope is needed.

6. RESULTS AND DISCUSSION

In order to gauge our success, we compare our results to that of a ZBLAN:Yb^{3+} sample with 2% ytterbium doping obtained from IPG Photonics which has shown substantial laser cooling in past experiments. The samples tested to date are given in TableX above. We will first focus on the results of our most recent sample, I267a, which has show reasonable cooling at room temperature. Shown in FigureX are the transients resulting from the TBDLT experiment performed on I267a (a) and the commercially procured IPG sample (b). As discussed in sectionX above, it is the slopes, -A/t of these transients which will be compared to determine which sample yields the lower ZCT. This result is shown in FigureX where data points above the dotted line represent heating and below it, cooling. For convenience, these results are fit to a single exponential. By interpolation, we find the ZCT of sample I267a to be XX and the commercial IPG sample to crossover at XX. This result by itself is not the final resultXX.

Better yet, we can compare/observe/X the progress in material synthesis over the course of only one year in FigureX. Here we compare, using our TBDLT experiment at room temperature, a number of samples produced in-house using our purification techniques described in sectionXX. With each iteration of our material development/characterization cycles, we produce a significantly better sample.

In order to further gauge our success in removing impurities, a sample (H262a) was prepared using commercial off the shelf fluorides which were not further purified. From the results, it is reasonable to conclude that our wet chemistry techniques do yield a sample with reduced impurities.

7. CONCLUSIONS

In summary, we have successfully developed material synthesis … The TBDLT method we have developed enables rapid and reliable feedback on the quality of our rare-earth glasses. FINISH.

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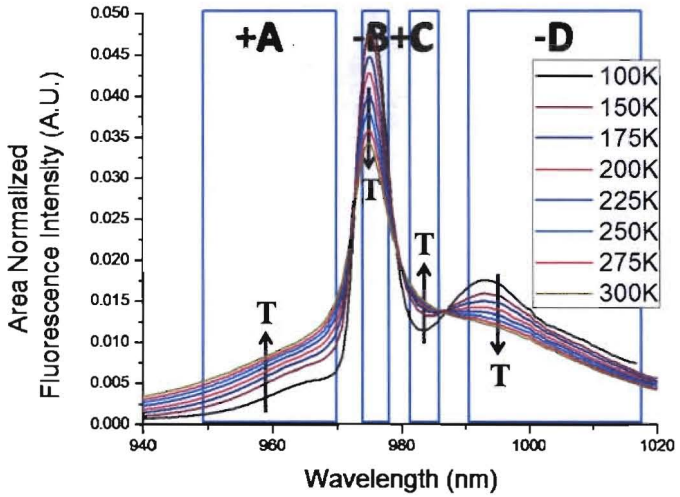
FIGURES



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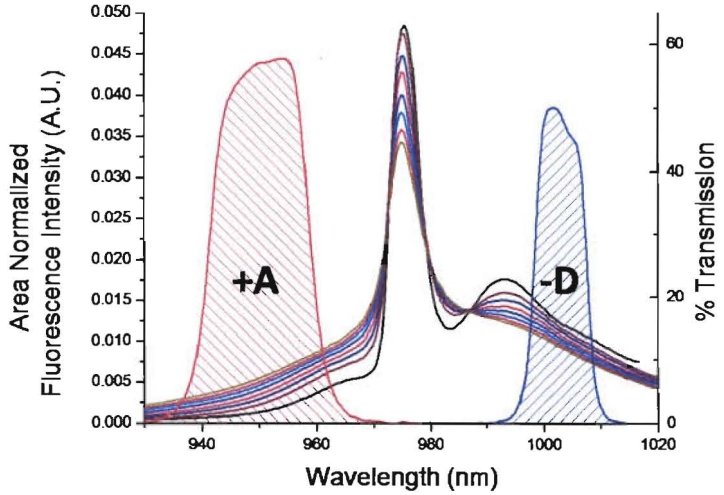

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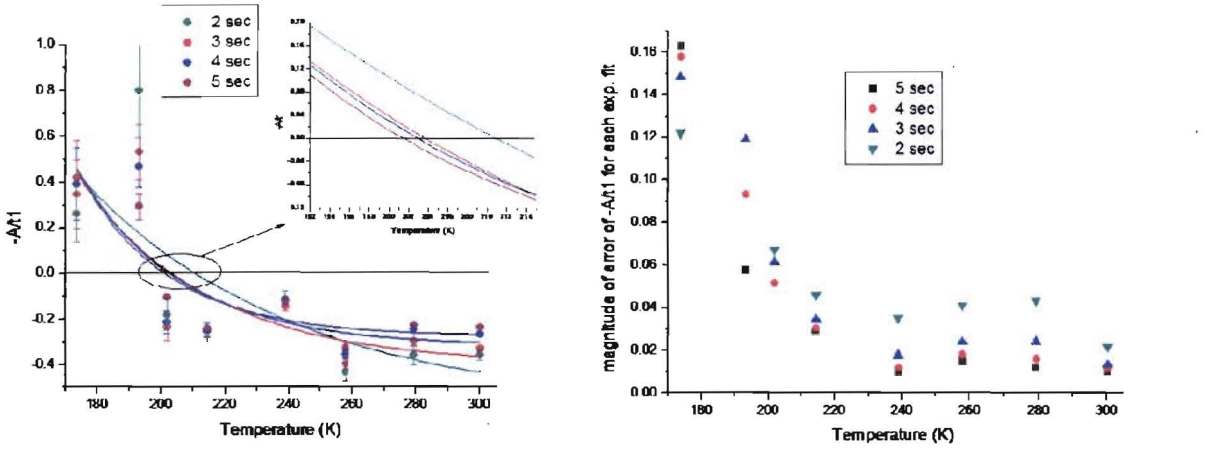

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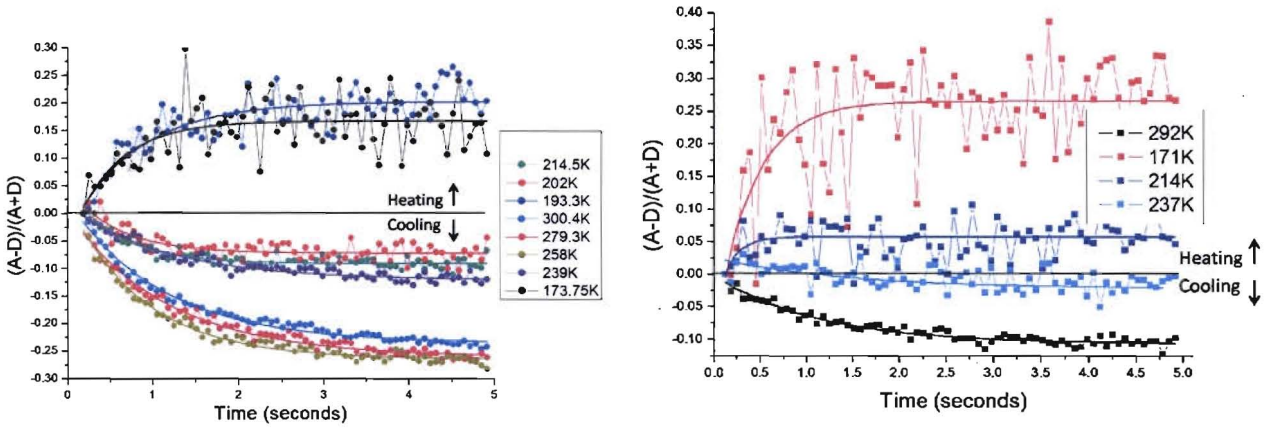

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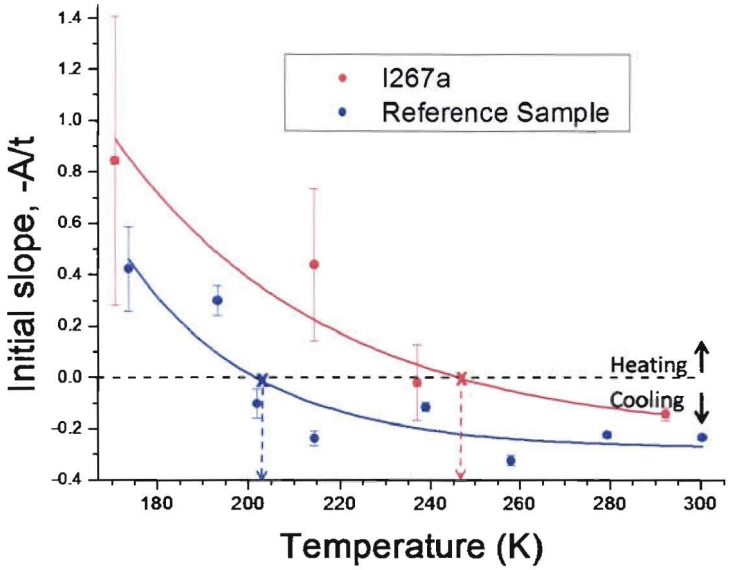

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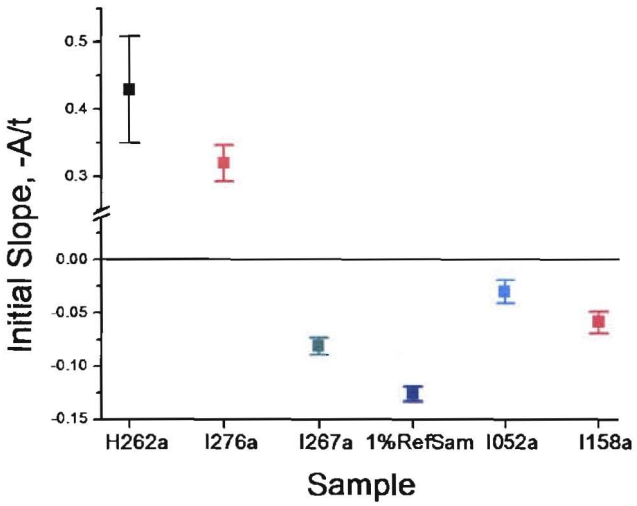

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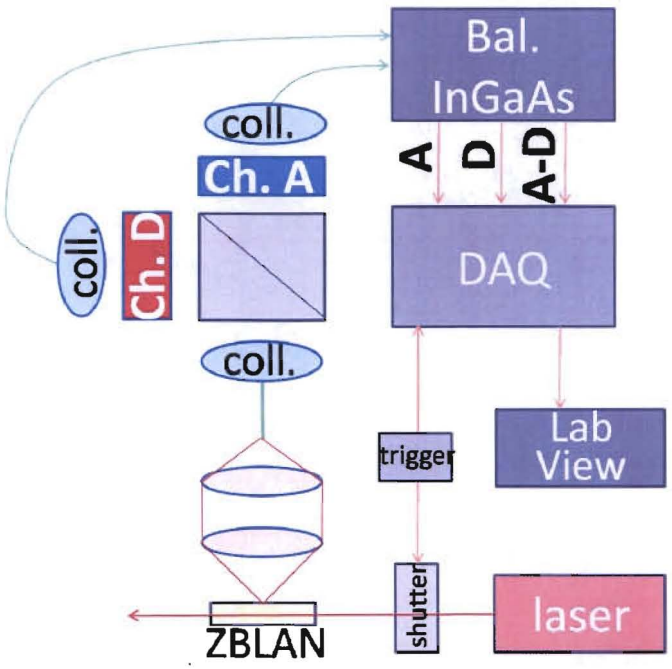

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