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Electrochemical purification of heavy metal fluoride glasses for laser-induced fluorescent cooling applications

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Abstract

An electrochemical purification stage has been incorporated into the conventional fabrication process of heavy metal fluoride glasses. This change was undertaken to reduce the absorption losses associated with residual transition metal impurities, particularly the Fe^{2+} band at 1.0 μm . Purified samples doped with ytterbium exhibited net cooling due to anti-stokes fluorescence and a relative cooling efficiency of about 2% was observed via photothermal deflection spectroscopy. Pumping to the lower Stark levels of the $^2\text{F}_{5/2}$ manifold, followed by population redistribution across this manifold and fluorescence to the ground state, results in net cooling. This cooling can be achieved only if energy transfer and the extrinsic absorptive component of the host glass are suppressed.

1. Introduction

The process of fluorescent cooling, in which the temperature of a material is decreased by the absorption of incident photons and a subsequent emission of photons of greater energy, was discussed in 1929 by Pringsheim [1]. After much controversy over the topic, Landau established that it does not violate any laws of thermodynamics through his introduction of the concept of radiation entropy [2–4]. It was not until 1995 that there had been an actual verification of net fluorescent cooling in a solid substance [5]. The system which successfully exhibited fluorescent cooling, ytterbium-doped ZBLANP glass, is an attractive candidate for the development of a first-gen-

eration optical cooler. A fluorozirconate glass host is utilized in this work because of the solubility of rare earths in it and the large spectral overlap between the absorption and emission of Yb^{3+} . The advantages over the conventional coolers operating below 100 K (e.g., Stirling-cycle cryogenic systems) include the absence of vibrations, minimal weight (less than 3 kg/W), a longer lifetime under continuous operation and freedom from electromagnetic interference.

The multiphonon emission rates, W_{mp} , of rare earths have been found to exhibit exponential dependence on the energy gap, ΔE , to the next lower level:

$$W_{\text{mp}} = W_0 e^{-\beta \Delta E}, \quad (1)$$

where W_0 and β are empirical parameters [6]. With the large energy gap between the $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ levels in ytterbium ($\Delta E \sim 10^4 \text{ cm}^{-1}$), the multi-

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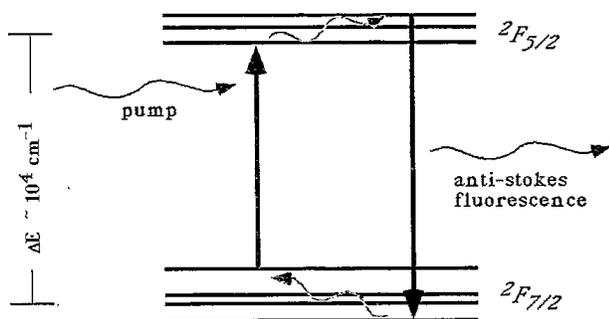


Fig. 1. Fluorescent cooling cycle of Yb^{3+} .

phonon emission rate is negligible and the radiative efficiency should be close to unity. As shown in Fig. 1, the ground state and excited state in Yb^{3+} are split into four and three levels, respectively, due to Stark effects. At room temperature, the splitting between levels is, at most, a few times kT . Excitation from the upper Stark levels of ${}^2F_{7/2}$ to the lower levels of ${}^2F_{5/2}$ is followed by population redistribution across the ${}^2F_{5/2}$ manifold through phonon absorption. The thermalization time is much less than the fluorescent lifetime of ${}^2F_{5/2}$, hence at room temperature, the mean emission energy is the same regardless of where the ion is pumped within the manifold. Radiative emission is followed by equilibration of the ground state, completing the process. The net result of this cycle is the removal of heat from the material [7,8].

Phonon-emitting, non-radiative decays are competing processes which can completely overwhelm

the fluorescent cooling effect. A pump photon that does not lead to radiative emission produces heat which is at least 50 times greater than the energy lost during the Yb^{3+} cooling cycle. Extrinsic absorption due to transition metals and energy transfer between excited Yb^{3+} and impurity species, such as Fe^{2+} and Cu^{2+} , can lead to heating and must be reduced for fluorescent cooling. Zhou et al. [9–12], have suggested achieving ultra-low transition metal content in fluoride melts through electrochemical processing. A fluoride liquid is exposed to a voltage gradient, which allows transition metal species to plate out onto a platinum electrode immersed in the liquid. This approach has been utilized in the preparation of materials for the present work.

2. Experimental

Ytterbium-doped ZBLANP (in mol%: 53% ZrF_4 , 18% BaF_2 , 3% LaF_3 , 3% AlF_3 , 20% NaF , 2% PbF_2 , 1% YbF_3) glass samples were fabricated using UHP starting materials (EM Fluortran). 20 g batches were melted in a vitreous carbon crucible at 950°C for 1 h under an inert atmosphere. Reactive atmosphere processing was carried out with $\text{SF}_6(\text{g})$ for 1 h at 700°C for the elimination of reduced zirconium and residual moisture. Prior to casting, the liquid was placed into an electrochemical purification cell as shown in

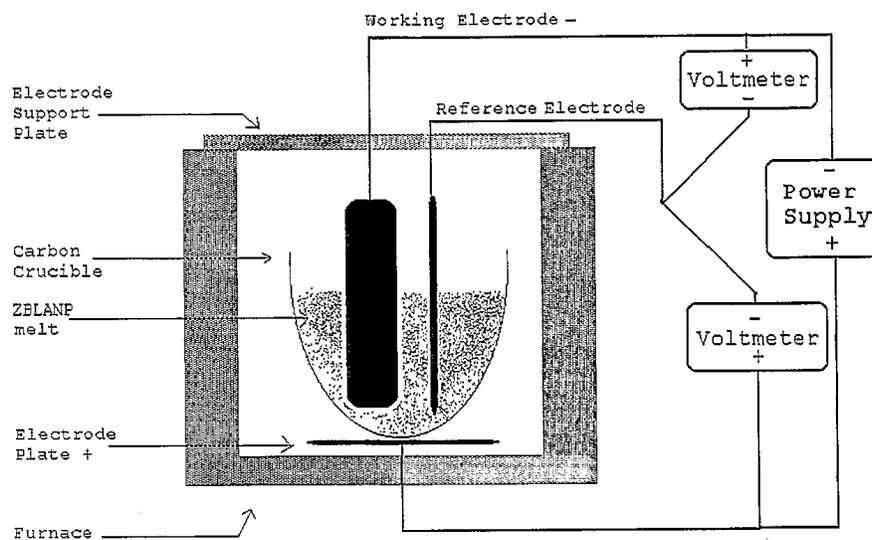


Fig. 2. Three electrode electrochemical purification cell.

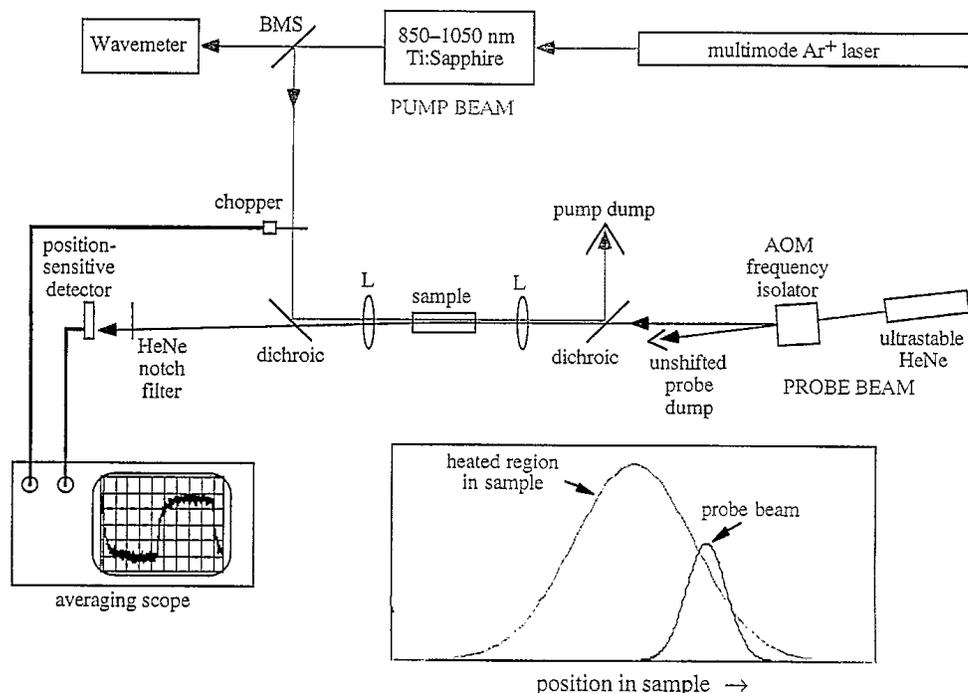


Fig. 3. Schematic diagram of photothermal deflection spectroscopy set-up.

Fig. 2. The liquids were exposed to a voltage for 1, 6, 12 and 24 h at 600°C. The dc power supply was connected to a 2 mm² Pt plate which was immersed in the melt and the carbon crucible which worked as a counter electrode. Since there is an electrochemical window between 400 and -1300 mV, the potential was slowly increased to go above the cathodic deposition potential of iron (-650 mV between the Pt plate and reference electrode), yet stay below 400 mV between the reference and crucible [9].

Cast samples were cut and polished for optical measurements. Absorption of the samples was measured using a spectrophotometer (Perkin-Elmer Lambda 9 UV/VIS/NIR). Fluorescence acquisition was done with an argon ion-pumped Ti-sapphire laser. A sensitive scheme, known as photothermal deflection spectroscopy (PTDS), has been used in the past to measure low absorption coefficients in optically thin media [13]. It was employed here to measure cooling in a local volume in the interior of the samples. Fig. 3 shows a schematic diagram of the PTDS set-up. The pump beam, which was at a wavelength between 900 and 1030 nm for Yb excita-

tion, was collinear and anti-parallel to a HeNe probe beam. The fluorescence causes a temperature gradient in the focal volume and the associated index of refraction gradient deflects the probe beam slightly. The pump was chopped at 1.25 Hz and the deflection of the probe was measured synchronously with the chopper using a position sensitive detector. This measurement was done at various pump wavelengths and wavelengths which resulted in net cooling would show an unmistakable 180° shift in the phase of the signal with respect to heating. The deflection amplitudes and waveform phases were measured for the glasses subjected to electrochemical processing and compared to untreated samples.

3. Results

The room temperature absorption and fluorescence spectra of 1 mol% Yb³⁺ measured in ZBLANP are shown in Fig. 4. The fluorescence properties were identical when pumped at various wavelengths

within the ${}^2F_{7/2} - {}^2F_{5/2}$ absorption band. The mean emission photon energy could thus be calculated by:

$$E_f = \frac{\int I_\nu h\nu d\nu}{\int I_\nu d\nu} \quad (2)$$

or

$$\lambda_f = \frac{\int I_\lambda d\lambda}{\int I_\lambda d\lambda/\lambda}. \quad (3)$$

As shown in Fig. 4, the mean emission wavelength was 995 nm, where the absorption coefficient was about 0.2 cm^{-1} . When the pump was at 995 nm, the sample should neither heat nor cool and cooling should be observed for lower pump-photon energies than E_f . If the radiative quantum efficiency is reduced due to trace impurities, the onset of net fluorescent cooling will take place at a longer wavelength.

The waveforms from the photothermal deflection of the 1% Yb ZBLANP sample which was processed in the electrochemical cell for 24 h are shown in Fig. 5. The first curve is the deflection within the sample when pumped at 960 nm. As expected, the deflection amplitude was large due the high absorption coefficient

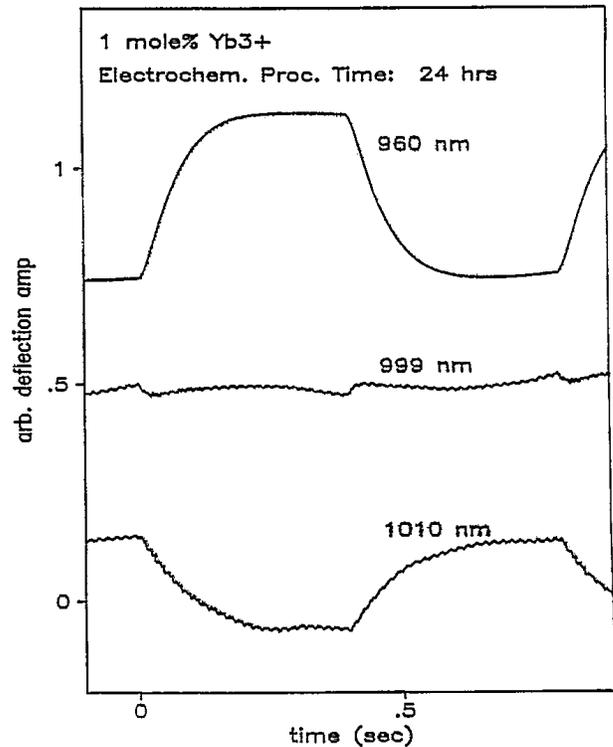


Fig. 5. Photothermal deflection waveforms from a 1% Yb ZBLANP glass.

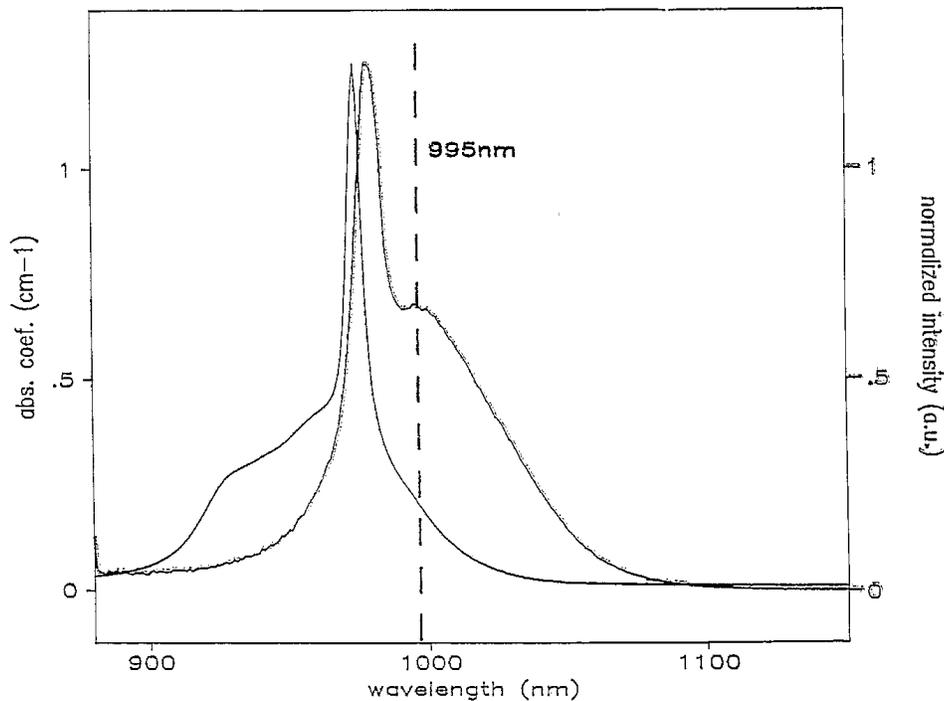


Fig. 4. Room temperature absorption and fluorescence spectra of 1% Yb in ZBLANP.

cient at 960 nm and indicates a large heating signal (pump is on the heating side of the fluorescence spectra.) A very slight heating signal was also observed at the theoretical null wavelength of 995 nm. The second waveform in Fig. 5 is from the same sample when pumped at 999 nm. Although the deflection signal is weak at this wavelength, the 180° shift is evident. This shift is an indication that the probe beam is now bending the other direction with respect to the optic axis and is due to a net decrease in the temperature of the focal volume. The deviation from the theoretical null point is $\leq 0.4\%$ and is attributed to the decrease in efficiency due to transition metal content still in the sample or possible surface contamination. At 1010 nm, the deflection amplitude is much greater and the 180° shift in the waveform is even better resolved.

4. Discussion

The theoretical cooling power, P_{cool} , is related to the absorbed power by

$$P_{\text{cool}} = P_{\text{abs}} \left(\frac{\lambda - \lambda_f}{\lambda_f} \right) \quad (4)$$

and thus the theoretical relative cooling efficiency is

$$\eta_r = \frac{P_{\text{cool}}}{P_{\text{abs}}} = \frac{\lambda - \lambda_f}{\lambda_f} \quad (5)$$

The cooling power is proportional to the deflection amplitude of the PTDS signal, hence the relative cooling efficiency can also be determined experimentally by

$$\eta_r \propto \frac{A}{P_{\text{inc}}(1 - e^{-\alpha L})} \quad (6)$$

where A is the deflection amplitude in mV, P_{inc} is the pump power and the bracketed term is the absorbance. Fig. 6 is the measured cooling efficiency for 1 mol% Yb^{3+} in ZBLANP after electrochemical processing for 24 h. The data were calibrated on the heating side to match theory (Eq. (5)), which is shown as the solid line. The results fall below expectations beyond the onset of cooling (i.e., where η_r is greater than zero), again indicating a decrease in quantum efficiency due to trace impurity effects. The impurity effects become more pronounced at the longer wavelengths, where the absorption due to ytterbium approaches zero. The measured cooling efficiency of about 2% suggests that a practical optical cooler, utilizing high transparency fluoride base glasses, may be feasible.

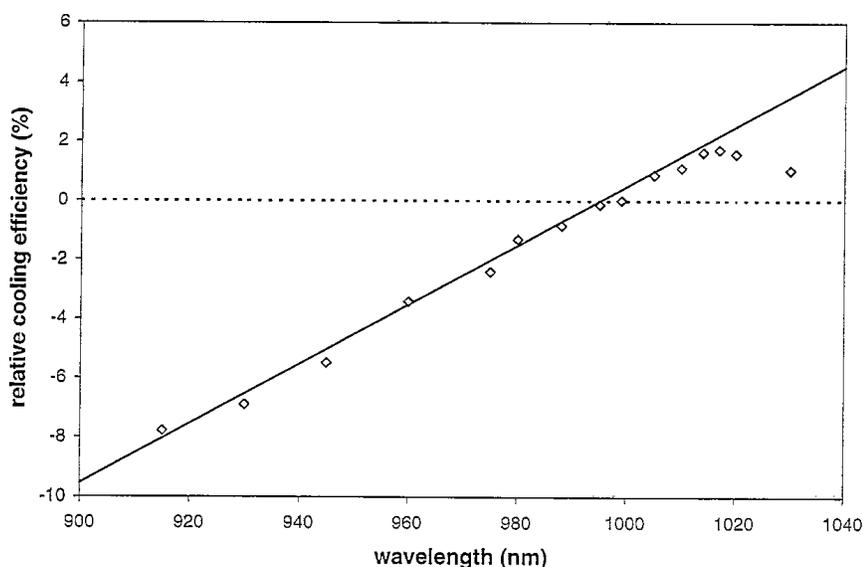


Fig. 6. Relative cooling efficiency of 1% Yb in ZBLANP. The line is drawn as a guide for the eye.

The samples exposed to the electrochemical treatment for less than 6 h (or not treated at all) did not exhibit fluorescent cooling at any pump wavelength. The electrochemical processing is obviously eliminating a detrimental component of non-radiative relaxation around 1000 nm. The work of Zhou et. al, suggests a reduction in trace Fe^{2+} and Cu^{2+} content is responsible for the improved transparency of the base glass.

5. Summary

High-purity fluoride glasses have been synthesized and evaluated for fluorescent cooling applications. An electrochemical purification technique has been successfully employed to reduce extrinsic host absorption in the vicinity of 1.0 μm . Measured cooling efficiency of 2% in Yb-doped ZBLANP makes this host attractive for practical cryogenic applications.

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