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Author(s): Markus P. Hehlen

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Novel materials for laser refrigeration

Markus P. Hehlen*

Los Alamos National Laboratory, Chemistry Division, Mailstop J565,
Los Alamos, NM, USA 87545.

ABSTRACT

The status of optical refrigeration of rare-earth-doped solids is reviewed, and the various factors that limit the performance of current laser-cooling materials are discussed. Efficient optical refrigeration is possible in materials for which $\hbar\omega_{max} < E_p/8$, where $\hbar\omega_{max}$ is the maximum phonon energy of the host material and E_p is the pump energy of the rare-earth dopant. Transition-metal and OH⁻ impurities at levels >100 ppb are believed to be the main factors for the limited laser-cooling performance in current materials. The many components of doped ZBLAN glass pose particular processing challenges. Binary fluoride glasses such as YF₃-LiF are considered as alternatives to ZBLAN. The crystalline system KPb₂Cl₅:Dy³⁺ is identified as a prime candidate for high-efficiency laser cooling.

Keywords: Optical refrigeration, laser cooling, binary fluoride glasses, halide crystals, ZBLAN, YLF, infrared sensors.

1. INTRODUCTION

Many refrigeration technologies are available to reduce the thermal noise and thus to improve the sensitivity of infrared sensors by cooling. Space-based sensor systems pose particularly difficult thermal-management challenges because of demanding size, weight, power, lifetime, and reliability constraints, and in some cases due to sensitivity to mechanical vibrations. Stored coolants (such as liquid or solid cryogenics) or active refrigerators (such as Stirling, pulse tube, Brayton, and Joule-Thomson devices) can provide cooling to cryogenic temperatures. However, these techniques are often not well suited because of their limited lifetime or vibrations introduced by moving parts. Multi-stage thermo-electric coolers (TECs) are a mature solid-state refrigeration technology that avoids some of these problems. But the minimum cold-side temperature of TECs is limited to ~170 K for ~100 mW cooling capacities [1]. Solid-state optical refrigerators with comparable cooling capacities are an attractive alternative to TECs because they can potentially cool to 70 K or below [2], have no moving parts, are expected to be very reliable, and offer the lowest spacecraft system mass of any cooling technology [3]. Such optical cryocoolers are poised to enable the detector sensitivities needed for emerging space-based threat reduction, treaty verification, and climate monitoring missions.

Over the past 14 years, solid-state optical refrigeration has been reported for a variety of rare-earth doped glasses and crystals ([4] and references therein) of which some have shown net bulk cooling starting from room temperature (Figure 1). In 2009, record laser-cooling by 98.5 K to 203 K has been reported by Seletskiy et al in an Yb³⁺-doped YLiF₄ crystal using a resonant cavity pumping scheme [10]. Efficient optical refrigeration of a bulk cooling element to below 170 K, the practical temperature limit for TECs, however remains to be demonstrated. This paper reviews the factors that limit the cooling performance of current materials (Section 2) and explores novel material systems that could enable optical refrigeration to application-relevant temperatures (Section 3).

2. LIMITATIONS OF EXISTING LASER-COOLING MATERIALS

The cooling efficiency of a material is affected by many factors that span a diverse range of disciplines. They include (1) the intrinsic ideal laser-cooling properties of the material, (2) the fabrication of the material, and (3) the integration of the material into an optical cryocooler device. Some of the associated challenges and limitations are discussed in the following.

*hehlen@lanl.gov; phone 1 505 665-1737; www.lanl.gov

Fig. 1. Lowest temperatures achieved in rare-earth doped solids by optical refrigeration from room temperature. The results are compared to the ~170 K temperature limit of thermoelectric coolers and the theoretical ~70 K temperature limit for cooling with Yb³⁺. The figure is not intended as a direct quantitative comparison between materials because the various studies compiled here used different sample geometries, absorbed pump powers, and temperature measurement methods (TC=thermocouple, IR=infrared imaging, DLT=differential luminescence thermometry). YLiF₄:Yb³⁺ (203 K) [10] and ZBLAN:Yb³⁺ glass (208 K) [5] are the leading crystal and glass, respectively.

2.1 Intrinsic material limitations

Optical refrigeration occurs upon absorption of a pump photon of energy E_p , followed by rapid excited-state thermalization and subsequent emission of an anti-Stokes photon at energy E_F . This ideal cooling cycle is illustrated in Figure 2 and has an efficiency $\Delta E/E_p$, where $\Delta E = E_F - E_p$. Alternatively, the excited state can decay non-radiatively via interaction with the optical phonons of the host material (typically the highest-energy optical mode with energy $\hbar\omega_{max}$) and introduce undesired heating through multi-phonon emission. The internal quantum efficiency $\eta = w_r/(w_r + w_{mp})$ resulting from this competition between radiative (w_r) and multi-phonon (w_{mp}) relaxation rates reduces the cooling efficiency to $\eta_{cool} = (\eta E_F - E_p)/E_p$.

Fig. 2. Ideal cooling cycle involving the ground-state and first excited-state multiplet of a rare-earth ion. Absorption at energy E_p is followed by thermalization and anti-Stokes fluorescence at energy E_F . Radiative relaxation (straight arrow) and multi-phonon relaxation (wiggly arrow) occur at rates w_r and w_{mp} , respectively.

It is instructive to estimate the parameter space of E_p and $\hbar\omega_{max}$ values that are suited for optical refrigeration. Assuming that a material that realizes $\gamma = 0.9$ of its maximum possible cooling efficiency $\Delta E/E_p$ qualifies as a suited laser-cooling system yields $\eta = [\gamma\Delta E + E_p]/E_p$. By substituting the internal quantum efficiency we find $w_{mp} = w_r\Delta E(1 - \gamma)/(\gamma\Delta E + E_p)$. First we note that oscillator strengths of $4f-4f$ transitions of rare-earth ions are $\sim 10^{-6}$ [17], and the corresponding rates for spontaneous radiative relaxation are on the order of $w_r = 100 \text{ s}^{-1}$. Second, the rate of multi-phonon relaxation is given by the energy gap law, $w_{mp} = \beta \exp(-\alpha E_p/\hbar\omega_{max})$, where α and β are constants and $\hbar\omega_{max}$ is the maximum phonon energy of the host material [18]. Noting that $\Delta E \approx 2.5kT$ we find that $\hbar\omega_{max} \approx \alpha E_p/\ln\beta$ at $T = 300 \text{ K}$. A survey of many different materials [19] suggests typical values for α and β on the order of 3.5 and 10^{12} s^{-1} , respectively. Therefore, a material can only provide efficient optical refrigeration if

$$\hbar\omega_{max} < E_p/8. \quad (1)$$

Figure 3 illustrates this relationship and can be a useful guide in the search for novel laser-cooling materials. It shows the maximum phonon energy $\hbar\omega_{max}$ of different glasses and crystals (horizontal lines) and the energy of the first excited $4f$ multiplet of different rare-earth ions (vertical lines). Systems below the bold line indicating $\hbar\omega_{max} < E_p/8$ have the potential to be efficient optical refrigerators. The circles indicate rare-earth doped solids for which laser cooling has been observed experimentally, confirming the rule of thumb [Eq.(1)] derived above. The most efficient materials are those with a small E_p , but correspondingly lower $\hbar\omega_{max}$ are required to enable efficient optical refrigeration in such systems.

acceptors in non-radiative energy transfers from nearby excited rare-earth ions, followed by multi-phonon relaxation; and (3) the aforementioned metal ions can also directly absorb pump light (background absorption) and subsequently release this energy as heat into the solid by multi-phonon relaxation. Model calculations suggest that the concentration of such impurities must be on the order of 100 parts-per-billion (ppb) or less in order for laser cooling to reach practical efficiencies [2]. Such purities far exceed those of most commercially available precursor materials and, as a consequence, require additional purification during the preparation of the laser-cooling material.

The situation is complicated by the complexity of some of the laser-cooling materials studied to date, in particular ZBLAN, a fluoroaluminate glass with a typical composition 53%ZrF₄–20%BaF₂–4%LaF₃–3%AlF₃–20%NaF (mol%). The ZBLAN glass composition has been widely studied in the 80s and 90s, and it has been optimized for the fabrication of ultra-low-loss optical fibers [20]. The first laser-cooling materials used ZBLAN glasses from this development, and this legacy persists to this date. ZBLAN, however, is a difficult material to produce in the purity required for laser cooling. First, ZBLAN has 5 basic components to which the metal fluoride of the active ion (e.g. YbF₃ or TmF₃) and an oxidizer (e.g. InF₃) are added. The latter is used at typically 2–3 mol% levels to prevent the chemical reduction of ZrF₄ to ZrF₃ and ZrF₂ species that cause undesired black precipitates in the glass matrix [21]. Second, the relative chemical inertness of most of these 7 precursors precludes the direct purification of the metal fluorides. Rather, aqueous solutions of the respective metal ions or solutions of organo-metallic precursors have to be purified individually before the respective metal fluoride is synthesized [4]. The many steps involved in purification and processing of ZBLAN precursors are not only extraordinarily laborious but also prone to recontamination. As a result, impurity levels of <100 ppb are extremely challenging to achieve in practice. The residual impurities are believed to be the main reason why laser cooling to <170 K has not yet been realized.

2.3 Device limitations

A number of additional challenges arise during the incorporation of a high-quality laser-cooling material into an optical cryocooler device. First, a reliable, high-power, and preferably tunable laser is needed to pump the cooling element at the design wavelength. Semiconductor lasers and optical parametric oscillators (OPOs) are well suited for pumping in the 1.0 – 4.5 μm wavelength range [22], i.e. for the excitation of Yb³⁺, Er³⁺, Tm³⁺, Ho³⁺, and Dy³⁺ (see Figure 3). The non-linear materials used in OPOs however absorb at wavelengths beyond 4.5 μm and make OPO systems impractical for pumping ions with smaller energy gaps (such as Ce³⁺). Second, the pump light must be confined in the sample to maximize the absorbed power. This is particularly difficult because pumping typically occurs in the long-wavelength tail of the absorption spectrum where absorption coefficients are very low. Various geometries have been successfully demonstrated, such as directly deposited parallel mirrors [5] or resonant cavities [10], but they all involve at least one mirror in close proximity or direct contact with the laser-cooling element. Residual absorption of pump light by the mirror causes heating that in turn reduces the net cooling power available from the device. Third, the device geometry and choice of materials is critical in order to (1) minimize radiative and conductive heat loads from the warm device enclosure, (2) properly manage and dissipate the fluorescent light emanating from the cooling element, and (3) achieve efficient thermal contact to the object to be cooled. Respective designs and actual implementations are in their infancy, and further progress in device design will be critical for realizing practical optical cryocoolers.

3. NOVEL MATERIALS

Advancing the performance of rare-earth-doped laser-cooling materials involves both further development of precursor purification processes and exploration of novel material systems. The focus of this section is on the latter. The search for novel materials can be guided by the following four principles:

1. The internal quantum efficiency criterion $\hbar\omega_{\text{max}} < E_p/8$ (Figure 3) is satisfied
2. A high-power laser technology is available at the design pump wavelength
3. The number of precursors and processing steps is minimal
4. The material is chemically inert and has optical-quality bulk and surface properties.

3.1 Binary fluoride glasses

Fluoride glasses are an attractive class of host materials for laser cooling. With phonon energies in the 500–600 cm^{-1} range, they satisfy the $\hbar\omega_{\text{max}} < E_p/8$ criterion for Yb^{3+} , Er^{3+} , and Tm^{3+} ions for which high-power pump lasers are available. In addition, fluoride glasses are chemically quite inert, mechanically durable, and can be fabricated in high optical quality. However, traditional fluoride glasses such as ZBLAN suffer from complexities in material composition and processing (Section 2.2). Fluoride glasses having fewer components would offer critical advantages in processing and, therefore, would be less difficult to produce in the required high purities.

The formation of a stable glass depends on both the *glass-forming ability* of the composition upon cooling from the liquid state and the *glass stability* against crystallization. The dynamics of these processes is poorly understood on an atomic scale. Almost any material can be produced in the glassy state if the rate of cooling from the liquid to the solid phase is sufficiently high. Glass-forming ability is therefore often described in the context of a critical cooling rate, q_{cr} , that is required to produce a sufficiently crystallite-free sample [23]. Likewise, many descriptions for glass stability exist and attempt to capture the complex interplay of phase segregation, nucleation, and crystal growth in glassy systems. Hrubý, for example, defined the parameter $K_H = (T_c - T_g)/(T_m - T_c)$ as a measure for glass stability that can be calculated from the crystallization (T_c), glass-transition (T_g), and melting (T_m) temperatures measured upon heating a glass [24]. Cabral et al found for silicate glasses that the higher the glass stability (K_H) the lower the critical cooling rate (q_{cr}) [23], indicating that the concepts of glass-forming ability and glass stability are related. Possible heterogeneous nucleation on bulk and surface defects however further adds to the complexity of these processes. The development of compositions that can form stable glasses is therefore still carried out largely by laborious trial-and-error experimentation.

McNamara and Mair have developed a semi-empirical model for *glass stability* in fluoride systems [25]. They define a parameter $G_s = (N_c - N)(X_c - X_g)$ that is the product of a nucleation and a crystallization factor. The nucleation parameter (N) and the crystal-growth parameter (X_g) are calculated from known bond strengths, cation radii, latent heat of fusion, and melting temperatures of the individual glass constituents, and $N_c = 8$ and $X_c = 1.9$ are empirical parameters derived from an analysis of a large number of fluoride compositions. G_s can thus be easily calculated and serve as an indicator of glass stability: compositions with $G_s > 0.4$ are expected to form stable glasses, while compositions with $G_s < 0.4$ can be forced to form glasses by rapid cooling but are expected to be unstable and crystallize. The model successfully predicts compositional glass-forming regions in $\text{ZrF}_4\text{--BaF}_2\text{--GdF}_3$, $\text{AlF}_3\text{--CaF}_2\text{--SrF}_2$, and ZBLAN [25].

Fig. 4. Calculated glass-stability parameter G_s [25] for binary glasses of YF_3 and LuF_3 with LiF and AlF_3 and doped with YbF_3 at 0% (solid lines), 2% (dashed lines), and 5% (dotted lines). The $G_s = 0.467$ glass stability of the standard ZBLAN composition is indicated by the horizontal line.

Fig. 5. Calculated glass-stability parameter G_s [25] for the binary YF_3 -LiF glass doped with 2% of different rare-earth fluorides.

A computational survey of binary fluoride compositions using above model [25] finds that YF_3 and LuF_3 are expected to form glasses with exceptionally high stability. Figure 4 shows the calculated glass-stability parameter G_s for the binary glasses YF_3 -LiF and YF_3 -AlF₃ as well as LuF_3 -LiF and LuF_3 -AlF₃ for 0%, 2%, and 5% doping with YbF_3 . The model suggests that all these systems form stable glasses over a wide compositional range. The binary 47% YF_3 -53%LiF is predicted to be the most stable glass in this family, and it significantly exceeds the $G_s = 0.467$ glass stability of the standard ZBLAN composition 53% ZrF_4 -20% BaF_2 -4% LaF_3 -3% AlF_3 -20% NaF (indicated by horizontal line). Similarly high glass stability is predicted for percent-level doping of YF_3 -LiF with other rare earths such as TmF_3 , ErF_3 , and HoF_3 (see Figure 5).

Despite the predicted high glass stability in the YF_3 -LiF system, our preliminary experiments have not produced any glasses. The composition 47% YF_3 -53%LiF was melted under inert atmosphere in a lidded platinum crucible for 3 hours at 1170 °C, i.e. above the individual melting temperatures of YF_3 (1152 °C) and LiF (842 °C). The visually clear melt readily crystallized during cooling at rates ranging from 20 to 50 K/s in both platinum and glassy-carbon molds. From the results of Cabral et al on silicate glasses we infer that the predicted high glass stability of 47% YF_3 -53%LiF should correlate with a low critical cooling rate (with respect to the cooling rate that is used for fabricating ZBLAN, for example). The observed crystallization of the samples, therefore, may be due to heterogeneous nucleation. In particular, microscopic YF_3 crystallites that remain due to incomplete melting of the YF_3 precursor may act as seeds for crystal growth during cooling. Longer melting times and higher melting temperatures are currently being explored.

3.2 Dy^{3+} -doped chloride and bromide crystals

Theoretical cooling efficiencies are $\sim 3\times$ higher in Dy^{3+} than in Yb^{3+} because its lower energy of the first excited state compared to Yb^{3+} . Pumping wavelengths for Dy^{3+} are around 3.1 μm where high-power OPO systems are available. Furthermore, the ${}^6\text{H}_{13/2}$ first excited state may be substantially less sensitive to quenching by multi-phonon relaxation via metal-ion impurities. The transition-metal ions Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , V^{3+} , Cr^{3+} , and Ti^{3+} that are problematic for Yb^{3+} have negligible absorption beyond $\sim 2.7 \mu\text{m}$ [26] and are neither expected to be efficient acceptors in non-radiative energy transfers from Dy^{3+} nor contribute significantly to background absorption. The challenging purity requirements of Yb^{3+} systems may therefore be greatly relaxed in Dy^{3+} and substantially facilitate the material preparation.

Chloride or bromide materials with phonon energies in the 150–300 cm^{-1} range are needed to satisfy the $\hbar\omega_{\text{max}} < E_p/8$ criterion for Dy^{3+} (see Figure 3). Crystals and glasses of these halides are typically extremely moisture-sensitive and pose respective challenges in handling and device integration. Despite of that, some chlorides and bromides have been

developed into commercial products, such as the gamma-ray scintillator crystals $\text{LaCl}_3:\text{Ce}^{3+}$ and $\text{LaBr}_3:\text{Ce}^{3+}$. One attractive chloride system is KPb_2Cl_5 , a material that is unique among the heavy halides as it is not hygroscopic [27]. KPb_2Cl_5 has already shown some optical refrigeration with Er^{3+} [9] and Yb^{3+} [14, 28] dopants. Its low phonon energy of 203 cm^{-1} is expected to enable an internal quantum efficiency of 100% for the emitting ${}^6\text{H}_{13/2}$ excited state of Dy^{3+} . KPb_2Cl_5 also has only two precursors (plus the dopant) and can be produced in cm^3 sizes by zone refining and Bridgman growth. However, quenching of the ${}^6\text{H}_{13/2}$ first excited state by OH^- impurities has been reported [27]. With proper control of OH^- impurities, $\text{KPb}_2\text{Cl}_5:\text{Dy}^{3+}$ is expected to be a prime candidate for efficient laser cooling.

4. CONCLUSIONS

Optical refrigerators based on rare-earth-doped solids have the potential to cool to $<100\text{ K}$ and offer an attractive alternative to TECs that are limited to $\sim 170\text{ K}$. Efficient optical refrigeration is possible in materials for which $\hbar\omega_{\text{max}} < E_p/8$, a criterion that can be a useful guide in the search for novel laser-cooling materials. Residual transition-metal and OH^- impurities at levels exceeding 100 ppb are believed to be the main reason why laser cooling to $<170\text{ K}$ has not yet been realized. The many precursors of doped ZBLAN glass pose particular challenges in purification and material processing and emphasize the need for systems with fewer components. A computational study of glass formation in binary fluorides finds several YF_3 and LuF_3 binary glasses with high glass stabilities. Heterogeneous nucleation was likely limiting the glass formation in preliminary experiments with the $\text{YF}_3\text{--LiF}$ system. Finally, the non-hygroscopic $\text{KPb}_2\text{Cl}_5:\text{Dy}^{3+}$ crystal was identified as a prime candidate laser cooling. It is expected to be less sensitive to transition-metal impurities and has the potential to surpass the laser-cooling efficiency of Yb^{3+} materials by a factor of three.

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