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Infrared to visible up-conversion in thulium and holmium doped lutetium aluminum garnet

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Abstract

We report on the up-converted emissions at 367, 458 and 483 nm in thulium doped lutetium aluminum garnet (LuAG) under infrared excitation in the range of 730–800 nm. We also observe blue and strong green emission in thulium and holmium codoped LuAG with near infrared excitation. Excitation spectra, power dependence, temporal behavior and temperature dependence of up-converted emissions were measured to explain the up-conversion mechanisms. Several cross-relaxation mechanisms and excited state absorption are found to be responsible for the observed up-conversion processes.

Keywords: Tm:LuAg; Tm; Ho:LuAG; Up-conversion; Energy transfer

1. Introduction

Rare earth ion doped lutetium garnets, $Lu_3Al_5O_{12}$ (LuAG), are efficient materials in generating near-infrared laser radiation at room temperature [1]. In particular, Tm or Tm,Ho doped LuAG has been proven to be most promising for laser action around 2 μm [2–4]. While spectroscopic studies have been scarce in these materials, Patel et al. [5] reported the photon avalanche up-conversion in Tm^{3+}:LuAG under 618 nm excitation. The same group reported the spectroscopic and up-conversion studies in Ho^{3+}:LuAG [6]. So far most of the up-conversion studies in Tm doped materials were concerned with the excitation in the region 617–650 nm [5,7] or dual wavelength pumping at 785 and 628–648 nm [8,9] as they provide good energy matching for pumping mechanism. To our knowledge there is no report on the infrared to blue (483 and 458 nm) up-conversion emission from $^1G_4$ and $^1D_2$ states in the Tm-doped materials with single wavelength excitation around 780 nm. This wavelength matches with the strong ground state absorption of Tm^{3+} ion. Here we report on the up-conversion in 4%Tm^{3+}:LuAG with near infrared excitation in the range 750–800 nm. The dynamics of up-conversion is explained by taking into account various cross-relaxation and excited state absorption (ESA) processes. We also report on the blue–green visible up-conversion in 6%Tm,0.36%Ho co-doped LuAG using near infrared excitation.

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The up-conversion process results from the Tm^{3+} to Ho^{3+} energy transfer and ESA in Ho^{3+} ions.

2. Experimental

The crystals used in the present study, 4%Tm:LuAG, and 6%Tm,0.36%Ho:LuAG were purchased from Scientific Materials Corporation. Absorption spectra were measured with an UV–VIS spectrophotometer (UVIKON, Contron) in the range 300–850 nm. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a tunable CW Ti:sapphire laser pumped by an Ar^{+} laser operating in the range 700–800 nm. Low temperature measurements were made by using a closed cycle He optical cryostat. Lifetime measurements of Tm:LuAG were performed with a Nd:YAG laser-pumped dye laser, and temporal buildup of up-conversion emission under CW excitation was measured using an electronic shutter and a digital oscilloscope.

3. Results and discussion

The up-conversion emission spectra of Tm:LuAG under 780 nm excitation measured at both room temperature (RT) and 40 K are shown in Fig. 1. The bands observed at 365, 458, 483 and 521 nm correspond to $^1D_2\rightarrow{}^3H_6$, $^1D_2\rightarrow{}^3F_4$, $^1G_4\rightarrow{}^3H_6$ and $^1D_2\rightarrow{}^3H_5$ transitions, respectively. The blue bands at 458 and 483 nm are very intense and overlap. A very weak green band observed at 540 nm is probably due to a small holmium impurity as there is no such possible emission in the case of the Tm^{3+} ion. The spectrum of Tm^{3+}:LuAG indicates that both $^1G_4$ and $^1D_2$ levels are populated in the up-conversion process. From Fig. 1 it is clear that up-conversion emission is less at 40 K compared to RT. This is due to the reduced probability for cross-relaxation processes at low temperatures that are the main energy transfer mechanisms in the up-conversion.

Fig. 2 shows the absorption of $^3H_6\rightarrow{}^3H_4$ and PLE spectra for 483 and 458 nm emissions of Tm^{3+}:LuAG at RT. The PLE spectra are similar except intensity and the up-conversion is predominant in the strong ground state absorption (GSA) region. A difference between PLE spectra for 483 and 458 nm is that the weak band present around 763 nm for 483 nm blue emission is not observed for 458 nm emission. This difference arises due to weak GSA in the ~763 nm region which cannot populate the $^1D_2$ level.

Fig. 3 shows the pump power dependence of blue emissions (483 and 458 nm) at both 15 K and

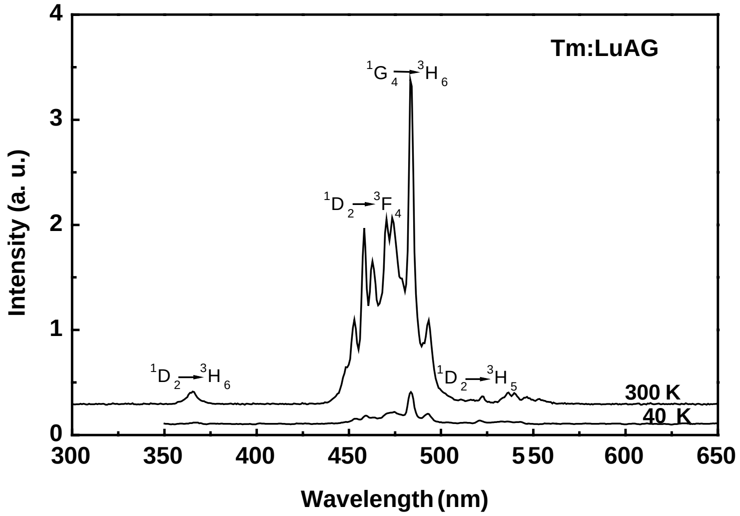


Fig. 1. Up-conversion emission spectra of Tm:LuAG under 780 nm excitation at 40 K and RT.

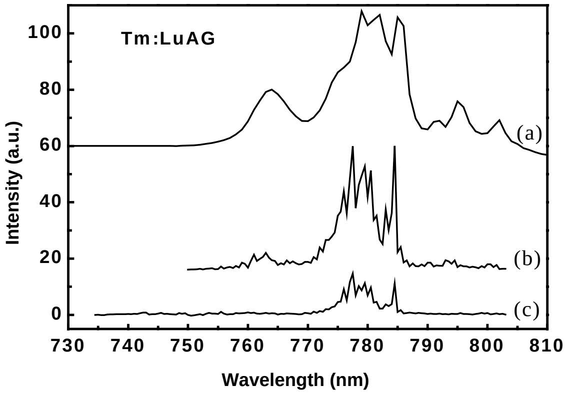


Fig. 2. (a) Absorption and PLE spectra at (b) 483 nm and (c) 458 nm in Tm:LuAG at RT.

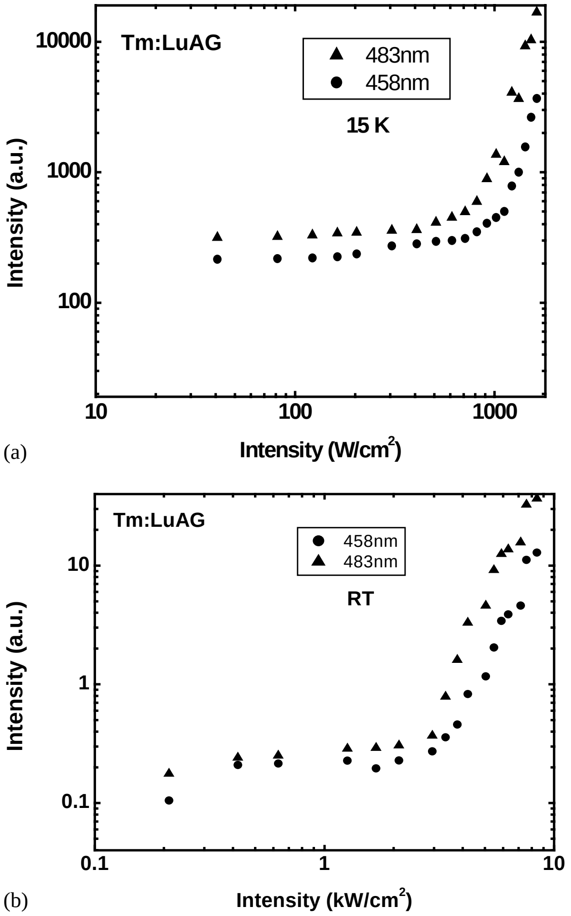


Fig. 3. Pump power dependence of blue up-conversion emissions of Tm:LuAG at (a) 15 K and (b) RT.

RT. The slopes of log–log plots of power and intensity shows some unusal behavior. At 15 K, the slopes of 483 and 458 nm emissions are very small up to 800 W/cm^2 intensity and then increase to 4 and 6, respectively. At RT, both the slopes of 483 and 458 nm emissions are 0.2 up to 2 kW/cm^2 intensity and then also increase to 4. These results indicate that there exists some avalanche type up-conversion but we could not observe the saturation point within our power limitations.

We measured the temporal behavior of two blue up-converted emissions in Tm^{3+}:LuAG at RT and the results are shown in Fig. 4 for a CW pump intensity of 6.3 kW/cm^2 at 780 nm. We observed rise times of 430 and 450 μs for 483 and 458 nm emissions, respectively, after taking account the shutter response time. The rise time implies that the feeding level for $^1G_4$ or $^1D_2$ levels has a lifetime of about 100 μs. The $^3H_4$ and $^1G_4$ levels could be responsible for 483 and 458 nm, respectively, because the lifetime of $^3H_4$ is a little bit longer than that of $^1G_4$. The rise times of both the emissions are found to decrease with increase in power as shown in the inset, which indicates the shortening of the lifetimes of the feeding levels due to effective energy transfer. For example, the rise time for 483 nm decreases from 2200 to 400 μs when the pump intensity is increased from 3 to 7 kW/cm^2. The experimental decay curves of the

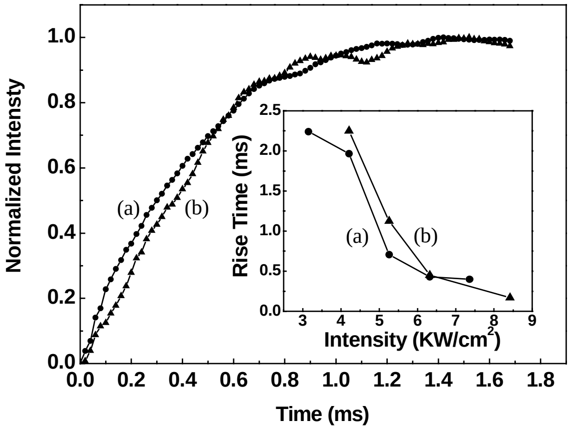


Fig. 4. Temporal behavior of: (a) the 483, and (b) 458 nm emission buildups in Tm:LuAG at an intensity of 6.3 kW/cm^2. Inset shows the variation of rise time with pump intensity.

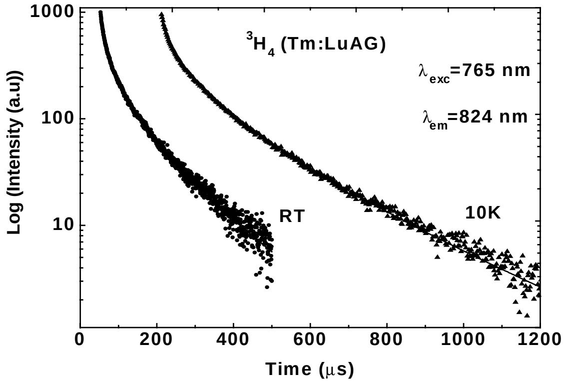


Fig. 5. Inokuti–Hirayama model fitting of decay curves of the $^3H_4$ level of Tm:LuAG at 10 K and RT. The excitation and emission wavelengths are 765 and 824 nm, respectively.

$^3H_4$ level at RT and 10 K as shown in Fig. 5 have been analyzed in the frame work of the Inokuti–Hirayama model [10] for energy transfer processes. In this model, the time dependence of the donor emission is

$$I(t) = I_0 \exp\left[-\frac{t}{\tau_0} - \alpha\left(\frac{t}{\tau_0}\right)^{3/s}\right] \tag{1}$$

in which τ_0 is the intrinsic lifetime of donors in the absence of acceptors. This value is taken as 645 μs reported for the $^3H_4$ level of 0.1 at% Tm^{3+}:YAG at 10 K [11] as the intrinsic value is not available for low concentrated Tm^{3+}:LuAG and both hosts have the same structure. The fitting parameter α is given by

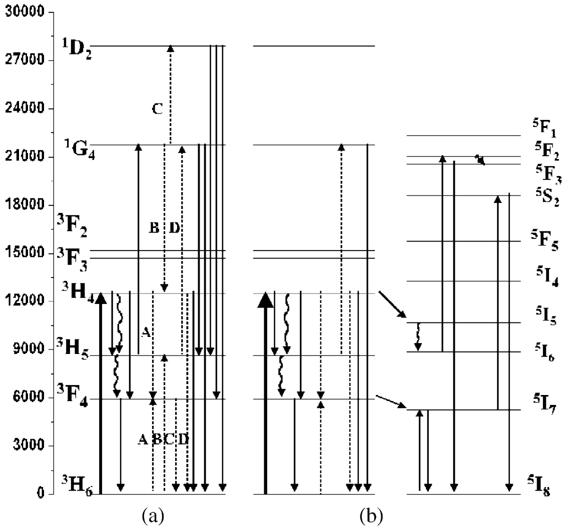
$$\alpha = \frac{4}{3}\pi\Gamma\left(1 - \frac{3}{s}\right)N_0 R_0^3, \tag{2}$$

where Γ is the gamma function, N_0 is the concentration of acceptors (8.2×10^{20} ion/cm^3), and R_0 is the critical distance defined as a donor–acceptor separation for which the rate of energy transfer to the acceptors is equal to the rate of intrinsic decay of the donor. We considered the interaction between Tm^{3+} ions as dipole–dipole type ($s = 6$) and obtained a good fit between the model and experimental curves. A fitting procedure gave α and R_0 as calculated from Eq. (2). The dipole–dipole interaction parameter C_{da} was evaluated from the relation, $C_{da} = R_0\tau_0^{-1}$. The values for the lifetime (τ), α, R_0, and C_{da} are presented in Table 1. The decrease in lifetime and increase in C_{da} parameter from 10 to 300 K are measures of increasing cross-relaxation quenching of the $^3H_4$ level.

We propose the model shown in Fig. 6a to explain the above up-conversion process. The pump photon excites the ions to the $^3H_4$ level. Subsequent non-radiative and radiative relaxation populates the $^3H_5$ level. This level has short lifetime of 13 μs [12] due to fast non-radiative decay to the next lower level, $^3F_4$. Though the $^3H_5$ level has very small initial population, the energy gap between $^3H_5$ and $^1G_4$ is well matched to the excitation wavelength. Thus, the second photon pumps the ions from the $^3H_5$ to the $^1G_4$ level. There is another possible cross-relaxation (CR) excitation mechanism D, $^3H_4$–$^3H_6$ and $^3H_5$–$^1G_4$

Table 1
Parameters of decay curve analysis of the $^3H_4$ level

Parameter	10 K	RT
α	3.56	5.40
R_0 (nm)	84	96
C_{da} (cm^6/s)	5.37×10^{-40}	12.2×10^{-40}
τ (μs)	210	55



(a) (b)

Fig. 6. Partial energy level diagram showing the up-conversion mechanisms in: (a) Tm:LuAG, and (b) Tm,Ho:LuAG. A, B, C, and D are different cross-relaxation processes.

which can populate the $^1G_4$ level. Due to energy matching and large branching ratio of the $^3H_4 \rightarrow {}^3H_6$ transition, this CR D also plays a prominent role in the excitation process. Once the $^1G_4$ level is populated, another process, CR B, $^1G_4$–$^3H_4$, followed by relaxation to $^3H_5$, and $^3H_6$–$^3H_5$, can repopulate the $^3H_5$ level. This feedback mechanism may increase the population of $^3H_5$ for a while to reach the steady state. Though we could not observe the $^1G_4 \rightarrow {}^3H_5$ transition in up-conversion emission since it has the same wavelength as the pumping laser light, this is the next most probable transition from $^1G_4$ after $^1G_4 \rightarrow {}^3H_6$ [11]. These mechanisms, ESA, CR B and CR D explain strong blue emission (483 nm) in the up-conversion spectrum. The CR C, $^3F_4$–$^3H_6$ and $^1G_4$–$^1D_2$ populates the $^1D_2$ level. This appears to be a reasonable pumping mechanism to $^1D_2$ due to matching of energies, high population in the meta-stable state $^3F_4$ and strong emission of $^3F_4 \rightarrow {}^3H_6$ with a lifetime of a few ms [12]. Also, the well known CR A process, $^3H_4$–$^3F_4$ and $^3H_6$–$^3F_4$ causes large population to build up in the $^3F_4$ level. Three transitions from $^1D_2$ (365, 458, and 521 nm) are observed in the up-conversion spectrum, in which the weak 521 nm transition, $^1D_2 \rightarrow {}^3H_5$, again helps to populate the $^3H_5$ level. Recently Wyss et al. [13] also observed the bluish-green emission (~480 nm) in a Tm^{3+}:$GdVO_4$ crystal with 797 nm quasi-CW excitation. They also proposed CR B and ESA from $^3H_5$ to $^1G_4$ levels to explain the up-conversion process. The slower rise time observed for 483 nm compared to 458 nm emission in Fig. 4 may be due to the process that the $^1G_4$ level is populated first and then $^1D_2$ level which is in accordance with our model. Competition between three cross-relaxation processes, B, C and D, as well as the difference in intrinsic lifetimes of the $^3H_5$ and $^1G_4$ levels. The observation of relative increase of 458 nm emission with temperature compared to 483 nm in Fig. 1 may result from the increase of CR C. The decrease in lifetime of $^3H_4$ level from 210 μs at 10 K to 55 μs at 300 K in Fig. 5 is due to increase in CR A and D in which CR A is more efficient. This implies that the population of the $^3F_4$ level increases with temperature which in turn favors CR C processes. The increase of overall emissions with temperature may be due to the increase of CR B and D processes which support our model.

The up-conversion spectrum of Tm,Ho:LuAG under 780 nm excitation is shown in Fig. 7 consists of an intense green band at 540 nm and a weak band at 483 nm. Fig. 8 shows the PLE spectra of green emission for Tm,Ho:LuAG at 15 K and RT. The region of 760–800 nm corresponds to GSA of Tm^{3+} and the 735–765 nm corresponds to ESA of $^5I_7 \rightarrow {}^5S_2$ transition. At room temperature, there are some weak bands at around 780 nm whereas at low temperature, there is no green emission in this

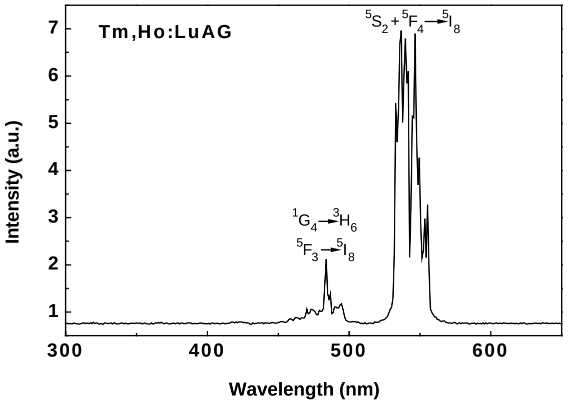


Fig. 7. Up-conversion emission spectra of Tm,Ho:LuAG at RT with excitation intensity of 7.4 kW/cm^2 at 780 nm.

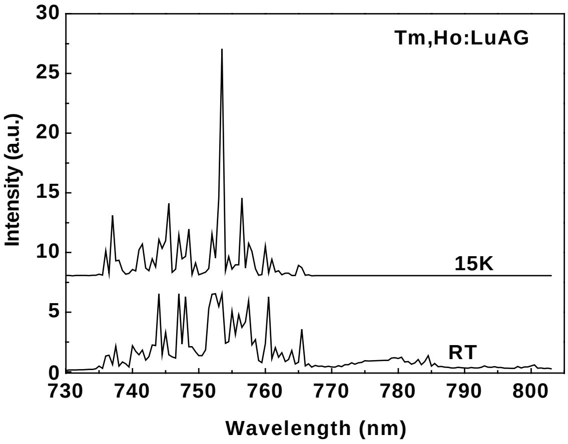


Fig. 8. PLE spectra for the green emission in Tm,Ho:LuAG at 15 K and RT.

region. Tyminski et al. [14] and Jani et al. [15] observed green fluorescence in Tm,Ho:YAG crystal when excited in the range of 745–785 nm. They explained the green up-conversion as due to both ESA of the $^5I_7 \rightarrow {}^5S_2$ transition and cooperative energy transfer between Tm^{3+} and Ho^{3+} ions. We also explain the green emission with both ESA and cooperative energy transfer processes. Fig. 9 shows the pump power dependence of the green emission. The slopes of log–log plot are about 1.5 at both 15 K and RT, suggesting a two photon excitation process. The rise time of the green emission was measured at different powers and the results are presented in Fig. 10. The rise time at 6.3 kW/cm^2 intensity under CW excitation is found to be about 0.9 ms and it decreases with increasing intensity as shown in the inset. The increase can be explained by a fast accumulation in $^3F_4$ level of Tm which is the feeding level for the $^5I_7$ of Ho. We summarize the up-conversion mechanism as shown in Fig. 6b. The pump photons first populate the $^3H_4$ level of Tm^{3+}. The excited ion relaxes to the $^3F_4$ level producing two ions in the $^3F_4$ level by cross-relaxation energy transfer between neighboring Tm^{3+} ions. The excited Tm^{3+} ions then transfer their excitation energy to the $^5I_7$ level of Ho^{3+} ions. The pump photons can also excite the ions from $^5I_7$ to $^5S_2$ level causing green emission, at 540 nm. The peak at 484 nm is the overlapping region of $^1G_4 \rightarrow {}^3H_6$ of Tm^{3+} and $^5F_3 \rightarrow {}^5I_8$ of Ho^{3+} ions. There are two possible mechanisms for the origin of this peak. One is cross-relaxation energy transfer between Tm^{3+} ions, $^3H_4$–$^3H_6$ and $^3H_5$–$^1G_4$ which was previously described. The second one is energy transfer from the Tm^{3+} $^3H_4$ to the Ho^{3+} $^5I_5$ level followed by non-radiative decay to the $^5I_6$ level. Then ESA populates $^5F_2$ level which decays non-radiatively to $^5F_3$. The ions then decay to ground state producing the blue emission.

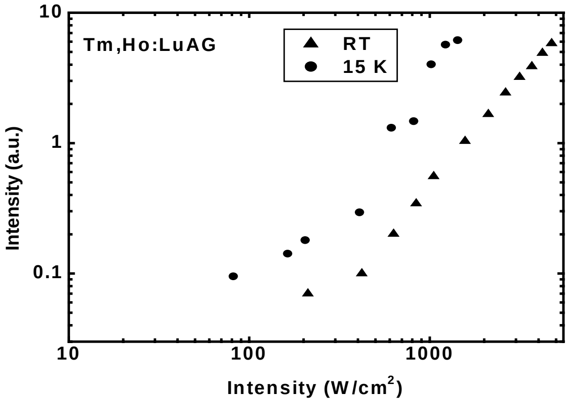


Fig. 9. Pump power dependence of the 540 nm emission of Tm,Ho:LuAG at 15 K and RT.

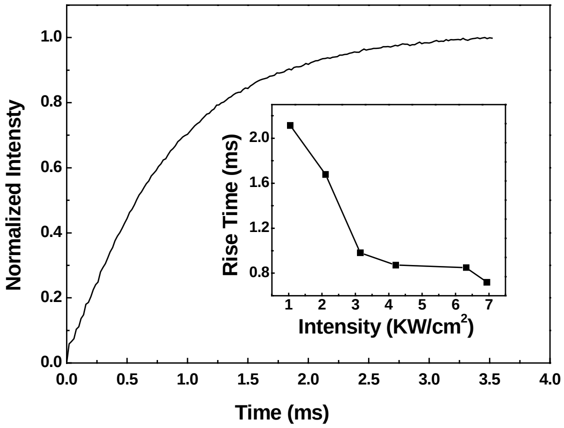


Fig. 10. Temporal behavior of the 540 nm emission buildup in Tm,Ho:LuAG at an intensity of 6.3 kW/cm^2. Inset shows the variation of rise time with pump intensity.

Acknowledgements

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