

Novel approach towards cross-relaxation energy transfer calculation applied on highly thulium doped tellurite glasses

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Abstract: In this paper we calculated, for the first time to the best of our knowledge, the cross relaxation parameter of Tm³⁺ ions in tellurite glasses over a wide range of concentrations: from 0.36 mol% up to 10 mol%. A new measurement approach based on emission spectra monitoring is proposed. This method is very simple and allows to measure even very highly doped samples. The obtained values of cross-relaxation parameter show a linear dependence with respect to dopant concentration over the full investigated interval, suggesting a dipole-dipole interaction process. The measured slope is $1.81 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ mol\%}^{-1}$.

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OCIS codes: (160.5690) Rare-earth-doped materials; (160.2750) Glass and other amorphous materials.

References and links

1. D. C. Hanna, I. M. Jauncey, R. M. Percival, I. R. Perry, R. G. Smart, P. J. Suni, J. E. Townsend, and A. C. Tropper, "Continuous-wave oscillation of a monomode thulium-doped fibre laser," *Electron. Lett.* **24**(19), 1222–1223 (1988).
2. S. D. Jackson and A. Lauto, "Diode-pumped fiber lasers: a new clinical tool?" *Lasers Surg. Med.* **30**(3), 184–190 (2002).
3. J. Y. Allain, M. Monerie, and H. Poignant, "Tunable CW lasing around 0.82, 1.48, 1.88 and 2.35 μm in thulium-doped fluorozirconate fibre," *Electron. Lett.* **25**(24), 1660–1662 (1989).
4. E. R. M. Taylor, L. N. Ng, J. Nilsson, R. Caponi, A. Pagano, M. Potenza, and B. Sordo, "Thulium-doped tellurite fiber amplifier," *IEEE Photon. Technol. Lett.* **16**(3), 777–779 (2004).
5. M. Yamane and Y. Asahara, *Glasses for Photonics* (Cambridge University Press, 2004).
6. A. Jha, S. Shen, and M. Naftaly, "Structural origin of spectral broadening of 1.5- μm emission in Er³⁺-doped tellurite glasses," *Phys. Rev. B* **62**(10), 6215–6227 (2000).
7. T. Yamamoto, Y. Miyajima, and T. Komukai, "1.9 μm Tm-doped silica fibre laser pumped at 1.57 μm ," *Electron. Lett.* **30**(3), 220–221 (1994).
8. J. Wu, S. Jiang, T. Luo, J. Geng, N. Peyghambarian, and N. P. Barnes, "Efficient thulium-doped 2- μm germanate fiber laser," *IEEE Photon. Technol. Lett.* **18**(2), 334–336 (2006).
9. Q. Huang, Q. Wang, J. Chang, X. Zhang, Z. Liu, and G. Yu, "Optical parameters and upconversion fluorescence in Tm³⁺/Yb³⁺ co-doped tellurite glass," *Laser Phys.* **20**(4), 865–870 (2010).
10. B. Richards, Y. Tsang, D. Binks, J. Lousteau, and A. Jha, "Efficient 2 μm doped tellurite fiber laser," *Opt. Lett.* **33**(4), 402–404 (2008).
11. P. F. Moulton, G. A. Rines, E. V. Slobodtchikov, K. F. Wall, G. Frith, B. Samson, and A. L. G. Carter, "Tm-Doped Fiber Lasers: Fundamentals and Power Scaling," *IEEE J. Sel. Top. Quantum Electron.* **15**(1), 85–92 (2009).
12. A. S. S. de Camargo, S. L. de Oliveira, D. F. de Sousa, L. A. O. Nunes, and D. W. Hewak, "Spectroscopic properties and energy transfer parameters of Tm³⁺ ions in gallium lanthanum sulfide glass," *J. Phys. Condens. Matter* **14**(41), 9495–9505 (2002).
13. R. R. Petrin, M. G. Jani, R. C. Powell, and M. Kokta, "Spectral dynamics of laser pumped Y₃Al₅O₁₂: Tm: Ho lasers," *Opt. Mater.* **1**(2), 111–124 (1992).
14. C. A. Evans, Z. Ikončić, B. Richards, P. Harrison, and A. Jha, "Theoretical modeling of a 2 μm Tm³⁺ doped Tellurite fiber laser: the influence of cross relaxation," *J. Lightwave Technol.* **27**(18), 4026–4032 (2009).

15. D. A. Simpson, G. W. Baxter, S. F. Collins, W. E. K. Gibbs, W. Blanc, B. Dussardier, and G. Monnom, "Energy transfer up-conversion in Tm³⁺-doped silica fiber," *J. Non-Cryst. Solids* **352**(2), 136–141 (2006).
16. H. Gebavi, D. Milanese, R. Balda, S. Chaussedent, M. Ferrari, J. Fernandez, and M. Ferraris, "Spectroscopy and optical characterization of thulium doped TZN glasses," *J. Appl. Phys.* **43**, 135104 (2010).
17. S. D. Jackson and T. A. King, "Theoretical modeling of Tm-doped silica fiber lasers," *J. Lightwave Technol.* **17**(5), 948–956 (1999).
18. H. Gebavi, D. Milanese, G. Liao, Q. Chen, M. Ferraris, M. Ivanda, O. Gamulin, and S. Taccheo, "Spectroscopic investigation and optical characterization of novel highly thulium doped tellurite glasses," *J. Non-Cryst. Solids* **355**(9), 548–555 (2009).
19. J. Wu, S. Jiang, T. Luo, J. Geng, N. Peyghambarian, and N. P. Barnes, "Efficient thulium-doped 2 μm germanate fiber laser," *IEEE Photon. Technol. Lett.* **18**(2), 334–336 (2006).
20. J. Wu, Z. Yao, J. Zong, and S. Jiang, "Highly efficient high-power thulium-doped germanate glass fiber laser," *Opt. Lett.* **32**(6), 638–640 (2007).
21. J. Wu, S. Jiang, T. Qiu, M. Morrell, A. Schulzgen, and N. Peyghambarian, "Cross-relaxation energy transfer in Tm³⁺ doped tellurite glass," in *Optical Components and Materials II* (San Jose, CA, USA, 2005) 152–161.
22. G. X. Chen, Q. Y. Zhang, G. F. Yang, and Z. H. Jiang, "Mid-infrared emission characteristic and energy transfer of Ho³⁺-doped tellurite glass sensitized by Tm³⁺," *J. Fluoresc.* **17**(3), 301–307 (2007).
23. C. R. Giles, C. A. Burrus, D. DiGiovanni, N. K. Dutta, and G. Raybon, "Characterization of erbium-doped fibers and application to modeling 980-nm and 1480-nm pumped amplifiers," *IEEE Photon. Technol. Lett.* **3**(4), 363–365 (1991).
24. C. R. Giles and E. Desurvire, "Propagation of signal and noise in concatenated erbium-doped fiber optical amplifiers," *J. Lightwave Technol.* **9**(2), 147–154 (1991).
25. F. Auzel, F. Bonfigli, S. Gagliari, and G. Baldacchini, "The interplay of self-trapping and self-quenching for resonant transitions in solids; role of a cavity," *J. Lumin.* **94–95**, 293–297 (2001).
26. F. Auzel, G. Baldacchini, L. Laversenne, and G. Boulon, "Radiation trapping and self-quenching analysis in Yb³⁺, Er³⁺, and Ho³⁺ doped Y₂O₃," *Opt. Mater.* **24**(1-2), 103–109 (2003).

1. Introduction

Thulium (Tm³⁺) is an excellent candidate for infrared domain applications thanks to its broad emission spectrum at around 1.8 micron [1] that makes this kind of laser very appealing for several application from precise cut and ablation of biological tissues to LIDAR and sensing applications [2–5]. In addition, Tm³⁺ has the advantage of efficient absorption at 790 nm which is available by using commercial diodes. Various glasses including silica, fluoride and germanate have been used as laser host material [6,7]. An alternative host material is tellurite glass. Amongst of all oxide glasses, tellurite glasses have the lowest phonon energies (~750 cm⁻¹), which lead to increase in optical efficiency and decrease in probability of non-radiative multiphonon decay. Another feature of tellurite glasses is the high rare earth ions solubility comparing with silicate and germanate glasses. That explains why the thulium laser based on tellurite glass is of a great interest [8–10]. Whatever is the kind of glass used, laser development and design optimization relies on accurate modeling and comparison of different concentration levels. Whilst lifetimes and cross-sections are well known, the investigation of cross-relaxation (CR) over a wide range of concentration is still missing, despite its importance [11]. Several methods have been proposed from those based on lifetime measurements [12,13] to the one which were taking into account numerical fitting of fluorescence dynamic versus pump power [14]. Several crystals [13] and glass hosts, including silica [15] and TeO₂ – ZnO – Na₂O (TZN) glass [14], were investigated. The first method however, is limited by the fast quenching of Tm pump level for very high doping concentrations [16] and the second one was, so far, applied to a single relatively low-doped glass sample. Therefore, modeling for different doping levels was relying on approximated data considering this fundamental parameter which has a strong impact on the pumping efficiency [17]. The aim of this paper is to investigate and characterize a set of highly Tm³⁺ doped tellurite glasses with doping level ranging from 0.36 mol% up to 10 mol% and to provide the corresponding value of cross-relaxation parameters. The investigation was based on our previous papers [16,18], especially regarding cross-sections and branching ratios values. To overcome limitation of usual measurement methods we develop the theory of and we propose a new method to calculate the cross-relaxation parameters. This method is based on steady-state fluorescence measurement and is very simple allowing to measure the cross-relaxation parameter even for very highly-doped samples. The presented method allow us to find for the first time, to the best of our knowledge, a general formula for the cross relaxation

parameter. The measurements show that it has a clear linear dependence on the doping level up to 10 mol%. The proposed method has a more general validity and can be applied to other kind of glasses.

2. Theoretical modeling and measurement procedures

Figure 1 shows for sake of clarity the energy-level diagram of the Tm^{3+} ion pumped at 790 nm to the $^3\text{H}_4$ level. The $^3\text{F}_4 \rightarrow ^3\text{H}_6$ emission of the neighboring ion is due to the cross-relaxation process: $^3\text{H}_4, ^3\text{H}_6 \rightarrow ^3\text{F}_4, ^3\text{F}_4$ as indicated in Fig. 1. As the result of this process for one pump photon it is possible to achieve two ions into the $^3\text{F}_4$ manifold [19].

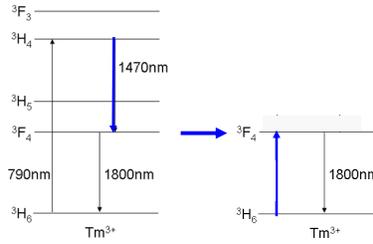


Fig. 1. Simplified energy level diagram of Tm^{3+} ion and scheme of the cross-relaxation process involving two Tm ions.

Since the average distance between two neighboring Tm^{3+} ions plays an important role in co-operative processes, the cross-relaxation parameter should depend on the doping level and this dependency has to be understood. The doping concentration range starts from a very low for long fiber lasers to extremely high for ultra - compact single-frequency lasers. In addition, evaluation of the cross-relaxation process will improve the predictions for a laser performance [20,21]. Tm^{3+} has a quite complex system of energy levels [14] but we can consider empty $^3\text{H}_5$ level due to non radiative fast relaxation to $^3\text{F}_4$ without losing in model accuracy. The corresponding rate-equation system used to analyze our experimental data is:

$$\frac{dN_0}{dt} = -W_{03}N_0 + \frac{N_3}{\tau_{30}} + \frac{N_1}{\tau_1} - C_R N_3 N_0 \quad (1)$$

$$\frac{dN_1}{dt} = \frac{N_3}{\tau_{31}} - \frac{N_1}{\tau_1} + 2C_R N_3 N_0 \quad (2)$$

$$\frac{dN_3}{dt} = W_{03}N_0 - \frac{N_3}{\tau_{30}} - \frac{N_3}{\tau_{31}} - C_R N_3 N_0 \quad (3)$$

where N_0 , N_1 , and N_3 are the populations of Tm^{3+} ions in the $^3\text{H}_6$, $^3\text{F}_4$, and $^3\text{H}_4$ levels respectively, W_{03} is the pump rate (s^{-1}) and C_R the cross relaxation parameter, τ_{xy} is the lifetime of the x to y transition and τ_x is the lifetime of level x. Note that $\tau_3 = (\tau_{31}^{-1} + \tau_{30}^{-1})^{-1}$. The C_R parameter is a function of the Tm doping level. At steady state the time derivatives in the rate equations are equal to zero. Considering the conservation law of Tm^{3+} ions populations, we can also write $N_t = N_0 + N_1 + N_3$. The above rate equations system can be solved using a suitable numerical program. However, to optimize doping level it is important to have available parameters as a function of the concentration. Here, we were focused on the C_R parameter. The cross-relaxation rate $C_R N_0$ can be estimated by using a standard model and the relation from the measurement of the experimental lifetime of $^3\text{H}_4$ level [12,22]:

$$C_R = \frac{1}{N_0} \left(-\frac{1}{\tau_3} + \frac{1}{\tau_3^*} \right) \quad (5)$$

where τ_3^* is the measured lifetime of the $^3\text{H}_4$ level. However, as we will discuss later this requires an experimental set-up with time resolution of the order of 1 μs or below [16] and the sensitivity fail to provide reliable values for very highly-doped samples. To overcome this limitation we propose to investigate the steady-state emission from $^3\text{H}_4$ and the $^3\text{F}_4$ levels. In steady-state condition from Eq. (2) follows:

$$C_R = \frac{1}{2N_0} \left[-\frac{1}{\tau_{31}} + \frac{N_1}{N_3\tau_1} \right] \quad (6)$$

We can now use the Fuchtbauer-Landenburg rule [23] and the relationship that provides the amount of the spontaneous emission [24]. The first rule relates the transition lifetime to emission spectra and emission cross section, the second one the amount of emitted spontaneous photons to the number of excited ions and their emission cross section. Therefore, the emission cross section can be written as:

$$\sigma_{e,ij}(\lambda_{p,ij}) = K \frac{\lambda_{p,ij}^4}{A_{i,j, \text{norm}} n^2(\lambda_{p,ij}) \tau_{ij}} = H \frac{\Phi_{ij}(\lambda_{p,ij})}{N_i \Delta\nu} \quad (7)$$

where σ_{ij} , $A_{ij, \text{norm}}$, τ_{ij} are the emission cross section, the area of emission spectrum normalized to the maximum and the transition radiative lifetime of the transition from level i to level j ; respectively. The parameters H and K are constants independent from the transition, n is the glass refractive index at the transition wavelength; Φ_{ij} is the number of photons emitted at peak wavelength in the frequency interval $\Delta\nu$, N_i is the excited ion population, and $\lambda_{p,ij}$ is the emission peak wavelength of the transition labeled as 'ij'. By combining the two above written equations we have:

$$\frac{N_i}{\tau_{ij}} \propto \frac{\Phi_{ij}(\lambda_{p,ij})}{\Delta\nu_p \lambda_{p,ij}^4} A_{ij, \text{norm}} n^2(\lambda_{p,ij}) \quad (8)$$

Please, note we are not interested in the exact value of the ratio. If we now rewrite the Eq. (6) and use Eq. (8) for the 1800 nm ($i = 1, j = 0$) and 1470 nm ($i = 3, j = 1$) transitions, we have:

$$C_R = \frac{\beta_{31}}{2N_0 \tau_3} \left[\frac{\Delta\nu_{p,31} \Phi_{10} \lambda_{p,31}^4 A_{10, \text{norm}} n^2(\lambda_{p,10}) \tau_{1,0}}{\Delta\nu_{p,10} \Phi_{31} \lambda_{p,10}^4 A_{31, \text{norm}} n^2(\lambda_{p,31}) \tau_1} - 1 \right] \quad (9)$$

where β_{31} is the branching ratio of the 1470 nm transition and is equal to 0.076 [20] and τ_{10} is the lifetime of $^3\text{F}_4$ level for an isolated ion. In the paper we will use this formula to calculate the cross relaxation even for the highest doped samples were Eq. (5) fails due to experimental resolutions limits.

3. Experimental set-up

All samples had the same host composition 75TeO₂-20ZnO-5Na₂O (mol%), labeled as TZN, and were doped with Tm³⁺ concentrations ranging from 0.36 mol% to 10 mol% [16]. In our set-up the excited pump beam from a 785 nm laser diode was first collimated and then focused on the sample edge to reduce undesired effects of radiation trapping and re-absorption that may alter the measurement. The signal was collected orthogonally with respect to the excited beam by a low N.A. lens (N.A. = 0.25). This reduced the signal intensity but at the same time reduced the lifetime measurement errors due to reabsorption. Before the photodiode a long-pass filter with cut-off at around 1500 nm was used to measure the $^3\text{F}_4$ level lifetime whilst a 1450 nm pass-band filter was used to measure the $^3\text{H}_4$ lifetime. The spectra were recorded by an array of ccd covering the 900 nm – 2500 nm wavelength interval.

4. Cross-relaxation measurement

As it is described in the theoretical investigation, in order to obtain the C_R parameter it is necessary to measure the lifetime of ${}^3\text{H}_4$ level for all samples or, alternatively, the lifetime of ${}^3\text{F}_4$ level and the emission spectra. We measured the lifetime of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ levels and fitted the experimental lifetime values using the formula proposed by Auzel et al [25]:

$$\tau = \frac{\tau_0}{\left(1 + \frac{9}{2\pi} \left(\frac{N}{N_q}\right)^2\right)} \quad (10)$$

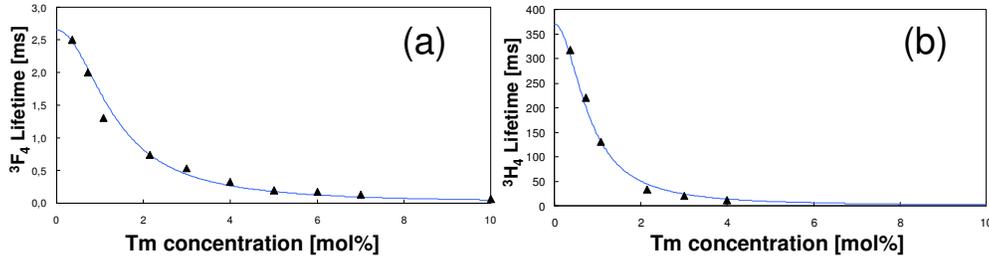


Fig. 2. Measured lifetimes for: (a) ${}^3\text{F}_4$ level, and (b) ${}^3\text{H}_4$ level versus Tm^{3+} concentration.

where τ is the measured lifetime at a given concentration N , τ_0 is the lifetime of a single isolated ion, and N_q the quenching concentration. Figure 2a and Fig. 2b show the measured values. Note that for our purpose we do not need to measure the highest-doped samples.

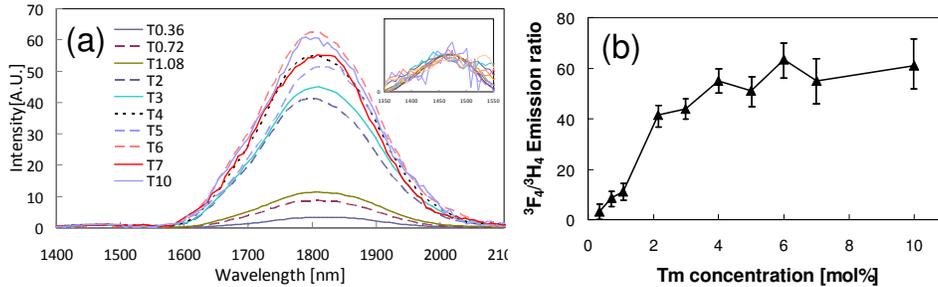


Fig. 3. (a) Emission spectra, inset magnifies the of ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition at 1.47 μm ; (b) Ratio between the emission from ${}^3\text{F}_4$ and ${}^3\text{H}_4$ levels.

The quenching concentration for ${}^3\text{F}_4$ and ${}^3\text{H}_4$ levels obtained by the Eq. (10) were ~ 1.6 and $1 \text{ mol}\%$, respectively. The lifetime τ_0 for ${}^3\text{H}_4$ was 0.37 ms whilst for ${}^3\text{F}_4$ equal to 2.7 ms . For the samples doped with concentrations higher than $4 \text{ mol}\%$ the lifetime of ${}^3\text{H}_4$ level was affected by the response time of our photodiode that is of about few microsecond. To calculate the cross-relaxation parameter for samples with higher doping concentration we measured the emission spectra. Again, samples of Tm-doped tellurite glasses were excited at the wavelength of 785 nm and the two transition bands centered at 1.47 and $1.8 \mu\text{m}$, which corresponding to ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ respectively, were observed and are shown in Fig. 3a where we normalized all curves to the peak of ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition at $1.47 \mu\text{m}$. The ratio between the emission peak from ${}^3\text{F}_4$ and ${}^3\text{H}_4$ levels is reported in Fig. 3b. We were using the peak ratios and not the integral value since the emission shape was not changing significantly.

Using data from emission spectra and Eq. (9) we calculated the C_R parameter. Since the detector bandwidth was similar at 1470 nm and at 1800 nm and the refractive index difference if less than 1% [16], we used the followed approximated equation:

$$C_R = \frac{1}{2N_0 \tau_{31}} [kR - 1] \quad (11)$$

Where $R = (\Phi_{10}/\Phi_{30})(\tau_{1,0}/\tau_1)$ depends on the measurements and ‘k’ contains all other constants $k = (\lambda_{p,31}/\lambda_{p,10})^4 (\Delta\nu_{p,31}/\Delta\nu_{p,10}) (A_{10,norm}/A_{31,norm})$. Since the two peak wavelengths are 1470 nm and 1800 nm and the normalized area of the $A_{31,norm}$ is half the normalized area $A_{10,norm}$ so we have $k = 1.33$. The final value of ‘k’ was also calculated considering frequency interval $\Delta\nu$. The measurement of output spectra were carried out using a similar interval in the wavelength domain, therefore the ratio between frequency intervals were scaled considering $\Delta\nu = c \Delta\lambda/\lambda^2$ where c is the speed of light. Figure 4 shows as triangles the values calculated by using Eq. (11). We can note a quite clear linear increase even for highest doped samples where, however the slope is slightly reduced.

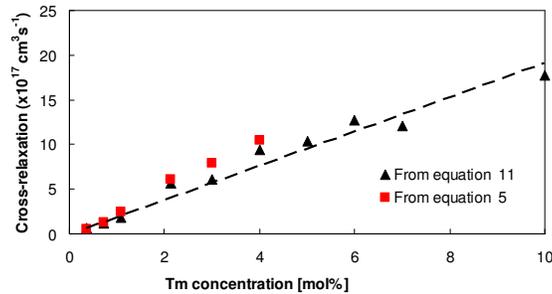


Fig. 4. Cross-relaxation parameter versus Tm concentration.

From the experimental data the fitted C_R is $1.81 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \text{ mol}^{-1}$ is obtained. This value is below the one previously reported in TZN glass [14] but is consisted with the one used for silica fiber modeling [17]. To verify our results further, we used the common method of calculating C_R parameter from Eq. (5) and results are shown in Fig. 4. The linear dependence on concentration of the cross-relaxation parameter is in agreement with the behavior of the concentration quenching of the lifetimes, as predicted by Auzel in the framework of dipole-dipole interaction processes [26]. We can notice an excellent agreement between the two methods until 4 mol%, the highest-doped sample we were able to measure with a suitable accuracy. We believe that the data here reported will be useful to model and design laser in TZN glasses. This measurement method can be easily extended to other type of glasses.

5. Conclusion

We experimentally calculated the cross relaxation parameter of Tm^{3+} ions in tellurite glasses over a wide range of concentrations: from 0.36 mol% up to 10 mol%. A new and simple approach based on the emission spectra measurements was developed to investigate samples with very high doping levels. This approach demonstrates to be very sensitive and can be further applied to other kind of glasses. The obtained values of cross-relaxation show a linear dependence with dopant concentration. The value of the linear fit slope was $1.81 \times 10^{-17} \text{ cm}^{-3} \text{ s}^{-1} \text{ mol}^{-1}$. This value allows a proper modeling of Tm-doped tellurite glass laser using a suitable value for the cross-relaxation parameter.

Acknowledgments

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