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Spectroscopic study of local thermal effect in transparent glass ceramics containing nanoparticles

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Local thermal effect influencing the fluorescence of triply ionized rare earth ions doped in nanocrystals is studied with laser spectroscopy and theory of thermal transportation for transparent oxyfluoride glass ceramics containing nanocrystals. The result shows that the local temperature of the nanocrystals embedded in glass matrices is much higher than the environmental temperature of the sample. It is suggested that the temperature-dependent thermal energy induced by the light absorption must be considered when the theory of thermal transportation is applied to the study of local thermal effect.

Keywords: Fluorescence emission, local thermal effect, nanocrystals, transparent glass ceramics
PACC: 7855H, 6590, 4270F

1. Introduction

Rare earth doped oxyfluoride glass ceramics containing LaF_3 nanocrystals have attracted much attention due to their unique optical properties and potential applications.[1−3] By combining the optical advantages of fluoride crystal with chemical and mechanical merits of oxide glass, oxyfluoride glass ceramics can offer some unique features, for example, they possess a low phonon energy of a fluoride and the durability and mechanical properties of an oxide glass. Previous investigations have shown that the spectral characteristics and luminescence processes of rare earth ions doped in nanocrystals can be affected by the confinement effect or size of nanoparticles, surface effects and defects, distribution of optical active ions, and the materials that nanoparticles are embedded in, etc. Thermal effect and its influence on the luminescence are attracting more and more attention in the study of luminescence and the development of optical materials.[4−7] The local thermal effect on the excitation spectra of Pr^{3+} doped LaF_3 nanoparticles embedded in transparent glasses has been mentioned in Ref.[8], but the mechanism behind it has not been investigated systematically. In this paper, the local thermal effect induced by the laser radiation in a transparent glass ceramics is studied by using laser spectroscopy and theory of thermal transportation. Local temperature and its influence on the luminescence and luminescent dynamics of rare earth ions doped in the nanocrystals are also discussed.

2. Experiments

Samples used in our study are transparent oxyfluoride glasses containing Tm^{3+}: LaF_3 nanocrystals, which were offered by Corning, Inc., New York.[3] The nanocrystal size is about 20 nm, that can be controlled by annealing temperature. The concentration of Tm^{3+} is 0.5 mol%. Nd^{3+}: YAG pulsed dye laser is used as an excitation source. Fluorescence emissions from $^3H_4$(I) and $^3H_4$(II) to $^3H_6$, located at 796.1 nm and 795.5 nm respectively, are chosen for investigating the local thermal effect. An SPEX1702 monochrometer and SR400 photon counter are employed for collecting and recording spectroscopic signals. Fluorescence lifetime measurement is carried out with a TDS 460 A digital oscilloscope. The low temperature environment is supplied with a closed-cycle cooling system.

3. Results and discussion

Fluorescence emissions of Tm^{3+} ions doped inside LaF_3 nanocrystals from the states $^3H_4$(I) and $^3H_4$(II) to $^3H_6$, which has a 9 cm^{-1} separation in between, are chosen for the local thermal effect study (see Fig.1).

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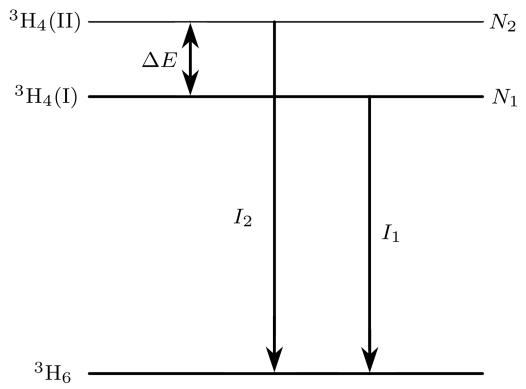


Fig.1. Energy levels and corresponding transitions of Tm^{3+} ions. ΔE is the energy gap, and N_1 and N_2 are ion populations.

Because of the small energy gap between two excited states $^3H_4$(I) and $^3H_4$(II), the population of rare earth ions on the higher excited state $^3H_4$(II) is very sensitive to the local temperature. Therefore, the relative intensity of fluorescence emissions from $^3H_4$(I) and $^3H_4$(II) offers us a practical way to investigate the influence of local temperature by using laser spectroscopy. Fluorescence intensities of the chosen transitions and their corresponding lifetimes can be measured experimentally at various sample bath temperatures. The local temperatures of Tm^{3+} ions under various bath temperatures can be obtained by considering the relations between fluorescence intensity and the population of rare earth ions as well as their lifetimes. Based on this idea, we have measured relative variations of fluorescence intensities of transitions $^3H_4$(II) to $^3H_6$ and $^3H_4$(I) to $^3H_6$ under various sample bath temperatures. The ratio of ion populations, N_2/N_1, is derived from the measurements, and the corresponding local temperatures can be obtained thereby.[8] Table 1 gives the obtained measurements. Figure 2(a) shows the data listed in Table 1.

Local thermal effect and thermal transportation occurring inside the sample can be explored by analysing experimental results based on the theory of thermal transportation. Light absorption of the sample should be the source that causes a rise of local temperature when the sample is under a certain laser irradiation at a given bath temperature. In the case of pulsed laser irradiation, a higher repetition rate of the laser pulse gives a shorter time for the heat to release through the heat conduction and favours heat accumulation, which will help to keep local temperature at a higher level at equilibrium. In our case the repetition rate of the laser pulse is 10 Hz and its influence on the local thermal effect is included in the thermal source. According to the theory of thermal transportation,[9] Poisson equation for a system with a thermal source q_v is written in the following form:

$$\nabla \cdot [k\nabla T(r)] + q_v = 0. \tag{1}$$

Here k is the thermal conductivity, $T(r)$ is the sample temperature at position r, and q_v is the density of thermal power which can be expressed as

$$q_v = Q\mathrm{e}^{-2r^2/b^2} \tag{2}$$

with r being the distance from the point to the symmetric axis of thermal source, and b the radius of the Gauss beam.[10]

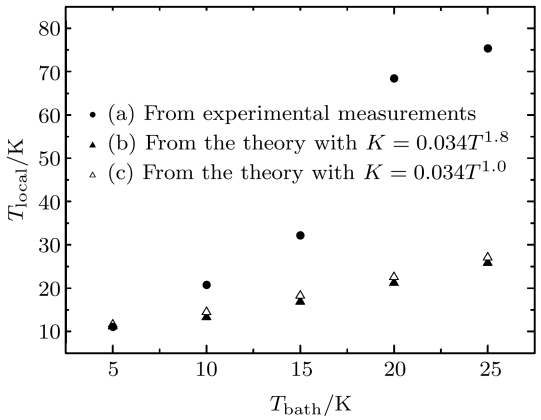


Fig.2. Local temperature T_{local} versus bath temperature T_{bath}, where the data are obtained (a) from experimental measurements (also see Table 1) and (b, c) from the theory of thermal transportation under the condition that the thermal source is independent of the sample bath temperature.

Table 1. Local temperatures vs. sample bath temperatures.

T_0/K	1.5	2.0	5.0	10.0	13.0	15.0	20.0
T_{local}/K	11.0	11.0	11.1	20.7	27.8	32.2	68.4

To acquire the numerical solution, we consider the sample as an infinitely long cylinder with a thermal source along its axis. In our case the thermal source is the excitation laser. Because of the Gauss spatial profile of the laser beam and the cylindrical symmetry of the sample, heat flow is along the radical direction, and the temperature at the surface of cylindrical sample equals the bath temperature. Based on the quasilinear temperature dependence of the homogeneous linewidth and the thermal properties of analogous glass systems,[11–14] we assume that the thermal conduction coefficient is related to the temperature through the equation of $K = A \cdot T^b$, where the value

of parameter b is between 1 and 2. To solve the Poisson equation (1), we introduce a new parameter U and let

$$U = \int_{T_0}^{T} \frac{K_{(T')}}{K_0} \mathrm{d}T', \tag{3}$$

$$\frac{\partial U}{\partial T} = \frac{K(T)}{K_0} \Rightarrow \frac{\partial T}{\partial U} = \frac{K_0}{K(T)}, \tag{4}$$

where T_0 is the reference temperature and K_0 is the value of $K(T)$ at the reference temperature T_0. For $K = 0.034\,T^{1.8}$, let $T_0 = 1$, then we will have $K = K_0 \beta T^{1.8}$.

At the surface of the cylinder, $r = R$ (the radius of the cylindrical sample), $T = t$ (the sample bath temperature), thus

$$T(R) = t \Rightarrow U(R) = \frac{\beta}{2.8}\left(t^{2.8} - 1\right). \tag{5}$$

At the place where the excitation laser passes, $r = b$, and

$$\frac{\partial T}{\partial r} = -\frac{\rho}{K} \Rightarrow \frac{\partial U}{\partial r} = -\frac{\rho}{K_0}, \tag{6}$$

where b is the radius of the light spot, and ρ is the density of the thermal flow resulted from the laser irradiation. Solving the thermal equation (1) under the above boundary conditions yields

$$\frac{q_v}{4K}\left(R^2 - r^2\right) + \frac{q_v b^2 - 2q_v b}{2K} \ln\left(\frac{r}{R}\right) + \frac{1}{2.8}\left(t^{2.8} - 1\right) = \frac{\beta}{2.8}\left(T^{2.8} - t_0^{2.8}\right), \tag{7}$$

which can be expressed as

$$2.8\frac{q_v}{4K}\left(R^2 - r^2\right) + 2.8\frac{q_v b^2 - 2q_v b}{2K} \ln\left(\frac{r}{R}\right) + \frac{1}{2.8}t^{2.8} = T^{2.8}. \tag{8}$$

If the heat absorbed by the sample at the site of the laser irradiation is independent of the bath temperature, then the relation between the local temperature and the sample bath temperature can be obtained by solving the equation with given boundary conditions. Figures 2 shows the experimental (a) and theoretical results obtained with $K = 0.034\,T^{1.8}$ (b) and $0.034\,T^{1.0}$ (c).

Obviously, the experimental results (see case (a) in Fig.2) show that as the bath temperature increases, the local temperature becomes higher and higher, which implies that more and more incident light absorbed by the sample is converted into thermal energy. This is inconsistent with theoretical calculations that the rise of local temperature is almost independent of the sample bath temperature (see cases (b, c) in Fig.2). This inconsistency may result from the specific form of the thermal conductivity, or the preconditions used for the calculation (i.e. the thermal source is independent of temperature). Indeed, the thermal conductivity used for the original calculation is obtained from that of an analogous glass material rather than a glass ceramics containing nanocrystals.[8] The study of glass ceramics has shown that the thermal conductivity of transparent glass ceramics is very close to that of the analogue glass materials at low temperatures, and its homogeneous linewidth also follows a quasilinear temperature dependence. Therefore, the formula of thermal conductivity we have used in the calculation is not likely to be the main cause of the inconsistence between cases (a) and (b, c) in Fig.2. Thus, it is necessary to re-examine the preconditions of the temperature-independent thermal source.

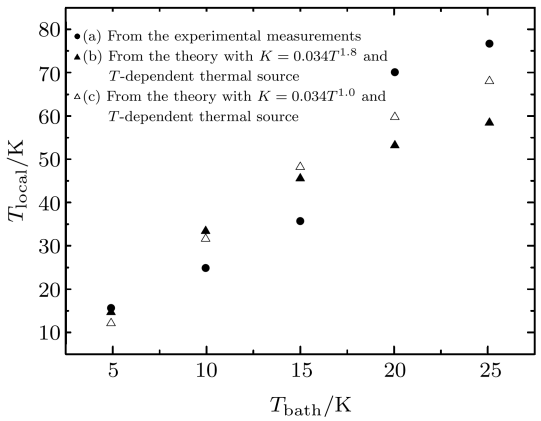


Fig.3. Local temperature T_{local} versus sample bath temperature T_{bath}, where the results are obtained (a) from the measurements (also see Table 1) and (b,c) from the calculations, with the temperature-dependent thermal source adopted in calculation.

As we have pointed out, the rise of local temper-

ature mainly results from the absorption of incident laser light by optically active ions doped in nanocrystals and glass matrices. Only part of the light that is absorbed by the sample can excite optical active ions, the remaining is mainly converted into thermal energy through nonradiative transition and lattice vibration, which actually increases with temperature. Following this idea leads to some necessary correction to the preconditions used in our calculation. Thus, we modify the temperature-independent thermal source by introducing a temperature-dependent thermal source[9] $q_v = q_{\rm ab}(1 + {\rm e}^{T_{\rm m}/T})^{-1}$, where $T_{\rm m}$ is a constant that is 32 K for our case. Substituting the corrected thermal source into the calculations yields the results shown in Fig.3(b, c), indicating good agreement with experimental results.

4. Concluding remarks

Local thermal effect in transparent glass ceramics containing nanocrystals has been studied by using laser spectroscopy and the theory of thermal transportation. It is found that the property of thermal conduction for transparent glass ceramics is similar to that of glass materials. The local temperature of nanocrystals embedded in glass matrices is much higher than the environmental temperature of the sample. The influence of nanosized crystals embedded in glass matrices is not significant for transparent glass ceramics in the study of thermal conduction and diffusion. Since nonradiative relaxation and lattice vibration increase with temperature, the temperature dependence of the thermal energy induced from the light absorption must be considered when the theory of thermal transportation is applied to the study of the relation between the local temperature and sample environmental temperature.

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References

[1] Dejneka M J 1998 *J. Non-Crystalline Solids* **239** 149
[2] Wang Y and Ohwaki J 1993 *Appl. Phys. Lett.* **63** 3268
[3] Zheng H R, Wang X J, Qu S X, Dejneka M J and Meltzer R S 2006 *J. Luminescence* **119** 153
[4] Xu S Q, Fang D W, Zhang Z X, Zhao S L, Zhang L Y, Wang B L and Jiang Z H 2005 *Chin. Phys.* **14** 2246
[5] Peng H S, Song H W, Chen B J, Huang S H, Wang X J, Lu L Z and Yen W M 2003 *Acta Phys. Sin.* **52** 1009 (in Chinese)
[6] Peng H S, Song H W, Chen B J, Wang J W, Lu S Z, Kong X G and Li D C 2002 *Acta Phys. Sin.* **51** 2875 (in Chinese)
[7] Pei Y, Chen X F, Qin L S, Yao D M and Ren G H 2006 *Chin. Phys.* **15** 2756
[8] Zheng H R, Wang X J, Qu S X, Dejneka M J and Meltzer R S 2004 *J. Luminescence* **108** 395
[9] Yu C M 1984 *Heat Conduction* (Beijing, Higher Education Publisher) p 88 and p 472
[10] Li L, Shi P and Bai J T 2004 *J. Xian Jiaotong University* **38** 369 (in Chinese)
[11] Meltzer R S, Zheng H R and Dejneka M J 2004 *J. Luminescence* **107** 166
[12] Zeller R C and Pohl R O 1971 *Phys. Rev.* B **4** 2029
[13] Schmidt T, Baak J, Straat D A, Brom H B and Volker S 1993 *Phys. Rev. Lett.* **71** 3031
[14] Li C, Huo Y J and He S F 1999 *J. Luminescence* **19** 243 (in Chinese)