The Fabrication of Nano-Particles in Aqueous Solution From Oxyfluoride Glass Ceramics by Thermal Induction and Corrosion Treatment

Hua Yu · Nan Hu · Ya-Nan Wang · Zi-Lan Wang · Zong-Song Gan · Li-Juan Zhao

Received: 6 July 2008 / Accepted: 3 October 2008 / Published online: 25 October 2008 © to the authors 2008

Abstract An innovative route is reported to fabricate nano-particles in aqueous solution from oxyfluoride glass by the thermal induction and corrosion treatment in this letter. The investigations of X-ray diffraction and transmission electron microscope based on nano-particles in glass ceramics (GCs) and aqueous solution indicate that the nano-particles formed in glass matrix during the thermal induction process are released to aqueous solution and their structure, shape and luminescent properties in glass host can be kept. Owing to the designable composition of the nano-particles during glass preparation process, the method is a novel way to obtain nano-particles in aqueous solution from GCs.

Keywords Nano-particles · Glass ceramics · Thermal induction and corrosion treatment

Introduction

Since Wang and Ohwaki [1] reported that transparent oxyfluoride glass ceramics (GCs) showed more efficient upconversion (UC) from infrared to visible than fluoride glass in 1993, many researchers have paid attention to oxyfluoride GCs. [2–5] The advantages of these materials are that the rare earth (RE) ions can be incorporated selectively in the fluoride crystal phase with lower phonon energy after thermal induction and the materials remain transparent due to the nano-scale size of precipitated crystals much smaller than the wavelength of visible light. Unlike multiphoton absorption in organic dyes or semiconductor quantum dots (QDs), photon UC involves real intermediate quantum states to generate efficient visible light by near infrared (NIR) excitation. High-efficient luminescent intensity, adjustable size, narrow size distribution and unique optical properties are helpful to practical applications of UC materials, especially RE-ion-doped inorganic nano-particles after heat-treatment, in the fields of flat-panel display, light-emitting diodes, temperature sensors, biolabels, DNA detection, photodynamic therapy, etc [6–10]. Moreover, different nano-particles composition could be designed in glass matrix [11–14]. Unfortunately, ever since the first report on oxyfluoride GCs, there have been much research on the properties of nano-particles in GCs but no publication has been reported about how to obtain free nano-particles in aqueous solution from the GC-host and how to apply it to the fields mentioned above, especially in biological field. Therefore, it is of great significance to develop convenient routes to fabricate inorganic nano-particles doped RE-ion in aqueous solution from GCs in order to meet their practical application requirements.

Silicate oxyfluoride glass is selected here and (Pb,Cd)F$_2$:Er$^{3+}$,Yb$^{3+}$ nano-particles were formed in glass matrix after thermal induction. Acid corrosion treatment was employed to remove the glass matrix in order to obtain free (Pb,Cd)F$_2$:Er$^{3+}$,Yb$^{3+}$ nano-particles in aqueous...
solution. The UC emissions of (Pb,Cd)F$_2$:Er$^{3+}$, Yb$^{3+}$ nanoparticles in aqueous solution have been well characterized by pumping the intermediate $^4I_{11/2}$ state of the Er$^{3+}$ ion via a facile 980 nm NIR diode laser. The 980 nm excitation wavelength is fairly transparent for most large biomolecules and does no damage to them. The UC emissions of (Pb,Cd)F$_2$:Er$^{3+}$, Yb$^{3+}$ nano-particles in aqueous solution are convenient to observe. Additionally, different nanoparticles composition and different RE-ion-dope can be employed for cellular and intracellular target.

**Experimental Details**

Oxyfluoride glasses with composition of 45.5SiO$_2$–40PbF$_2$–10CdF$_2$–0.5Er$_2$O$_3$–4Yb$_2$O$_3$ were prepared. About 20 g of starting material were fully mixed and melted in a covered platinum crucible in air atmosphere at 1,000 °C for 2 h, and then cast into a steel plate. [1–5] To obtain nano-particles in glass ceramic, the glass samples were subsequently heat-treated at 470 °C for 8 h at the nucleation temperature measured by differential thermal analysers (DTA). Using DTA equipment (TA-Inst 2100), samples were held in a Pt crucible and analysed against a calcined Al$_2$O$_3$ reference at a heating rate of 20 °C min$^{-1}$. The nano-particles in aqueous solution were fabricated with the following method. Firstly, the GCs (about 500 mg) were immersed into 5.65 mol/L hydrofluoric acid for 20 h to get rid off silicate glass host. After corrosion treatment, the nano-particles were deposited by solid–liquid separation. Then pH value was adjusted to neutrality by repeated adding distilled water. Finally, the nano-particles in aqueous solution were dispersed using sodium lauryl benzenesulphate. A small quantity of the nano-particles in aqueous solution were dispersed using ultrasonic wave and dispersion of surface active agent. Figure 2 shows the XRD spectrum and TEM image of nano-particles after corrosion treatment process. Phase identification of the nano-particles has been studied by using XRD. The typical XRD patterns show strong diffraction peaks that can be indexed to the $\beta$-(Pb,Cd)F$_2$:Er$^{3+}$,Yb$^{3+}$ phase due to the appreciable shift of XRD peaks position and former research results [15, 16]. No additional or intermediate phase is detected in the sample. The peaks position and half peak breadth of XRD are in concordance with those measured in GCs, which indicates that nano-particles are released from glass matrix to aqueous solution. Moreover, the baseline of XRD is nearly a straight line compared with that of XRD of GCs, which also indicates that silicate glass host is corroded completely. The Fig. 2b is the TEM image of nano-particles after hydrofluoric acid corrosion treatment, adjusting pH value and dispersion of surface active agent. Figure 2 shows the XRD spectrum and TEM image of nano-particles after corrosion treatment process. Phase identification of the nano-particles has been studied by using XRD. The typical XRD patterns show strong diffraction peaks that can be indexed to the $\beta$-(Pb,Cd)F$_2$:Er$^{3+}$,Yb$^{3+}$ phase due to the appreciable shift of XRD peaks position and former research results [15, 16]. No additional or intermediate phase is detected in the sample. The peaks position and half peak breadth of XRD are in concordance with those measured in GCs, which indicates that nano-particles are released from glass matrix to aqueous solution. Moreover, the baseline of XRD is nearly a straight line compared with that of XRD of GCs, which also indicates that silicate glass host is corroded completely. The Fig. 2b is the TEM image of nano-particles in aqueous solution and Fig. 2c reveals the size distribution. The average particle size is obtained as 41.7 nm, which is very close to the former calculation result of nano-particles existing in glass matrix 42.6 nm.

The nano-particles in aqueous solution were obtained by hydrofluoric acid corrosion treatment, adjusting pH value and dispersion of surface active agent. Figure 2 reveals the main UC emission of the $^2H_{11/2}/^4S_{3/2}$ to $^4I_{15/2}$ transition in GCs and in aqueous solution under 980 nm diode laser excitation. The weak ultraviolet UC radiation of the $^4G_{11/2}$ to $^4I_{15/2}$ transition were not shown here, since we focus on the ratio of red and
Fig. 1  a XRD patterns of GCs after thermal induction. The asterisks correspond to JCPDS file NO.06-0251 (β-PbF₂). b TEM micrographs of nano-particles existing in glass matrix. c The size distribution of nano-particles in glass matrix.

Fig. 2  a XRD patterns of dried nano-particles after corroding treatment. The asterisks correspond to JCPDS file NO.06-0251 (β-PbF₂). b TEM micrographs of nano-particles, showing highly dispersive nano-scale quasi-sphere. c The size distribution of nano-particles in aqueous solution.
green fluorescent intensities, which could show the variation of crystal lattice field around the RE-ion. Compared to GCs, the red fluorescent intensity of nano-particles in aqueous solution dramatically increases as shown in Fig. 3. The UC mechanisms of the green and red emissions had been researched by our groups [16, 17]. And the Er³⁺ ion can be promoted to the ⁴I₁₅/₂ state through ground state absorption (GSA) of laser photons, and then to the ⁵H₁₁/₂ state by use of the excited state absorption (ESA) or energy transfer UC (ETU) processes. The ⁴S₃/₂ state can also be populated by relaxations from the upper ⁵H₁₁/₂ state. The green luminescence is emitted by the transition from ⁵H₁₁/₂ and ⁴S₃/₂ state to ⁴I₁₅/₂ ground state. Hence, the green UC luminescence seldom subjects to influence of phonon energy difference of crystal field around the RE ions. The red UC luminescence, however, comes from the phonon-assisted quantum cutting (PQC) process and is primarily generated in low phonon energy crystal lattice field [16]. It is worthwhile to point out that luminescent signal includes emission from RE ions in glass host and fluoride nano-particles at luminescent spectra. In GCs, most of RE ions are incorporated in the fluoride crystal phase, which mainly emit red UC luminescence. Nevertheless, a part of RE ions exists in glass host and mainly emits green UC luminescence. As Fig. 3 shows, the ratio value of red and green UC luminescent intensities increase from 1:1.31 in GCs to 1:0.61 in nano-particles aqueous solution. The key reason for the red UC enhancement arises from the fact that the glass host is corroded by hydrofluoric acid, the fluoride nano-particles formerly embedded in glass matrix are released to aqueous solution and eventually red UC luminescent intensities increase sharply. These results are consistent with the conclusion drawn by XRD and TEM. The nano-particles in aqueous solution have the same luminescent properties as those existing in glass host.

From a practical point of view, it is possible for the nano-particles in aqueous solution from the GC-host to have a potential application as nano-sized probes used in the drug targeting after appropriate modification during the exploration of cellular and intracellular targeting. Under ideal circumstances, nano-particles for site-specific drug delivery, mediated by a targeting sequence, should deliver their payload only to specific target cells, tissues or organs [9, 18]. Moreover, nano-particles may optimize the bio-availability and the bio-distribution of the drug. The nano-particles in aqueous solution from the GC-host also apply in non-invasive imaging by detecting the luminescence of nano-particles inside biological systems, like cells, tissues or whole organisms. The further work for digging out the properties and applications of the nano-particles in aqueous solution is under way.

**Conclusion**

In summary, β-(Pb,Cd)F₂:Er³⁺,Yb³⁺ nano-particles in aqueous solution were prepared by means of thermal induction to produce nano-particles in glass matrix and corroding the glass host by hydrofluoric acid. The nano-particles in aqueous solution have the same structure and luminescent properties as nano-particles existing in glass matrix. Although thermal induction and corrosion treatment were used to prepare β-(Pb,Cd)F₂:Er³⁺,Yb³⁺ nano-particles in aqueous solution in this letter, it may directly apply to any other silicate GCs doped with other RE ions and embedded various composition of nano-particles, since the preparation method is based on a fundamental consideration.

**Acknowledgement** The work is supported by the National Natural Scientific Foundation of China under Grant No. 10574074, 973 Program (No. 2007CB613403), the 111 Project (B07013), Changjiang Scholars and Innovative Research Team in University, the Cultivation Fund of the Key Scientific and Technical Innovation Project from the Ministry of Education of China under Grant No. 704012, Key International Science and Technology Cooperation Project under award No. 2005DFA10170, and National College Students Innovation Project from the Ministry of Education of China under Grant No. NK0713. The authors also thank Cui Guoxin (Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Science) for many helpful suggestions.

**References**

1. Y. Wang, J. Ohwaki, Appl. Phys. Lett. 63, 3268 (1993). doi: 10.1063/1.110170
2. W. Luo, Y. Wang, Y. Cheng, Y. Cheng, F. Bao, L. Zhou, Mater. Sci. Eng. B 127, 218 (2006). doi:10.1016/j.mseb.2005.10.034
3. F. Lahoz, I.R. Martín, U.R. Rodríguez-Mendoza, I. Iparraúirre, J. Azkargorta, A. Mendioroz, R. Balda, J. Fernández, V. Lavín, Opt. Mater. 27, 1762 (2005). doi:10.1016/j.opt.mat.2004.11.047
4. M. Beggionra, I.M. Reaney, Appl. Phys. Lett. 83(3), 467 (2003). doi:10.1063/1.1594842
5. J. Méndez-Ramos, V. Lavín, I.R. Martín, U.R. Rodríguez-Men- doza, V.D. Rodríguez, A.D. Lozano-Gorrín, P. Núñez, J. Appl. Phys. 94(4), 2295 (2003). doi:10.1063/1.1592298
6. F. Liu, E. Ma, D.Q. Chen, Y.L. Yu, Y.S. Wang, J. Phys. Chem. B 110, 20843 (2006). doi:10.1021/jp063145m
7. S. Sivakumar, F.C.J.M. van Veggel, M. Raudsepp, J. Am. Chem. Soc. 127, 12464 (2005). doi:10.1021/ja052583o
8. B. Dong, D.P. Liu, X.J. Wang, T. Yang, S.M. Miao, C.R. Li, Appl. Phys. Lett. 90, 181117 (2007). doi:10.1063/1.2735955
9. D.A. Groneberg, M. Giersig, T. Welte, U. Pison, Curr. Drug Targets 7, 643 (2006). doi:10.2174/138945006777435245
10. L.Y. Wang, Y.D. Li, Comput. Chem. Eng. 24, 2557 (2006)
11. L. Huang, T. Yamashita, R. Jose, Y. Arai, T. Suzuki, Y. Ohishi, Appl. Phys. Lett. 90, 131116 (2007). doi:10.1063/1.2719028
12. D. Karmakar, S.K. Mandal, R.M. Kadam, P.L. Paulose, A.K. Rajarajan, T.K. Nath, A.K. Das, I. Dasgupta, G.P. Das, Phys. Rev. B 75, 144404 (2007). doi:10.1103/PhysRevB.75.144404
13. T.R. Oliveira, L. de S. Menezes, Cid B. de Araújo, A.A. Lipovskii, Phys. Rev. B 76, 134207 (2007). doi:10.1103/PhysRevB.76.134207
14. S. Bhattacharya, A. Ghosh, Phys. Rev. B 75, 092103 (2007). doi:10.1103/PhysRevB.75.092103
15. H. Yu, L.J. Zhao, J. Meng, Q. Liang, X.Y. Yu, B.Q. Tang, J.J. Xu, Chin. Phys. 14(9), 1799 (2005). doi:10.1088/1009-1963/14/9/019
16. H. Yu, L.J. Zhao, Q. Liang, J. Meng, X.Y. Yu, B.Q. Tang, L.Q. Tang, J.J. Xu, Chin. Phys. Lett. 22(6), 1500 (2005). doi:10.1088/0256-307X/22/6/056
17. H. Yu, L.J. Zhao, J. Meng, Q. Liang, X.Y. Yu, B.Q. Tang, J.J. Xu, Chin. Opt. Lett. 3(8), 469 (2005)
18. A.M. Derfus, W.C.W. Chan, S.N. Bhatia, Adv. Mater. 16, 961 (2004). doi:10.1002/adma.200306111