Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 5973–5977

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Microwave-assisted preparation of nearly monodisperse flower-like CaF_2 microspheres

Lin Ma[a,*], Lin-Lin Yang[b], Yong-Gang Wang[b], Xiao-Ping Zhou[a], Xu-Yao Xu[a]

[a]*Chemistry Science and Technology School, Development Center for New Materials Engineering & Technology in Universities of Guangdong, Zhanjiang Normal University, Zhanjiang 524048, PR China*

[b]*Department of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, PR China*

Received 14 November 2012; received in revised form 14 December 2012; accepted 14 December 2012
Available online 26 December 2012

Abstract

Nearly monodisperse flower-like CaF_2 microspheres with average diameter of 1.2 μm were successfully synthesized via a rapid microwave route using ethylenediaminetetraacetic acid disodium (Edta) as a complexing reagent. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and photoluminescence (PL). The XRD results indicated that the as-prepared CaF_2 microspheres were of cubic phases and had good crystallinity and purity. The TEM and SEM results revealed that these flower-like CaF_2 microspheres had uniform morphologies and sizes and consisted of many nanosheets. It was found that both Edta and $NaBF_4$ had great influences on the formation of these flower-like microspheres. A possible formation mechanism was initially proposed. In addition, rare-earth ions such as Ce^{3+} or Tb^{3+} doped CaF_2 microspheres were also prepared similarly and their luminescent properties were characterized.

Keywords: A. Microwave processing; B. X-ray methods; C. Optical properties

1. Introduction

Inorganic nanomaterials with controllable sizes and shapes have attracted vast attention due to the strong correlation between these parameters and their properties and potential applications [1,2]. The fluoride nanomaterials have a wide range of potential optical applications due to their high transparency arising from low energy phonons and high ionicity, which lead to less fundamental absorption than other oxide or sulphide materials [3].

Among the various fluorides, calcium fluoride (CaF_2) has a low refractive index and a wide band gap and is optically transparent over a wide wavelength range from mid-infrared to vacuum ultraviolet [4,5]. So CaF_2 has been widely used in UV-transparent optical lenses, UV lithography, surface conditioning of glass, promoting agents for bone/tooth reconstruction, and biocompatible luminescent markers [6,7]. Specially, the CaF_2 crystal, with an optically isotropic structure, is suitable as a phosphor host because it exhibits outstanding transmission characteristics for a wide range of wavelength (0.3–8 μm) [8]. Moreover, the lanthanide ions doped CaF_2 will cause an increase in the refractive index compared with the pure CaF_2, which makes it very attractive as an active waveguide to realize optical integrated devices [9]. Up to now, CaF_2 and rare-earth ions doped CaF_2 nanomaterials with various morphologies have been successfully fabricated, such as nanoparticles [10–12], nanocubes [7], thin films [5] and hollow nanospheres [13]. Various methods including flame synthetic method [10], chemical co-precipitation method [11], reverse micelle method [14], hydrothermal and solvothermal methods [7,13,15] have been developed to synthesize CaF_2 micro/nanostructures. However, it is still a challenge to fabricate CaF_2 with controlled morphologies in mild reaction conditions.

In the past two decades, the use of microwave (MW) energy to heat chemical reactions had attracted great attention, owing to its successful application in organic synthesis, polymer chemistry, material sciences and nanotechnology. In many

---

*Corresponding author. Tel.: +86 759 3183 205; fax: +86 759 3183 510.
E-mail address: ml_buct@126.com (L. Ma).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.12.056

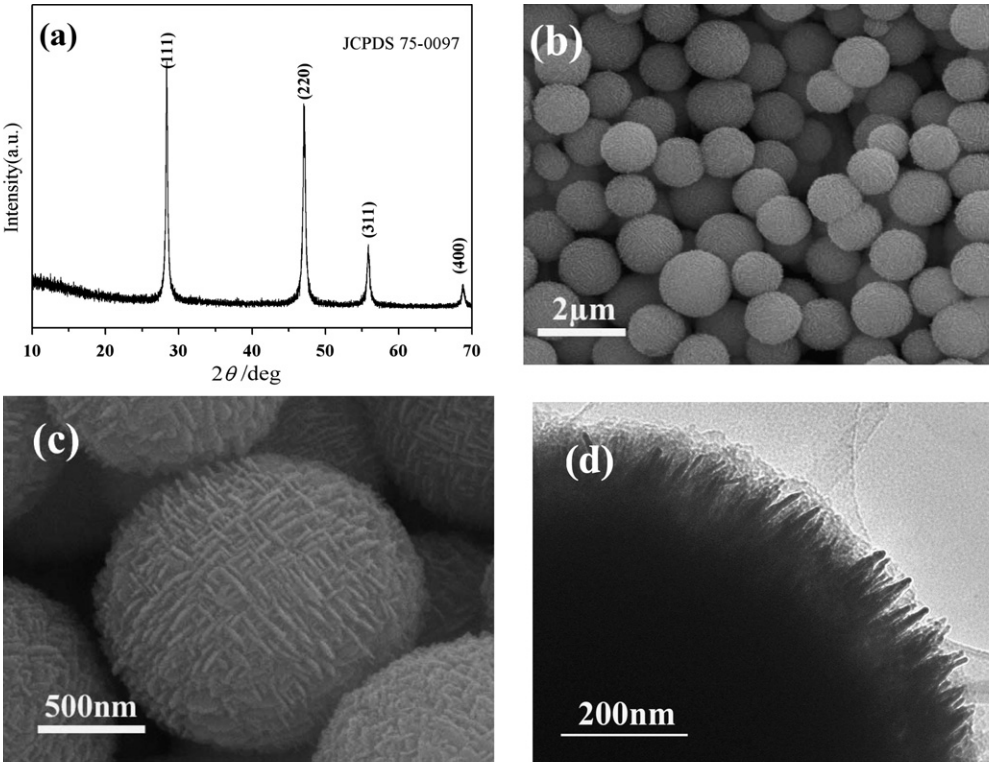

Fig. 1. (a) XRD pattern and ((b)–(d)) SEM and TEM images of the as-prepared CaF_2 sample.

cases, it has been demonstrated that MW dielectric heating can dramatically reduce processing time, increase product yields, and enhance material properties compared with conventional heating method [16]. In this paper, we first report a rapid microwave irradiation method to prepare nearly monodisperse flower-like CaF_2 microspheres using Edta as a complexing reagent.

2. Experimental procedure

2.1. Microwave-assisted synthesis of nearly monodisperse flower-like CaF_2 microspheres

All the chemical reagents used were of analytical grade. In a typical synthesis, $CaCl_2 \cdot 2H_2O$ (2 mmol) was dissolved in 50 ml deionized water to form a solution. Then ethylenediaminetetraacetic acid disodium (4 mmol) was added to above solution under vigorous stirring to form a clear solution. After that, 50 ml $NaBF_4$ (4 mmol) solution was slowly added to the above solution under vigorous stirring. The pH value of the final solution was adjusted to 6.0 with 10% HNO_3 solution. After stirring about 30 min, the solution was finally transferred into a 250 ml round flask and placed in a microwave oven (650 W, 2.45 GHz) with a refluxing apparatus. The solution was heated by microwave irradiation for 40 min at 80% of the maximum power under refluxing. The resulting product was collected by centrifuge and washed three times using deionized water and absolute ethanol, then dried in vacuum at 60 °C for 12 h.

Rare-earth ions such as Ce^{3+} or Tb^{3+} doped CaF_2 samples (doping concentration of 10%, molar ratio) were prepared by the same procedure, except that an additional Ce_2O_3 or Tb_4O_7 was dissolved in concentrated HNO_3 first, then evaporating the solvent and added to the Ca^{2+}-containing solution.

2.2. Characterization of CaF_2 samples

XRD analysis was performed on a D/Max-2550 X-ray diffractometer with monochromatized CuK_α radiation ($\lambda = 0.1540562$ nm). TEM images were taken with a transmission electron microscopy (TEM, JEOL JEM -200CX). Samples for TEM were obtained by dispersing the products in ethanol with 15 min ultrasonicating, and then dropping a few drops of the resulted suspension onto a copper grid precoated with amorphous carbon and allowing them to dry naturally. SEM images were taken with FEI SIRION-100 field-emission scanning electron microscope. The emission spectra were recorded on the F-2500 luminescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The CaF_2:Ce and CaF_2:Tb samples were dispersed into absolute ethanol with 15 min ultrasonicating for PL measurement.

3. Results and discussions

The crystal structure and the phase purity of the product were determined by X-ray diffraction (XRD). A typical XRD pattern of the as-prepared sample is presented in Fig. 1(a). The major detectable diffraction peaks can be readily indexed to the pure cubic phase of CaF_2 consistent with the standard powder diffraction file of CaF_2 (JCPDS 75-0097). No impurity phase could be found. The high and sharp peaks indicate that the sample was well crystallized. The XRD pattern indicates that the pure and well-crystallized CaF_2 product can be easily obtained in our synthetic route. The morphology and microstructure of the as-prepared CaF_2 sample were investigated with SEM and TEM. Fig. 1(b) exhibits a low-magnification SEM image of the as-prepared CaF_2 sample, which displays well-dispersed and uniform spherical morphology with rough surfaces. The yield of the spheres is closed to 100%. It is estimated that these CaF_2 microspheres have a mean diameter about 1.2 μm. Fig. 1(c) clearly reveals the surface structures of these CaF_2 microspheres. It can be seen that the surfaces of the flower-like microspheres are covered with many interlaced nanosheets. Fig. 1(d) clearly displays the edge structure of the single microsphere, from which it is observed that tens of nanosheets with thickness about 15 nm radially stretch out towards the edges of the sphere. The experimental results suggest that the as-prepared CaF_2 flower-like microspheres should be assembled by nanosheets in a certain way.

In order to investigate the effect of the complexing reagent (Edta) and $NaBF_4$ on the formation of the flower-like CaF_2 microspheres, two control experiments were carried out. Fig. 2(a) shows the XRD pattern of the CaF_2 sample prepared without Edta. The major detectable diffraction peaks also can be readily indexed to the pure cubic phase of CaF_2 (JCPDS 75-0097), which reveals that the Edta has little influence on the crystalline phase of CaF_2 samples in our synthetic route. Fig. 2(b) and (c) showed that the obtained CaF_2 sample exhibited not a spherical but an irregularly polyhedral morphology when no Edta was used in the reaction process. Additionally, as NH_4F instead of $NaBF_4$ was used a fluoride source, the obtained CaF_2 samples were aggregated nanoparticles as shown in Fig. 2(d). Therefore, both Edta and $NaBF_4$ played a crucial role in the formation of the flower-like CaF_2 microspheres.

Based on the experimental results, the probable reaction process in our current experiment can be summarized as following expressions:

$$Ca^{2+}\text{-Edta} \rightarrow Ca^{2+} + \text{Edta} \tag{1}$$

$$BF_4^- + 3H_2O \rightarrow 3H^+ + 4F^- + H_3BO_3 \tag{2}$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \tag{3}$$

As an efficient chelator for Ca^{2+}, Edta could react with Ca^{2+} to form stable Ca^{2+}-Edta complex. Under microwave irradiation conditions, Ca^{2+} ions were continuously supplied at a slow rate by gradual dissociation of the Ca^{2+}-Edta complex. Meanwhile, because the hydrolysis of $NaBF_4$ was also a slow process, F^- ions were slowly produced by hydrolysis of $NaBF_4$. Then Ca^{2+} reacted with F^- to form amorphous CaF_2 primary nanoparticles. This slow process was probably helpful to the two dimensional growth of the CaF_2 crystals and then these primary nanoparticles grew into nanosheets. Afterwards, these

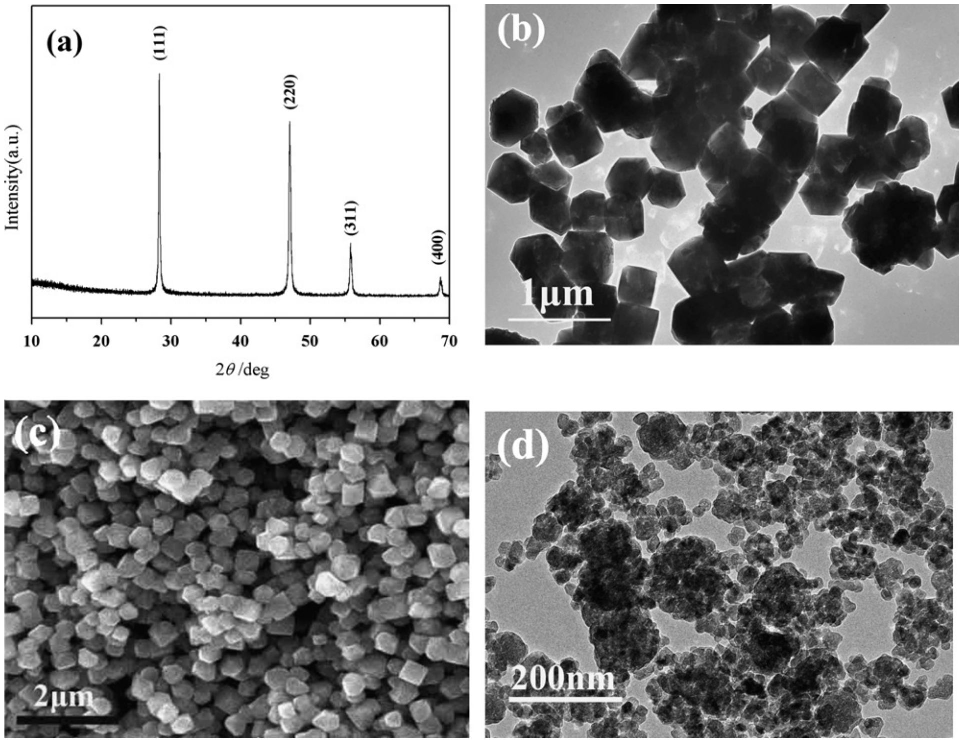

Fig. 2. (a) XRD pattern and ((b) and (c)) TEM and SEM image of the CaF_2 sample prepared without Edta and (d) TEM image of the CaF_2 sample prepared with NH_4F as fluoride source.

nanosheets began to assemble in a certain way under the effect of Edta, probably by electrostatic gravitation and intermolecular force, and finally flower-like microspheres were formed. The exact formation mechanism needs to be further investigated.

The crystal structures and morphologies of the rare-earth ions such as Ce^{3+} or Tb^{3+}, doped CaF_2 samples (CaF_2:Ce or CaF_2:Tb) were also investigated. Fig. 3(a) shows that the major detectable diffraction peaks can be readily indexed to the cubic phase of CaF_2 consistent with the standard powder diffraction file of CaF_2 (JCPDS 75-0097). In comparison with the standard diffraction pattern, no diffraction peaks from CeF_3 or TbF_3 which may exist as impurities, are observed from the doped samples, suggesting that Ce^{3+} or Tb^{3+} were successfully doped into the CaF_2 matrix in our synthetic route. The high and sharp peaks indicate that the samples were well crystallized. In addition, it is noted that the diffraction peaks of CaF_2:Tb slightly shift to a higher angle than those of CaF_2:Ce because CaF_2:Tb possesses smaller *d*-spacings than CaF_2:Ce. Fig. 3(b) and (c) show the morphologies and sizes of the as-prepared CaF_2:Ce and CaF_2:Tb

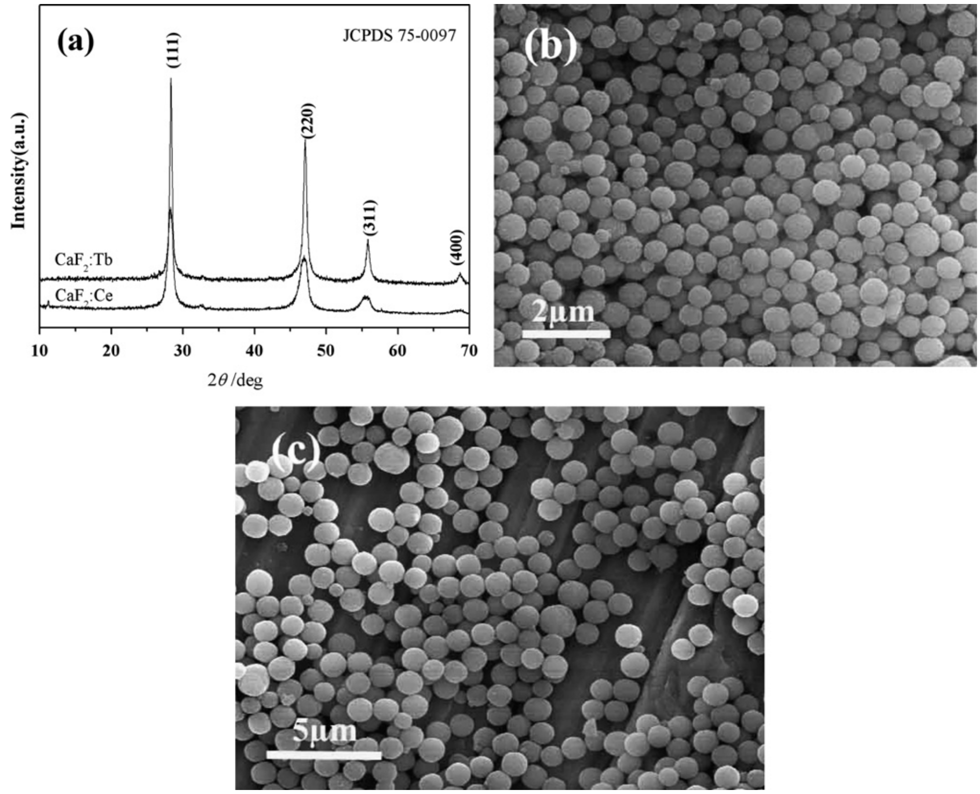

Fig. 3. (a) XRD pattern and SEM images of the samples (b) CaF_2:Ce and (c) CaF_2:Tb.

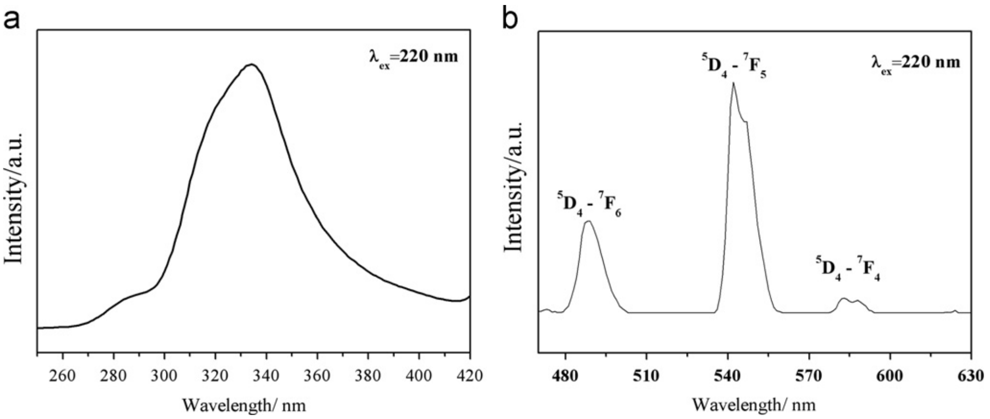

Fig. 4. Emission spectra of the samples (a) CaF_2:Ce and (b) CaF_2:Tb.

samples, respectively. Compared with the undoped sample, the CaF_2:Ce or CaF_2:Tb sample displays similar spherical morphology except with reduced sizes.

The luminescent properties of the CaF_2:Ce and CaF_2:Tb sample were also investigated. It is observed from Fig. 4(a) that the emission of Ce^{3+} presents a broad band consisting of two overlapped peaks which corresponds to the transitions from the lowest excited 5d state to the 4f ground state, that is, the $^2F_{5/2}$ and $^2F_{7/2}$ levels of Ce^{3+} [17]. The emission spectrum of Tb^{3+} (Fig. 4(b)) exhibits three peaks centered at 489, 542, 583 nm, respectively, originating from transitions from the $^5D_4$ excited state to the ^7F_J ($J=6, 5, 4$) ground states of Tb^{3+} [18], among which the $^5D_4 \rightarrow {}^7F_4$ transition at 542 nm is the most prominent.

4. Conclusions

In summary, novel CaF_2 flower-like microspheres were successfully synthesized via a rapid microwave irradiation route using Edta as a complexing reagent. The obtained CaF_2 flower-like microspheres had good crystallinity and purity and were assembled by nanosheets. The experimental results indicated that not only Edta but also $NaBF_4$ played a crucial role in the formation of the flower-like CaF_2 microspheres. A possible formation mechanism was initially proposed. In addition, rare-earth ions such as Ce^{3+} or Tb^{3+} doped CaF_2 microspheres were also prepared similarly and their luminescent properties were also characterized. The strategy presented in this work is easily controllable and well reproducible and may be feasible to develop into the scale-up production.

Acknowledgement

This work was financially supported by Guangdong Natural Science Foundation for Ph.D Start-up Research Program (No. 10452404801004521) and Program for Innovative Research Team in Zhanjiang Normal University.

References

[1] M.A. El-Sayed, Some interesting properties of metals confined in time and nanometer space of different shapes, Accounts of Chemical Research 34 (2001) 257–264.

[2] A.P. Alivisatos, Semiconductor clusters, nanocrystals, and quantum dots, Science 271 (1996) 933–937.

[3] M.F. Joubert, Y. Guyot, B. Jacquier, J.P. Chaminade, A. Garcia, Fluoride crystals and high lying excited states of rare earth ions, Journal of Fluorine Chemistry 107 (2001) 235–239.

[4] N.S. Sokolov, S.M. Suturin, MBE-growth peculiarities of fluoride (CdF_2–CaF_2) thin film structures, Thin Solid Films 367 (2000) 112–119.

[5] T. Pilvi, K. Arstila, M. Leskel, M. Ritala, Novel ALD process for depositing CaF_2 thin films, Chemistry of Materials 19 (2007) 3387–3392.

[6] W.S. Wang, L. Zhen, C.Y. Xu, J.Z. Chen, W.Z. Shao, Aqueous solution synthesis of CaF_2 hollow microspheres via the ostwald ripening process at room temperature, ACS Applied Materials & Interfaces 1 (2009) 780–788.

[7] X.M. Sun, Y.D. Li, Size-controllable luminescent single crystal CaF_2 nanocubes, Chemical Communications 14 (2003) 1768–1769.

[8] M.Y. Sharonov, Z.I. Zhmurova, E.A. Krivandina, A.A. Bystrova, I.I. Buchinskaya, B.P. Sobolev, Spectroscopic properties of nonstoichiometric multicomponent fluoride crystals withfluorite structure doped with Pr^{3+} ions, Optics Communications 124 (1996) 558–562.

[9] T. Balaji, G. Lifante, E. Daran, R. Legros, G. Lacoste, Growth by molecular beam epitaxy andcharacterization of CaF_2:Pr^{3+} planar waveguides, Thin Solid Films 339 (1999) 187–193.

[10] R.N. Grass, W.J. Stark, Flame synthesis of calcium-, strontium-, barium fluoride nanoparticles and sodium chloride, Chemical Communications 13 (2005) 1767–1769.

[11] F. Wang, X.P. Fan, D.B. Pi, M.Q. Wang, Synthesis and luminescence behavior of Eu^{3+}-doped CaF_2 nanoparticles, Solid State Communications 133 (2005) 775–779.

[12] G.L. Zhi, J.H. Song, B.C. Mei, W.B. Zhou, Synthesis and characterization of Er^{3+} doped CaF_2 nanoparticles, Journal of Alloys and Compounds 509 (2011) 9133–9137.

[13] C.M. Zhang, C.X. Li, C. Peng, R.T. Chai, S.S. Huang, D.M. Yang, Z.Y. Cheng, J. Lin, Facile and controllable synthesis of monodisperse CaF_2 and CaF_2:Ce^{3+}/Tb^{3+} hollow spheres as efficient luminescent materials and smart drug carriers, Chemistry - A European Journal 16 (2010) 5672–5680.

[14] A. Bensalah, M. Mortier, G. Patriarche, P. Gredin, D. Vivien, Synthesis and optical characterizations of undoped and rare-earth-doped CaF_2 nanoparticles, Journal of Solid State Chemistry 179 (2006) 2636–2644.

[15] G.A. Kumar, C.W. Chen, J. Ballato, R.E. Riman, Optical characterization of infrared emitting rare-earth-doped fluoride nanocrystals and their transparent nanocomposites, Chemistry of Materials 19 (2007) 1523–1528.

[16] M. Baghbanzadeh, L. Carbone, P. Davide Cozzoli, C. Oliver Kappe, Microwave-assisted synthesis of colloidal inorganic nanocrystals, Angewandte Chemie International Edition 50 (2011) 2–50.

[17] A. Gektin, N. Shiran, V. Nesterkina, Y. Boyarintseva, V. Baumer, G. Stryganyuk, K. Shimamura, E. Villora, Luminescence of heavily Ce-doped alkaline-earth fluorides, Journal of Luminescence 129 (2009) 1538–1541.

[18] L. Zhu, Q. Li, X.D. Liu, J.Y. Li, Y.F. Zhang, J. Meng, X.Q. Cao, Morphological control and luminescent properties of CeF_3 nanocrystals, The Journal of Physical Chemistry C 111 (2007) 5898–5903.