Available online at www.sciencedirect.com

Ceramics International 35 (2009) 521–525

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

# Synthesis and emission analysis of $RE^{3+}$ ($Eu^{3+}$ or $Dy^{3+}$):$Li_2TiO_3$ ceramics

G. Bhaskar Kumar, S. Buddhudu [*]

*Department of Physics, Sri Venkateswara University, Tirupati 517502, India*

Received 25 July 2007; received in revised form 5 August 2007; accepted 14 September 2007
Available online 15 January 2008

---

## Abstract

The development and photoluminescence analysis of $Eu^{3+}$or $Dy^{3+}$ ions in the matrix of lithium titanate ($Li_2TiO_3$) ceramics by using a solid state reaction method are reported. Emission spectra of $Eu^{3+}$:$Li_2TiO_3$ ceramics have shown strong *red* emission at 611 nm ($^5D_0 \rightarrow {}^7F_2$) with $\lambda_{exci} = 392$ nm ($^7F_0 \rightarrow {}^5L_6$) and from the $Dy^{3+}$:$Li_2TiO_3$, a *blue* emission at 493 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and also an *yellow* emission at 582 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) have been observed with $\lambda_{exci} = 366$ nm ($^6H_{15/2} \rightarrow {}^6P_{5/2}$). Both the rare-earth ions containing ceramics have displayed their brighter emission performance from their measured spectral results. In addition, X-ray diffraction (XRD), Fourier transform infra red (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) have been used to characterize the structural properties of ($Eu^{3+}$ or $Dy^{3+}$):$Li_2TiO_3$ ceramics.

*Keywords:* A. Solid state reaction; B. Spectroscopy; $RE^{3+}$:ceramic

---

## 1. Introduction

Rare-earth (RE) luminescent materials have considerable practical applications involving the production of different visible fluorescent colors, such as cathode ray tubes, lamps and X-ray detectors etc [1]. Photoluminescence in such optical materials could be attributed to f–f or f–d transitions of rare-earth ions and their photoluminescence intensity would depend on the site symmetry or nature of ligands, i.e. the covalency between the rare-earth ions and the ligands around them [2]. Rare-earth ion containing materials could perform well in respect of efficient and narrow emissions from them in the visible region [3]. From the literature, it is noted that AlN, GaN, ZnO and $TiO_2$ could be found more attractive semiconductor host matrices for RE ions because of their possessing relatively wide band gaps and also their high refractive indices [4–7]. Among them, $TiO_2$ could be a good host to excite RE ions more efficiently to result in with intense luminescence phenomenon from them [8–10]. Luminescence of the titanate-type compounds has the potential for their use in optoelectronic applications [11]. $TiO_2$ possesses a good mechanical resistance and stability even in some corrosive environments and therefore it has widely been used in the development of stable host matrices such as $BaTiO_3$, $SrTiO_3$, $CaTiO_3$ and $TiO_2$-based oxide composites, namely $TiO_2$–$SiO_2$, $TiO_2$–$CeO_2$, $TiO_2$–$ZrO_2$ and $TiO_2$–$Fe_2O_3$ have been synthesized [12–15]. $BaTiO_3$ and $SrTiO_3$ are well known examples with a renewed focus to explore luminescence studies in the titanate perovskite [16–18].

Several groups have investigated the effect of lithium ion on the luminescent properties and reported the enhancement of photoluminescent efficiency [19–21]. Photoluminescence studies on lithium tantalate, lithium niobate, lithium aluminate and lithium tetra borate have extensively been carried out [22–27]. Since there exists no reports so far on lithium titanate ($Li_2TiO_3$) with rare-earth ions, we have undertaken the present work to prepare and analyze the emission spectral properties of $Eu^{3+}$:$Li_2TiO_3$ and $Dy^{3+}$:$Li_2TiO_3$ ceramic powders.

## 2. Experimental

Rare-earth ion containing lithium titanate ceramics were prepared by heating a mixture with a ratio of 1 mol of lithium carbonate ($Li_2CO_3$) and 1 mol of titanium dioxide ($TiO_2$) and 0.2 mol of rare-earth oxide of 99.99% purity in an ambient

---

[*] Corresponding author. Tel.: +91 877 2261611.
*E-mail address:* drsb99@hotmail.com (S. Buddhudu).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.09.107

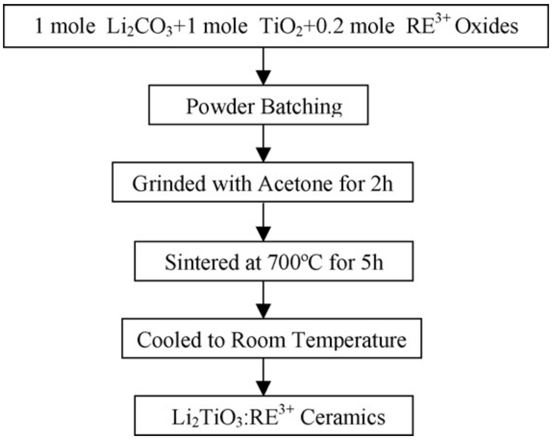

Fig. 1. Synthesis of $RE^{3+}$:ceramics.

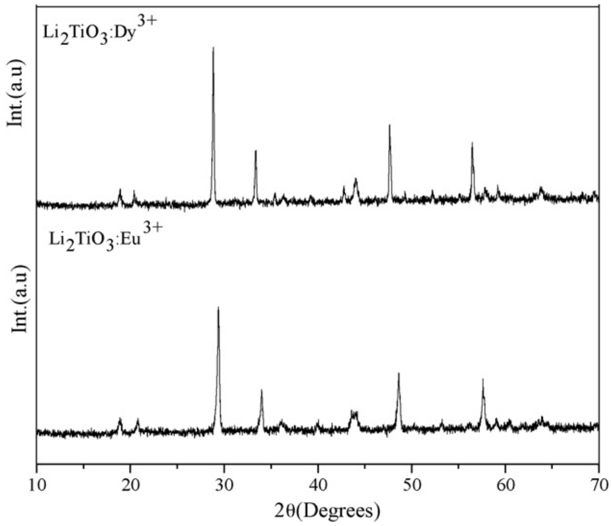

Fig. 2. XRD pattern of (a) $Eu^{3+}$:$Li_2TiO_3$ and (b) $Dy^{3+}$:$Li_2TiO_3$ ceramics.

atmosphere. The chemicals weighed were powdered with acetone in an agate mortar for 2 h to obtain homogeneous mixture and then those were collected into porcelain crucibles each separately. It was gradually raised to 700 °C, at which the finely powdered mixtures were kept for 5 h. We have heated the samples at 600 °C, 700 °C and 850 °C, respectively and found that emission intensity was good enough at 700 °C, hence this temperature is preferred. The synthesis method has clearly been shown in Fig. 1. Structural characterization of these samples has been carried out from the X-ray powder diffraction measurements on a XRD 3003TT Seifert diffractometer with CuKα radiation ($\lambda$ = 1.5406 Å) at 40 kV and 20 mA and the $2\theta$ range was varied between 10° and 70°.

Morphology and average grain size of the ceramic powder were examined on a Philips XL30 ESEM. For an average grain size analysis, the sample was coated with a thin layer of gold by using a JEOL fine coat ion sputter FC-1100 unit to avoid the possible charging of the specimen. The scanning electron microscopy (SEM) image was obtained for samples by using a 35 m camera attached to a high resolution recording system. Fourier transform infra red (FTIR) spectrum of the sample was carried out on a Thermo Nicolet -5700 Spectrophotometer using the KBr pellet technique in the range of 4000–400 $cm^{-1}$. Both the excitation and the emission spectra of lithium titanate:$RE^{3+}$ ceramics were recorded on a SPEX Fluorolog-3 fluorimeter attached with a Xe-arc lamp (450 W) with the datamax software for acquiring the spectral data.

## 3. Results and discussion

X-ray diffraction (XRD) patterns of $Eu^{3+}$:$Li_2TiO_3$ and $Dy^{3+}$:$Li_2TiO_3$ powders are shown in Fig. 2. By using XRD analysis software namely POWD, we have observed that the structures of them are orthorhombic natured. SEM micrographs of the $Eu^{3+}$:$Li_2TiO_3$ and the $Dy^{3+}$:$Li_2TiO_3$ ceramics are shown in Fig. 3. The obtained micrographs show that the particles are agglomerated and the average diameter of the grain size is in the range of 100–200 nm. The elemental analysis of the synthesized products was performed using the energy dispersive X-ray analysis (EDAX) technique which is attached to the SEM system for its use, when desired and the measured patterns are presented in Fig. 4. EDAX analysis was carried out mainly to confirm the presence of RE ions in the ceramics prepared and the results confirm their presence. However, the EDAX of the matrix could not show the presence of lithium because of its lighter weight [28,29]. Fig. 5 shows the FTIR spectra of $Eu^{3+}$:$Li_2TiO_3$ and $Dy^{3+}$:$Li_2TiO_3$ ceramics. FTIR bands have been analyzed for identifying the functional groups.

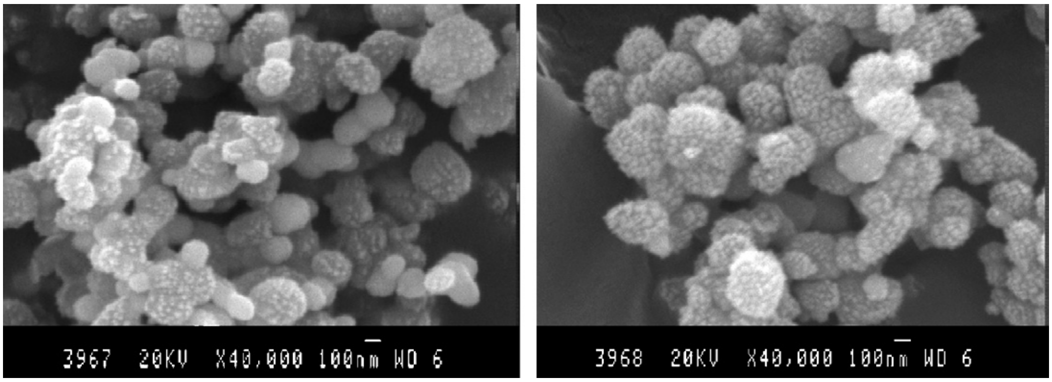

Fig. 3. SEM images of (a) $Eu^{3+}$:$Li_2TiO_3$ and (b) $Dy^{3+}$:$Li_2TiO_3$ ceramics.

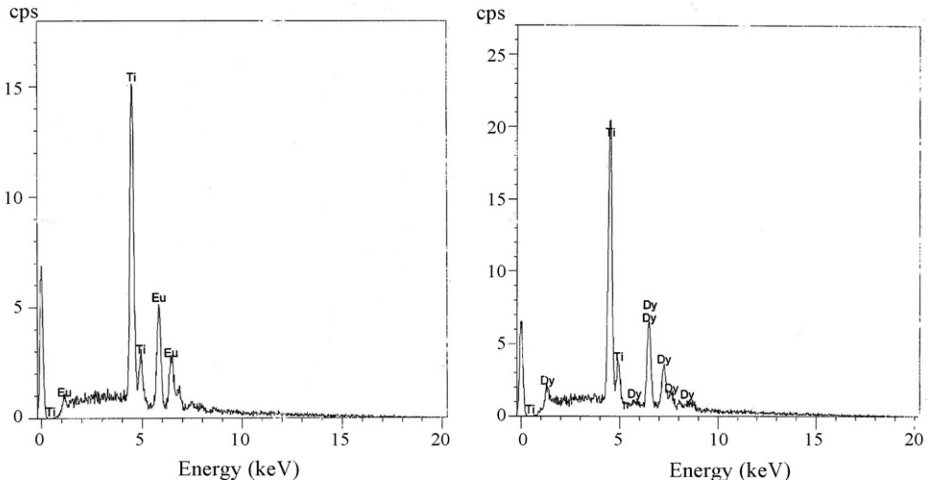

Fig. 4. EDAX spectra of (a) $Eu^{3+}$:$Li_2TiO_3$ and (b) $Dy^{3+}$:$Li_2TiO_3$ ceramics.

The bands at 1426 $cm^{-1}$ and 866 $cm^{-1}$ are due to the vibration of $CO_3^{2-}$ anions, indicating the absorption of $CO_2$ molecules on the surface of the samples [30]. The band at 2360 $cm^{-1}$ is due to the Ti–O vibrations [31]. The band at 3460 $cm^{-1}$ is attributed to the absorption of OH molecules [32].

The excitation spectrum with an emission band at 611 nm ($^5D_0 \rightarrow {}^7F_2$) has shown a broader and intense excitation band at 299 nm and it has been identified as a charge transfer band (CTB). In oxides, it has been reported that a *charge transfer band* due to $Eu^{3+}$–$O^{2-}$ interaction might arise [33]. The other bands that are located at 360 nm, 380 nm, 392 nm, 413 nm and 463 nm are assigned to the electronic transitions of $^7F_0 \rightarrow {}^5L_9$, $^7F_0 \rightarrow {}^5G_3$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively. The emission spectrum of $Eu^{3+}$:$Li_2TiO_3$ ceramics with excitation at 392 nm has been shown in Fig. 6. The intense emission bands in the range of 570–700 nm are assigned to the electronic transitions of ($^5D_0 \rightarrow {}^7F_{J=1–4}$) and the transitions such as $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are electric dipole (ED) transitions. Among them, $^5D_0 \rightarrow {}^7F_2$ has been a hypersensitive transition that follows the selection rule of $\Delta J = 2$ and hence it demonstrates a bright red emission from $Eu^{3+}$:$Li_2TiO_3$ ceramics. The other emission bands at 579 nm, 590 nm, 650 nm and 704 nm are assigned to $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_3$ and $^7F_4$ transitions, respectively [34].

The excitation spectrum of $Dy^{3+}$:$Li_2TiO_3$ is shown in Fig. 7 with excitation bands at 325 nm, 354 nm, 366 nm and 387 nm, and which are assigned to the electronic transitions of $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$ and $^4I_{13/2}$, respectively. A broadband in the region of 280–320 nm has been attributed to be a *charge transfer band* of $Dy^{3+}$–$O^{2-}$ interaction [35]. Among them, $^6H_{15/2} \rightarrow {}^6P_{5/2}$ at 366 nm is an intense one and with this, an emission spectrum has been recorded with emission bands $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 493 nm (blue) and 582 nm (yellow), respectively. $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is mainly a magnetically allowed which varies a little with the crystal field strength change around the $Dy^{3+}$ ion and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is a forced electric dipole transition with $\Delta J = 2$, which is strongly influenced by the host environment [36].

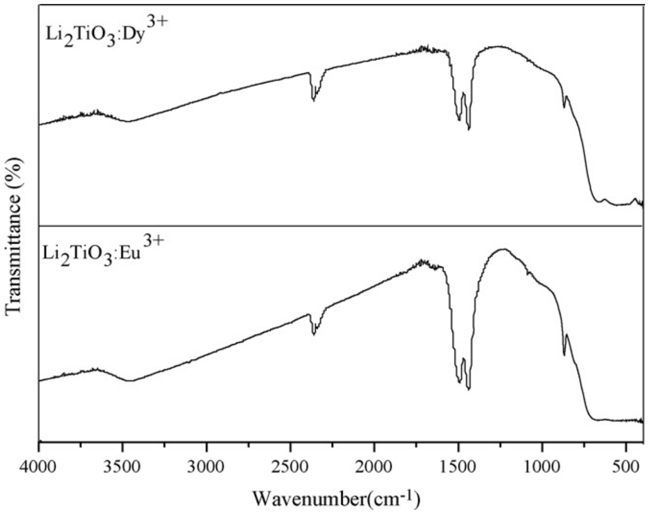

Fig. 5. FTIR spectra of (a) $Eu^{3+}$:$Li_2TiO_3$ and (b) $Dy^{3+}$:$Li_2TiO_3$ ceramics.

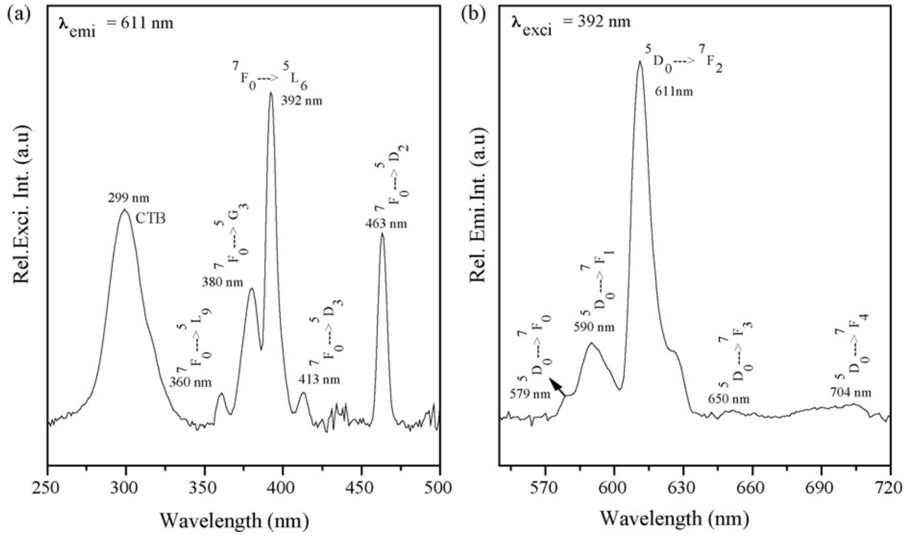

Fig. 6. (a) Excitation and (b) emission spectra of $Eu^{3+}$:$Li_2TiO_3$ ceramics.

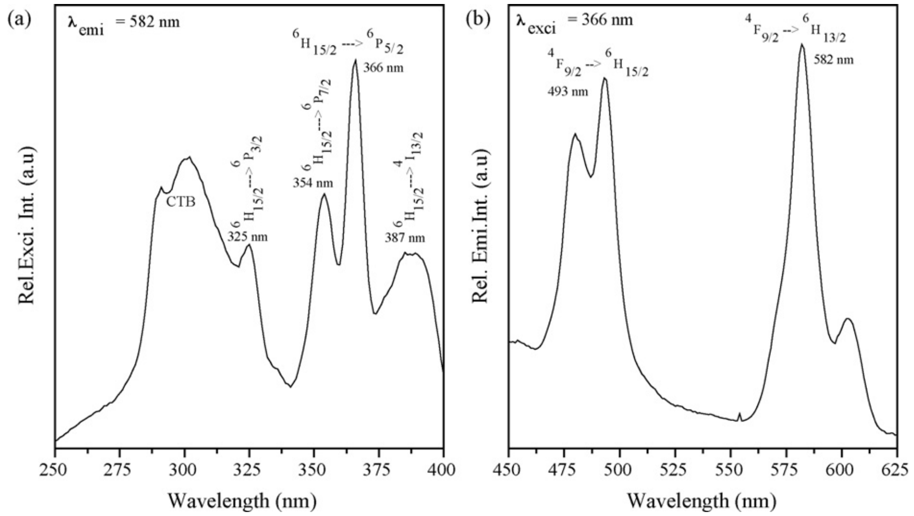

Fig. 7. (a) Excitation and (b) emission spectra of $Dy^{3+}$:$Li_2TiO_3$ ceramics.

## 4. Conclusions

We summarize that the rare-earth ($Eu^{3+}$ or $Dy^{3+}$) ions containing $Li_2TiO_3$ ceramics have been synthesized by using a solid state reaction method and these materials have shown orthorhombic structure and the average diameter of the grain size of the material is in the range of 100–200 nm. Based on the emission results, we suggest these ceramics are brightly luminescent and novel optical materials.

## References

[1] B. Yan, X.Q. Su, $LuVO_4$:$RE^{3+}$ (RE = Sm, Eu, Dy, Er) phosphors by in-situ chemical precipitation construction of hybrid precursors, Opt. Mater. 29 (2007) 547–551.

[2] Y. Inaguma, T.T. Suchiya, T. Katsumata, Systematic study of photoluminescence upon band gap excitation in perovskite-type titanates $R_{1/2}Na_{1/2}TiO_3$:Pr (R = La, Gd, Lu, and Y), J. Solid State Chem. 180 (2007) 1678–1685.

[3] K.M. Lin, C.C. Lin, C.Y. Hsiao, Y.Y. Li, Synthesis of $Gd_2Ti_2O_7$:$Eu^{3+}$, $V^{4+}$ phosphors by sol–gel process and its luminescent properties, J. Lumin. 127 (2) (2007) 561–567.

[4] C.W. Jia, E.Q. Xie, J.G. Zhao, Z.W. Sun, A.H. Peng, Visible and near-infrared photoluminescence of europium-doped titania film, J. Appl. Phys. 100 (2006) 023529.

[5] A.K. Singh, G. Tripathi, S.B. Rai, A. Rai, Enhancement of upconverted luminescence in $Er^{3+}$:$TeO_2$ glass on increasing the temperature and concentration of $Yb^{3+}$ beyond the critical limit, J. Appl. Phys. 101 (2007) 103–105.

[6] P. Che, J. Meng, L. Guo, Oriented growth and luminescence of ZnO: Eu films prepared by sol-gel process, J. Lumin. 122–123 (2007) 168–171.

[7] A. Podhorodecki, M. Nyk, J. Misiewicz, W. Strek, Optical investigation of the emission lines for $Eu^{3+}$ and $Tb^{3+}$ ions in the GaN powder host, J. Lumin. 126 (2007) 219–224.

[8] L. Hu, H. Song, G. Pan, B. Yan, R. Qin, Q. Dai, Photoluminescence properties of samarium-doped TiO2 semiconductor nanocrystalline powders, J. Lumin. 127 (2) (2007) 371–376.

[9] N. Wang, H. Lin, J. Li, X. Yang, L. Zhang, Photoluminescence of $TiO_2$:Eu nanotubes prepared by a two-step approach, J. Lumin. 122–123 (2007) 889–891.

[10] S. Yi, J.S. Bae, B.K. Moon, J.H. Jeong, J.H. Kim, Highly enhanced luminescence of nanocrystalline $TiO_2:Eu^{3+}$ phosphors, Opt. Mater. 28 (2006) 610–614.

[11] R.C. Lima, J.W.M. Espinosa, M.F.C. Gurgel, E.C. Paris, E.R. Leite, Photoluminescence in disordered sm-doped $PbTiO_3$: experimental and theoretical approach, J. Appl. Phys. 100 (2006) 034917.

[12] A.T. de Figueiredo, V.M. Longo, S. de Lazaro, V.R. Mastelaro, F.S. De Vicente, A.C. Hernandes, M. Siu Li, J.A. Varela, E. Longo, Blue-green and red photoluminescence in $CaTiO_3$:Sm, J. Lumin. 126 (2007) 403–407.

[13] Z. Liu, J. Zhang, B. Han, J. Du, T. Mu, Y. Wang, Z. Sun, Solvothermal synthesis of mesoporous $Eu_2O_3$-$TiO_2$ composites, Microporous Mesoporous Mater. 81 (2005) 169–174.

[14] S.O.Y. Matsuo, T. Omata, M. Yoshimura, Photocatalytic behavior of cerium titanates, $CeTiO_4$ and $CeTi_2O_6$ and their composite powders with $SrTiO_3$, J. Alloys Compd. 376 (2004) 262–267.

[15] Y. Cong, B. Li, B. Lei, W. Li, Long lasting phosphorescent properties of Ti doped $ZrO_2$, J. Lumin. 126 (2007) 822–826.

[16] R. Pazik, D. Hreniak, W. Strek, A. Speghini, M. Bettinelli, Structural and luminescence properties of $Eu^{3+}$ doped $BaxSr_{1\_x}TiO_3$ (BST) nanocrystalline powders prepared by different methods, Opt. Mater. 28 (2006) 1284–1288.

[17] H. Guo, N. Dong, M. Yin, W. Zhang, L. Lou, S. Xia, Green and red upconversion luminescence in $Er^{3+}$-doped and $Er^{3+}/Yb^{3+}$-codoped $SrTiO_3$ ultrafine powders, J. Alloys Compd. 415 (2006) 280–283.

[18] M. Qureshi, H.Y. Chen, C.H. Lu, Synthesis and photoluminescent properties of neodymium- ion doped perovskite oxides, Solid State Commun. 142 (2007) 85–88.

[19] J.S. Bae, J.H. Jeong, K.S. Shim, B.K. Moon, S. Yi, J.H. Kim, Crystallinity and morphology dependent luminescence of Li-doped $Y_{2\_x}Gd_xO_3:Eu^{3+}$ thin film phosphors, Appl. Surf. Sci. 252 (2006) 4564–4568.

[20] B. Liu, M. Gu, X. Liu, C. Ni, D. Wang, L. Xiao, R. Zhang, Effect of $Zn^{2+}$ and $Li^+$ codoping ions on nanosized $Gd_2O_3:Eu^{3+}$ phosphor, J. Alloys Compd. 440 (2007) 341–345.

[21] K.A. Hyeon, S.H. Byeon, J.C. Park, D.K. Kim, K.S. Suh, Highly enhanced photoluminescence of $SrTiO_3$: Pr by substitution of ($Li_{0.5}$, $La_{0.5}$) pair for Sr, Solid State Commun. 115 (2000) 99–104.

[22] I. Sokolska, S. Kuck, G.D. Dzik, M. Baba, The up-conversion processes in Ho doped $LiTaO_3$, J. Alloys Compd. 323–324 (2001) 273–278.

[23] W.R. Romanowski, I. Sokolska, G.D. Dzik, S. Golab, Investigation of $LiXO_3$(X = Nb, Ta) crystals doped with luminescent ions Recent results, J. Alloys Compd. 300–301 (2000) 152–157.

[24] D. Hreniak, A. Speghini, M. Bettinelli, W. Strek, Spectroscopic investigations of nanostructured $LiNbO_3$ doped with $Eu^{3+}$, J. Lumin. 119–120 (2006) 219–223.

[25] L. Tsonev, Luminescent activation of planar optical waveguides in $LiNbO_3$ with rare earth ions $Ln^{3+}$—a review, Opt. Mater. (2007), corrected proof.

[26] X. Yang, G. Ning, X. Li, Y. Lin, Synthesis and luminescence properties of a novel $Eu^{3+}$-doped $\gamma$-$LiAlO_2$ phosphor, Mater. Lett. 61 (25) (2007) 4694–4696.

[27] M. Ignatovych, V. Holovey, T. Vidoczy, P. Baranyai, Spectral study on manganese-and silver-doped lithium tetraborate phosphors, Radiat. Phys. Chem. 76 (2007) 1527–1530.

[28] A. Fini, G. Fazio, M.A. Holgado, M.J.F. Herva, Fractal and reactive dimensions of some ursodeoxycholic acid salts, Int. J. Pharm. 171 (1998) 45–52.

[29] Y. Kojima, K. Suzuki, Y. Kawai, Hydrogen generation from lithium borohydride solution over nano-sized platinum dispersed on $LiCoO_2$, J. Power Sources 155 (2006) 325–328.

[30] D.R. Zhang, H.L. Liu, R.H. Jin, N.Z. Zhang, Y.X. Liu, Y.S. Kang, Synthesis and characterization of nanocrystalline $LiTiO_2$ using a one-step hydrothermal method, J. Ind. Eng. Chem. 13 (2007) 92–96.

[31] Y. Li, H. Zhao, Z. Tian, W. Qiu, X. Li, Solvothermal synthesis and electrochemical characterization of amorphous lithium titanate materials, J. Alloys Compd. (2007), corrected proof.

[32] X. Liu, P. Jia, J. Lin, G. Li, Monodisperse spherical core -shell structured $SiO_2$-$CaTiO_3:Pr^{3+}$ phosphors for field emission displays, J. Appl. Phys. 99 (2006) 124902.

[33] B.V. Rao, U. Rambabu, S. Buddhudu, Photoluminescence spectral analysis of $Eu^{3+}$: phosphors, Physica B 382 (2006) 86–91.

[34] G.S.R. Raju, S. Buddhudu, A. VaradaRajulu, Red emission from $Eu^{3+}$: PVA polymer film, J. Appl. Polym. Sci 102 (2006) 3273–3276.

[35] X.Q. Su, B. Yan, Matrix-induced synthesis and photoluminescence of $M_3Ln(VO_4)_3$:RE (M = Ca, Sr, Ba; Ln = Y, Gd; RE = $Eu^{3+}$, $Dy^{3+}$, $Er^{3+}$) phosphors by hybrid precursors, J. Alloys Compd. 421 (2006) 273–278.

[36] S.D. Han, S.P. Khatkar, V.B. Taxak, G. Sharma, D. Kumar, Synthesis, luminescence and effect of heat treatment on the properties of $Dy^{3+}$-doped YVO4 Phosphor, Mater. Sci. Eng. B 129 (2006) 126–130.