Indian Journal of Pure & Applied Physics
Vol. 45, June 2007, pp. 496-500

Emission spectra of Eu^{3+} and Tb^{3+}: Borophosphate oxyfluoride glasses

B Sudhakar Reddy & S Buddhudu*

Department of Physics, Sri Venkateswara University, Tirupati 517 502

*E-mail: profsb_svuniv@hotmail.com

Received 23 January 2007; accepted 20 March 2007

The development and luminescence properties of (0.2 mol %) of $Eu^{3+}$and Tb^{3+} ions doped borophosphate oxyfluoride (BPOF) optical glasses have been reported in the following general compositions:

69.8 B_2O_3.10 P_2O_5-10 ($ZnO/CdO/TeO_2$)-10 (AlF_3/LiF)

Measured emission spectra of Eu^{3+}: BPOF optical glasses have revealed five emissions ($^5D_0 \rightarrow {}^7F_{0,1,2,3\&4}$) at 580, 591, 613, 654 and 701 nm, respectively with λ_{exci} = 392 nm ($^7F_0 \rightarrow {}^5L_6$). In case of Tb^{3+}:BPOF optical glasses, four emissions ($^5D_4 \rightarrow {}^7F_{6,5,4\&3}$) that are located at 489, 545, 584 and 622 nm have been measured with λ_{exci} = 374 nm. For the red (Eu^{3+}) and green (Tb^{3+}) emission bands, decay curves have been recorded to compute their lifetimes. By using relevant energy level diagrams, emission processes in the glasses have been explained.

Keywords: Borophosphate oxyfluoride glasses, Eu^{3+}, Tb^{3+} ions, Optical analysis, Emission spectra
IPC Code: G01J3/28

1 Introduction

More recently, there has been a great deal of interest on the preparation and characterization of a wide variety of optical glasses comprising oxides, silicates, borates, phosphates and fluorides etc., for their potential applications[1-5]. Studies on the optical characterization of certain phosphate and fluoride glasses have earlier been reported[6-11]. Glasses based on phosphate and fluorides have been identified as ideal optical systems because of their good glass forming ability, hardness, transparency and resistance towards the moisture without any degradation on their surfaces. In order to improve glass quality and its optical performance from borophosphate oxyfluoride glasses, suitable quantity (10 mol%) of ZnO, CdO and TeO_2, have been added separately as the network modifiers (NWF) along side two other properly improving network modifiers namely AlF_3 and LiF. Rare-earth ions are incorporated into these borophosphate oxyfluoride glasses in order to characterize their optical behaviour. For quite some time it has been known that rare– earth ions doped optical glassy materials have attracted a great deal of attention in different laboratories for a wide variety of potential applications[12-16]. The red colour emitting rare-earth Eu^{3+} ($4f^{6}$) ion, has a lower lying excited level ($^5D_0$) to exhibit intense and sharp emission transitions[13] with the $^7F_6$ as the ground state. Similarly the green colour emitting Tb^{3+} ($4f^{8}$) ion exhibits more bright and line like excitation and emission bands[17-18] with the $^7F_0$ as the ground state. Since there are no reports in analyzing Eu^{3+} and Tb^{3+} ions doped borophosphate oxyfluoride optical glasses, we have undertaken the present work to analyze their optical properties.

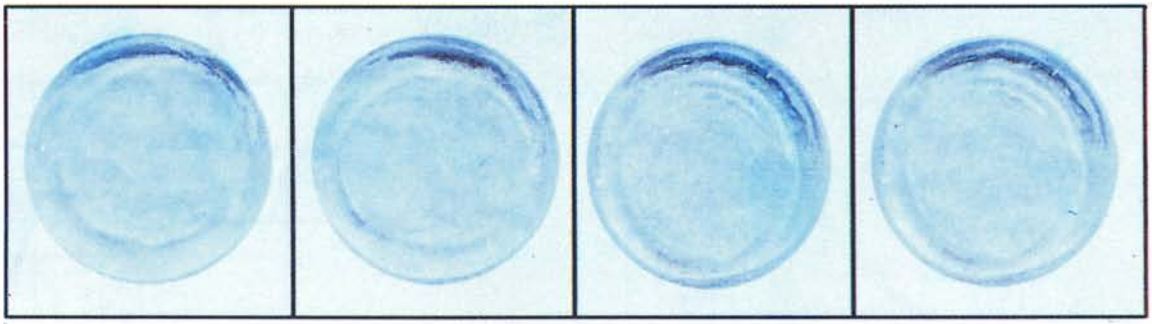
2 Experimental Details

2.1 Glasses preparation

0.2 mol % of Eu^{3+} and Tb^{3+} ions doped in borophosphate oxyfluoride (BPOF) glasses were prepared in the following chemical compositions:

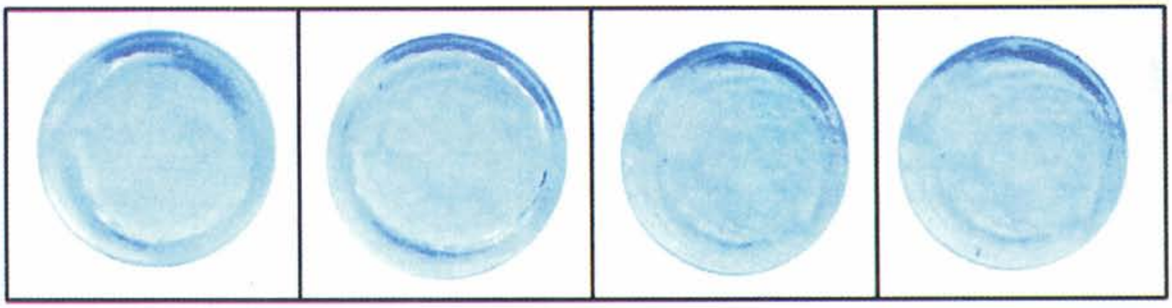
69.8 B_2O_3-10P_2O_5-10($ZnO/CdO/TeO_2$)-10(AlF_3/LiF)

The starting materials in the present work were reagent grade of H_3BO_3, $(NaPO_3)_6$, ZnO, CdO, TeO_2, AlF_3, LiF, Eu_2O_3 and Tb_2O_3. All chemicals were weighed appropriately powdered finely and mixed thoroughly. Each batch weighing about 10 g was melt in ceramic crucibles in an electrical furnace for about an hr, at 950°C. These melts were quenched in between two brass plates to produce 2-3 cm diameter glass discs of 0.3 cm thickness each. These glasses thus obtained were annealed to 200°C for an hour to remove thermal strains if any. Figures 1 and 2 shows the photographs of both reference and 0.2 mol % of Eu^{3+} and Tb^{3+} ions doped borophosphate oxyfluoride (BPOF) glasses studied in the present work.



(a) Eu^{3+}: ZnO - AlF_3 (b) Eu^{3+}: CdO - AlF_3 (c) Eu^{3+}: TeO_2- AlF_3 (d) Eu^{3+}: TeO_2- LiF

Fig. 1 — Photograph showing Four Eu^{3+} :BPOF optical glasses



(a) Tb^{3+}: ZnO - AlF_3 (b)Tb^{3+}: CdO - AlF_3 (c)Tb^{3+}: TeO_2- AlF_3 (d)Tb^{3+}: TeO_2- LiF

Fig. 2 — Photograph showing four Tb^{3+} :BPOF optical glasses

2.2 Measurement of optical spectra of glasses

For these glasses, the optical absorption spectra of Eu^{3+} and Tb^{3+} glasses were measured by JASCO V570 UV-VIS-NIR spectrophotometer. Both the excitation and emission spectra of Eu^{3+} and Tb^{3+} glasses were measured on a SPEX fluorolog-2 fluorimeter (Model-II) with a Datamax software to acquire the data with a Xe-are lamp (150 W) as the excitation source. To measure the lifetimes of the emission bands from this system, a Xe-flash lamp was arranged to the system along side a phosphorimeter attachment.

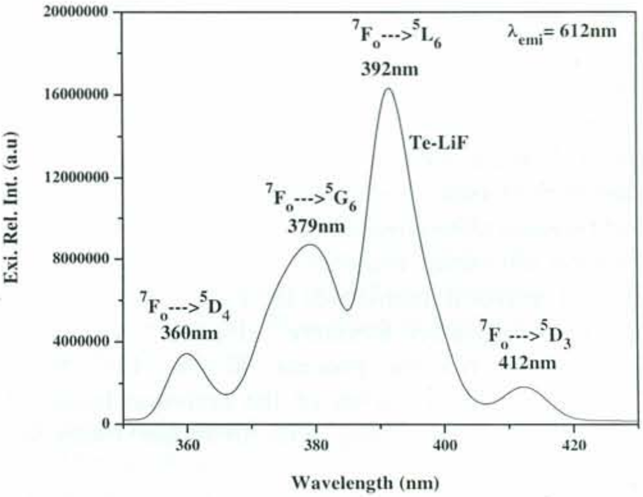


Fig. 3 — Excitation spectrum of Eu^{3+}: 69.8 B_2O_3-10P_2O_5-10 TeO_2 -10LiF glass

3 Results and Discussion

3.1 Eu^{3+}: BPOF glass

The excitation spectrum of Eu^{3+}:BPOF glass (Fig. 3) shows four excitation bands such as $^7F_0 \rightarrow {}^5D_4$ (360 nm), $^7F_0 \rightarrow {}^5G_6$ (379 nm), $^7F_0 \rightarrow {}^5L_6$ (392 nm) and $^7F_0 \rightarrow {}^5D_0$ (412 nm). Among these, a prominent excitation band at $^7F_0 \rightarrow {}^5L_6$ (392nm) has been chosen to measure the emission spectra of Eu^{3+}: BPOF glasses (Fig. 4) with five emission transitions of $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (591 nm), $^5D_0 \rightarrow {}^7F_2$ (614 nm), $^5D_0 \rightarrow {}^7F_3$ (654 nm) and $^5D_0 \rightarrow {}^7F_4$ (702 nm) as was reported previously in literature[19-21]. Due to the shielding effect of $4f^6$ electrons by 5s and 5p electrons in outer shells in the Eu^{3+} ion, narrow emission bands are arising. Among these five emission bands, the transition $^5D_0 \rightarrow {}^7F_2$ (614 nm) has shown a strong red emission. The $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions are electric dipole (ED) transitions and the red emission ($^5D_0 \rightarrow {}^7F_2$) is considered as the hypersensitive transition that follows the selection rules of $\Delta J = 2$ and another transition $^5D_0 \rightarrow {}^7F_1$ with $\Delta J = 1$ could be found as a magnetic dipole (MD)

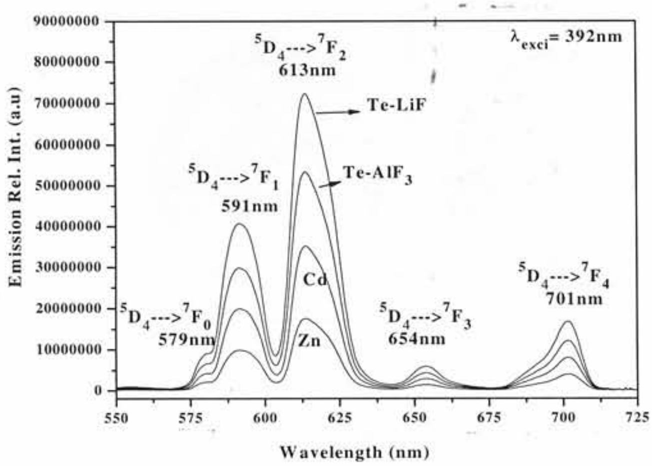


Fig.4 — Emission spectra of Eu^{3+}: 69.8 B_2O_3-10P_2O_5-10 (ZnO/CdO/TeO_2)-10 (AlF_3/LiF) glasses

transition[21]. In glassy materials, due to the absence of a centre of symmetry, a mixing of the 4f orbitals with opposite parity could be taken place and an electric dipole transition (ED) would be arising[21,22]. The absence of emission from the excited levels of $^5D_{J=1,2,3}$ could be due to the presence of high energy phonons found in the glasses, i.e. when the Eu^{3+} ions are excited to any level above the $^5D_0$, there could be a fast non-radiative multiphonon relaxation takes place at this level and also because of the fact that emission from $^5D_{3,2,1}$ to the ^7F_J levels would be found several orders of magnitude smaller compared to that of $^5D_0 \rightarrow {}^7F_J$ transitions, hence, the emissions from these three excited states could not take place and so those could remain to be suppressed. Therefore, $\sum {}^5D_0 \rightarrow {}^7F_J$ emission intensities could be considered to represent the total emission intensity of the Eu^{3+} glass studied as was down in earlier literature[21]. Figure 5 shows the emission mechanism process in the Eu^{3+}:BPOF glasses. The decay curves of the emission bands of Eu^{3+}:BPOF glasses along with their life times are shown in Fig. 6

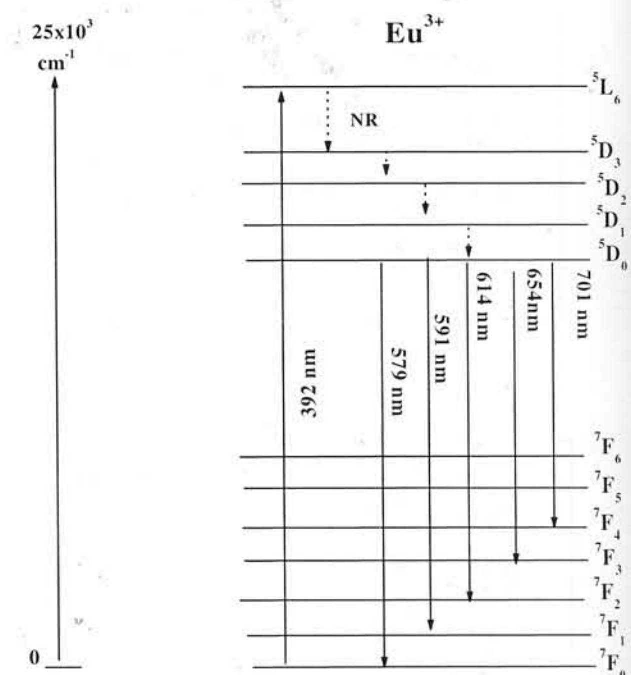


Fig. 5 — Energy level scheme for emission process in Eu^{3+}: BPOF glass

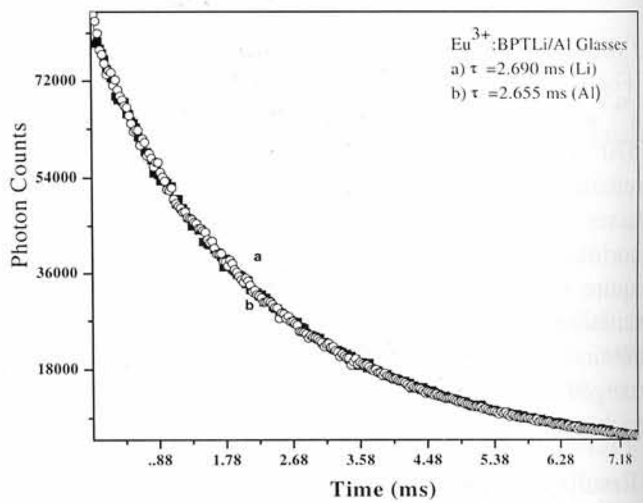


Fig. 6 — Decay curves of the emission transitions of Eu^{3+}: BPOF glasses with excitation at 392 nm

3.2 Tb^{3+}: BPOF glass

The excitation spectrum of Tb^{3+}:BPOF glasses (Fig. 7) shows three excitation bands such as ($^7F_6 \rightarrow {}^5H_7$) at 316 nm ($^7F_6 \rightarrow {}^5D_2$) at 350 nm and ($^7F_6 \rightarrow {}^5G_6$) at 374 nm. Among these, a prominent excitation band ($^7F_6 \rightarrow {}^5G_6$) at λ_{exci} = 374 nm has been chosen to measure the emission spectra of Tb^{3+}: BPOF glasses (Fig. 8) with the four emission transitions of ($^5D_4 \rightarrow {}^7F_6$) at 489 nm, ($^5D_4 \rightarrow {}^7F_5$) at 545 nm, ($^5D_4 \rightarrow {}^7F_4$) at 584 nm and ($^5D_4 \rightarrow {}^7F_3$) at 622 nm, has been identified[19,23-25]. The emission transitions are all found to be intense and sharp emission band due to the f-f inner shell transitions, from the excited level to the lower level such as $^5D_4 \rightarrow {}^7F_{J(J=0-6)}$ for Tb^{3+}. The intense green emission is at 545 nm, arises from the Laporte-forbidden $^5D_4 \rightarrow {}^7F_5$ transition[23]. The transition ($^5D_4 \rightarrow {}^7F_6$) obeys the magnetic dipole transition selection rule[26-28] of $\Delta J = \pm 1$. Figure 9 shows the emission process with 374 nm at the excitation wavelength. Figure 10 shows the decay curves of the emission transitions of Tb^{3+}: BPOF glasses along with their life times.

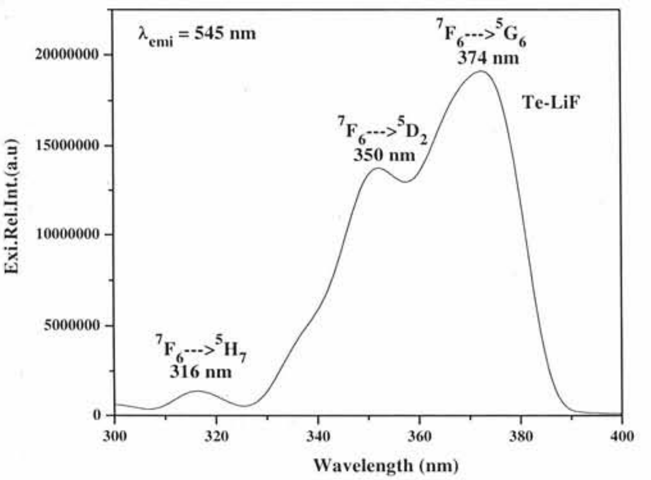


Fig.7 — Excitation spectrum of Tb^{3+}: 69.8 B_2O_3-10 P_2O_5-10 TeO_2 -10LiF glass

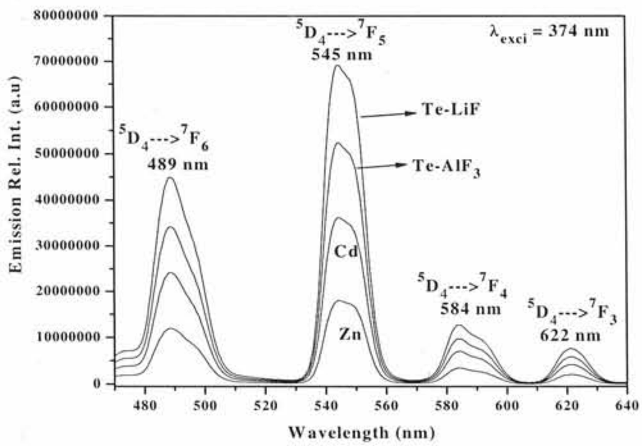


Fig.8 — Emission spectra of Tb^{3+}: 69.8 B_2O_3-10 P_2O_5-10 ($ZnO/CdO/TeO_2$)-10 (AlF_3/LiF) glasses

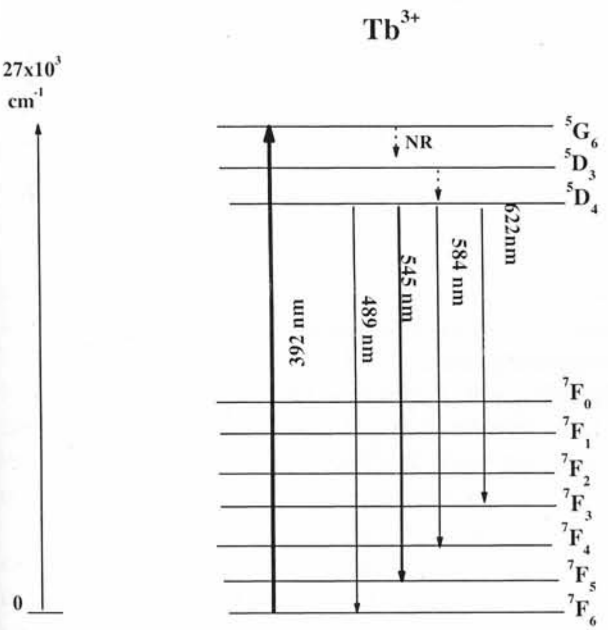


Fig. 9 — Emission process mechanism in Tb^{3+}: BPOF glass

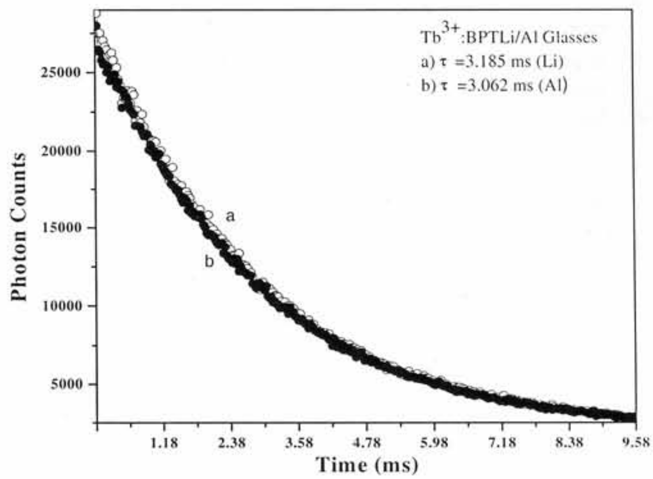


Fig. 10 — Decay curves of the emission transitions of Tb^{3+}: BPOF glasses with excitation at 374 nm

4 Conclusion

Highly transparent, moisture resistant and more stable 0.2 mol % of Eu^{3+} or Tb^{3+} ions doped borophosphate oxyfluoride glasses have been developed. Optical analysis of these glasses has been carried out based on the measurement of the absorption, excitation and emission spectra. Apart from analyzing the optical properties of these glasses, we have watched a bright red (Eu^{3+}:BPOF glasses) and a green (Tb^{3+}:BPOF glasses) emissions from these glasses when those are placed under an UV source. We have plotted the decay curves of the emission bands of Eu^{3+}or Tb^{3+}:BPOF glasses. We could suggest that these BPOF glasses are highly potential enough towards the display of green (Tb^{3+}) and red (Eu^{3+}) luminescent colours. Such primary (green, red) colors emitting materials are of significant importance in the development of emission rich optical systems.

Acknowledgement

This work was supported by the University Grants Commission; Hyderabad in the form of a Minor Research Project sanctioned to one of the author (BSR) who would like to thank Dr S Jelani, Deputy Secretary (UGC-SERO) and Sri A Gangi Reddy, Principal S V Degree College, Kadapa, for their kind support and co-operation in the present work.

References

1 Belliveau T F & Simkin, D J, *J Non-Cryst Solids*, 110 (1989) 127.
2 Ainslie B J, Craig, S P, Davey, S T & Wakefield, B, *Mater Lett*, 6 (1988) 139.
3 Dexpert-Ghys, J, Piriou, B, Fracillon, N J & Sombret C, *J Non-Cryst Solids*, 125 (1990) 117.

4 Shelby J E & Downie L K, *Phys Chem Glasses*, 30(4) (1989) 151.

5 Staske R, Frobel P, Dirke M V, Mullor S & Barner K, *Solid State Commun*, 78 (1991) 647.

6 Saltberg M A, Haw Hu & Ameer Y J, *Ceram Soc*, 73 (1990) 2970.

7 Penz B & Zhou Z, *J Mater Sci Lett*, 21 (2002) 1863.

8 Fernandez J, Balda R & Ariandiaga M A, *Opt Mater*, 4 (1994) 91.

9 Binnemans K, Van Deun R, Gorller-Walrand C & Adam J L, *J Alloys Compd*, 275-277 (1998) 455.

10 Rao A S, Ahammed Y N, Reddy R R & Rao T V R, *Opt Mater*, 10 (1998) 245.

11 Yong Gyu Choi, Jung Hyun Baik & Jong Heu, *Chem Phys Lett*, 406 (2005) 436.

12 Kam C H & Buddhudu S, *J Quant Spectrosc Radiat Trans*, 87 (2004) 325.

13 Jiwei Wang, Song H, Kong X, Wu Xu & Haiping Xia, *J Appl Phys* 91 (2002) 9466.

14 Wang J, Song H, Kong X, Peng H, Sun B, Chen B, Zhang J & Xu Wu & Haiping Xia, *J Appl Phys*, 93 (2003) 1482.

15 Kohei Soga, Inove H & Makishima Akio, *J Appl Phys*, 89 (2001) 3730.

16 Abdulatif Y Hamad, James P Wicksted, Robert Ascio, Joel J Martin, Charles Hunt & George S Dixon, *J Appl Phys*, 92 (2002) 2235.

17 Rai V K, Rai S B & Rai D K, *J Mater Sci*, 39 (2004) 4971.

18 Balaji T & Buddhudu S, *Ferroelectric Lett Sect*, 19 (1995) 1.

19 Thulasiramudu A & Buddhudu S, *Spectrochim Acta, Part A*, 66 (2007).

20 Carnal W T, Fields P R & Rajnak K, *J Chem Phys*, 49 (1968) 1450.

21 Chen L & Liu Y, *J Alloy Comp*, 381 (2004) 266.

22 SoorajHussain N, Prabhakar Reddy Y & Buddhudu S, *Spectrosc Lett*, 35(2) (2002) 275.

23 Kam C H & Buddhudu S, *Phys B*, 344 (2004) 182.

24 Zhang X, Zhang J, Liang L & Su Q, *Mater Resear Bull*, 40 (2005) 281.

25 Xu Z, Li Y, Liu Z & Wang D, *J Alloy Comp*, 391 (2005) 202.

26 Aruna V & Buddhudu S, *Mater Lett*, 36 (1998) 24.

27 Sooraj Hussain N, Prabhakara Reddy Y & Buddhudu S *Mater Lett*, 48 (2001) 303.

28 ZhangH X, Buddhudu S, Kam C H, Zhou Y, Lam Y L, Wong K S, Ooi B S, Ng S L & Que W X, *Mater Chem Phys*, 68 (2001) 31.