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Luminescence studies on lithium-calcium borophosphate glasses doped with Fe^{2+}, Ni^{2+} and Zn^{2+} ions

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Abstract

Luminescence material is a solid which converts certain types of energy into electromagnetic radiation over and above thermal radiation. Due to the limited studies on luminescence properties of the transition metal ion doped glass, this present study aiming to understand further the effect of doping different transition metal ions to the luminescence properties. This paper report on the luminescence properties of $25Li_2CO_3$-$25Ca_2CO_3$-$30B_2O_3$-$20P_2O_5$ glasses doped with 1 mol % of different transition metal ions (Fe, Ni, and Zn) which had been prepared by melt quenching technique. The luminescence properties were analyzed based on emission spectra obtained from the photoluminescence spectroscopy. The luminescence spectra of $25Li_2CO_3$-$25Ca_2CO_3$-$30B_2O_3$-$20P_2O_5$: Fe^{2+} consists of three band regions in the range from 272 to 489 nm, 516 to 689 nm and 754 to 861 nm. It exhibits indigo emission band which is centered at 430 nm and this band has been assigned to the transition of $z^8D°_{5/2} \rightarrow z^6D°_{3/2}$. While for the luminescence spectra of $25Li_2CO_3$-$25Ca_2CO_3$-$30B_2O_3$-$20P_2O_5$: Ni^{2+}, it exhibits a strong orange emission band centered at 580 nm and this band has been assigned to the transition of ${}^2P°_{1/2} \rightarrow {}^4F_{9/2}$. Lastly, for the luminescence spectra of $25Li_2CO_3$-$25Ca_2CO_3$-$30B_2O_3$-$20P_2O_5$: Zn^{2+}, it exhibits a strong indigo emission band at 433 nm ad this band has been assigned to the transition of ${}^2S_{1/2} \rightarrow {}^2D_{3/2}$.

Keywords: Borophosphate glass, lithium, calcium, Fe^{2+}, Ni^{2+} and Zn^{2+} ions, luminescence.

1. Introduction

Glass can be understood as an amorphous solid which is completely lack of long range and periodic atomic structure. In the last 30 years, phosphate glasses have been investigated because of their interesting properties. However, pure phosphate network is very hygroscopic and therefore their application is limited. It has been demonstrated that the addition of B_2O_3 to a phosphate network improves the chemical durability as well as the thermal and mechanical stability of pure phosphate glass [1, 2]. Borophosphate glasses have been studied in preceding years due to their possible applications as low-melting glass solders or glass seals [3]. The structure and properties of glass can be altered in a desired way by addition of so-called network modifier such as lithium, sodium or potassium. Studies of oxide glasses with a high ionic conductivity are interesting because of their advantageous characteristics for energy conversion in solid state devices such as micro batteries [4]. Therefore, the adding of network modifier of lithium is necessary to obtain a glass with higher ionic conductivity. Besides adding modifier, doping of transition metal ions also has attracted a great deal of attention due to their potential applications in solid state laser

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luminescent solar energy concentrators and fiber optic communication devices [5]. In general, the presence of transition metal ions additives increases the refractive index and transmission range the expense of increasing the ultraviolet absorption. Furthermore, the most interesting features of transition metal ions are that they exhibit variable valency (oxidation state) and the valency changes in unit of one [6]. A great number of researches have been carried to understand the luminescence properties of various rare earth ions doped glasses. While on the other hand, the research on transition metal ions doped materials are still very few. In order to examine the importance of glass doped transition metal ions, we have recently investigated the luminescence properties on the lithium-calcium borophosphate glasses doped with transition metal ions.

2. Experiment

2.1 Experimental procedures

The glass samples were prepared from raw material of Li_2CO_3, CaO, B_2O_3 and P_2O_5 according to the compositional formula $25Li_2CO_3{:}25CaO{:}30B_2O_3{:}20P_2O_5$ doped with 1mol% of different transition metal ions (Fe, Ni, Zn). The corresponding weight of the starting material were weighed by the analytical balance and mixed thoroughly in porcelain crucible. This followed by placing the samples in an electric furnace at 400°C for 20 minutes to facilitate evaporation of water and CO_2.The samples were then melted in an electric furnace at 1100°C for 5 to 10 minutes depending on the types of dopant used. Finally, the melts were then poured onto a stainless steel plate and press quickly with another stainless steel plate.

The glass samples were polished with sand paper until the surface of the samples was flat to obtain the data from photoluminescence spectroscopy. Then, the glass samples of approximately 1cm× 1cm were selected to paste it onto a black paper as a holder. The photoluminescence properties of the glass samples were measured using Perkin-Elmer LS55 Spectroscopy in room temperature. Different excitation energy was employed to obtain the best spectra.

3. Results and Discussion

The sample was visually checked and found to be homogeneous, colored and physical stable (non-hygroscopic).

The emission spectrum of $25Li_2CO_3$-25CaO-$20B_2O_3$-$30P_2O_5$with (a) 1 mol % of Fe ions, (b)1 mol % of Ni ions and (c) 1 mol % of Zn ions are shown in Fig.1. The spectrum of Fe ions doped sample is obtained when the excitation of 260 nm radiation is used. While for the spectrum of Ni ions doped sample, the excitation of 250 nm radiation is used. Lastly, the spectrum of Zn ions doped sample, 270 nm radiations is used.

From Fig.1, it can be seen that the Zn ions spectrum exhibit fewer emission bands than the Ni ions and Fe ions spectrum. As going from Zn ions → Ni ions → Fe ions, the number of emission peaks becomes more. This might be due to the nature of hyperfine structure of the transition metal ions. The hyperfine structure of the ions, lead to small shifts and splitting in the energy levels of atoms, molecules and ions. Therefore, it is more peaks observed in the Fe ions spectrum.

The Fig. 1(a) shows the emission spectrum of $25Li_2O$-25CaO-$20B_2O_3$-$30P_2O_5$ with 1 mol % of Fe ions in the excitation of 260 nm. From the figure, it is clear that there are three main bands region which are from 272 to 489 nm, 516 to 689 nm and 754 to 861 nm respectively. The transition of the emission lines and their assignments are summarized in

Table 1. The emission spectrum of Fe ions exhibit blue emission (~ 473 nm), green emission (~ 517 nm), yellow emission (~ 577 nm), orange emission (~ 593 nm) and red emission (~ 650 nm).

The emission spectrum of 1 mol % Ni ions doped $25Li_2O$-$25CaO$-$20B_2O_3$-$30P_2O_5$ excited at 250 nm is shown in Fig. 1(b). The 250 nm excitation gives rise to two groups of peaks mainly in the range of ~289 to 507 nm and ~532 to 689 nm. The transition of the emission lines and their assignments are summarized in Table 2. As is shown in Fig. 1(b), the emission spectrum exhibits a indigo emission band (~ 449 nm), green emission band (~ 507 nm), yellow emission band (~ 575 nm), orange emission band (~ 610 nm) and red emission band (~ 645 nm).

The Fig. 1(c) shows the emission spectrum of $25Li_2O$-$25CaO$-$20B_2O_3$-$30P_2O_5$ with 1 mol % of Zn ions in the excitation of 270 nm. From the figure, it is clear that there are two main bands region which are from 307 to 586 nm and 624 to 752 nm respectively. The emission lines and their transitions are summarized in Table 3. The emission spectrum of Zn ions shows orange emission (~ 586 nm).

Table 1: Transitions of Fe ions in borophosphate glasses

Transition	Experimental Wavelength (nm)	Calculated Wavelength (nm)
$z^4D^{\circ}_{7/2} \rightarrow a^4F_{9/2}$	~ 237	234
$z^4H^{\circ}_{9/2} \rightarrow a^2D^2_{3/2}$	~ 254	252
$z^4D^{\circ}_{3/2} \rightarrow a^6S_{5/2}$	~ 256	257
$z^4G^{\circ}_{5/2} \rightarrow a^6S_{5/2}$	~ 260	265
$z^4G^{\circ}_{5/2} \rightarrow a^6S_{5/2}$	~ 260	265
$z^4H^{\circ}_{11/2} \rightarrow a^4G_{11/2}$	~ 280	282
$b^4G_{7/2} \rightarrow a^4H_{13/2}$	~ 296	302
$c^2G_{7/2} \rightarrow a^6D_{3/2}$	~ 307	306
$c^4F_{7/2} \rightarrow a^2P_{3/2}$	~ 319	314
$c^2P_{1/2} \rightarrow a^6S_{5/2}$	~ 321	325
$z^8P^{\circ}_{5/2} \rightarrow b^4F_{7/2}$	~ 340	337
$b^4G_{11/2} \rightarrow a^4G_{7/2}$	~ 354	353
$d^2G_{7/2} \rightarrow b^2G_{7/2}$	~ 357	358
$c^4P_{5/2} \rightarrow a^6S_{5/2}$	~ 373	372
$b^2H_{9/2} \rightarrow a^6D_{1/2}$	~ 398	394
$d^2D^1_{5/2} \rightarrow a^6S_{5/2}$	~ 414	404
$z^8D^{\circ}_{5/2} \rightarrow z^6D^{\circ}_{3/2}$	~ 430	433
$c^4D_{7/2} \rightarrow c^2D_{5/2}$	~ 451	452
$a^2H_{7/2} \rightarrow a^6D_{5/2}$	~ 473	475
$a^2H_{9/2} \rightarrow a^6D_{7/2}$	~ 492	489
$a^2H_{11/2} \rightarrow a^6D_{1/2}$	~ 517	516
$z^4F^{\circ}_{3/2} \rightarrow b^2H_{11/2}$	~ 525	523
$z^4I^{\circ}_{15/2} \rightarrow z^6P^{\circ}_{7/2}$	~ 533	535
$a^2H_{11/2} \rightarrow a^4F_{9/2}$	~ 543	541
$a^2P_{3/2} \rightarrow a^6D_{7/2}$	~ 557	556
$c^2D_{5/2} \rightarrow a^2D^2_{5/2}$	~ 568	567
$a^2P_{3/2} \rightarrow a^6D_{1/2}$	~ 577	575
$z^4I^{\circ}_{9/2} \rightarrow z^4D^{\circ}_{7/2}$	~ 593	585
$z^4I^{\circ}_{9/2} \rightarrow c^2F_{5/2}$	~ 601	603
$a^2P_{3/2} \rightarrow a^4F_{9/2}$	~ 604	606
$a^2P_{1/2} \rightarrow a^4F_{5/2}$	~ 619	623
$a^2P_{3/2} \rightarrow a^4F_{7/2}$	~ 631	627
$b^2F_{7/2} \rightarrow a^2G_{7/2}$	~ 641	639
$a^2G_{7/2} \rightarrow a^6D_{1/2}$	~ 650	649
$a^2G_{9/2} \rightarrow a^6D_{3/2}$	~ 663	667
$d^2D^1_{5/2} \rightarrow c^2G_{7/2}$	~ 685	687
$a^2G_{7/2} \rightarrow a^4F_{9/2}$	~ 690	689
$z^8P^{\circ}_{7/2} \rightarrow z^6D^{\circ}_{9/2}$	~ 713	708
$a^4P_{1/2} \rightarrow a^4F_{9/2}$	~ 833	831
$a^4P_{3/2} \rightarrow a^4F_{9/2}$	~ 844	847
$a^4P_{5/2} \rightarrow a^4F_{9/2}$	~ 859	861

Table 2: Transitions of Ni ions in borophosphate glasses

Transition	Experimental Wavelength (nm)	Calculated Wavelength (nm)
$^4F^{\circ}_{3/2} \rightarrow {}^4P_{5/2}$	~ 289	300
$^2G_{7/2} \rightarrow {}^2D_{3/2}$	~ 324	322
$^2F^{\circ}_{5/2} \rightarrow {}^2P_{3/2}$	~ 333	339
$^4G^{\circ}_{5/2} \rightarrow {}^4P_{3/2}$	~ 381	385
$^2G^{\circ}_{9/2} \rightarrow {}^2G_{7/2}$	~ 437	440
$^4G^{\circ}_{5/2} \rightarrow {}^2G_{9/2}$	~ 449	444
$^4F_{5/2} \rightarrow {}^2G_{9/2}$	~ 484	487
$^4D^{\circ}_{7/2} \rightarrow {}^4F_{9/2}$	~ 507	506
$^4D^{\circ}_{7/2} \rightarrow {}^4F_{7/2}$	~ 532	539
$^4F_{9/2} \rightarrow {}^2G_{7/2}$	~ 549	540
$^2P^{\circ}_{1/2} \rightarrow {}^4F_{9/2}$	~ 575	580
$^4F_{9/2} \rightarrow {}^2G_{7/2}$	~ 549	540
$^2P^{\circ}_{1/2} \rightarrow {}^4F_{9/2}$	~ 575	580
$^2P^{\circ}_{1/2} \rightarrow {}^4D^{\circ}_{7/2}$	~ 594	598
$^2D^{\circ}_{3/2} \rightarrow {}^4D^{\circ}_{7/2}$	~ 610	603
$^2P^{\circ}_{1/2} \rightarrow {}^4F_{7/2}$	~ 621	622
$^4D^{\circ}_{7/2} \rightarrow {}^4G^{\circ}_{5/2}$	~ 632	635
$^4D^{\circ}_{7/2} \rightarrow {}^2G^{\circ}_{9/2}$	~ 645	646
$^2D_{3/2} \rightarrow {}^4F_{9/2}$	~ 655	649
$^4P^{\circ}_{5/2} \rightarrow {}^4D^{\circ}_{7/2}$	~ 669	666
$^4P_{5/2} \rightarrow {}^4F_{9/2}$	~ 689	680

Table 3: Transitions of Zn ions in borophosphate glasses

Transition	Experimental Wavelength (nm)	Calculated Wavelength (nm)
$^2D_{3/2} \rightarrow {}^2D_{5/2}$	~ 307	293
$^2D_{3/2} \rightarrow {}^2D_{3/2}$	~ 323	317
$^2F^{\circ}_{7/2} \rightarrow {}^2S_{1/2}$	~ 349	347
$^2S_{1/2} \rightarrow {}^2D_{3/2}$	~ 433	434
$^2F^{\circ}_{7/2} \rightarrow {}^2D_{3/2}$	~ 496	491
$^2D_{3/2} \rightarrow {}^2P^{\circ}_{1/2}$	~ 586	591
$^2D_{3/2} \rightarrow {}^2P^{\circ}_{3/2}$	~ 624	623
$^2D_{5/2} \rightarrow {}^2P^{\circ}_{3/2}$	~ 752	748

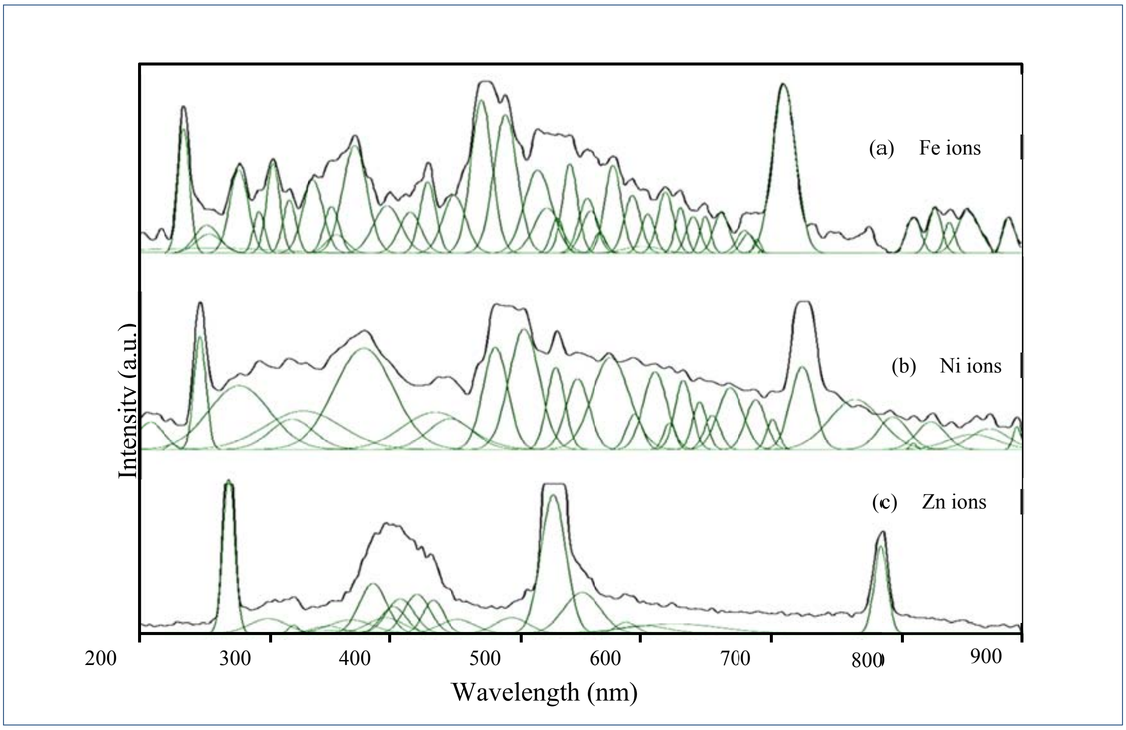

Figure 1: The emission spectrum of $25Li_2CO_3:25CaO:20B_2O_3:30P_2O_5$ with 1 mol % of (a) Fe ions (b) Ni ions (c) Zn ions.

4. Conclusion

In summary, it can be concluded that we have developed transparent and colored Fe, Ni and Zn ions doped lithium-calcium borophosphate glasses for studying their photoluminescence properties. Due to the doping of transition metal ions in the glasses, they have been found that glasses are more stable.

Besides that, the doping of different transition metal ions does influence the photoluminescence spectra. From the spectra obtained, as the transition metal ions goes from Zn to Ni and to Fe, more peaks are observed. This might be due to the structure becomes more hyperfine. Hence, the splitting of energy level becomes more.

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