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Photoluminescence Studies on Lithium- Calcium Borophosphate Glasses doped with Transition Metal Ions

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ABSTRACT

The mixed alkali borophosphate $25Li_2CO_3$:$25Ca_2O_3$:$30B_2O_3$:$20P_2O_5$ glasses doped with 1 mol% of different transition metal ions were prepared and studied using photoluminescence techniques. The transition metal ions used included chromium, manganese and iron. Chromium doped glass exhibits a violet emission band at ~ 316 nm and this band has been assigned to the transition of $z^6D^{\circ}_{1/2} \rightarrow a^4P_{5/2}$. While manganese doped glass show a violet emission band at ~ 408 nm which is assigned to $z^7P^{\circ}_4 \rightarrow a^5D_4$ and a red emission band at ~ 632 nm which is assigned to the transition of $z^5P^{\circ}_3 \rightarrow a^5G_6$. Lastly, for the iron doped glass shows many emission bands along the visible range.

| Borophosphate glass| Lithium | Calcium | transition metal ions | photoluminescence |

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1. INTRODUCTION

Glass can be understood as an amorphous solid which is completely lack of long range and periodic atomic structure. Glasses are important optical materials usually made to be transparent in the visible spectrum [1]. Phosphate glasses have a wide range of technical applications [2]. However, it is well known that a pure phosphate network is very hygroscopic and therefore is not stable. 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[3,4]. Borophosphate glasses belong to interesting glassy materials, e.g. zinc-calcium borophosphate glasses were studied as candidates for applications as low-melting glass solders or glass seals [5]. Adding of network modifier to the glasses such as Lithium, Sodium or Potassium alters fundamentally the glass properties. 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 luminescent solar energy concentrators and fiber optic communication devices [6].

Furthermore, the most interesting features of transition metal ions is that they exhibit variable valency(oxidation state) and the valency changes in unit of one. When the transition metal ions are coordinated with other glass ions, the energy levels of the 3d electrons are split by the electric field of the coordinating ions. The d-electron orbitals are strongly directional, so the splitting is sensitive to the arrangement of the surrounding ions. Thus, transition metal ions are used to probe the glass structure and to study the coordination numbers of the central ions due to their outer d electron orbital functions have a broad radial distribution. In general, the presence of transition metal ions additives increases the refractive index and transmission range the expense of increasing the ultraviolet absorption [7]. 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 [8]. 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. EXPERIMENTAL

2.1 Materials, method and instruments

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 1 mol % of different transition metal ions (Cr, Mn, Fe). 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.

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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.

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3. RESULTS & DISCUSSION

The sample was visually checked and found to be homogeneous, colored and physical stable (non-hygroscopic). Table 1 summarized the samples composition that has been prepared.

Table 1 Nominal compositions (mol%) of lithium calcium borophosphate glasses doped with transition metal ions.

No	Composition (mol %)				TMI
	Li_2CO_3	Ca_2O_3	B_2O_3	P_2O_5	(1 mol%)
S1	25	25	30	20	Cr
S2	25	25	30	20	Mn
S3	25	25	30	20	Fe

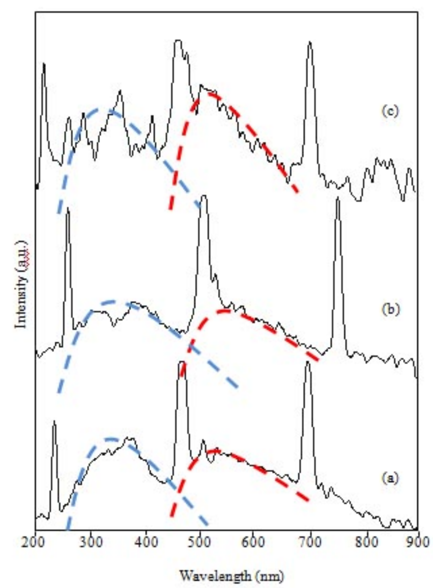

Fig. 1 The emission spectrum of $25Li_2CO_3$:25CaO :$20B_2O_3$:$30P_2O_5$with (a) 1 mol% of Cr ions, (b)1 mol% of Mn ions and (c) 1 mol% of Fe ions

The emission spectrum of $25Li_2CO_3$-25CaO-$20B_2O_3$-$30P_2O_5$with (a) 1 mol % of Cr ions, (b)1 mol % of Mn ions and (c) 1 mol % of Fe ions are shown in Fig.1. The spectrum of Cr ions doped sample is obtained when the excitation of 240 nm radiation is used. While for the spectrum of Mn ions doped sample, the excitation of 260 nm radiation is used. Lastly, the spectrum of Fe ions doped sample, 260 nm radiations is used.

From Fig.1, it can be seen that the Cr ions spectrum exhibit fewer emission bands than the Mn ions and Fe ions spectrum. As going from Cr ions → Mn 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.

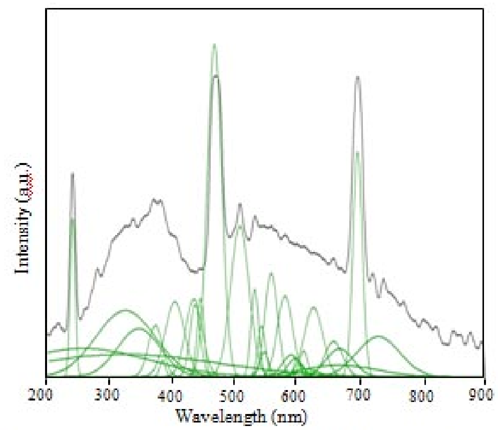

Fig. 2 The emission spectrum of $25Li_2CO_3$:25CaO: $20B_2O_3$:$30P_2O_5$ with 1mol% of Cr ions in the excitation of 240 nm.

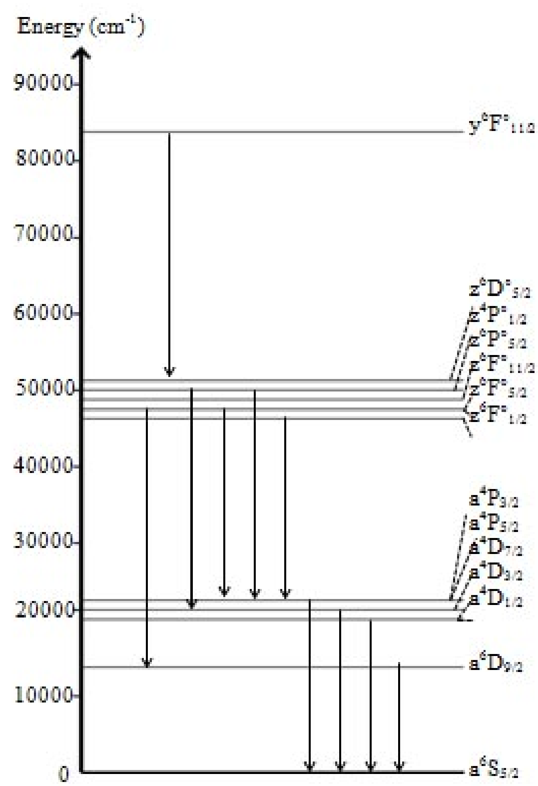

Fig. 3 Energy level diagram of the sample doped Cr ions.

Table 2: Experimental and calculated wavelength of Cr ions in borophosphate glasses

Transition	Experimental Wavelength (nm)	Calculated Wavelength (nm)
$y^6F^{\circ}_{11/2} \rightarrow a^6D_{9/2}$	~ 258	283
$y^6F^{\circ}_{11/2} \rightarrow z^6D^{\circ}_{5/2}$	~ 325	300
$z^4P^{\circ}_{1/2} \rightarrow a^4D_{3/2}$	~ 347	343
$z^6F^{\circ}_{5/2} \rightarrow a^4D_{7/2}$	~ 373	370
$z^6P^{\circ}_{5/2} \rightarrow a^4P_{5/2}$	~ 384	374
$z^6F^{\circ}_{1/2} \rightarrow a^4P_{3/2}$	~ 404	400
$a^4P_{5/2} \rightarrow a^6S_{5/2}$	~ 468	458
$a^4D_{7/2} \rightarrow a^6S_{5/2}$	~ 508	499
$a^4D_{1/2} \rightarrow a^6S_{5/2}$	~ 532	512
$a^6D_{9/2} \rightarrow a^6S_{5/2}$	~ 780	800

The emission spectrum of 1 mol % Cr ions doped $25Li_2CO_3$-25CaO-$20B_2O_3$-$30P_2O_5$ excited at 240 nm is shown in Fig. 2. The 240 nm excitation gives rise to three groups of peaks mainly in the range of ~283 to 377 nm, ~410 to 787 nm and ~808 to 857 nm. The location of the emission lines and their assignments are indicated in the energy level diagram in Fig.3 and are summarized in Table 2.

From the transition of energy level obtained, it can be seen that, the transition of Cr ions in the ultraviolet region centered at 325, 347, 373 and 384nm respectively. As is shown in Fig.1, the emission spectrum exhibits a blue emission band (~ 499 nm) and green emission band (~ 512 nm).

The Fig.4 shows the emission spectrum of $25Li_2CO_3$-25CaO-$20B_2O_3$-$30P_2O_5$ with 1 mol% of Mn ions in the excitation of 260 nm. From the figure, it is clear that there are three main bands region which are from 293 to 419 nm, 551 to 698 nm and 754 to 888 nm respectively. The emission lines and their transitions are indicated in Fig.5 and are summarized in Table 3.

From the Table 3, it shows that the transition of Mn ions emitted at ultraviolet region which is at ~ 235, ~ 261, ~ 282, ~ 352 and ~ 367 nm. The emission spectrum of Mn ions shows yellow emission (~ 552 nm), orange emission (~ 626 nm) and red emission (~ 669 nm).

Figure 5: The emission spectrum of $25Li_2CO_3$:25CaO:$20B_2O_3$:$30P_2O_5$ with 1 mol% of Fe ions in the excitation of 240 nm.

The Fig.5 shows the emission spectrum of $25Li_2CO_3$-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 location of the emission lines and their assignments are indicated in the energy level diagram in Fig.5 and are summarized in Table 4.

As summarized in Table 4, there are emissions bands appear at ultraviolet region (~ 237, ~ 254, ~ 256, ~ 260, ~ 280, ~ 296, ~ 307, ~ 319, ~ 321, ~ 340, ~ 354, ~ 357, ~ 373 and ~ 398 nm). 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).

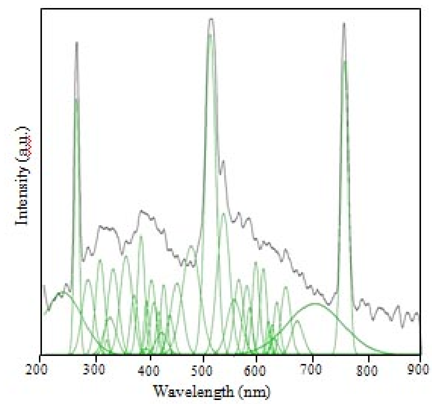

Fig. 4 The emission spectrum of $25Li_2CO_3$:25CaO:$20B_2O_3$:$30P_2O_5$ with 1 mol% of Mn ions in the excitation of 260 nm.

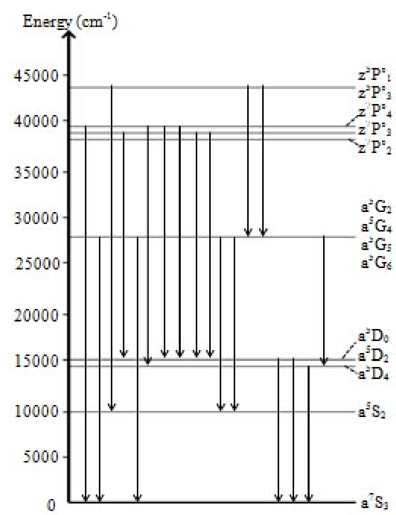

Fig. 5 Energy level diagram of the sample doped Mn ions.

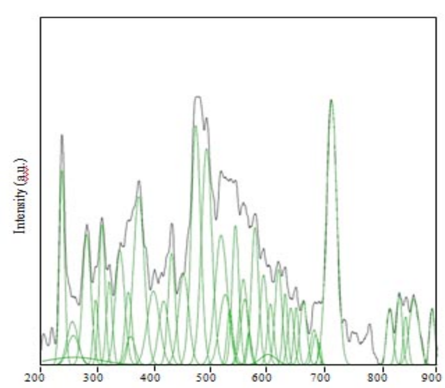

Fig. 5 The emission spectrum of $25Li_2CO_3$:25CaO:$20B_2O_3$:$30P_2O_5$ with 1 mol% of Fe ions in the excitation of 240 nm.

Table 3: Experimental and calculated wavelength of Mn ions in borophosphate glasses *(continued)*

Transition	Experimental Wavelength (nm)	Calculated Wavelength (nm)
$z^5P^{\circ}_3 \rightarrow a^7S_3$	~235	231
$a^5G_4 \rightarrow a^7S_3$	~261	261
$z^5P^{\circ}_1 \rightarrow a^5S_2$	~282	293
$z^5P^{\circ}_3 \rightarrow a^5D_0$	~352	352
$a^5G_6 \rightarrow a^7S_3$	~367	363
$z^7P^{\circ}_4 \rightarrow a^5D_4$	~404	408
$z^7P^{\circ}_4 \rightarrow a^5D_2$	~413	416
$z^7P^{\circ}_4 \rightarrow a^5D_0$	~418	419
$z^7P^{\circ}_3 \rightarrow a^5D_2$	~422	421
$z^7P^{\circ}_2 \rightarrow a^5D_0$	~433	427
$a^5D_2 \rightarrow a^5S_2$	~551	551
$a^5D_6 \rightarrow a^5S_2$	~552	553
$z^5P^{\circ}_1 \rightarrow a^5G_2$	~626	626
$z^5P^{\circ}_3 \rightarrow a^5G_2$	~631	634
$a^5D_0 \rightarrow a^7S_3$	~669	668
$a^5D_2 \rightarrow a^7S_3$	~687	677
$a^5D_4 \rightarrow a^7S_3$	~702	698
$a^5D_5 \rightarrow a^5D_4$	~757	754

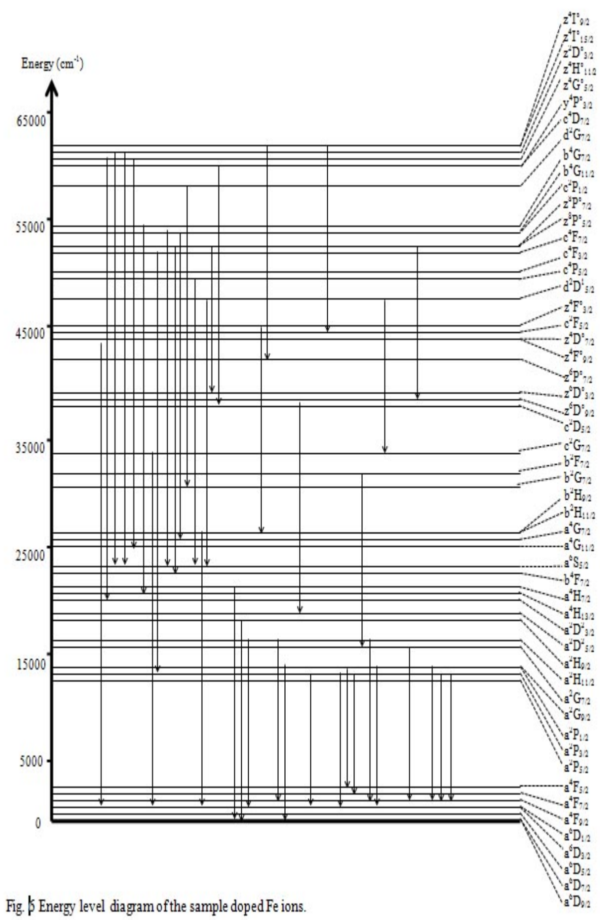

Fig. 5 Energy level diagram of the sample doped Fe ions.

Table 4: Experimental and calculated wavelength of Fe ions in borophosphate glasses *(continued)*

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

4. CONCLUSION

In summary, it is concluded that we have developed transparent and colored Cr, Mn and Fe 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 left to right along the series, 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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