

of 0.0001-0.0005 moles) in strontium aluminate (SrAl_2O_4 : Eu, Dy, Y) was investigated.

2. EXPERIMENTAL

SrCO_3 , $\alpha\text{-Al}_2\text{O}_3$, H_3AlO_3 , Eu_2O_3 , Dy_2O_3 , Y_2O_3 , Pr_6O_{11} and H_3BO_3 with high purity were used as starting materials because the solid-state reaction route was chosen to prepare long afterglow phosphorescent pigments co-doped with Pr^{3+} . The thoroughly weighed recipes including Pr_6O_{11} and coded as A-E were milled in zirconium oxide bowls using zirconium oxide balls and isopropyl alcohol at 200 rpm for 1 hour in a planetary mill. The mixed solutions were dried in an oven at 90 °C for 12 hours. The dried powder mixtures were then fired in alumina crucibles in a laboratory type tunnel furnace at about 1400-1550 °C for 1-5 hours.

The crystalline structure of the phosphors powders was analyzed by X-ray diffractometer (XRD at 40 kV and 30 mA with Rigaku Rint 2000 using Cu $K\alpha$ radiation). The morphology and size of the powders were observed employing a scanning electron microscope (SEM-Zeiss EVO50).

After sintering and sieving, the particle size distributions of phosphors were determined by using Malvern Instruments Mastersizer Hydro 2000G laser particle size analyzing instrument.

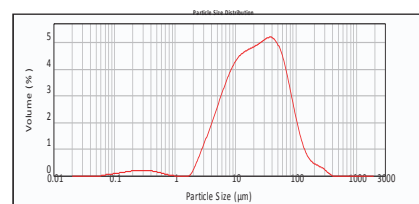
The excitation and emission spectra were recorded on the powder samples using a fluorescence spectrophotometer (Perkin Elmer LS55). All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

After sintering the samples at certain temperatures for determined time, dry-ground phosphors were analyzed by laser particle size analysis and a scanning electron microscope (SEM) to investigate particle size distributions and element analysis, respectively.

The particle size analysis results, XRD graphs, SEM images and EDX results of the phosphorescence base and C sample including

Pr^{3+} (the best one in terms of luminescence) after sintering and grinding are given in Figs. 2-4. As seen in both systems, the major crystal phase is SrAl_2O_4 and secondary ones seem to be AlYO_3 , SrAl_4O_7 and SrB_2O_4 . The excitation and emission spectra of SrAl_2O_4 : Eu^{2+} , Dy^{3+} , Y^{3+} versus SrAl_2O_4 : Eu^{2+} , Dy^{3+} , Y^{3+} , Pr^{3+} phosphors are shown in Fig. 5.



(a)

(b)

Figure 2. The particle size analysis results of the phosphorescence base sample in the SrAl_2O_4 : Eu^{2+} , Dy^{3+} , Y^{3+} (a) and C one (with 0.0003 moles Pr_6O_{11}) in the SrAl_2O_4 : Eu^{2+} , Dy^{3+} , Y^{3+} , Pr^{3+} systems (b) after sintering and dry-grinding.

Figure 3. The XRD results of the phosphorescence base and C one (with 0.0003 moles Pr_6O_{11}) samples after sintering.

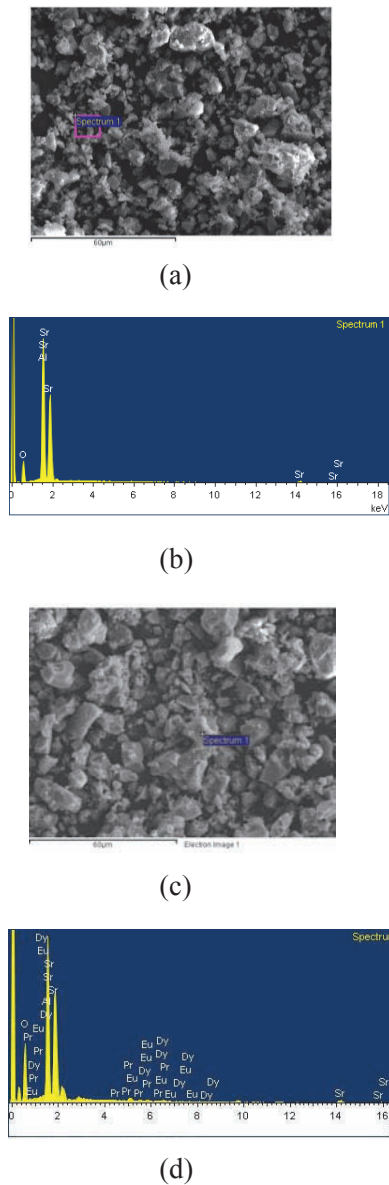
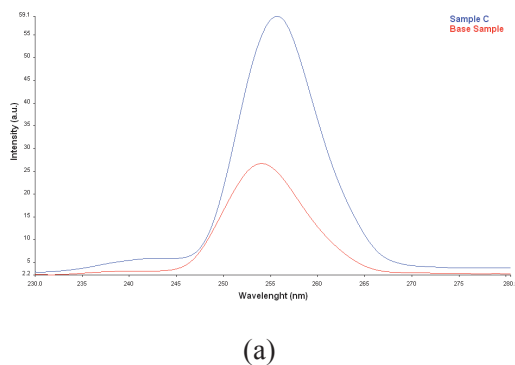
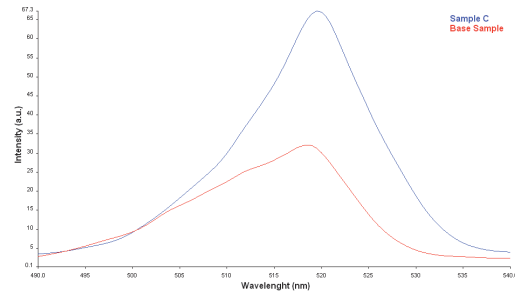


Figure 4. (a-b) SEM photographs and EDX results of the phosphorescence base and (c-d) C (with 0.0003 moles Pr_6O_{11}) samples after sintering.



(a)



(b)

Figure 5. (a) The excitation and (b) emission analysis results of the base sample and the one co-doped (sample C) with 0.0003 moles Pr_6O_{11} .

It can be clearly seen that the crystal exhibits a broad band emission from Eu ions peaking at λ : 520 nm, which is thought to be due to the 5d–4f transition of Eu ions. The peak wavelength of the phosphorescence does not vary with Pr_6O_{11} , the auxiliary activator element in the crystals. Consequently, the results present that the intensity of excitation and emission peaks of the samples co-doped Pr^{3+} are stronger than those of the base one. The peak intensity of the photoluminescence varies greatly with adding the auxiliary activator element, Pr. It is thought that the formation of Al_2O_3 increases with the addition of Pr_6O_{11} and has an increasing effect on the phosphorescence according to the excitation and emission analysis results. The emission can, thus, be said to originate from the same Eu^{2+} center as then on co-doped SrAl_2O_4 : Eu^{2+} [18]. This implies that the crystal field, which affects the 5d electron states of Eu ions, is not changed by the auxiliary activator element of Pr_6O_{11} .

4. ARTISTIC GLASS APPLICATIONS

Glass art works with Pr_6O_{11} -doped SrAl_2O_4 : Eu^{2+} , Dy^{3+} , Y^{3+} yellowish-green phosphor (sample C) in this study were made by using the hot glass blowing and fusion techniques. When employing the hot glass blowing method, phosphorescent pigments were sprinkled onto a glass hump at the edge of blowing pipe and then, fixed after heating up in

a glory hole. At this stage it seems that fixing treatment on the surface of the art form must be gradually done since the pigments tend to get together due to their high surface tension values. Therefore, splashing should be repeated several times with certain amount of pigments. After making sure of the fact that the pigments were homogenously sprinkled on the glass surface another hot glass layer was applied on the initial one and the object was enlarged by blowing. As a result of this treatment, a relief appearance was achieved thanks to both crackling and layering effects. In such a sense *Graal Technique can be suggested especially to the glass artists dealing with hot glass work. The photos of the artworks with the phosphorescence ability are given in Fig. 6.

As seen from Fig. 6, no matter what was done to overcome agglomeration problem of the pigments on the glass surface their inhomogeneous distribution could not be completely prevented. Even so, the final works seem to be of artistic importance in terms of both attractive appearances and the surface textures. As to fusion methods, the phosphorescent pigments were mixed with a suitable low temperature transparent frit and then sprinkled onto the bulls eye-shot and window glass surfaces. At this stage, different pigment layers were applied onto the surface and the thickness effect was investigated. When the thickness increases the sticking ability of pigment-frit mixture to the surface weakens. In the primary works, with which a single glass layer was handled, firings were conducted in a fusion furnace at 960 °C for 5 min holding time. In the secondary works, after the first firing of the single glass layer, another layer was placed on the top of the primary one and fusion was conducted at 920 °C (Fig. 7). The bubble formation at inter-phase was observed, which may be commented that is caused by the high surface tension the phosphorescent pigments.

*Graal Technique is a decoration method, with which glasses initially decorated either by cold treatment or painting, are heated up to their annealing point and then rolled by another hot glass layer and finally blown.

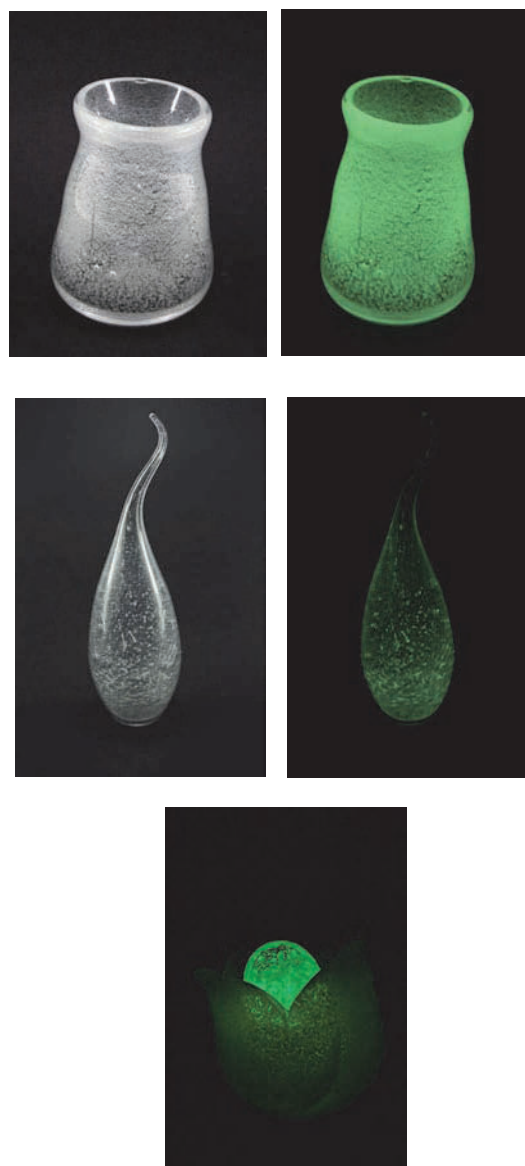


Figure 6. The appearances of the artistic glass forms made by the hot glass blowing method in the daylight (left) and the dark (right).

5. CONCLUSION

A novel yellowish-green color emitting long-lasting phosphorescent pigment, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}, \text{Y}^{3+}, \text{Pr}^{3+}$, was successfully synthesized and produced. The trivalent rare-earth ion, Pr^{3+} co-doping would effectively enhance the persistent luminescence intensity considering the phosphor with no Pr^{3+} ions. It was seen that art glass works with phosphorescence ability could be made by using both glass blowing and fusion techniques supplying different surface effects.

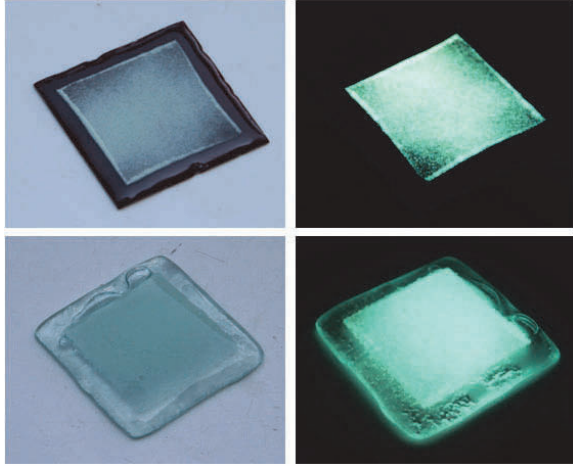


Figure 7. The appearances of the artistic glass forms produced by the fusion technique in the daylight (left) and the dark (right). Upper ones were produced with a single glass layer and lowers with double ones by direct firing where bubble formation is obvious.

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