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A STUDY ON THE FORMATION OF LUMINESCENT ZINC SILICATE

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A study to understand the mechanism of formation of zinc ortho silicate green phosphor has been attempted. Samples with different mole ratios of ZnO and SiO_2 ranging from 2:1 to 0.25:1 in steps of 0.25 respectively have been prepared. Characterisation of the samples were done by emission and excitation spectra and XRD analysis.

Key words: Zinc silicate, photoluminescence, fluorescent lamps

INTRODUCTION

Zinc silicate-willemite (Zn_2SiO_4) activated by Mn^{2+} phosphor having its green emission is still evaluated as an unreplaceable green phosphor for its cost to performance ratio. Although it is one of the oldest phosphor materials known, it has got numerous applications in fluorescent lamps, CRT, Radar screens etc. by its compatibility to a number of dopants such as Mn^{2+}, Al^{3+}, Ti^{3+} [1]. Enhancement of emission intensity by the addition of $AlPO_4$ is of practical importance with regard to applications in fluorescent lamps, screens in electronic devices [2]. The green emission in Zn_2SiO_4:Mn is due to the spin flip transition of 'd' orbital electron associated with Mn^{2+} ion.

The main advantage of zinc silicate:Mn phosphor is its favourable emission in the 520-525 nm region. Because of this it finds use in modern trichromatic lamps [3], to satisfy the condition that of the three primary colour components, blue and red components should have narrow band emission and the green components should be a broad one having λ_{max} around 520-540 nm [4].

It is quite suggestive that for the formation of zinc ortho sillicate ($2ZnO + SiO_2 \longrightarrow Zn_2SiO_4$) the ratio between ZnO and SiO_2 is 2:1 to be stoichiometric. Contrary to this, in actual practice, it has been observed that samples prepared even with the ratio as low as 0.25:1 gives peak emission at 523 nm, characteristic of Zn_2SiO_4:Mn^{2+}. A detailed study has been therefore attempted with different ratios between ZnO and SiO_2 to understand the formation process and its effect on the photoluminescence of the phosphor.

EXPERIMENTAL

To study the formation of zinc ortho silicate phosphor samples with the variation in zinc oxide (A.R., B.D.H.) from 2 moles to 0.25 mole in steps of 0.25 mole were mixed thoroughly with fixed proportions of optical grade silica supplied by (CGCRI, India) 1 mole in all the cases. The various samples presented in this paper are labelled in Table I. The activator divalent manganese is added in the form of manganese sulphate (A.R., B.D.H.). The optimum activator concentration has earlier been found to be 4 m/o and this optimised amount of manganese is added in all the cases. In each case, corresponding amounts of the ingredients (of about 10g in all were taken in powder form) were mixed thoroughly. These mixtures were fired in silica crucibles at 1250°C for an hour in a muffle furnace under normal atmospheric conditions. The final products were air cooled and pulverized.

TABLE-1: Effect of ZnO/SiO_2 on the emission intensity of zinc ortho silicate on 254 nm excitation

Sample	ZnO/SiO_2	Intensity at λ_{max} = 523 nm (Arb units)
b	2:1	28
c	1.75:1	47
d	1.5:1	73
e	1.25:1	83
a	1.0:1	80
f	0.75:1	79
g	0.5:1	68
h	0.25:1	59

Fluorescence measurements (both emission and excitation spectra) on these samples were made with the help of fluorescence spectrophotometer Hitachi 650-10S in conjunction with 150W xenon lamp source. Diffuse reflectance measurements were made with double beam UV-VIS-NIR spectrophotometer Hitachi U-3400 with high alumina pellet as the reference. X-ray diffraction studies (XRD) for our phosphor samples were made with the help of Philips X-ray Diffractometer with Cu K radiation, with Ni filter.

RESULTS AND DISCUSSION

Emission and excitation characteristics

As it is the normal method to evaluate a phosphor by its luminosity and other allied properties here the results of emission and excitation spectra are presented. To get the emission spectra, these samples were excited with 254 nm UV radiation from the xenon lamp source of the fluorescence spectrophotometer and their emissions were recorded from 440 nm to 600 nm in all the cases. Emission spectra of various samples are given in Fig.1.

Though no change has been found in the peak emission (λ_{max} = 523 nm) for all these samples, their relative luminosity varied in accordance with the state of completion of the reaction of Zn_2SiO_4:Mn.

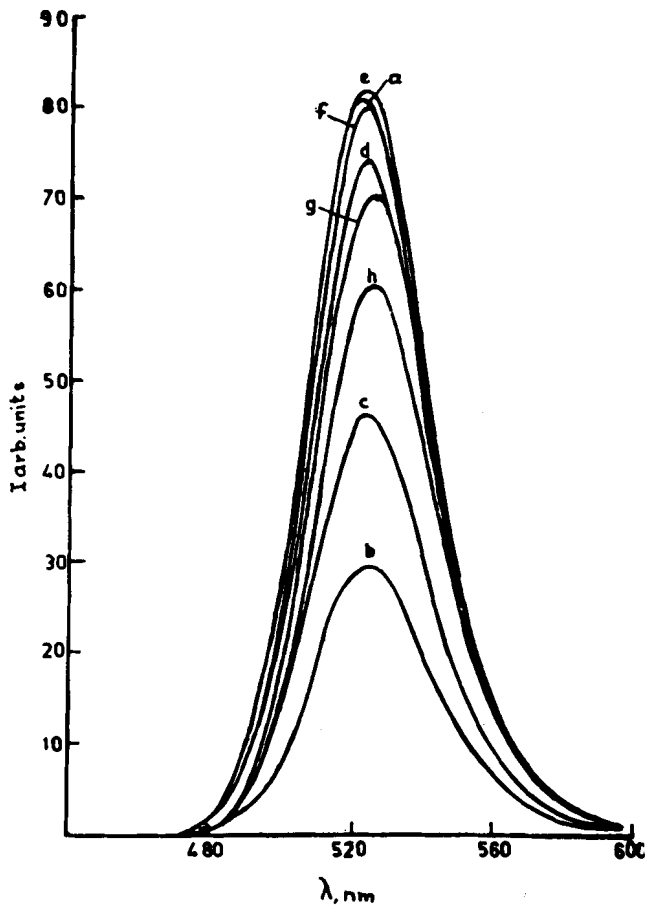

Fig. 1: Emission spectra of samples with various mole ratios between ZnO and SiO_2 (a) 1:1 (b) 2:1 (c) 1.75:1.0 (d) 1.5:1.0 (e) 1.25:1.0 (f) 0.75:1.0 (g) 0.5:1.0 (h) 0.25:1.0 on 254 nm UV excitation

Of all these samples (with the only difference of ZnO content) the sample (e) is found to be having maximum emission intensity whereas the sample (b) with the theoretical mole ratio of 2:1 is only having about 30% intensity to that of sample (e), while that of sample (a) with $ZnO:SiO_2$ = 1:1 is 95% of sample (e). The other samples (c), (d), (f), (g) and (h) exhibited the same fluorescent characteristics, satisfying the condition that if more is the deviation is the ZnO content from the optimum ratio of 1.25:1, more will be the decrease in intensity as can be seen from Table I.

The decrease in luminosity may be partly attributed to discoloration of the samples observed in some cases. But the discoloration has been found to have some gradation from deep yellow to white as the ratio is decreased from 2:1 to 1.25:1. Products obtained with proportions below the optimal value are found not to have any discoloration. This gradation in the discoloration suggests the presence of an intermediate phase having a decreasing tendency as it is approached towards the optimum proportion of 1.25:1. This discoloration has been found to disappear with better luminosity in the subsequent firings under the same conditions. To confirm this, the sample with $ZnO:SiO_2$ = 1.75:10 having yellow body colour in the first firing became white in subsequent firing at 1250°C, under same conditions, with about 40% improvement in its intensity from its previous value, indicating the completion of Zn_2SiO_4 formation.

Hence it is quite clear from the above results that for proportions higher than the optimal value, the reaction takes a sluggish pace and it could be improved slightly by the addition of either suitable flux like MgF_2 or by the application of external pressure [5]. Excitation spectra for these samples have been recorded from 220 to 320nm, by fixing the emission at 523 nm. Again, maximum excitation intensity has been obtained in the case of sample (e) as seen in Fig. 2.

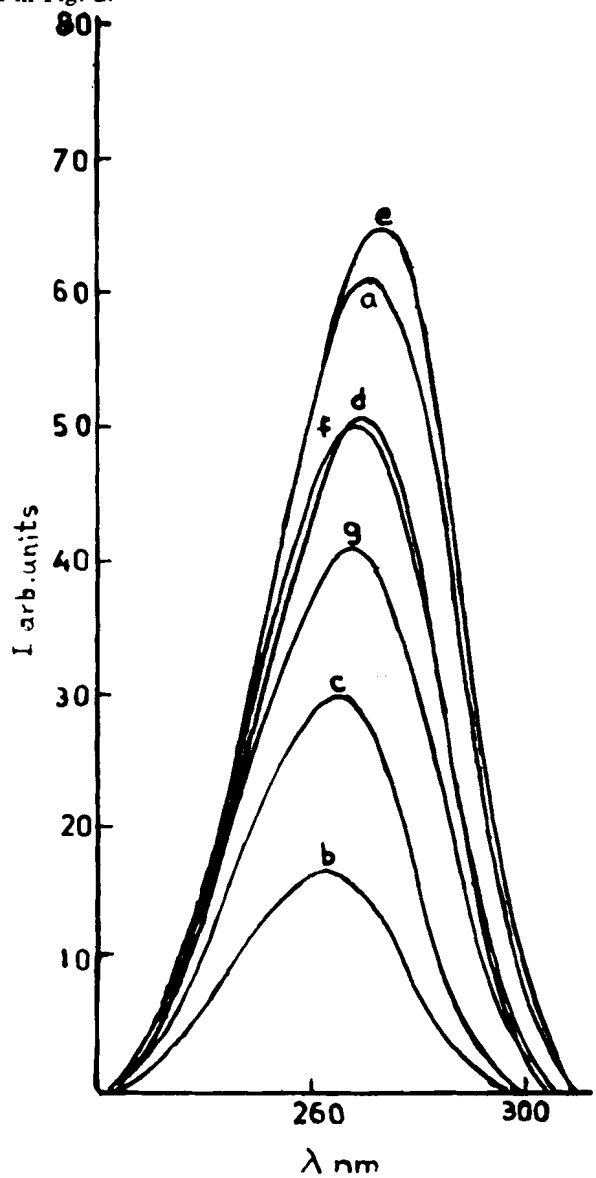

Fig. 2: Excitation spectra of samples with various mole ratios between ZnO and SiO_2 . (a) 1:1 (b) 2:1 (c) 1.75:1 (d) 1.5:1.0 (e) 1.25:1.0 (f) 0.75:1.0 (g) 0.5:1.0 (h) 0.25:1.0 with emission fixed at 523 nm

Excitation spectra of other samples are also given in the same figure.

Diffuse reflectance spectra

Diffuse reflectance spectra of the phosphor samples were taken 350-800 nm, and the diffuse reflectance curves are given in Fig. 3.

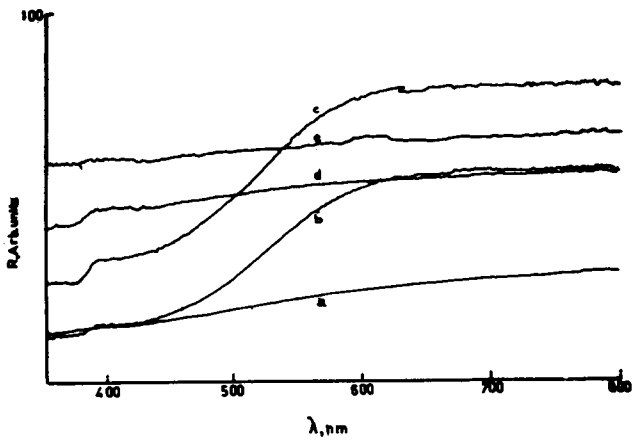

Fig. 3: Diffuse reflectance spectra of samples with ZnO/SiO_2 (a) 1:1 (b) 2:1 (c) 1.75:1.0 (d) 1.5:1.0 (e) 1.25:1.0

From the reflectance spectra, it can be seen, that samples (b), (c), and (d) with $ZnO:SiO_2$ 2:1, 1.75:1.0 and 1.5:1.0 have pronounced ZnO phase, as indicated by the absorption edge around 380 nm, this can be compared with the diffuse reflectance spectra of bare ZnO given in Fig.4. In addition, for the samples (a) and (e) with $ZnO:SiO_2$ = 1:1 and 1.25:1.0 respectively (Fig. 3) absorption edge due to ZnO is not seen.

To confirm this, XRD studies were made on the samples with $ZnO:SiO_2$ 2:1 and 1:1 the results revealed that the former samples had, lines due to ZnO, while the latter did not have any XRD lines corresponding to ZnO. In addition the sample (b) is not having any XRD lines corresponding to any of the phases of silica. Hence it is quite convincing to conclude that for the former sample, the presence of ZnO is attributed to the sluggishness of the reaction,

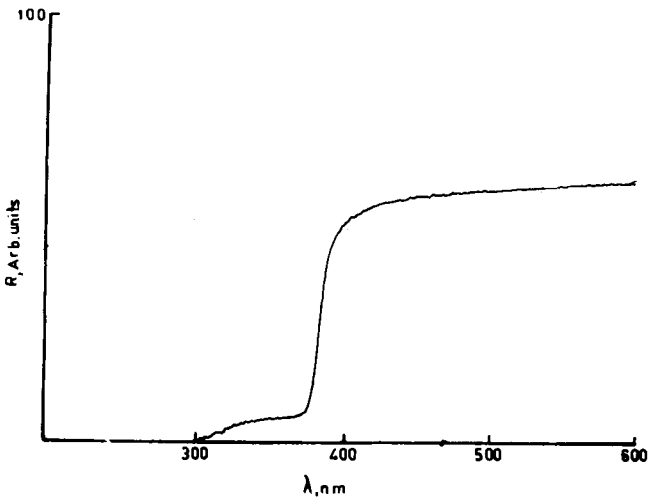

Fig. 4: Diffuse reflectance spectra of bare zinc oxide

while in the latter case, the reaction had reached a stage of completion. However at least three XRD lines corresponding to one of the phases of silica were found to be present in the case of sample with the ratio 1:1.

CONCLUSION

In conclusion, it is suggested that the sample with zinc oxide, silica in the mole ratio 1.25:1.0 is having the best fluorescence properties. Formation of zinc ortho silicate takes an impeded pace when tried with the thoretical proportions of ingredients and avoidable phases are found to be present, as observed from the discoloration in the body colour of the product.

REFERENCES

1. H Hess, A Helm, M Scala, *J Electrochem Soc,* **130** (1983) 2443

2. I F Chang, M W Shafer, *J Appl Phys Letter,* **35** (1979) 229

3. Junrokoike, Takehirokojima, Ryuya Toyonaga, A. Kiyasukagami, Takashi Hase and Shujilnaho, *J Electrochem Soc,* **126** (1979) 1008

4. J M P Verstegen, *J Electrochem Soc,* **121** (1974) 1621

5. W A McAllister, *J Electrochem Soc,* **118** (1971) 474