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Luminescence and XRD studies of some (ZnS:1% wt CaS) and (CaS : 1% wt ZnS) phosphors

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The results of luminescence, absorption and XRD studies of some (ZnS : 1% wt CaS) and (CaS : 1% wt ZnS) phosphors when doped with impurities like Cu, Sm/Pr and Cl have been presented. Emission peaks at 420 nm (due to Cu), 480 nm (due to Zn) and in the region 730-740 nm (due to Sm Sm/Pr) have been found. Absorption spectra consists of a number of peaks due to native lattice alongwith the presence of different ingredients used. ZnS based systems have been found to be more susceptible to oxidation.

1 Introduction

Both alkaline earth sulphide and zinc sulphide phosphors are well known phosphors[1-4]. The crystal structure, ionic radii, ionicity and band gaps of these materials are such that possibility of solid solutions may be expected which may generate new systems for phosphors. Such a possibility was anticipated by Lehmann[5] also. However, not much efforts were made in this direction. Viney *et al.*[6], attempted to mix CaS with CdS. Sen and Bhushan[7,8] recently reported luminescence in ZnS mixed CaS when doped with impurities like Cu, La and Cl. It was found that CaS affected the emission profoundly. Possibilities of replacement of Ca by Zn up to a certain proportion, Ca going into interstitials of ZnS and CaS and ZnS with impurities used giving their own emissions were shown. They also reported structural studies of these systems. It was found that due to oxidation of original materials, formation of ZnO and $CuSO_4$ took place. However, explanation given on the origin of emission bands remained valid. To enhance such studies, the present paper deals with luminescence and structural studies of ZnS:CaS phosphors when doped with impurities like Cu, Pr/Sm and Cl.

2 Experimental Details

The phosphors were prepared by firing a mixture of appropriate amounts of CaS (From National Physical Laboratory, New Delhi, maximum impurities Cu 20 ppm and Fe 50 ppm, firing of CaS alone gave no emission), ZnS (grade I, Johnson and Matthey, U K), copper acetate (AR, BDH), samarium/praseodymium nitrate (Indian Rare Earths Ltd, 99.99% pure) and ammonium chloride (AR, BDH) at a temperature of about 1050 °C under the continuous flow of N_2 and H_2S gases. 99.99% pure sulphur was also added in the above mixture up to 5%. All the concentrations used were by weight of CaS/ZnS. Emission spectra were studied under the excitations of 3650 Å Hg radiations photo-luminescence (Pl) and ac electric field electroluminescence (EL) using a Jarell-Ash monochromator and RCA 6217 photo-multiplier tube. For the absorption spectral studies a Varian (VIS-UV) DMS-100 spectrophotometer was used and XRD studies were made at RSIC Nagpur using Fe Kα radiation from a computerized diffractometer.

3 Results and Discussions

3.1 Spectral studies

It has been observed that PL spectrum[9] of CaS: Cu, Cl shows a peak at 420 nm which is related to the presence of Cu. Due to mixing of ZnS a peak at 480 nm appears which has been related to the presence of Zn in CaS. With the increase in concentration of ZnS this peak becomes maximum at a concentration of 1 to 1.25% after that concentration quenching takes place. This means that luminescence centres due to Zn are formed giving rise to emission at 480 nm. In Sm/Pr doped samples[9,10] a peak in the red region (730-740 nm) has been observed. EL spectra are also found to show similar behaviour. Since gradual shift in emission colours due to increasing concentration of ZnS has not been observed, therefore, possibility of forming a common lattice i.e. monophasic structure has been ignored. In ZnS:Cu,Cl peaks at 440 nm and 620 nm are observed[11] whose intensities reduce due to addition of CaS. In

presence of Sm/Pr, a red peak (720-730 nm) alongwith the 440 nm peak has been observed. Peak at 620 nm is suppressed completely. In this system also, no gradual shift in emission colours is observed due to increasing concentration of CaS.

Absorption spectra for the two kinds of systems are shown in Figs 1 and 2 and their corresponding data are presented in Tables 1 and 2. Band gaps of CaS and ZnS are 4.8 eV and 3.72 eV respectively. Peaks corresponding to exact values of band gaps are not seen mostly. However, peaks which are shifted from band gap values may be due to creation native lattice defects. Other peaks may be due to impurities. Changes in absorbance values are also observed due to the presence of impurities.

3.2 XRD studies

The XRD diffractograms for different CaS phosphors are shown in Figs 3-5 and corresponding data are presented in Tables 3-6. On comparing with powder diffraction file (PDF) in CaS:Cu. Cl prominent lines of CaS alongwith some prominent lines of Cas, some lines of

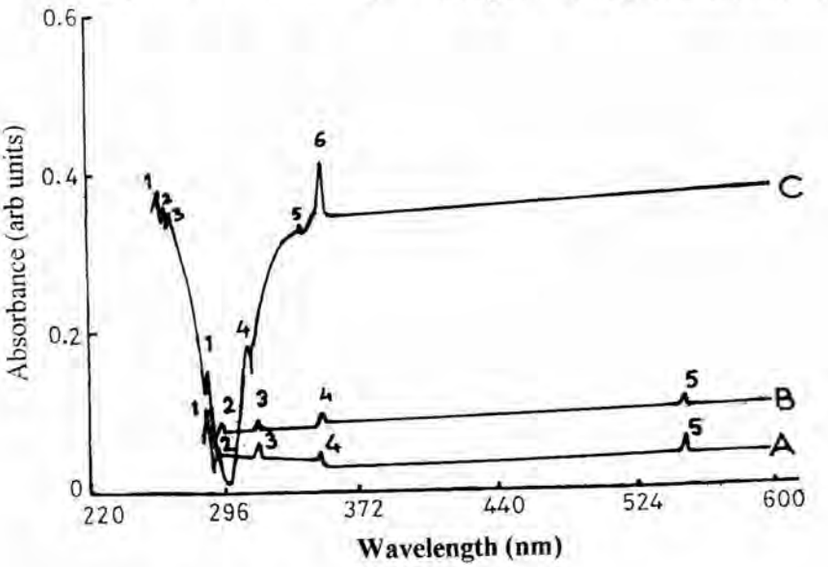

Fig. 1 — Absorption spectra of different CaS phosphors.
A. (CaS : 1% wt ZnS): Cu. Cl; B. (CaS: 1% wt ZnS): Cu. Sm. Cl; C. (CaS : 1% wt ZnS): Cu. Pr. Cl

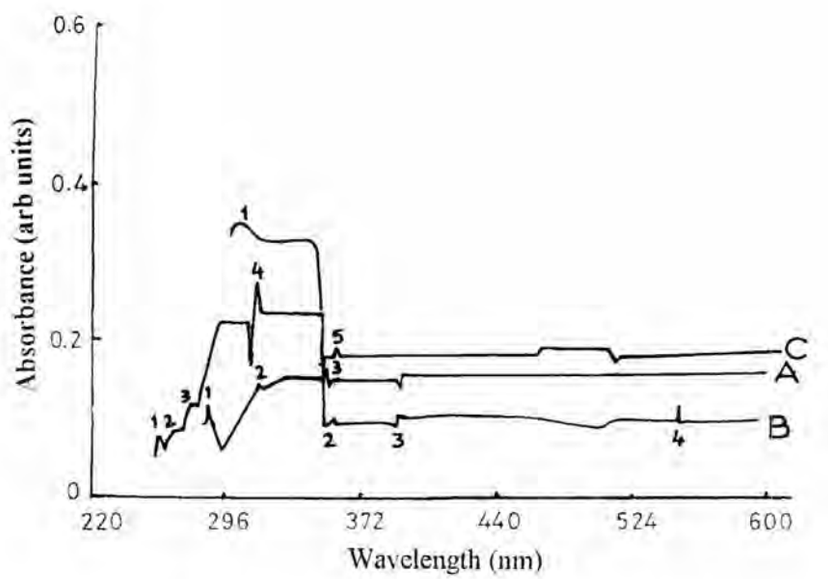

Fig. 2 — Absorption spectra of different ZnS phosphors.
A. (ZnS : 1% wt CaS): Cu. Cl; B. (ZnS: 1% wt CaS): Cu. Sm. Cl; C. (ZnS: 1% wt CaS): Cu. Pr. Cl

Table 1 — Absorption data of different CaS phosphors

(CaS:1% wt Zns): Cu(1%), Cl (1%)			(CaS: 1% wt Zns): Cu(1%), Sm(1%),Cl(1%)			(CaS: 1% wt ZnS): Cu(1%), Pr (1%), Cl(1%)		
Peak Values			Peak values			Peak values		
(nm)	E(eV)	Absorbance	(nm)	E(eV)	Absorbance	(nm)	E(eV)	Absorbance
286.00	4.336	0.113	287.7	4.310	0.149	260.6	4.762	0.369
292.7	4.236	0.048	294.4	4.212	0.081	265.7	4.670	0.334
314.7	3.940	0.060	314.7	3.940	0.095	269.9	4.597	0.331
355.4	3.489	0.032	355.4	3.489	0.081	309.7	3.007	0.191
						338.4	3.667	0.343
551.7	2.248	0.050	551.7	2.248	0.109	351.1	3.534	0.427

Table 2 — Absorption data of different ZnS phosphors

(ZnS:1 % wt CaS): Cu(1%), Cl(1%)			(ZnS: 1% wt CaS):Cu(1%),Sm (1%), Cl(1%)			(ZnS:1% wt CaS): Cu (1%), Pr(1%), Cl(1%)		
Peak Values			Peak Values			Peak Values		
(nm)	E(eV)	Absorbance	(nm)	E(eV)	Absorbance	(nm)	E(eV)	Absorbance
286.00	4.339	0.107	311.4	3.985	0.347	261.4	4.747	0.098
312.2	3.972	0.128	358.8	3.456	0.096	268.2	4.627	0.089
354.5	3.498	0.131	392.6	3.158	0.106	286.2	4.432	0.112
			551.7	2.248	0.114	313.0	3.964	0.270
						354.3	3.500	0.180

Table 3 — XRD data of Cas:Cu, Cl Phosphor
General tension : 35 kV, Generator Current : 20 mA

Observed values			Reported values		Assigned Materials / (*hkl*)	PDF	Lattice constant (Å)
2θ	*d*(Å)	I/I_0	*d*(Å)	I/I_0			
32.155	3.496	62	3.549	100	$CuSO_4$/(111)	15-775	-
34.410	3.279	5	3.28	< 1	CaS(Cubic)/(111)	8-464	5.6799
37.240	3.032	8	3.02	13	$CaCl24H_2O$/(112)	25-1090	-
39.760	2.847	279	2.846	100	CaS(Cubic)/(200)	8-464	5.6934
49.140	2.328	12	2.321	10	$CuSO_4$/(012)	15-775	-
51.925	2.212	4	2.238	4	NH_4Cl/(111)	7-7	3.8230
57.465	2.014	119	2.013	70	CaS(Cubic)/(220)	8-464	5.6956
67.375	1.745	6	1.733	6	NH_4Cl (210)	7-7	3.9024
72.170	1.643	41	1.6439	21	CaS(Cubic)/(222)	8-464	5.6933
75.605	1.579	4	1.582	25	NH_4Cl/(211)	7-7	3.8685
85.655	1.424	17	1.4238	10	CaS(Cubic)/(400)	8-464	5.6960

$CuSO_4$, NH_4Cl and $CaCl_2.H_2O$ appear although some prominent lines of the latter materials are missing. Comparison has been made from the reported values in terms of nearest available values. As far as possible the assignments have also been ascertained by evaluation of the lattice constants, which are in accordance with the observed values. The XRD data of (CaS:1% wt ZnS): Cu,Cl phosphors presented in Table 4 show that ob-

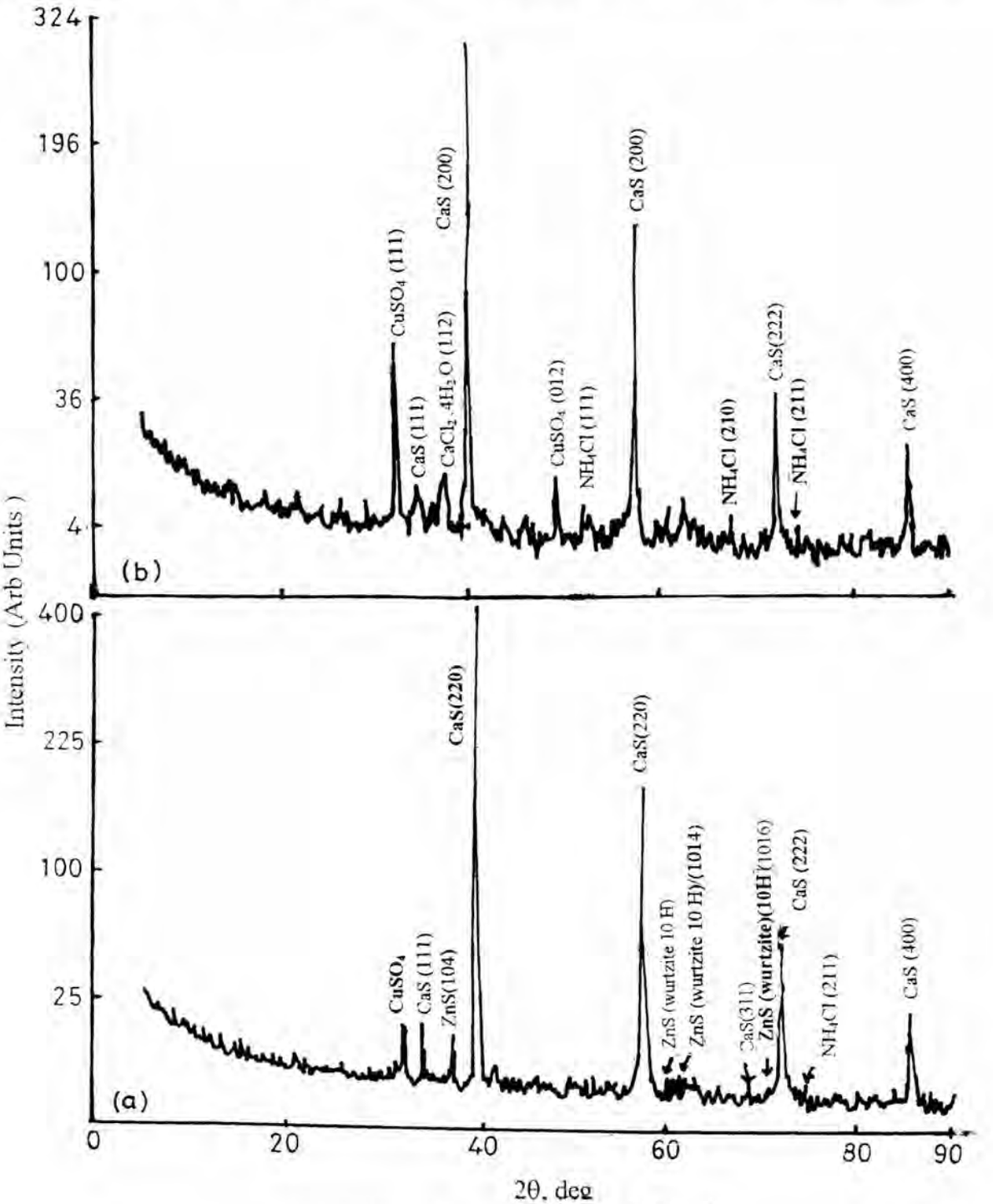

Fig. 3 — X-ray diffractogram of different CaS phosphors (a) CaS: Cu, Cl; (b) (CaS: 1% wt ZnS): Cu, Cl

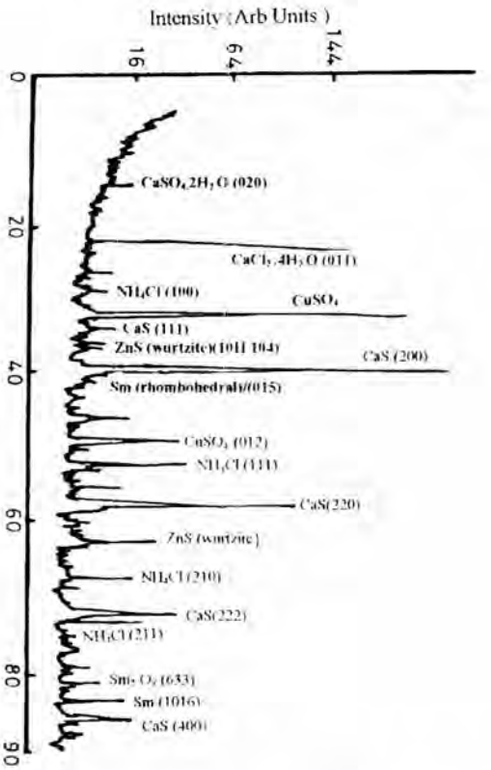

Fig. 4 — X-ray diffractogram of (CaS: 1% wt ZnS): Cu, Sm, Cl

Table 4 — XRD data of (CaS: 1% wt ZnS): Cu, Cl phosphor
Generator tension: 35 kV, Generator Current: 20 mA

Observed values			Reported values		Assigned Materials / (*hkl*)	PDF	Lattice constant (Å)
2θ	*d*(Å)	I/I_1	*d*(Å)	I/I_1			
32.190	3.492	14	3.549	100	$CuSO_4$/(111)	15-775	–
34.275	3.285	13	3.28	< 1	CaS(Cubic)/(111)	8-464	5.6899
37.195	3.035	12	3.05	4	ZnS(Wurtzite-10 H)/(104)	12-688	–
39.770	2.846	416	2.846	100	CaS(Cubic)/(200)	8-464	5.6900
57.480	2.013	182	2.013	70	CaS(Cubic)/(220)	8-464	5.6940
62.240	1.873	02	1.871	02	ZnS(wurtzite-10 H)	12-688	–
63.260	1.846	03	1.841	02	ZnS(Wurtzite-10H)/(1014)	12-688	–
68.775	1.714	03	1.717	< 1	CaS(Cubic)/(311)	8-464	5.6866
70.635	1.675	03	1.678	02	ZnS(Wurtzite-10H)/(1016)	12-688	–
72.160	1.644	52	1.6439	21	CaS(Cubic)/(222)	8-464	5.6939
74.750	1.595	1	1.582	25	NH_4Cl(211)	7-7	3.9062
85.650	1.424	23	1.4238	10	CaS(Cubic)/(400)	8-464	5.6934

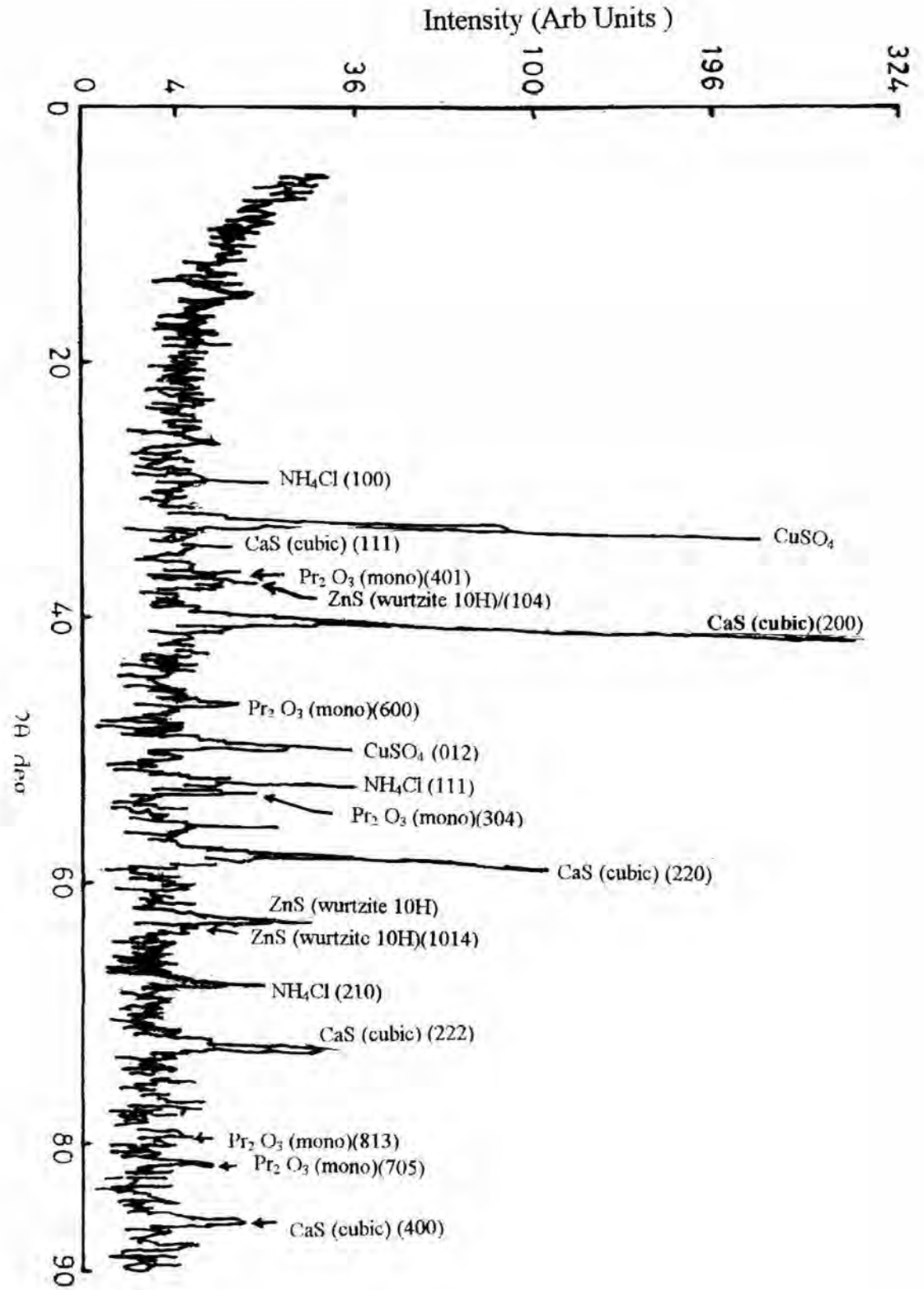

Fig. 5 — X-ray diffractogram of (CaS: 1% wt ZnS): Cu, Pr, Cl

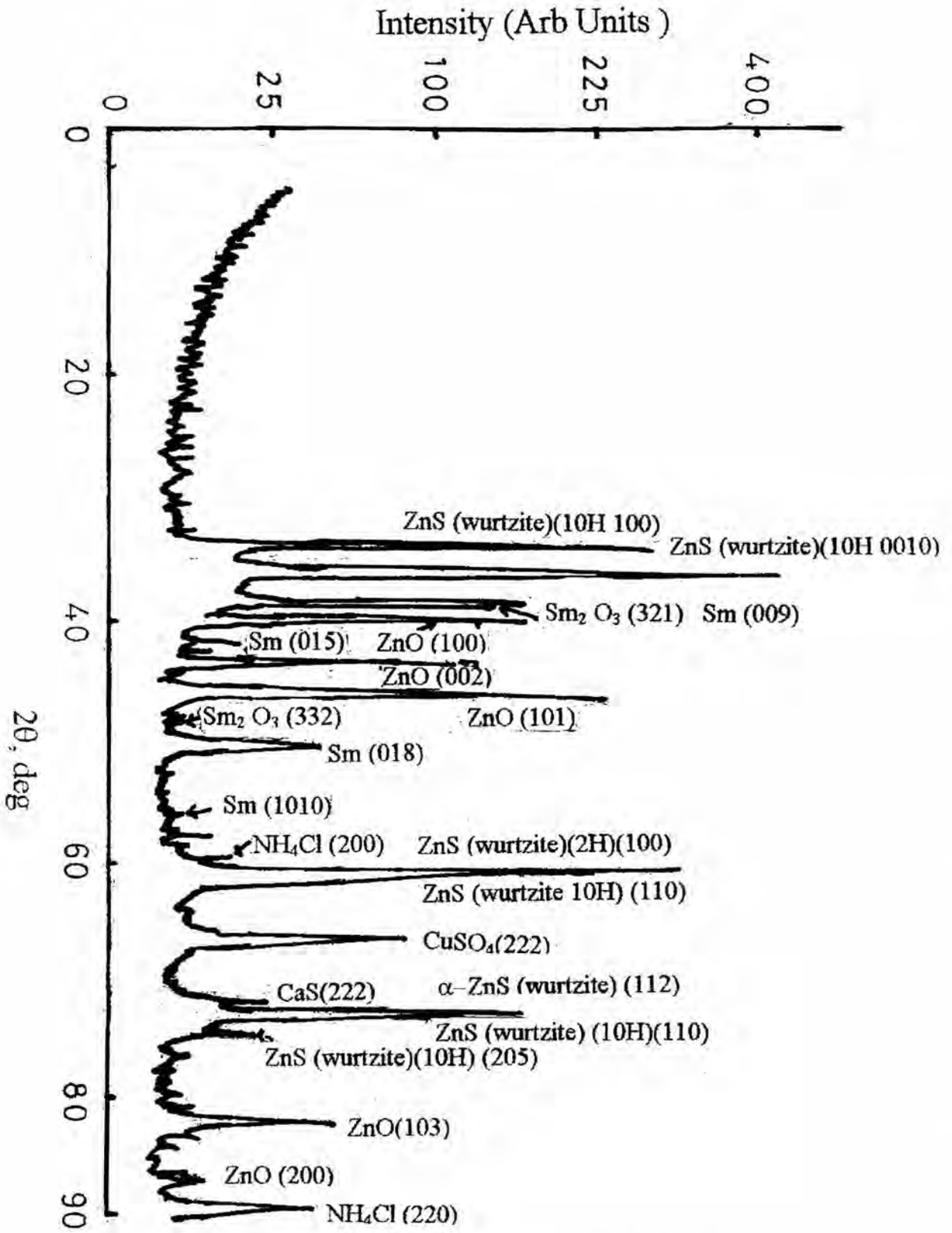

Fig. 6 — X-ray diffractogram of (ZnS: 1% wt CaS); Cu, Sm, Cl

Table 5 — XRD data of (Cas: 1% wt ZnS): Cu, Sm, Cl phosphor

General tension: 35 kV, Generator Current: 20 mA

Observed values			Reported values		Assigned Materials/ (*hkl*)	PDF	Lattice constant (Å)
2θ	*d*(Å)	I/I_0	*d*(Å)	I/I_0			
14.680	7.577	11	7.59	77	$CaSO_4.2H_2O$/(020)	36-432	–
21.875	5.102	156	5.20	20	$CaCl_2.4H_2O$/(011)	25-1090	–
29.014	3.865	08	3.87	25	NH_4Cl(Cubic)/(100)	7-7	3.8649
32.195	3.491	225	3.549	100	$CuSO_4$/(111)	15-775	–
34.335	3.280	07	3.28	< 1	CaS(Cubic)/(111)	8-464	5.680
37.025	3.049	04	3.05	04	ZnS(Wurtzite-10H)/(104)	12-688	–
39.760	2.847	253	2.846	100	CaS(Cubic)/(200)	8-464	5.6934
42.380	2.678	02	2.68	40	Sm(Rhombohedral/(1015)	6-419	–
49.215	2.325	35	2.321	10	$CuSO_4$/(012)	15-775	–
52.070	2.210	30	2.238	4	NH_4Cl(Cubic)/(111)	7-7	3.8277
57.505	2.012	114	2.013	70	CaS(Cubic)/(220)	8-464	5.6910
62.485	1.866	25	1.871	02	ZnS(Wurtzite-10H)	12-688	–
67.340	1.746	12	1.733	02	NH_4Cl (Cubic)/(210)	7-7	3.9042
72.105	1.645	34	1.6439	21	CaS(Cubic)/(222)	8-464	5.6977
74.820	1.593	02	1.582	25	NH_4Cl(Cubic)/(211)	7-7	3.9030
81.145	1.488	06	1.487	01	Sm_2O_3(Cubic)/(633)	43-1029	–
83.330	1.465	71	1.453	50	Sm/(1016)	6-419	–
85.715	1.423	14	1.4238	10	CaS(Cubic)/(400)	8-464	5.6960

Table 6 — XRD data of (CaS:1% wt ZnS): Cu, Pr, Cl phosphor,

Generator Tension: 35 KV, Generator current : 20 mA

Observed values			Reported values		Assigned Materials/ (*hkl*)	PDF	Lattice constant (Å)
2θ	*d*(Å)	I/I_0	*d*(Å)	I/I_0			
28.970	3.870	14	3.870	25	NH_4Cl(Cubic)/(100)	7-7	3.8701
32.195	3.4912	210	3.549	100	$CuSO_4$ (Orthorhombic)/(111)	15- 775	–
34.265	3.286	06	3.28	< 1	CaS(Cubic/(111)	8-464	5.691
36.105	3.1301	09	3.13	30	Pr_2O_3(Monoclinic)/(401)	24-912	–
36.870	3.0611	12	3.05	04	ZnS(Wurtzite-10H)/(104)	12-680	–
39.775	2.8470	243	2.846	100	CaS(Cubic)/(200)	8-464	5.694
46.150	2.469	8	2.373	05	Pr_2O_3(Monoclinic)/(600)	24-912	–
49.200	2.3254	30	2.321	10	$CuSO_4$(Orthorhombic)/(012)	15-775	–
52.015	2.2076	36	2.238	4	NH_4Cl(Cubic)/(111)	7-7	3.8277
52.770	2.1783	10	2.181	15	Pr_2O_3(Monoclinic)/(304)	24-912	–
57.470	2.0135	92	2.013	70	CaS(Cubic)/(220)	8-464	5.695
62.240	1.868	24	1.871	02	ZnS(Wurtzite-10H)/	12-688	–
63.140	1.8490	4	1.841	02	ZnS(Wurtzite-10H)/(1014)	12-688	–
67.305	1.7468	14	1.733	06	NH_4Cl(Cubic)/(210)	7-7	3.905
72.130	1.6443	37	1.6439	21	CaS(Cubic)/(222)	8-464	5.6977
79.185	1.5189	2	1/519	5	Pr_2O_3 (Monoclinic)/(813)	24-912	–
81.210	1.4873	5	1.481	15	Pr_2O_3 (Monoclinic)/(705)	24-912	–
85.690	1.4235	12	1.4238	10	CaS(Cubic)/(400)	8-464	5.6940

Table 7 — XRD data of (ZnS:1% wt CaS): Cu, Sm, Cl phosphor
Generator tension: 35 kV, Generator Current: 20 mA

Observed values			Reported values		Assigned Materials/ (*hkl*)	PDF	Lattice constant (Å)
2θ	*d*(Å)	I/I_0	*d*(Å)	I/I_0			
34.045	3.037	279	3.31	02	ZnS(Wurtzite 10H)/(100)	12-0688	–
36.145	3.120	400	3.120	100	ZnS(Wurtzite 10H)/(0010)	12- 0688	–
38.685	2.993	156	2.920	04	Sm_2O_3 /(321)	43-1029	–
38.780	2.916	137	290	100	Sm/(009)	06-0419	–
40.235	2.815	177	2814	57	ZnO(Zincite,Syn)/(100)	36-1451	3.4299
42.060	2.698	10	2.68	40	Sm/(015)	06-0419	–
43.670	2.603	100	2.603	44	ZnO(Zincite, Syn)/(002)	36-1451	–
46.040	2.475	288	2.4759	100	ZnO(Zincite,syn)/(101)	36-1451	–
48.880	2.340	01	2.330	04	Sm_2O_3/(332)	43-1029	
50.420	2.273	38	226	05	Sm/(018)	06-0419	–
58..810	1.9986	32	1.998	05	Sm/(1010)	06-0419	–
59.810	1.942	41	1.939	08	NH_4Cl/(200)	07-0007	–
60.900	1.910	279	1.911	65	ZnS(Wurtzite-2H)/(110)	10-434	–
61.070	1.905	174	1.904	50	ZnS(Wurtzite-10H)/110)	12-0688	–
66.630	1.763	72	1.77	33	$CuSO_4$(Chalcocyanite,Syn)/(22)	15- 0775	–
71.700	1.653	20	1.644	21	CaS(Cubic)/(222)	08-0464	5.7258
72.885	1.630	166	1.63	45	α-ZnS(Wurtzite)/(112)	5-492	–
73.105	1.625	132	1.626	35	ZnS(Wurtzite-10H)/(110)	12-0688	–
74.540	1.599	23	1.598	02	ZnS(Wurtzite-10H)/(205)	12-0688	–
81.905	1.477	48	1.477	29	ZnO(Zincite, Syn)/(103)	36-1451	–
86.975	1.407	06	1.407	04	ZnO(Zincite, Syn)/	36-1451	3.249
89.170	1.379	38	1.370	06	NH_4Cl/(200)	07-0007	–

served lines have been assigned to CaS, ZnS, NH_4Cl and $CuSO_4$. Due to addition of ZnS some changes in lattice constants of CaS although not in a regular way are observed. As is known when a small atom is substituted for a large one, the lattice parameter smoothly decreases and in the reverse case it increases[12]. In case a mixed lattice is formed, a regular shift should have appeared in the lattice parameter. This result is also in accordance with the results of luminescence studies and thus possibility of forming a common lattice has been ignored.

From the diffractograms of (CaS:1% wt ZnS): Cu, Sm, Cl (Fig. 4 and Table 5) diffraction lines corresponding to ZnS, CaS, $CaSO_4$, $CaCl_2$, $CuSO_4$, Sm, NH_4Cl and Sm_2O_3 are recognized. Similarly in case of (CaS:1% wt ZnS): Cu, Pr, Cl (Fig. 5 and Table 6) diffraction lines due to ZnS, CaS, $CuSO_4$, NH_4Cl and P_2O_5 are found. Lattice constants have also been calculated which are found to match with the standard values. Thus, alongwith the used materials in the preparation of samples. Thus, alongwith the used materials in the preparation of samples, existence of some other materials are also found which might have occurred due to chemical reactions during the process of preparation.

The XRD data of (ZnS:1% wt CaS): Cu, Sm, Cl and (ZnS: 1% wt CaS): Cu, Pr, Cl prepared separately were also investigated and such observations for a representative samples of (ZnS:1% wt CaS): Cu, Sm, Cl are shown in Fig. 6. The corresponding data are summarized in Table 7. In these cases, alongwith the lines associated to ingredients used. Those of ZnO are also found. Although these samples were prepared under the strict conditions of CaS phosphors, it appears that ZnS compounds are more susceptible to oxidation. Assignments in these cases also have been confirmed by calculating the lattice constants.

4 Conclusion

The XRD studies of different ZnS mixed CaS and CaS mixed ZnS phosphors show the existence of differ-

ent ingredients used in such systems. Considering luminescence studies also, possibility of forming a common lattice i.e. monophasic structure has not been found. It is also found that ZnS based systems are more susceptible to oxidation.

Acknowledgement

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