

## Laser-excited transition probabilities and oscillator strengths of calcium sulphide doped phosphors

H S Bhatti<sup>a</sup>, Sukhwinder Singh<sup>a</sup>, N K Verma<sup>b</sup>, Sunil Kumar<sup>b</sup>

<sup>a</sup>Department of Physics, Punjabi University, Patiala 147 002, India

<sup>b</sup>School of Basic and Applied Sciences, Thapar Institute of Engineering & Technology, Patiala, 147 004, India.

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Pulse excitation method has been used to find out the transition probabilities and oscillator strengths of calcium sulphide phosphors, doped with different activators having variable concentrations using ultraviolet laser as the excitation source. These investigations have been carried out at room temperature and at liquid nitrogen temperature. Various strong transitions in these phosphors have been detected and the corresponding oscillator strengths for these transitions have been calculated in terms of emission wavelengths, index of refraction and the transition probability at room temperature and liquid nitrogen temperature. The effect of concentration of the various dopants and the effect of temperature on transition probability and oscillator strength is also studied.

CaS phosphors doped with different activators having variable concentrations are very useful. Transition probabilities and oscillator strengths of CaS phosphors doped with various impurities, using various techniques, have been reported by earlier workers<sup>1-7</sup>. The experimental determination of transition probabilities and oscillator strengths has become more reliable with modern laser spectroscopic techniques<sup>8-10</sup> which yield very accurate values. Pulsed Nitrogen laser having operating wavelength in UV region, short pulsewidth, large photon flux density and high repetition rate is especially useful for excitation of shallow trapping states and to record the transition probabilities at room as well as liquid nitrogen temperatures. The decay of luminescence in doped phosphors, following excitation by a short laser pulse, depends on trap distribution in the forbidden gap of the phosphor. The decay becomes comparatively faster as the temperature of the phosphor is lowered to liquid nitrogen temperature. As the pulsewidth of Nitrogen laser used for excitation of the phosphors is of a few nanoseconds in the present case, the transition probabilities of the doped phosphors under investigations could be measured very easily and accurately without taking into account the excitation pulse width. The present paper considers the measurement of transition probabilities very accurately under short laser pulse excitation at room as well as liquid nitrogen temperature. The transition probabilities along with the index of refraction and the emission wavelength have been used to calculate

the absolute oscillator strengths of various transitions in these phosphors.

### Experimental

The CaS doped phosphors were prepared by the well-known flux method<sup>11</sup> starting with spectroscopic grade non-luminescent CaS. At room temperature (300 K), the sample was taken in the form of a pellet. Nitrogen laser is the most suitable excitation source (337.1 nm) to irradiate the CaS phosphors, doped with the impurities, viz., Cu, Ag, Mn, Fe, Co, Ni, Sr, Ba, Al, Bi, as the laser energy matches the band-gap energy of these phosphors. High photon flux density of the laser is very useful to excite the short-lived shallow trapping states which otherwise are impossible to excite. The low-temperature studies at 77 K were carried out employing liquid nitrogen cryostat. The short-lived phosphorescence from the sample at an angle of 90° to the incident beam was collected by a fast photomultiplier tube through an assembly of monochromator and copper sulphate solution as a filter for UV radiation. The decay signals from phosphors were recorded by multi-channel analyser and analyzed accurately to calculate transition probabilities of the phosphors.

### Theoretical

The probability that, in certain time  $dt$ , an electron in the excited state comes back to the ground state with the emission of light is given by  $npdt$ , where  $n$  is the number of electrons in the excited state at time,  $t$ , after switching off the exciting radiation, and,  $p$ , is a constant for a crystal at a given temperature.

For this decay:

$$dI/dt = -pI \quad \dots (1)$$

$$I = I_0 e^{-pt} \quad \dots (2)$$

$$I = I_0 e^{-t/\tau} \quad \dots (3)$$

Where 'I' is the intensity of phosphorescence radiation at time,  $t$ , and  $I_0$  the intensity of radiation at cut-off position and the constant 'p' is the transition probability of the corresponding radiative transition.

If  $p_{ed}(ab)$  is the only radiative process from upper level 'a' to the lower level 'b', then  $p_{ed} = \tau_R^{-1}$  where  $\tau_R$  is the emission lifetime of the upper state and  $p_{ed}$  is the transition probability for electric dipole transition.

A dimensionless quantity called the oscillator strength 'f' in case of electric dipole transitions is given by

$$f_{ed}(V) = 1.5 \times 10^4 \lambda_0^2 \cdot \frac{9}{(n^2 + 2)^2 \cdot n} P_{ed} \quad \dots (4)$$

where  $\lambda_0$  is the emission wavelength given by  $c/\nu$ ,  $p_{ed}(ab) = 1/\tau_R(V)$  is transition probability and 'n' is the index of refraction of CaS material. For magnetic dipole transitions the above relation reduces to:

$$f_{md} = 1.5 \times 10^4 \lambda_0^2 \cdot \frac{1}{n^3} P_{md} \quad \dots (5)$$

An electric dipole transition will have a lifetime of  $10^{-8}$  to  $10^{-7}$  second, while a magnetic dipole transition  $10^{-3}$  to  $10^{-1}$  second and a quadruple transition an even longer lifetime. Eq. (4) has been used to calculate the oscillator strengths of weak electric dipole transitions while Eq. (5) is preferred for calculating the oscillator strengths of the magnetic dipole transitions. The measured values of the transition probabilities for strong transitions at 300 K and 77 K have been listed in Table 1. The calculated values of the oscillator strengths for different transitions have been shown in Table 2.

### Results and Discussion

In the present paper, in most of the cases, three transition probabilities have been observed except in case of CaS:Ag and CaS:Ni at low temperature (Table 1). Transition probability is found to increase with the lowering of the temperature and it generally increases with the increase in dopant concentration whereas oscillator strength also increases with the lowering of temperature but have a mixed effect of dopant concentration. The short-lived phosphorescence decay measurements yield three exponential components in most of the cases except CaS:Ag and CaS:Ni where

Table 1—Transition probabilities of CaS doped phosphors at 300 K and 77 K

Phosphor	300 K			77 K		
	$p_1 \times 10^3 s^{-1}$	$p_2 \times 10^3 s^{-1}$	$p_3 \times 10^3 s^{-1}$	$p_1 \times 10^3 s^{-1}$	$p_2 \times 10^3 s^{-1}$	$p_3 \times 10^3 s^{-1}$
<b>CaS(Cu)</b>						
0.03 %	8.7	42.5	210.1	23.6	112.3	558.6
0.10 %	11.1	53.7	245.7	24.8	123.4	588.2
0.20 %	12.2	55.5	243.0	24.2	123.9	625.1
0.30 %	13.8	52.9	210.5	24.3	124.8	621.1
0.40 %	16.3	59.2	246.9	24.4	124.7	613.4
<b>CaS:(Ag)</b>						
0.03 %	38.7	59.7	232.0	854.7	2777.8	*
0.10 %	43.4	82.6	259.1	900.9	3846.1	*
0.20 %	46.7	84.4	324.7	813.0	3448.3	*
0.30 %	50.0	97.1	323.6	826.4	4000.0	*
0.40 %	56.1	101.1	328.9	862.1	4347.8	*
<b>CaS:(Mn)</b>						
0.03 %	60.6	178.6	341.3	290.7	507.6	1282.0
0.10 %	95.7	202.0	347.2	275.5	427.3	1149.4
0.20 %	98.4	198.8	355.9	284.1	502.5	1234.6
0.30 %	103.6	205.3	374.5	268.8	480.8	1190.5
0.40 %	111.2	208.3	373.1	286.5	505.0	1204.8

Contd.-

Table 1—Transition probabilities of CaS doped phosphors at 300 K and 77 K—*Contd*

Phosphor	300 K			77 K		
	$p_1 \times 10^{3s^{-1}}$	$p_2 \times 10^{3s^{-1}}$	$p_3 \times 10^{3s^{-1}}$	$p_1 \times 10^{3s^{-1}}$	$p_2 \times 10^{3s^{-1}}$	$p_3 \times 10^{3s^{-1}}$
<b>CaS:(Fe)</b>						
0.03 %	46.2	92.1	324.7	79.6	305.8	613.5
0.10 %	49.1	92.0	289.0	76.4	239.8	595.2
0.20 %	53.0	108.3	346.0	77.4	248.1	574.7
0.30 %	58.0	110.0	355.9	72.1	235.3	529.1
0.40 %	57.9	109.0	359.7	76.8	244.5	537.6
<b>CaS:(Co)</b>						
0.03 %	64.6	171.8	497.5	141.4	319.5	609.7
0.10 %	66.4	230.9	346.0	146.0	320.5	621.1
0.20 %	66.5	205.3	371.7	145.1	323.6	641.0
0.30 %	66.7	213.2	370.4	147.5	322.6	657.9
0.40 %	67.3	216.4	369.0	146.2	320.5	625.0
<b>CaS:(Ni)</b>						
0.03 %	31.6	127.7	401.6	48.9	*	*
0.10 %	31.0	112.2	291.5	46.3	*	*
0.20 %	33.0	123.0	343.6	51.2	*	*
0.30 %	33.5	126.4	318.5	50.1	*	*
0.40 %	34.9	124.7	310.5	47.9	*	*
<b>CaS:(Mg)</b>						
0.03 %	31.2	87.6	258.4	104.8	454.5	1098.9
0.10 %	32.1	95.9	332.2	102.2	444.4	1052.6
0.20 %	33.3	106.1	395.2	104.3	452.5	1086.9
0.30 %	34.2	110.6	416.7	104.8	450.4	1111.1
0.40 %	34.4	111.2	414.9	106.3	458.7	1111.1
<b>CaS:(Sr)</b>						
0.03 %	97.9	261.1	322.6	115.1	293.2	416.7
0.10 %	103.9	216.4	308.6	134.8	303.0	429.2
0.20 %	96.0	277.0	373.1	124.5	311.5	434.8
0.30 %	107.7	324.7	510.2	121.3	312.5	434.8
0.40 %	108.7	331.1	526.3	123.9	316.4	446.4
<b>CaS:(Ba)</b>						
0.03 %	26.9	93.0	288.2	86.0	285.7	485.4
0.10 %	32.2	109.4	291.6	85.2	280.1	471.7
0.20 %	34.5	110.5	335.6	85.5	278.5	478.5
0.30 %	36.4	111.0	326.8	85.6	279.3	490.2
0.40 %	41.4	114.3	393.7	85.3	277.8	483.1
<b>CaS:(Al)</b>						
0.03 %	31.3	202.4	549.4	77.8	363.6	869.6
0.10 %	32.0	255.7	546.4	74.3	353.3	819.7
0.20 %	33.5	216.9	561.8	77.2	357.1	833.3
0.30 %	35.1	255.7	653.6	75.5	352.1	840.3
0.40 %	36.8	268.1	813.0	74.6	357.1	862.1
<b>CaS:(Bi)</b>						
0.03 %	53.2	202.0	320.5	34.1	125.0	418.4
0.10 %	58.2	234.2	346.0	36.6	140.6	423.7
0.20 %	58.9	244.5	334.4	35.2	127.5	421.9
0.30 %	62.5	248.7	347.2	34.5	128.2	423.7
0.40 %	62.5	251.9	348.4	35.8	135.3	427.3

Table 2—Oscillator strengths ( $\times 10^{-6}$ ) of CaS phosphor doped with different concentrations of activators

Phosphor	300 K			77 K		
	$f_1$	$f_2$	$f_3$	$f_1$	$f_2$	$f_3$
<b>CaS(Cu)</b>						
0.03 %	3.5	17.2	84.8	9.4	45.4	225.6
0.10 %	4.5	21.7	99.2	10.0	49.8	237.5
0.20 %	4.9	22.4	98.5	9.8	50.0	252.4
0.30 %	5.6	21.4	85.0	9.8	50.4	250.8
0.40 %	6.6	23.9	99.7	9.9	50.3	247.7
<b>CaS(Ag)</b>						
0.03 %	19.7	30.4	118.3	435.8	1416.5	*
0.10 %	22.1	42.1	132.1	459.4	1961.3	*
0.20 %	23.8	43.0	165.6	414.6	1758.4	*
0.30 %	25.5	49.5	165.0	421.4	2039.8	*
0.40 %	28.6	51.6	167.7	439.6	2217.2	*
<b>CaS(Mn)</b>						
0.03 %	31.6	93.2	178.2	151.8	265.0	669.4
0.10 %	50.0	105.5	181.3	143.8	223.1	600.1
0.20 %	51.4	103.8	185.8	148.3	262.4	644.6
0.30 %	54.1	107.2	195.5	140.3	251.0	621.6
0.40 %	58.1	108.8	194.8	149.6	263.7	629.1
<b>CaS(Fe)</b>						
0.03 %	18.5	36.9	130.1	31.9	122.5	245.8
0.10 %	19.7	36.9	111.3	30.6	96.1	238.5
0.20 %	21.2	43.4	138.6	31.0	99.4	230.3
0.30 %	23.2	44.1	142.6	28.9	94.3	212.0
0.40 %	23.2	43.7	144.1	30.8	98.0	215.4
<b>CaS(Co)</b>						
0.03 %	28.4	75.6	218.9	62.2	140.5	268.2
0.10 %	29.2	101.6	152.2	64.2	141.0	273.2
0.20 %	29.2	90.3	163.5	63.8	142.4	282.0
0.30 %	29.3	93.8	162.9	64.9	141.9	289.4
0.40 %	29.6	95.2	162.3	64.3	141.0	274.9
<b>CaS(Ni)</b>						
0.03 %	13.0	52.5	165.3	20.1	*	*
0.10 %	12.8	46.2	120.0	19.1	*	*
0.20 %	13.6	50.6	141.4	21.1	*	*
0.30 %	13.8	52.0	131.0	20.6	*	*
0.40 %	14.3	51.3	127.8	19.7	*	*
<b>CaS(Mg)</b>						
0.03 %	11.4	32.0	94.2	38.2	165.8	400.8
0.10 %	11.7	35.0	121.2	37.3	162.1	384.0
0.20 %	12.1	38.7	144.2	38.0	165.0	396.5
0.30 %	12.5	40.3	152.0	38.2	164.3	405.3
0.40 %	12.6	40.6	151.3	38.8	167.3	405.3
<b>CaS(Sr)</b>						
0.03 %	37.8	100.7	124.4	44.4	113.0	160.6
0.10 %	40.1	83.4	119.0	51.9	116.8	165.5
0.20 %	37.0	106.8	143.8	48.0	120.1	167.6
0.30 %	41.5	125.2	196.7	46.8	120.5	167.6
0.40 %	41.9	127.6	202.9	47.8	122.0	172.1

Contd

Table 2—Oscillator strengths ( $\times 10^{-6}$ ) of CaS phosphor doped with different concentrations of activators—*Contd*

Phosphor	300 K			77 K		
	$f_1$	$f_2$	$f_3$	$f_1$	$f_2$	$f_3$
CaS(Ba)						
0.03 %	12.1	41.8	129.6	38.7	128.5	218.3
0.10 %	14.5	49.2	131.1	38.3	125.9	212.1
0.20 %	15.5	49.7	150.9	38.5	125.2	215.1
0.30 %	16.4	49.9	146.9	38.5	125.6	220.4
0.40 %	18.6	51.4	158.3	38.3	124.9	217.2
CaS(Al)						
0.03 %	12.9	83.6	226.9	32.1	150.2	359.2
0.10 %	13.2	84.8	225.7	30.7	145.9	338.6
0.20 %	13.8	9.6	232.0	31.9	147.5	344.2
0.30 %	14.5	105.6	270.0	31.2	145.4	347.1
0.40 %	15.2	110.7	335.8	30.8	147.5	356.1
CaS(Bi)						
0.03 %	24.4	92.8	147.2	15.7	57.4	192.2
0.10 %	26.7	107.6	159.0	16.8	64.6	194.7
0.20 %	27.1	112.3	153.6	16.2	58.6	193.8
0.30 %	28.7	114.3	159.5	15.8	58.9	194.7
0.40 %	28.7	115.7	160.1	16.5	62.2	196.3

two and one exponential component is found respectively at liquid nitrogen temperature. The largest of the three calculated transition probabilities is interpreted to be due to the transition in nearest neighbour coupled pairs while the smallest of the transition probability is attributed to the decay of single ions. The intermediate probability is explained as due to the less effective coupling between the radical ions and their nearest neighbours. When the temperature of the phosphor is lowered to liquid nitrogen temperature, all the transition probabilities are increased in magnitude indicating thereby the reduction in trap-depths, which indicates that the radiative transitions play a dominant role in the decay of these phosphors.

This trend shows that the radiative transitions corresponding to the nearest neighbour coupled-pairs are stronger than the radiative transitions due to less effective coupling between the radical ions and their nearest neighbours, which in turn is stronger than the radiative transitions from the single ions. As the temperature of the material is lowered, the corresponding values of the oscillator strengths have the increasing tendency, which yields the information that radiative transitions have a stronger role to play in the decay processes of these luminescent materials. As the concentration of the dopant is decreased below the optimum value, the phosphors after excitation by the suitable UV radiation show no emission leading to the conclusion that at such low concentration, the

trapping states are not introduced in the band gap. At a concentration higher than the optimum value, the concentration quenching starts and the emission intensity starts decreasing with the increase of concentration of the dopant radicals. A stage is reached when at certain concentration the quenching of the phosphorescence emission is complete.

### Conclusions

The concentration of the dopant is to be kept at some optimum values so that the phosphorescence emission is free from the trapping states introduced in the bandgap of the phosphor and it is independent of the concentration of the dopant radicals. The selective excitation of these phosphors under suitable conditions can make them the most suitable coating materials for various applications.

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