

## A review of X-ray imaging phosphors

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**Abstract.** The important methods of X-ray imaging use various phosphors. The phosphors give light proportional to the amount of radiation. The light is emitted either as X-ray excited fluorescence, phosphorescence, or due to stimulated, radiative recombinations of defects generated by X-ray exposures. The role of phosphors in improving image quality and reducing exposures to patients is important. Properties of various phosphors which can be used for X-ray imaging applications are reviewed here.

**Keywords.** X-ray imaging; phosphors.

### 1. Introduction

Almost immediately after the discovery of X-rays by Röntgen, it was realized that this radiation is not very efficient in affecting photographic emulsions. A search for phosphors, which are able to convert X-rays into visible radiation, was started. Pupin (as quoted by Brixner 1987) found that  $\text{CaWO}_4$  emits light upon X-ray incidence, which affects photographic film more effectively than the X-rays themselves. Several materials have since then been developed (Smets 1991). These will be reviewed under the section on screen phosphors. Later, more effective ways of X-ray detection and imaging using scintillators and photostimulatable phosphors were invented; these will be discussed in the subsequent sections.

### 2. Screen phosphors

#### 2.1 Mechanism

High energy ionizing radiation in the form of X-rays is absorbed by the lattice and secondary charge carriers such as electron and hole pairs are created. After thermalization, these pairs recombine, and this process ultimately results in the emission of photons. Energy efficiency  $\eta$  of the overall process is given (Robins 1980)

$$\eta = (1 - r_b) \frac{h\nu_a}{E} \eta_i Q,$$

where  $r_b$  is the fraction of primary radiation scattered back,  $h\nu_a$  the quantum emitted,  $E$  the average energy to generate one e–h pair,  $\eta_i$  the efficiency for transfer of e–h recombination energy to the activator, and  $Q$  the quantum efficiency of luminescence centre. Practically, screen phosphors are characterized by their speeds given by

$$S = AQD,$$

where  $A$  is the absorption coefficient of phosphor and  $D$  the detection efficiency

defined as

$$D = \int D_{\lambda} \phi d_{\lambda} / \int \phi d_{\lambda},$$

where  $D_{\lambda}$  and  $\phi$  are sensitivity and flux respectively.

Screen phosphors should thus have high absorption of X-rays, high densities and stopping power, high luminescence efficiency, emission matching with the most sensitive range of the photographic materials (300–480 nm), not very long decay time ( $> 1$  s), good radiation resistance, non-toxicity, good mechanical and chemical stability, etc.

Needless to say, a single material possessing all these characteristics has not been found, but compromising on some factor or the other, a phosphor can be found to suit the application.

## 2.2 Materials

2.2a *CaWO<sub>4</sub>*: This is the earliest known phosphor, discovered by Edison (see Harvey 1957). Both excitation and emission take place in  $\text{WO}_4^-$  group. Emission is at 430 nm giving a  $D$  of 81%. Of the constituent atoms only W ( $Z = 74$ ) gives dominant contribution to X-ray absorption. The energy efficiency is rather poor, being only about 5%. Radiation resistance is also rather poor, but can be improved by adding  $\text{NaHSO}_4$  which introduces shallow traps which are emptied at RT itself.

Efforts were made to replace  $\text{CaWO}_4$  (Dutch patent 6917280, 1970; US patent 3,527,710, September 1970; Bates 1968; Ludwig 1972; Ludwig and Prener 1972; Stevels 1976). The materials have been systematically reviewed by Stevels and Pingault (1975). However, these materials were not found to be better than  $\text{CaWO}_4$ , due to one drawback or the other, e.g.  $\text{ZnS:Ag}$  is more sensitive than  $\text{CaWO}_4$  at lower energies but image is sharper with  $\text{CaWO}_4$ . Better materials were found only after the seventies.

2.2b *LaOBr:Re*:  $\text{LaOBr}$  doped with rare earths (Tb, Tm or Dy) were studied by Blasse and Bril (1967). An X-ray screen using  $\text{LaOBr:Ce, Tb}$  was reported by Rabatin (1971). The method of preparation of the phosphor and more detailed properties were given by Holsa *et al* (1980, 1981).

2.2c *M'ReTaO<sub>4</sub>*: Rare earth tantalates crystallize in two types of structures designated as M type and M' type (Wolten 1967). Blasse and Bril (1970) studied  $\text{M'ReTaO}_4$  for  $\text{Re} = \text{Gd, Y and Lu}$ . Application to X-ray screens is described by Brixner and Chen (1983). These compounds have high density ( $7.56 \text{ g/cm}^3$ ) and little afterglow. The excitation and emission is in  $\text{TaO}_4$  luminescence centre which is excited via charge transfer process. Emission is at 337 nm which is suitable for blue sensitive X-ray films. When small quantities ( $\approx 2\%$ ) of Nb are incorporated, all the energy is transferred to niobate group emitting at 410 nm. Energy efficiency is 9% and the detection efficiency 95%.

2.2d *Gd<sub>2</sub>O<sub>2</sub>S:Tb*: Rare earth oxysulphides doped with Tb were studied by Klassem and de Groot (1947) and Wickersheim *et al* (1969, 1970). They found 13% efficiency for La oxysulphide and 18% for the Gd compound. These materials also have high

densities. Screens using these materials were made by Wang (1969) and Wang *et al* (1979). Buchanan *et al* (1972) and Stevels (1975) demonstrated the use of this phosphor using green sensitive films.

Lammers *et al* (1987) and Lammers and Blasse (1987) reported other Tb doped compounds such as Gd silicate and germanate which are suitable as screen phosphors.

**2.2e BaFCL:Eu<sup>2+</sup>:** Blasse and Brill (1974) reported this phosphor. Stevels and Pingault (1975) proposed its use for X-ray screens. It becomes more important in the context of photostimulatable phosphors which will be discussed later. Properties of various screen phosphors are given in table 1.

### 3. Phosphors for computed tomography

#### 3.1 X-ray scintillators

In 1973, Housefield (1973) described a new technique for X-ray imaging. In this technique (computed tomography, CT), the recording of the image is electronic and not photographic. An array of detectors consisting of phosphors coupled with photodiodes replaces the screen. X-ray exposure produces 'scintillations' which originate in prompt recombinations of lattice defects produced by X-rays. The photodiode current signals can be stored and processed. The use of photodiodes changes some of the requirements drastically. Green-yellow emitters are more suitable than the blue ones. Phosphors for X-ray detectors in CT are basically scintillators. There are some important differences in the requirements for these two types of phosphors. In scintillation detection of nuclear radiation, fast decay is important. If

**Table 1.** X-ray screen phosphors.

Material	Density (g/cm <sup>3</sup> )	X-ray attn. co-eff. (at 75 keV) (cm <sup>-1</sup> )	Conversion efficiency	Emission (nm)
CaWO <sub>4</sub>	6.06	3.83	6.5	440
Zn <sub>2</sub> SiO <sub>4</sub>		1.64	11.5	
ZnS:Ag		1.97	17.0	
Zn <sub>0.58</sub> Cd <sub>0.42</sub> S:Ag		4.6	14.5	
Ba <sub>2</sub> SiO <sub>5</sub> :Pb		6.19	3.5	
CsI:Tl	4.52	11.7	10.0	550
La <sub>2</sub> O <sub>2</sub> S:Tb		9.2	12.5	543
Gd <sub>2</sub> O <sub>2</sub> S:Tb	7.34	8.1	13	414, 440, 543
LaOBr:Ce, Tb	7.56			543
M'GdTbO <sub>4</sub>	8.55	6.1		490, 543
M'YTbO <sub>4</sub>	7.56	4.5	9.0	337
Gd <sub>3</sub> Ga <sub>5</sub> O <sub>12</sub> :Tb	7.1			
Ba <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> :Eu <sup>2+</sup>				
CsI:Na	4.51		10.0	410
BaFCl:Eu <sup>2+</sup>			13	385
BaFBr:Eu <sup>2+</sup>			13	385
BaSO <sub>4</sub> :Eu <sup>2+</sup>			6	377

there is a weak afterglow, it does not interfere with the detection of the next particle due to use of pulse height discrimination. For phosphors in X-ray CT, on the other hand, fast clearing of the screen is important, otherwise the afterglow will contribute to the noise in the next frame. Afterglow is thus totally undesirable for CT. On the other hand, the decay in CT phosphor has to be just fast enough to enable the scanning of the frame without interfering signal from the previous scan (fraction of a millisecond).

### 3.2 Requirements

Besides the 'low afterglow' CT phosphors should possess properties (Rossner and Grabmaier 1991; Ishii and Kobayashi 1991) such as high quantum or radiant conversion efficiency, emission in the range of photodiodes (green-red), rapid decay ( $< 0.1$  ms), low afterglow (intensity less than 5% of the maximum value in 2 ms), high X-ray absorption coefficient, high transmittance of the emitted light, high radiation resistance, chemical and thermal stability, etc.

### 3.3 Materials

Phosphors CsF, NaI:Tl, BGO and  $\text{CdWO}_4$  which are good scintillators are also good phosphors for CT applications. Besides these, CsI:Tl which is not efficient as a scintillator due to its green emission is suitable in CT for this very reason.

$\text{ZnWO}_4$  and  $(\text{Y, Gd})_2\text{O}_3\text{:Eu}$  are other candidates as CT phosphors. Properties of various materials have been frequently reviewed (Farukhi 1982; Grabmaier 1984; Holl *et al* 1988). These are summarized in table 2. It is seen that none of the phosphors is free from drawbacks. CsI:Tl has the highest light output and emission matching with photodiode response, but it has a long afterglow. CsF, discovered by van Sciver and Hofstadter (1952), has low afterglow, but it is very hygroscopic. BGO has high X-ray attenuation necessary for compact detector assembly and good resolution, but its light output is low. Growth and properties of the single crystals of these materials have been recently reviewed by Ishii and Kobayashi (1991).

### 3.4 Recent developments

In recent years, hot pressed, transparent ceramics in place of single crystals have been developed for use in CT.  $(\text{Y, Gd})_2\text{O}_3\text{:Eu}$  in such form was reported by Greskovich and coworkers (Greskovich *et al* 1985, 1986; DiBianca *et al* 1985; Cusano *et al*).  $\text{Gd}_2\text{O}_2\text{S:Pr, Ce, F}$  introduced by Yamada *et al* (1989) can be prepared by hot pressing techniques using  $\text{LiGeF}_6$  as a sintering agent (Ito *et al* 1988). It has emission at 520 nm, density of  $7.34 \text{ g/cm}^3$ , good sensitivity and low afterglow (0.01% after 3 ms).

## 4. Photostimulatable X-ray phosphors

A new technique for X-ray imaging based on photostimulatable phosphors was described by Sonoda *et al* (1983). This allows the use of photomultiplier tubes (PMT) as detector instead of film (Takahashi *et al* 1985).

Table 2. Scintillators for X-ray CT.

Material	Density (g/cm <sup>3</sup> )	Attn. co-eff. (150 keV)	Relative light output	Emission (nm)	Decay time (ns)	Afterglow (%)	Radiation resistance (rad)	Light yield (ph/MeV)
NaI:Tl	3.67	2.20	118	415	230	90 in 150 ms	10 <sup>3</sup>	37700
CsI:Tl	4.52	3.21	100	550	980	15 in 20 ms	10 <sup>3</sup>	51800
CdWO <sub>4</sub>	7.99	7.93	30	480	5000	2 in 20 ms	10 <sup>3</sup>	15300
ZnWO <sub>4</sub>	7.87	7.80	20	480	5000	< 1 in 20 ms		9300
BGO	7.13	9.93	10	480	300	< 1 in 20 ms	10 <sup>4</sup> -10 <sup>5</sup>	8200
(Y, Gd) <sub>2</sub> O <sub>3</sub> :Eu	5.9	3.4	40	610	1 ms			
Gd <sub>2</sub> O <sub>3</sub> :S:Pr < Ce, F	7.34	6.86	60	520	3000	< 1 in 3 ms	> 10 <sup>8</sup>	
Gd <sub>2</sub> SiO <sub>5</sub> :Ce	6.71		20	430	60		< 10 <sup>4</sup>	
CsF	4.64	3.09	5	390	5	0.03 in 6 ms		38500
CsI:Na	4.52	3.21		420	63			23650
CaF <sub>2</sub> :Eu	3.18		25	520-580	70		10 <sup>7</sup>	9950
BaF <sub>2</sub>	4.89	3.3	16	310	62		10 <sup>6</sup> -10 <sup>7</sup>	
Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub>	6.8		2	480	100			
CeF <sub>3</sub>	6.16		5	375	30		10 <sup>7</sup>	
YAlO <sub>3</sub> :Ce	5.55		40	347	30		10 <sup>7</sup>	

Exposure to X-rays produces electron and hole trapped defects in the photostimulatable X-ray phosphors. The photostimulation liberates electrons (or holes), which recombine with holes (or electrons). The recombination, directly or indirectly, leads to light emission.

Photostimulatable X-ray phosphors should have (von Seggern 1989; Crawford and Brixner 1991) efficient X-ray absorption; high light output; short lifetime ( $< 2 \mu\text{s}$ ); low afterglow; optical stimulation spectrum in the range of commonly available, inexpensive lasers such as He/Ne laser; emission in the range of PMT (violet-blue), well separated from the stimulating light; good transmission for emitted as well as stimulating light; dose linearity; reusability following read out or suitable optical erasure; low fading during the time lapse between exposure and read out.

#### 4.1 Materials

Various types of materials have been considered for use as photostimulatable X-ray storage phosphors. These include alkali halides such as RbBr:Tl (Amitani *et al* 1986; von Seggern *et al* 1988a, 1989), CsI:Na (Brinkman 1965), alkaline earth halides doped with  $\text{Eu}^{2+}$  (Takahashi *et al* 1984; Takahashi and Miyahara 1988; Jianhu and Mianzeng 1988; Kano *et al* 1986; Iwabuchi *et al* 1991) or  $\text{Yb}^{2+}$  (Schipper and Blasse 1991), alkaline earth sulphides (Keller *et al* 1957; Gasiot *et al* 1982; Chakrabarti *et al* 1988), barium bromogermanate (Meijerink and Blasse 1991) or silicate (Garcia *et al* 1979, 1980; Meijerink and Blasse 1989b), or borate doped with  $\text{Eu}^{2+}$  (Meijerink and Blasse 1989a, 1990).

4.1a *RbBr: Tl*: Though RbBr:Tl phosphor was studied quite early (Inohara 1965; Sharan 1983), the photostimulation properties were studied only in 1986 (Amitani *et al* 1986). von Seggern *et al* (1989) proposed the following mechanism. The radiation creates F centres and  $\text{Tl}^{2+}$  centres. Photostimulation raises an F centre electron to the excited state, from which it tunnels to  $\text{Tl}^{2+}$  converting it to  $\text{Tl}^+$  in excited state ( $^2\text{P}_1, ^3\text{P}_0$ ). The light emission is obtained when  $\text{Tl}^+$  returns to ground state ( $^1\text{S}_0$ ). In earlier works, they proposed that  $\text{Tl}^{2+}$ -electron recombination is by transport of electron through conduction band (von Seggern *et al* 1988a). However, the observation that the temperature dependence of PSL was solely determined by lifetime of  $\text{Tl}^+$  in the range 50–500 K, and that there was no decrease in PSL below 80 K where release of electron into conduction band becomes less probable prompted them to propose the tunneling mechanism (von Seggern 1989; von Seggern *et al* 1989).

4.1b *Sulphides*: Infrared stimulatable phosphors based on sulphides and selenides had been known for a long time (e.g. see Fonda 1946; Garlick and Mason 1949; Keller *et al* 1957; for reviews see Mason 1965; Matsuoshi and Shinoya 1977). These phosphors could store energy for days and were used in wartime as light sources (Kroger 1947). A special session on these phosphors was held in the Cleveland meeting of the Optical Society of America on 7 March 1946. Use in IR detection was also proposed (Kunz and Urbach 1937).

The possibility of using these phosphors for X-ray storage, however, was indicated as late as 1982 (Gasiot *et al* 1982; Chakrabarti *et al* 1988). These phosphors, however, suffer from the drawback that they are sensitive to UV and visible light as well.

4.1c *BaFX:Eu<sup>2+</sup>*: *BaFCl:Eu<sup>2+</sup>* was studied as early as 1974 (Blasse and Brill 1974), and its use for X-ray screens was proposed in 1975 (Stevens and Pingault 1975). *BaFX:Eu<sup>2+</sup>* photostimulatable phosphors for CT were proposed by Takahashi *et al* (US Patent 4,239,968 and 4,236,078; Takahashi *et al* 1984, 1985). These workers also proposed the mechanism of luminescence in this phosphor. They suggested that creation of F centres by X-rays due to filling of existing vacancies by electrons and the release of the trapped electron during photostimulation is involved in PSL. It was also speculated that during irradiation *Eu<sup>2+</sup>* gets oxidized to *Eu<sup>3+</sup>*. Decrease in *Eu<sup>2+</sup>* luminescence and increase in that of *Eu<sup>3+</sup>* were observed (Takahashi *et al* 1984; de Leeuw *et al* 1987) which support the hypothesis. von Seggern *et al* (1988b) and von Seggern (1989) proposed that F centre electron is not released but it tunnels to *Eu<sup>3+</sup>*. Close association of F centres and *Eu<sup>3+</sup>* was suggested. The fact that the PSL lifetime has the same temperature characteristics as *Eu<sup>2+</sup>* emission was taken as the supporting evidence. Later works refute *Eu<sup>2+</sup>* → *Eu<sup>3+</sup>* conversion (Meijerink and Blasse 1991; Hangleiter *et al* 1990; Crawford and Brixner 1991). In fact Sun and Su (1988) found evidence for *Eu<sup>3+</sup>* → *Eu<sup>2+</sup>* conversion. Instead of *Eu<sup>3+</sup>*, intrinsic hole trapping sites such as *V<sub>k</sub>* centres were suggested (Crawford *et al* 1989). Reuter *et al* (1990) suggested that irradiation creates F centre interstitial pairs stabilized by *Eu<sup>2+</sup>* at Ba substitutional sites. F centre stimulation destabilizes the interstitial halogen centre. Electron tunneling from F centre converts the pair into *e + V<sub>k</sub>* pair which decays and the energy is transferred to nearby *Eu<sup>2+</sup>* ion. Crawford and Brixner (1991) pointed out that only the samples fired in nitrogen/hydrogen atmosphere show PSL, and thus speculated that the hole trap is hydrogen anion at fluorine substitutional site. Upon photostimulation F centre electron and hole recombine by tunneling and the energy of recombination is transferred to *Eu<sup>2+</sup>*.

## 4.2 Recent developments

In recent years Blasse and coworkers (Meijerink and Blasse 1989a, b, 1990, 1991; Schipper and Blasse 1991) studied several phosphors such as barium bromosilicate germanate, borate and *Eu<sup>2+</sup>* doped *BaFX* all of which show promising properties. Systems *M<sub>4</sub>O<sub>6</sub>X* (*M* = Ca, Sr or Ba and *X* = F or Cl) were also investigated (Schipper *et al* 1991). Properties of various photostimulatable phosphors are summarized in table 3.

**Table 3.** Photostimulatable X-ray phosphors.

Phosphor	Emission (nm)	Stimulation (nm)	Lifetime (ns)	Excitation energy ( $\mu\text{J}/\text{mm}^2$ )	Conversion efficiency ( $\text{pJ}/\text{mm}^2/\text{nr}$ )
RbBr: <i>Tl<sup>+</sup></i>	370	700	280		
BaFCl: <i>Eu<sup>2+</sup></i>	385				
BaFBr: <i>Eu<sup>2+</sup></i>	385	600	750	17	2
Ba <sub>5</sub> SiO <sub>4</sub> Br <sub>6</sub> : <i>Eu<sup>2+</sup></i>	440	500, 610	720	40	4
Ba <sub>2</sub> B <sub>5</sub> O <sub>9</sub> Br: <i>Eu<sup>2+</sup></i>	410, 440	620			1
Ba <sub>4</sub> O <sub>6</sub> Br: <i>Eu<sup>2+</sup></i>	454			300	0.04

## 5. Conclusions

The new techniques of X-ray imaging such as computed tomography and photo-stimulation offer several advantages such as electronic storing and image processing, speed, high resolution, etc. over the conventional screens. It is seen from this survey that there are very efficient phosphors available for X-ray imaging. Use of these phosphors in conjunction with new techniques will reduce exposure and increase image quality a great deal. Considering that about 90% of exposure to man-made radiations arise from X-rays, such reduction will be desirable. On the other hand, implementation of the new techniques and the new phosphors is costly. Major X-ray imaging work is still done using  $\text{CaWO}_4$  screens, the earliest known imaging device. Future efforts may be directed at obtaining cheaper phosphors and techniques.

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