RELATIVE EFFICIENCIES AND PHYSICAL CHARACTERISTICS FOR A SELECTED GROUP OF X-RAY PHOSPHORS

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We have measured the energy dependent conversion factors and quantum efficiencies for a number of selected phosphors in response to 0.7 to 6.0 keV X-rays. We have investigated the effects of deposition techniques, optical attenuation, dead layer material and front surface aluminization upon the light yield of the phosphor. From these measurements a simple model was derived that enables us to predict the light yield of a phosphor over a wide range of incident X-ray energies.

1. Introduction

In our detector development laboratory facility at the Smithsonian Astrophysical Observatory, we are studying several new types of soft X-ray detector systems [1]. One of these systems involves the use of a phosphor which converts individual soft X-ray photons to a number of visible light photons which are detected by a position sensitive low light level camera. The overall detector system has been described elsewhere in the literature [2], and is shown schematically in fig. 1.

In an attempt to maximize the detector quantum efficiency of this Phosphor X-ray Imaging detector system (PXI), it is necessary to investigate individual phosphor characteristics such as energy, spatial and temporal response in the conversion of X-rays to visible light. An ideal phosphor converter for this detector should have a high photon conversion yield, and it should be thick enough to absorb all of the incident X-rays, while remaining transparent to the visible light photons produced. The phosphor should also have a spectral output matched to the image intensifier photocathode response which immediately follows it. It is also important to select a phosphor that has a decay time (persistence) that is less than the integration time of the video readout system being used so that X-ray events are detected completely and uniquely in the camera. In the process of selecting a suitable phosphor, we have set up test facilities and procedures to:

1) determine the energy dependence of visible photon yield per incident X-ray photon conversion factors and efficiencies of a group of phosphors in response to excitation by ~ 0.7 to 6.0 keV X-rays;

2) determine the effects on X-ray absorption proper-
ties of varying phosphor grain size, deposition technique, dead layer thickness, binding agents surrounding the phosphor grains and optical attenuation;

3) develop a suitable model that enables us to characterize and predict the phosphor response to low energy X-rays.

2. Past results

Published data concerning phosphor response generally fall into two categories: 1) the response of a phosphor due to electron excitation for use in cathode ray tubes (CRTs); and 2) the phosphor response to higher energy X-rays (≥ 20 keV) for use in medical X-ray applications.

The CRT phosphor data generally consist of normalized emission spectra, persistence and a relative "color" output due to the excitation of the phosphor by 1 to 30 kV electron bombardment. For our purposes, the emission spectra are the most useful information contained in these data. The number of visible light photons emitted and the persistence information are strongly dependent on the accelerating voltages and the beam currents. No information on the quantum efficiencies for X-ray conversions are available from these data sets [3].

The references on the phosphors developed and selected for medical applications are optimized for higher energy X-rays (20-80 keV) and very different spectral response criteria (i.e. medical films). Again, the available data are given in small "normalized" sets covering a limited number of phosphors [4].

In both cases, none of the references surveyed adequately covers the effects of the physical characteristics (grain size, deposition techniques, visible light attenuation, etc.) or the energy conversion efficiencies so that a simple comparison between the referenced data can be made.

3. Energy response

When an X-ray is absorbed in the phosphor, visible light photons are emitted individually over a characteristic decay time ranging from a few nanoseconds (P47) to several hundred milliseconds (P39) depending upon the phosphor selected. An appropriate detection system for X-ray astronomy would determine both the total number of visible light photons emitted as a result of a single X-ray conversion and the position of the event. In order to measure light yields, we have constructed a system that consists of depositing phosphors on glass disks (or fiber optic face plates) which are then optically coupled to a low noise photomultiplier tube (PMT). The number of visible light photons is determined by using the PMT in a single photon counting mode. The incident X-ray flux is determined with a single wire proportional counter, as shown in the setup in fig. 2 and 3.

A group of phosphors for testing was selected primarily by their emission spectra (in the 3000 Å to 5000 Å range) and their persistence. All of the phosphors in this group were exposed to 5.9 keV X-rays and the average number of photoelectrons per incident X-ray photon was measured. The phosphors with maximum emission were then selected for further low energy X-ray tests and optical measurements.

We have defined the average conversion factor \( \langle CF \rangle \) as a figure of merit. The average conversion factor is the ratio of the average number of detected photoelectrons \( \langle I_{pe} \rangle \) produced by visible light photons striking the photocathode of the PMT to the X-ray flux \( \langle I_{x} \rangle \) impinging on the phosphor target:

\[
\langle CF \rangle = \frac{\langle I_{pe} \rangle}{\langle I_{x} \rangle}.
\] (1)

This conversion factor combined with knowledge of the PMT photocathode and the specific geometry factors of the detection system enables us to calculate the number of visible light photons emitted from each phosphor and the absolute energy conversion efficiency.

4. Experimental setup

4.1. X-ray sources – determining \( \langle I_{x} \rangle \)

Two experimental setups were constructed to produce the X-ray radiation and measure its flux. The first system uses radioactive, fixed energy sources and the second system uses a Henke fluorescent X-ray source in a vacuum system to permit irradiation at low energies.

4.2. Radioactive sources

In order to control the radioactive X-ray source intensity a "dark box" was constructed as shown in fig.
2. The source was mounted on a movable bench that was controlled by a lead screw. The source bench also contained two filters that could be placed in the beam path to attenuate or block the X-ray flux depending upon the filter combination used. Source intensities were calculated from the geometry factors of the detection system and verified by measurements made with two different proportional counters. The $^{55}$Fe (5.9 keV) flux rates in the dark box could be regulated from 0 to 600 counts/s with uncertainties in $\langle I_x \rangle$ of about 20%.

4.3. Fluorescent Henke source

Our adaptation of the Henke system (fig. 3) is designed to produce filtered fluorescent radiation from a selected set of targets; Fe Lα (0.70 keV), Al Kα (1.48 keV), Mo Lα (2.29 keV), Ti Kα (4.51 keV) and Fe Kα (6.40 keV). The X-ray flux is monitored with a proportional counter that is used to determine $\langle I_x \rangle$ with an uncertainty of $\sim$ 20%. X-ray intensities can be regulated from 0 counts/s to several thousand counts/s. A typical Al Kα spectra obtained by the monitor counter is shown in fig. 4.

4.4. The photomultiplier system – determining $\langle I_{pe} \rangle$

In choosing a photomultiplier tube to detect the single emitted photons from our test phosphors, one must consider the spectral response of the photo-
cathode, dark counts and the single photoelectron resolution of the tube. A selected low noise 2” EMI 9635QA photomultiplier tube was used for our phosphor tests. The bialkali photocathode of this tube is similar to the photocathode that will be used in the final PXI low light level camera, and is therefore well suited for our tests. The voltage dependent dark count over the entire 2” tube face at room temperature is about 100 to 200 counts/s.

5. Procedures

Systematically varying the PMT high voltage and observing the signal to noise (S/N) ratio as a function of the amplifier discriminator level, enables one to select an optimum operating point for the single photoelectron detection system. These data are shown in fig. 5, using the setup of fig. 2. The amplifier–discriminator electronics have a resolving time of 30 ns. Events occurring closer than 30 ns apart will be recorded as one event. The logic pulse produced from the fast amplifier–discriminator is fed to a 100 MHz counter–scaler. An experimental run begins by optically coupling the phosphor coated disk to the photomultiplier tube which is then placed in the dark box or attached to the vacuum chamber. The PMT and phosphor were allowed to settle a minimum of 8 h before any measurements are performed. In order to determine the average number of photoelectrons produced, it is necessary to subtract the noise of the system (electronic noise + dark counts) from the signal (electronics + dark counts + photoelectrons) produced by the phosphor. Accumulation times of 120 s corrected for dead time (<5%) are used to collect both signal and noise.

The overall gain of the system was monitored using a stabilized LED located in the dark box or in the Henke tube. Typical variations observed were less than 2%.

6. Results

Table 1 lists the phosphors tested and their corresponding average conversion factor \( <\text{CF} > \) for exposures

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Thickness (mg/cm**2)</th>
<th># MFP</th>
<th>( \langle I_{pe} \rangle ) (pe/s)</th>
<th>( \langle I_{s} \rangle ) (#/s/disk)</th>
<th>( \langle \text{CF} \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P45</td>
<td>5.80</td>
<td>1.32</td>
<td>5911.1</td>
<td>423</td>
<td>14.0</td>
</tr>
<tr>
<td>P22B</td>
<td>10.1</td>
<td>1.60</td>
<td>3711.1</td>
<td>455</td>
<td>8.15</td>
</tr>
<tr>
<td>LaOBr</td>
<td>5.33</td>
<td>2.49</td>
<td>4325.9</td>
<td>525</td>
<td>8.23</td>
</tr>
<tr>
<td>P11</td>
<td>11.0</td>
<td>1.74</td>
<td>3478.2</td>
<td>471</td>
<td>7.38</td>
</tr>
<tr>
<td>P44</td>
<td>6.00</td>
<td>1.40</td>
<td>2705.0</td>
<td>429</td>
<td>6.30</td>
</tr>
<tr>
<td>BaFCl</td>
<td>5.13</td>
<td>3.21</td>
<td>2917.2</td>
<td>548</td>
<td>5.33</td>
</tr>
<tr>
<td>P43</td>
<td>9.13</td>
<td>1.99</td>
<td>2100.1</td>
<td>429</td>
<td>4.26</td>
</tr>
<tr>
<td>P20</td>
<td>3.95</td>
<td>1.22</td>
<td>779.3</td>
<td>403</td>
<td>1.93</td>
</tr>
<tr>
<td>P39</td>
<td>13.6</td>
<td>1.41</td>
<td>650.5</td>
<td>432</td>
<td>1.51</td>
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<tr>
<td>P24</td>
<td>1.58</td>
<td>1.76</td>
<td>119.7</td>
<td>92</td>
<td>1.29</td>
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<tr>
<td>P47</td>
<td>5.92</td>
<td>1.19</td>
<td>337.5</td>
<td>398</td>
<td>0.85</td>
</tr>
<tr>
<td>P46</td>
<td>7.30</td>
<td>1.28</td>
<td>132.2</td>
<td>412</td>
<td>0.32</td>
</tr>
<tr>
<td>P22R</td>
<td>5.52</td>
<td>1.28</td>
<td>128.7</td>
<td>413</td>
<td>0.31</td>
</tr>
<tr>
<td>P36</td>
<td>4.50</td>
<td>1.35</td>
<td>5.01</td>
<td>423</td>
<td>0.11</td>
</tr>
</tbody>
</table>
to 5.9 keV X-rays. The number of photoelectrons detected $\langle I_{pe} \rangle$ was averaged over a two min integration time. The absorbed X-ray flux $\langle I_{x} \rangle$ is a fraction of the incident flux, and depends on the X-ray properties of each phosphor.

From this list, four of the top ranked phosphors were selected for further spectral studies on the Henke system. The results of these tests are shown plotted on a log-log scale in fig. 6.

General observations of this initial data set indicate that the P45 and P44 have an approximately linear response with energy; whereas the P22B and P11 do not (slope $\sim 1.5$). We interpret this difference as most probably due to optical attenuation effects in the phosphor and/or dead layer effects which reduce the low energy response as discussed below.

7. Phosphor modeling

There are two major processes we considered in attempting to model the phosphor response to low energy X-rays: 1) The X-ray attenuation and conversion of the active and dead layer absorbers; and 2) visible light attenuation once the X-rays have been converted. Our objective is to maximize the light output from a phosphor by determining the optimum thickness such that the absorption of the incident X-ray flux is at a maximum and the subsequent emission of the visible light photons is minimally attenuated. While this can be calculated for a monoenergetic X-ray flux, for a practical application, it is necessary to consider a range of energies and appropriate spectral weighting to select the best phosphor thickness.

We consider a simple model consisting of a slab of material that is characterized by a column density $x$, an energy dependent absorption coefficient and a visible light attenuation coefficient. The incident X-ray flux is exponentially attenuated as it penetrates the phosphor. The visible light photons that are generated from the X-ray conversions are then exponentially attenuated as they exit the remaining phosphor material. Using this model the exit visible light intensity $I_{pc}$ can be described by eq. (2):
where $I_{ow}$ is the incident X-ray flux, $\alpha$ is $\mu_e/\mu_v$ and $\tau = \int \mu_v X$.

8. Optical attenuation measurements and X-ray absorption calculations

In order to verify this model it is necessary to measure the optical transmission properties of a phosphor (and any binders/glues) to its emitted light which is characteristically concentrated in a few spectral lines. A $^{55}$Fe source was placed in front of a phosphor coated disk. The visible light emitted from this disk was then allowed to pass through a second phosphor coated disk. The amount of optical attenuation in the second disk was then measured with a PMT. The attenuation was measured from several phosphor thickness ranging from 0.0 to $\sim 20.0$ mg/cm$^2$. The results are shown in fig. 7. Optical attenuation coefficients for P44 and P45 were measured in this manner to be 0.0493 $\pm$ 0.0047 and 0.0875 $\pm$ 0.0134 cm$^2$/mg respectively.

X-ray mass absorption tables given by Henke et al. [5] were used to calculate the X-ray absorption coefficients. Uncertainties in the absorption coefficients are < 5%.

9. Results of the modeling program

Fig. 8 shows the visible light output in arbitrary units from two phosphors of a given thickness, for various values of optical absorption coefficient.

Modeling studies have been carried out which include the effects of dead layers. At low energies, most of the X-rays are absorbed and are converted into visible light photons in the front layers. The exit intensity of these photons is strongly dominated by the optical attenuation effects and loss of the primary X-rays which are absorbed in the dead layer. At the mid-energy range, one sees an optimum balance between the X-ray absorption and visible light attenuation. At the higher energies, the decrease in number of visible light photons is dominated by the decreasing X-ray absorption. The model was tested with data taken for four phosphor disks of various thicknesses as shown in fig. 9. Disks with 2.20, 4.93, 9.50 and 18.2 mg/cm$^2$ of P45 were used. At the higher energies, the decrease in light output as a function of increasing phosphor thickness is less pronounced than at the lower energies. The light output decreases by about 60% at 4.51 over the range of thicknesses studied, whereas at 0.7 keV the light output decreases by $\sim 75\%$. One would expect that at the lower energies a significant fraction of the X-rays will be absorbed and converted into visible light photons in the first few phosphor grains. The output intensity of these photons is strongly moderated by optical attenuation as they traverse the remaining layers of the phosphor and

$$I_{pe} = \frac{\alpha I_{ow}}{(\alpha - 1)} \exp[-\tau] \exp[(1 - \alpha)\tau] - 1,$$

where $I_{ow}$ is the incident X-ray flux, $\alpha$ is $\mu_e/\mu_v$ and $\tau = \int \mu_v X$. 

Fig. 7. Optical attenuation measurements for P44 and P45 showing the optical attenuation coefficient vs the phosphor thickness.
Fig. 8. Calculated phosphor response for a fixed thickness showing the relative light output vs energy for several optical attenuation factors. The dashed line shows the added effects of a dead layer.
binding materials. The higher energy X-ray photons are converted deeper in the phosphor layer and are less affected by this process. These data were fitted using the model developed above. The only free parameter used in matching the data were the dead layer thickness and the overall normalization point. All of the other parameters were measured or directly calculated as previously discussed. There is good agreement between the predicted and the measured energy dependence. The model is extremely sensitive to the input parameters, small changes have a pronounced effect when attempting to fit the observed data points over a large energy and phosphor thickness range.

The success of this simple model enables us to characterize the phosphor response over a wide range of X-ray energies and thicknesses from two basic measurements: 1) The light output from a single X-ray energy which is used to normalize the response; and 2) the optical attenuation coefficient.

10. Deposition techniques

Depositions are presently being done using a standard sedimentation technique in a Kasel solution (potassium silicate) with barium acetate as the cushion [6]. By varying the potassium silicate, barium acetate, and deionized water content, one can vary the wet/dry adhesion properties and reduce the number of surface pinholes. By increasing the silicate concentration, the dry adhesion can be increased at the expense of the wet adhesion.

Other deposition techniques were investigated with varying degrees of success. Depositing the phosphor grains in an acetone solution and then allowing the acetone to slowly evaporate provided the most uniform surface deposition. However, when comparing the light output from the two deposition techniques, the acetone deposition yielded 18% less light than the standard deposition technique. This effect is most probably due to the absence of the potassium silicate binding material. In the absence of a binding material, the difference in the index of refraction between the phosphor grain and the outside medium is greater than if the binder is
Table 2

<table>
<thead>
<tr>
<th>Phosphor condition</th>
<th>Normalized output</th>
</tr>
</thead>
<tbody>
<tr>
<td>P45 uncoated phosphor</td>
<td>1.00</td>
</tr>
<tr>
<td>P45 with ~ 500 Å Al overcoat</td>
<td>0.66</td>
</tr>
<tr>
<td>P45 with ~ 1200 Å Al overcoat</td>
<td>0.56</td>
</tr>
<tr>
<td>P45 with lacquer overcoat</td>
<td>1.32</td>
</tr>
<tr>
<td>P45 with lacquer + Al overcoat</td>
<td>0.85</td>
</tr>
<tr>
<td>P45 with Al poly film</td>
<td>1.52</td>
</tr>
<tr>
<td>P45 with lacquer + Al poly film</td>
<td>1.72</td>
</tr>
</tbody>
</table>

present. This difference can increase the amount of light trapped in the phosphor grain due to total internal reflection losses.

11. Aluminum overcoating techniques

Since approximately one half of the visible light photons escape through the front surface of the disk, several techniques were tested in an attempt to reflect these photons back through the disk. One technique was to vacuum deposit aluminum directly on the front surface of the phosphor. These tests were conducted for several different thickness of the aluminum ranging from 200 Å to 1500 Å (see table 2). In all cases where the Al was applied directly to the surface, the total light output decreased as a result of the overcoating. The most successful test involved aluminizing a thin polypropylene window which was placed over a phosphor disk which had a thin lacquer overcoat. This combination resulted in an increased light yield of a factor of 1.7.

12. Conclusions

We have measured the X-ray conversion factor at 5.9 keV for 16 phosphors in an attempt to characterize and select a suitable scintillator for the PXI detector system. Of the phosphors tested, P45 has the highest light yield in the spectral region of interest (~ 14 photoelectrons/incident X-ray in our detecting system under exposure to 5.9 X-rays). Further low energy measurements were performed on the top emitting phosphors in order to develop a suitable model to describe the response of a phosphor as a function of its material thickness, optical attenuation and X-ray absorption properties. This allows us to prepare a phosphor such that the light output is optimized for a given X-ray energy input spectrum.

We have investigated several techniques in an attempt to increase the light yield from the phosphor. By varying the deposition solutions and ratios, it is possible to reduce amount of light trapping that occurs, and surface pinhole defects. By overcoating the front surface with a lacquer plus an aluminized thin film, the light yield could be further increased by a factor of ~ 1.7.

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References