Ideal Distribution of Polycrystalline Phosphor Particles for Application to Phosphor Screens in CRT

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Abstract: Our daily activity is supported with information stored in tiny tips in computers that are invisible by the naked eyes. The stored information of PC and TV broadcasting images displays on lighted phosphor screens. Comfortable images on the phosphor screens for the naked eyes should be equivalent with the daytime scenery under slightly overcastting sky $\{10^{25}$ visible photons $(m^2, s)^{-1}\}$ that the eyes have adjusted for 5 million years. We have developed the CRTs that display the required images on the phosphor screen as the consequence of the statistical study on the sizes of the phosphor particles. Phosphor screens in CRT are constructed with the polycrystalline phosphor particles in the size at around 5×10^{-6} m. The phosphor powder in 1 gram contains 3×10^{20} particles that should distribute with a log-normal distribution. Then, we have significantly increased the luminance to 100 ft-L (equivalent to 330 lumens m^{-2}) from 7 ft-L by the change in the operation conditions of the phosphor particles after the measurements of the VD and CD curves of CL. The sharp and stable images on the lighted phosphor screen in CRTs are only obtained with the phosphor particles that have the clean surface chemically and physically.

Keywords: Phosphor Screens, Distribution of Particle Sizes, One-Directional Movement of Electrons,
Clean Surfaces of Phosphor Particles

1. Phosphor Particles in Screen of Established CRT

Human history backs to 5 million years. Our life activity is based on the historical results of the 5 million years. Human culture starts by development of artificial voices from roaring and yelling like as animals. By development of artificial voices, the human had developed the human culture by thinking with the artificial voices. Then, the voices had expressed symbolic pictures on wall in caves and surface of cliffs. The symbolic pictures changed to letters on surface of tablets and then on sheets of paper. Finally, the letters and symbols record in the tiny tips in computers. Developed voices and recorded letters in tips of the computers, including the broadcasting TV images, are essential necessity for our modern life activity. This is because human culture is significantly developing by thinking (abstraction) by the use of the words that are clearly defined with the advanced science. With this reason, we have attention to the phosphor screens of the display devices, like as CRTs, for the reading of the

information in the tips of computers and broadcasting TV images. When we had involved the phosphor screens of color CRT on 1950s, the color phosphor screens in CRT had the luminance at 7 ft-L, corresponding to the illuminance (10 lm, m^{-2}) of the luminance (10 cd, m^{-2}) that is less than one tenth of the required luminance (330 cd, m^{-2}). The improvement of the images on the color phosphor screens, we had studied the basics of the phosphor screens. The phosphor screens are constructed with the polycrystalline particles that distribute in the sizes at around 5×10^{-6} m. This report will describe about the details of the characteristic properties in the phosphor screens in CRT of which have ever discussed in the past [1, 2, 3]. The report will start from the overview of the established phosphor particles for a good understanding of the weak points of the study on the phosphor screens in CRT.

The typical phosphor screens in CRT are made with the layers of the phosphor particles that are not uniform size. The particle sizes spread at around 5×10^{-6} m that is invisible by the naked eyes. Furthermore, each phosphor particle contains the plural growing axes that form the polycrystalline particles. Consequently, unlighted phosphor screen is a white body color.

The huge numbers of the polycrystalline particles involve in the study on the phosphor particles. We will clarify the characteristic properties of the individual polycrystalline phosphor particles. The difficulty of the study on the individual polycrystalline phosphor particles comes from the luminescence from the phosphor screens.

The phosphor screens transduce the energy of invisible particles, like as electrons, photons of ultraviolet (UV) lights, and radioactive particles such as α-, β-, and γ-rays, to the lights in the visible spectral wavelengths; e.g., from the blue light to the red light, like as rainbow-color. The transduced lights by the phosphor screens are the scattered lights in the polycrystalline phosphor particles in the screen. Consequently, one may observe the similar images on the phosphor screens from the wide viewing angles. The phosphor screens by the polycrystalline particles have a great latent advantage as the display of the images on the lighted screens.

Here arises a serious problem for the study on the phosphor screen. The phosphor screen is constructed with a huge numbers of the phosphor particles that are the invisible sizes (5×10^{-6} m) by the naked eyes. We cannot find out a report that is the statistical calculation of the huge numbers of the phosphor particles in the CRT, including fluorescent (FL) lamps in the past publications [1, 2, 3], although the study on the phosphor screens has a history longer than 100 years. We may calculate the average numbers of phosphor particles in the phosphor powder in 1×10^{-3} kg (1 gram). The following calculations are made with the average particle size $\varphi = 5 \times 10^{-6}$ m. We may calculate the average volume of one phosphor particle under the assumption of the spherical particles. The volume of one phosphor particle V_{part} is 6.5×10^{-17} m^3 {$= (4/3)\pi (5 \times 10^{-6} \times 2^{-1})^3$ m^3}. Many phosphor particles have the density around $\rho = 5 \times 10^{-9}$ kg m^{-3} (= 5g cm^{-3}). We take the density $\rho = 5 \times 10^{-9}$ kg m^{-3} in the following calculations. The weight of one phosphor particle is calculated as 3.2×10^{-25} kg {$= (5 \times 10^{-9}$ kg m^{-3}) x $(6.5 \times 10^{-17}$ m^3)}. The numbers of the phosphor powder in 1 kg are 3.0×10^{24} {$= (3.2 \times 10^{-25})^{-1}$} particles, corresponding to 3.0×10^{21} (= $3.0 \times 10^{24} \times 10^{-3}$) particles per gram. The commercial phosphor powders usually produce with one tone (10^3 kg) that contains 3.0×10^{27} particles. The calculated numbers are more than the stars in our galaxy (the Milky Way) that contains 10^{22} stars. We must control the particle sizes of the huge numbers of the particles in the production of the phosphor powders.

The production volume of the phosphor powders changes from a few grams in the laboratory to a few tons per month in the phosphor factories. The fundamentals of the preparations of the phosphor powders do not change with the production volume of the phosphor powders. The invisible 10^{27} phosphor particles per 10^3 kg are produced with the heating of the blend mixture of the raw materials and fluxes in the heated crucibles in the furnace. The blend raw materials of about 1 kg put in the crucible of 1 liter. The produced phosphor powder by the one crucible is about 1 kg that contains around 10^{24} phosphor particles. The luminescence of the produced phosphor powders are examined under the UV lights from the UV lamp in air (PL) and/or under the irradiation of the electron beam in

vacuum (CL). The particle sizes are determined by the use of the commercial instruments that determine the medium (or average) particle sizes. The determined particle sizes by the commercial instruments somewhat deviate from the reality. The produced phosphor powders contain many clumped particles and small particles less than 1×10^{-6} m. Consequently, the characterizations of the commercial phosphor powders face the serious problems in the screening of the produced phosphor powders. The main problems are caused by (a) the luck of the chemistry and physics of the growth of the polycrystals in the heated blend mixtures in the crucibles, and (b) determination of the particle sizes of the produced phosphor powders as the statistical results. We will clarify them in this report.

At present, many scientists and engineers have studied the phosphor screens with the commercial phosphor powders of the CRT for more than 100 years. The phosphor powders are produced by a very simple way. The powders of the raw materials and fluxes are mechanically blended in the containers. The blended mixtures of the raw materials and fluxes put in the silica (or alumina) crucibles and then the crucibles heat up to the required temperatures in the heating furnace.
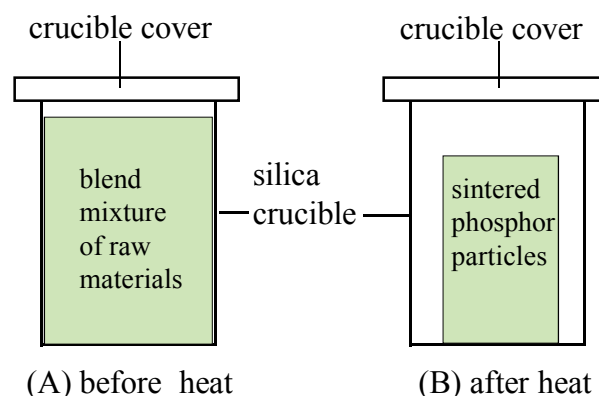

Figure 1. Schematic explanation of blend mixture of raw materials in un-heated crucible (A) and sintered phosphor powder in heated crucibles (B).

Figure 1 schematically illustrates the production of the phosphor powder in the silica crucible. The raw materials and the fluxes are mechanically blended by the ball-mill. Figure 1 (A) illustrates the blended powder in a silica crucible with the crucible cover. The crucibles set in the heating furnace. At the given temperatures, the components of the blended mixture chemically react in the heated crucibles for the growth of the phosphor particles. The produced phosphor particles in the crucibles are sintered with the solidified by-products that cover on the surface of the crystallized phosphor particles. Figure 1 (B) illustrates the sintered phosphor powder in the heated crucible. The by-products in the sintered products in the crucibles are the water soluble and phosphor particles are un-soluble in water. As the sintered phosphor powder puts in the deionized water, the solidified by-products of the fluxes and phosphor particles slowly dissolve into the agitated deionized water. In some cases, the rinsed phosphor powder puts in the dilute acid solution and agitates it for a while. The

by-products on the surface on the phosphor particles quickly dissolve in the dilute acid solution. The chemically cleaned phosphor particles settle down on the bottom of the washing container. The phosphor particles in the bottom of the container are rinsed with the deionized water for several times in order to remove completely the by-products from the surface of the phosphor particles. The rinsed phosphor particles separate from the water by the filtration. The filtrated phosphor powders dry in the heated oven at $110^{o}C$ for one overnight. Then, one may have the phosphor powder in his hands.
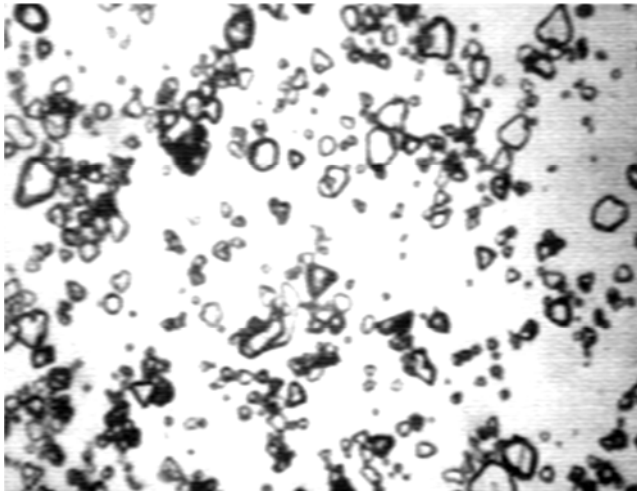

Figure 2. *Commercial phosphor particles under optical microscope (x 500).*

Figure 2 shows, as an example, the photopicture of the Japanese commercial phosphor particles under the optical microscope (x 500 times). The phosphor powders always contain the large and small sizes, and some amount of the thin plate particles. The phosphor particles by other producers are similar with the photograph in Figure 2. Many particles have the irregular shapes, indicating the heating conditions of the blend mixtures in the heated crucibles do not well controlled by the heat programs of the furnace.

According to their explanations, the irregular phosphor particles (especially flat and large particles) selectively and strongly adhere on the wet and flat glass surface in the early stage of the screening process. The adhered flat particles in the large sizes on the wet glass surface act as the anchor particles in the screening process at an early time of the screening process of the phosphor slurry. The small and irregular particles in the screening slurry gather up at around the anchor particles, resulting in the less pin holes in the dried phosphor screen. It has believed that some amount of the anchor flat particles in the large size is a necessity for the screening of the phosphor particles on the wet surface of the glass substrate. The numbers of the flat large particles as the anchors and the small particles less than 1×10^{-6} m are changed with the screening conditions by the users. The irregularity of the phosphor particles is the know-how for them. The present phosphor screens in CRT are predominantly produced by the commercial phosphor powders. Then, the optimal screen thickness of the phosphor particles has been studied.
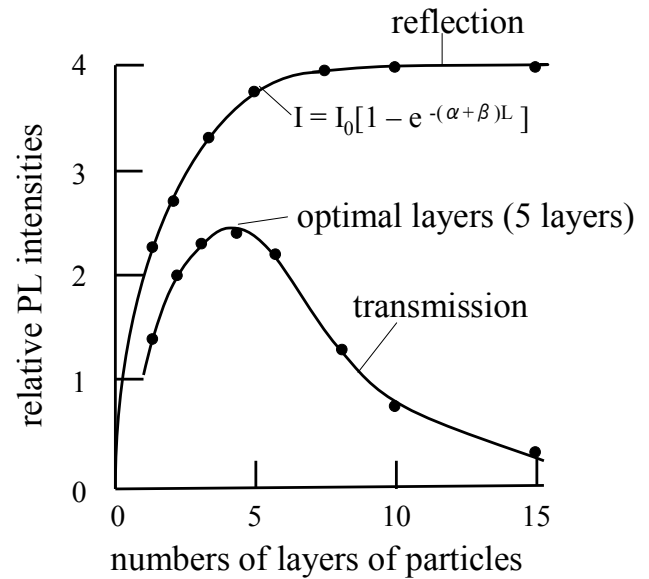

Figure 3. *Relative light intensities in transmission and reflection modes of phosphor screens as a function of numbers of layers of phosphor particles.*

Figure 3 shows the light intensities as the function of the screening layers of the phosphor particles. The numbers of the layers of the phosphor particles have been determined by the cross-section of the phosphor screens under the observation of the scanning electron microscope (> x 2000). The CRTs use the transmitted lights from the phosphor screen. It had concluded that the optimal phosphor screens for the CRT were made with around 5 layers of the phosphor particles.

Their studies on the optimization of the luminescence from the phosphor powders and screens have summarized in the publications, like as Phosphor Handbook [1] and typical text Books of the phosphor powders [2, 3]. It has believed that the quality of the luminescence from the phosphor screens in the commercial CRT have well optimized with the efforts by them. Their phosphor powders are well optimized technically with their know-how. A kind of the know-how is the surface treatment of the phosphor powders. They never discussed about the statistics of the sizes of the huge numbers of the phosphor particles. The statistical study remains as a future study.

The engineers and scientists of the phosphor powders have a serious problem that is the clumped particles during the storage. The phosphor particles in the storage for a long time contain many clumped particles in the large sizes. Their explanations are below. The phosphor particles in the produced phosphor powder contact each other with the small contact gaps. The small contact gaps may adsorb the water from air in the storage room by the capillary condensation. The water in the gaps dissolves the surface of the phosphor particles, forming the solution in the gap. As the amount of the absorbed water by the capillary condensation increases with the times, the concentration of the solved phosphor particles in the water also increases. And then, some amount of the water evaporates into air, the concentration of the solved phosphor particles in the condensed water increases with the time. When the concentration of the dissolved phosphor particles becomes

a high concentration, the particles strongly bind up by the crystallized products, giving rise to the largely clumped particles in the phosphor powder.

It had empirically found that the amount of the water by the capillary condensation at the contact gaps between the phosphor particles is significantly reduced by the coating of some amount of the SiO_2 gels (microclusters) on the surface of the phosphor particles. The sizes of the SiO_2 gels are less than 1×10^{-7} m. The solubility of the SiO_2 is very low, but they may make reclaimed gypsum ($CaSO_4$) in the gap. The formation mechanism of the gypsum is not clear. Then the narrow contact gap between SiO_2 particles and phosphor particles adsorbs the small amount of the condensed water by the capillary condensation, resulting in the less clumped phosphor particles in the storage. The solidified SiO_2 are insoluble in water.

The coating of the SiO_2 gels on the phosphor particles has been called as the "surface treatment". Figure 4 shows, as an example, the photograph of the scanning electron microscope (x 3000) of the commercial phosphor particles that have the surface treatment. We may observe the many solidified SiO_2 microclusters on the surface of phosphor particles. The troubles of the pine holes and clumped particles in the phosphor screens certainly reduce to the acceptable levels for the mass production of the CRTs. But the real trouble does not eliminate from the produced phosphor screens. The troubles of the SiO_2 and $CaSO_4$ microclusters on the surface of the phosphor particles are the electric insulators that electrically charge up under the irradiation of the electron beam. The details of the charge-up of the SiO_2 microclusters will describe later in this report.
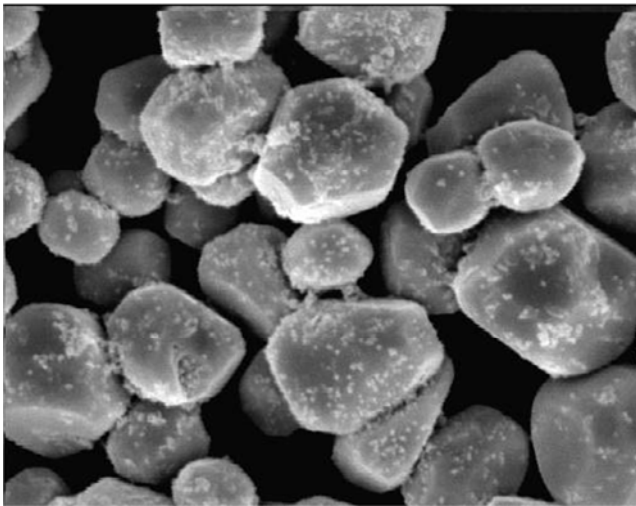

Figure 4. Photograph of scanning electron microscope (x 3000) of commercial phosphor particles.

2. Phosphor Particles Inherently Distribute with Log-Normal Distribution

As already mentioned, the phosphor screens are constructed

with huge numbers of the phosphor particles. 1 gram phosphor powder contains 3×10^{21} particles. Furthermore, at a glance of the photograph of the phosphor particles in Figure 2, the phosphor particles of the commercial phosphor powder distribute in a quite wide range in the diameters and shapes. We must find out the statistical results of 3×10^{21} particles per gram for a new handling of the phosphor particles in the screens.

The phosphor producers and users of the commercial phosphor powder measure the particle sizes of their phosphor powders by the commercial instruments. The most popular instruments are the determination of the average particle sizes in the sedimentation cell based on the equivalent particle sizes with the surface areas. The determinations are made by the surface areas of the precipitating particles in the dispersed fluid at a given distance from the bottom of the sedimentation cell. The determination is made with the decrease in the intensity of the Laser beam. Even though the average particles of the phosphor powders are strictly controlled by the determined average particle sizes, the quality of the produced phosphor screens varies with the production lots. The optimization of the quality of the phosphor screens in the CRT is limited by the statistical determination of the phosphor particles. We have the questions on the determination of the average phosphor particles by the commercial instruments. We have found the commercial instrument determines the particle sizes in the very narrow area in the precipitating particles in the precipitating space (equivalent with the diameter of the Laser beam). The preparation of the precipitating solution is not completed for the dispersion. Therefore, you do not get the reliable results.

After many trials of the finding of the real distribution of the particle sizes of the produced phosphor powders, we have reached a conclusion that the phosphor particles shown in Figure 2 do not distribute with a given statistical pattern. This means the particle sizes of the commercial phosphor powders do not monitor with the adequate conditions. This is a serious problem for the practical use of the phosphor screens in CRT. We cannot find out a commercial instrument that precisely and reciprocally determines the distribution of the sizes of the particles in the phosphor powder. We must find the production process of the phosphor powder that the phosphor particles distribute with a single distribution pattern statistically. Here we have a quite different approach for the determination of the particle sizes of the huge numbers of the phosphor particles (3×10^{21} particles per gram) in different sizes.

After many struggles, finally we have made a hand-made instrument that determines the proper distribution of the particle sizes of the phosphor powder. That is the precipitation of the suspending phosphor particles on the thin Al saucer from the undisturbed liquid with which it was previously mixed. We take the 200 ml glass cylinder. Figure 5 illustrates the hand-made instrument. The measurement of the particle sizes is made from the measurements of the change in the weights of the sediment particles on the Al saucer as a function of the deposit time. The Al saucer sets at 1×10^{-2} m above from the bottom of the precipitating cylinder. The

precipitating weights on the Al saucer at the given time are detected by the torsion balance. The measurements process and determination of the distribution of the particle sizes is the tedious works, but we may have the fruitful results on the study on the statistical distribution of the phosphor particles in the phosphor powders.
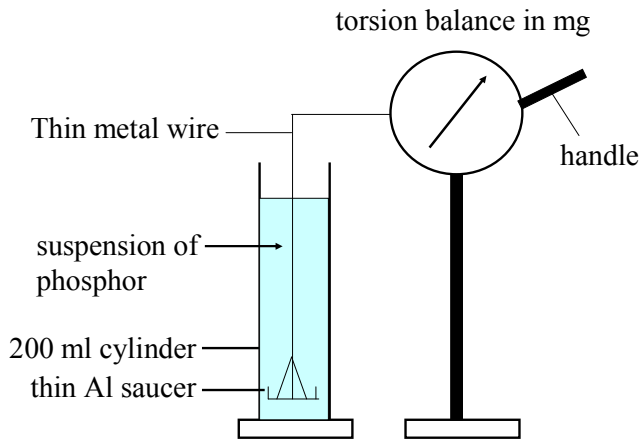

Figure 5. Hand-made instruments for determination of weights of sediment of particles on thin Al saucer as a function of precipitating time of particles.

We take the phosphor powder in 1 gram (e.g., 3×10^{21} particles). The phosphor powder puts in the bottom of the beaker of 200 ml. A small amount of the deionized water (about 10 ml) slowly adds to the stirring phosphor powder in the beaker. Then, the beaker is tightly covered with the plastic sheet. This is the aging process. The surfaces of each phosphor particle in the 10^{21} particles are well wetted with the deionized water by the aging process. After 60 minutes for the aging, the residual deionized water (140 ml) slowly added to the stirring powder. Total deionized water is 150 ml. Then, K-silicate solution in 0.5 ml, as a disperser of the phosphor particles, slowly adds to the suspension in the beaker. After the solution in the beaker strongly stir for 3 minutes, the suspending solution in the beaker pours in the cylinder in 200 ml, as illustrated in Figure 5.

The changes in the weights of the precipitating phosphor particles on the thin Al saucer are detected by the torsion balance. You may obtain the sedimentation curve as the function of the sedimentation times. Figure 6 shows the sediment curve of the commercial phosphor powder. The curve consists with three different groups of the sedimentations; (a) the large particles including clumped particles, (b) the primary particles, and (c) the extremely small particles less than 1×10^{-6} m. The commercial phosphor powders usually contain the extreme large particles and the clumped particles in the large sizes and the extreme small particles, as shown in Figure 2. The extreme large particles quickly deposit on the Al saucer within a few minutes. The extreme small particles will sediment on the Al saucer for longer than 60 minutes. After the sedimentation of the large particles, the primary phosphor particles in different sizes continuously deposit on the Al saucer. The intercept of the slopes of the curve at the given particle size corresponds to the

accumulation of the deposited weights of the phosphor particles on the Al saucer. We have the accumulation of the depositing weights of the primary particles that are total sediment weights in Figure 6. We have found that the curve of the deposit weights of the primary particles on the Al saucer fits to a log-normal distribution. The clumped particles and large particles and the extreme small particles are out of the log-normal distribution of the primary particles.
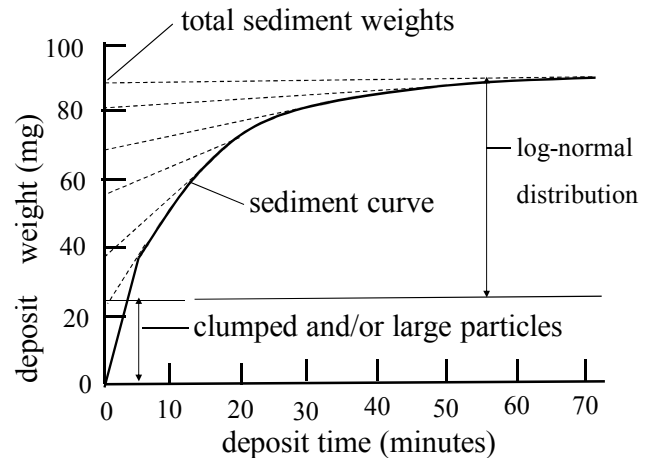

Figure 6. Precipitated curve of commercial phosphor particles on Al-saucer in suspension as a function of deposit time.

From the results in Figure 6, we have a conclusion that the commercial phosphor particles are gown with the unsuitable conditions in the heated crucibles. In the blend mixture in the crucibles, the raw materials of the phosphor particles and the fluxes have the different particle sizes and density. The blend powder charged in the crucible contains many air babbles in the different sizes. Consequently, the individual phosphor particles in the heated crucibles grow with the different conditions for the growth of the phosphor particles. The microscopic details of the uniformity of the blend mixtures in the heated crucibles ever studied in the phosphor production for last 80 years with the uncertainty of the determination of the particle sizes of the grown phosphor particles.

By referring the distribution of the particle sizes of the produced phosphor powders, we have found a new growth mechanism of the phosphor particles in the heated crucibles. Under the ideal heat programs of the heated crucibles, the produced phosphor powders do not contain the large particles and clumped particles, and extremely small particles. The sizes of the phosphor particles distribute with the log-normal distribution. The details are below.

When the blend mixture in the crucibles heats up in the furnace, the first consideration is thermal expansion of air babbles in the blend mixture. The crucibles in the furnace slowly heat up from the room temperature to 200°C. The next consideration is the melting points of the fluxes in the blend mixture. The melted fluxes have a high viscosity. The surface of the particles of the raw materials should be covered with the melted fluxes. We must keep the crucibles at the slightly higher temperature than the melting temperature of the fluxes for a while; hopefully more than 30 minutes. The surface of all

particles of the raw materials will be covered by the melted fluxes. Then the heating temperatures of the crucibles rise up to the high temperatures for the growth of the phosphor particles to the required sizes. The shapes of the grown particles are changed with the rate of the rising temperatures.
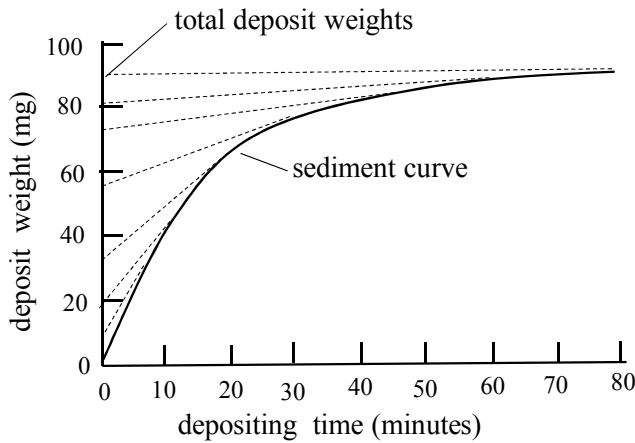

Figure 7. Ideal precipitated curve by improved phosphor powder.

By the consideration of the heating programs described above, we have obtained the improved phosphor powders. The all of the phosphor particles in the crucibles distribute with a log-normal distribution. The details of the heating programs of the phosphor powder refer to the references [4, 5]. Figure 7 shows the sediment curves of the new phosphor powder that does not contain the large and clumped particles and the particles smaller than 1×10^{-6} m.

Now we know the different sediment curves. The differences do not caused by the ratio of the blend mixtures of the raw materials in the heated crucibles. The variation of the quality of the produced phosphor powders comes from the heating programs of the crucibles in the furnace. The details of the mathematics of the log-normal distribution refer to the book [4]. The details of the heating programs of the blend mixtures in the crucibles refer to the book [5]. Figure 8 shows three log-normal distribution curves of the phosphor powders, which are produced with the same blend mixtures in the heating crucibles. The growth conditions of the phosphor particles are significantly changed with the heating programs of the crucibles. When the phosphor powder is produced with the ideal heating programs, the phosphor powder solely distribute with the log-normal distribution (A). Many commercial phosphor powders have two distributions (A) and (B). Some commercial phosphor powders are consisted with three distributions (A), (B), and (C) as shown in Figure 8.

If you study on the phosphor powders with the average or medium particle sizes, you never obtain the information shown in Figure 8. The reliably phosphor powders should be evaluated with the whole distribution of the phosphor particle sizes. This is a crucial point of the study of the produced phosphor powders. The commercial instruments of the determination of the particle sizes in the powders do not give the whole distribution with the difficulty of the detection of the large and clumped particles and extremely small particles.

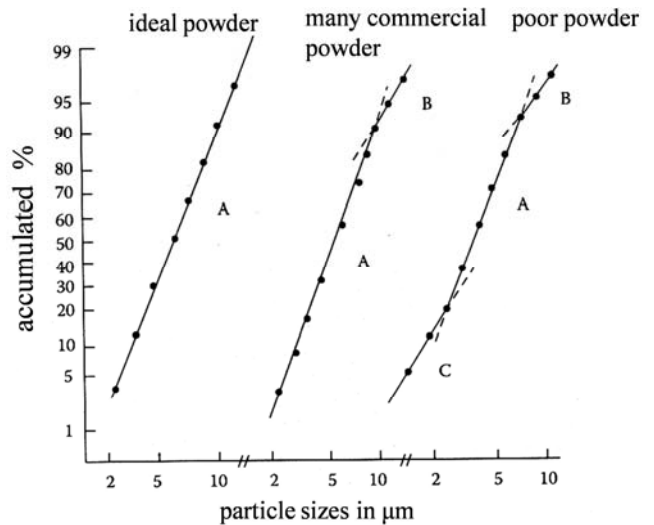The hand-made balance shown in Figure 5 only gives the whole distribution of the particle sizes.

Figure 8. Log-normal distribution curves of phosphor particles of ideal phosphor powder (A), many commercial phosphor powders have (A) and (B), and poorest phosphor powders have (A), (B) and (C).

It is mentioned again. The distribution of the sizes of the phosphor particles significantly changes with the heating conditions of the crucibles in the furnace. The heating conditions of the crucibles also change with the design of the heating furnaces. We have found that many furnaces for the phosphor productions in Asian Countries have the poor designs. Especially, we have found (a) the serious irregularity of the temperature profile, (b) the inadequate positions of the thermocouple in the furnace, (c) atmosphere in the furnace. The heating furnaces never have the leak holes for air circulation in the furnace. If you use the furnaces of the poor designs, you never produce the phosphor powders that distribute with the log-normal distribution. The selections of the furnace and heat program are the important considerations in the production of the phosphor powders. The improved phosphor powders should be composed with the primary particles that fit on the log-normal distribution. Then, we may study the increase of the required luminance (ft-L) of the phosphor screens in CRT.

3. Remarkable Improvement of Luminance of Phosphor Screens in CRT

Now, we have the phosphor powder that all particles distribute with the log-normal distribution, like as Figure 8 (A). So far as the phosphor particles distribute with the log-normal distribution, the quality of the phosphor screens is not change with the variation of the mean (or average) particle sizes within the variation ± a few μm. Therefore, you should consider the distribution of the phosphor particles, instead of the mean (or average) particle sizes, in the quality control of the phosphor powders. We will show the direct evidence of the quality of the practical phosphor screens.

We have produced, as an example, the Y_2O_2S:Tb white phosphor powder. Figure 9 shows the photograph of the Y_2O_2S:Tb white phosphor particles under the optical microscope (transmission mode) with the magnification (x 500). Since all phosphor particles sizes fit to the log-normal distribution, we may have the smooth phosphor screen as shown in Figure 10. The optimal screen thickness of the phosphor screen is 3 layers that reduce from the 5 layers of the phosphor powder as shown in Figure 3. We have found that the surface of the produced phosphor particles in Figure 9 is always covered with the very thin layer (0.01 μm) of the by-products that are the mixed compounds of the fluxes and phosphor particles. The by-products on the surface of the phosphor particles are the electric insulators and do not dissolve in the ionized water. The by-products only dissolve in the dilute acid solution. The by-products in the thin layer on the phosphor particles should etch out from the surface of the phosphor particles. The etched surface of the phosphor particles is unstable in water and air. The etched surface of the phosphor particles should be stabilized chemically and physically by the rinsed with H_3PO_4 solution.
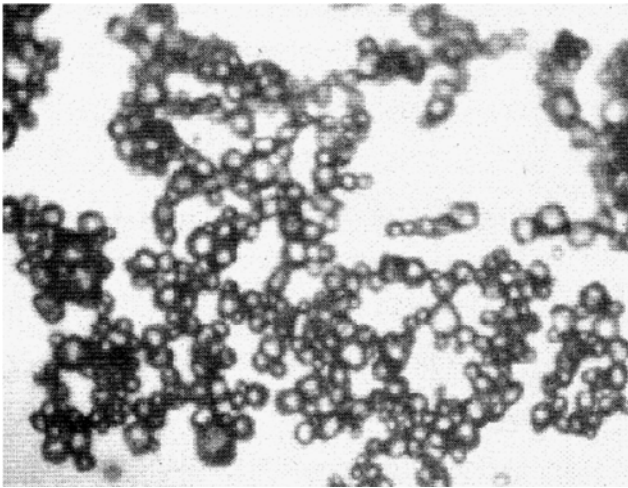

Figure 9. *Photograph of ideal phosphor powder under optical microscope (x 500).*
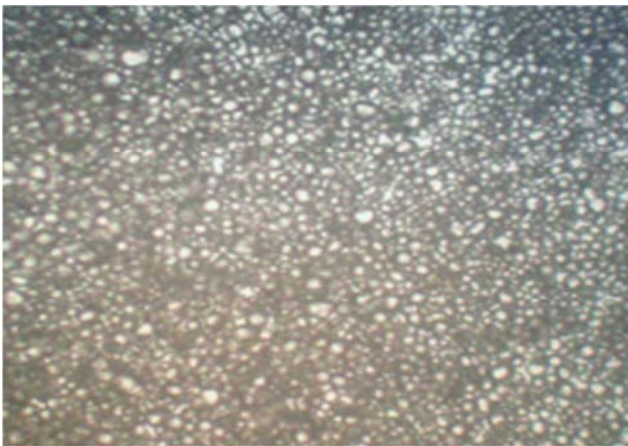

Figurer 10. *Photograph of Y_2O_2S:Tb phosphor particles arranged in phosphor screen (transmission mode) (x 300).*

With the thin phosphor screens, we may study on the characteristic properties of the phosphor screen in CRT. The studies on the cathodoluminescence (CL) may reveal the essential properties of the phosphor screen. Figure 11 shows the photopicture of the hand-made devices for the study on the properties of the CL from the phosphor screens.
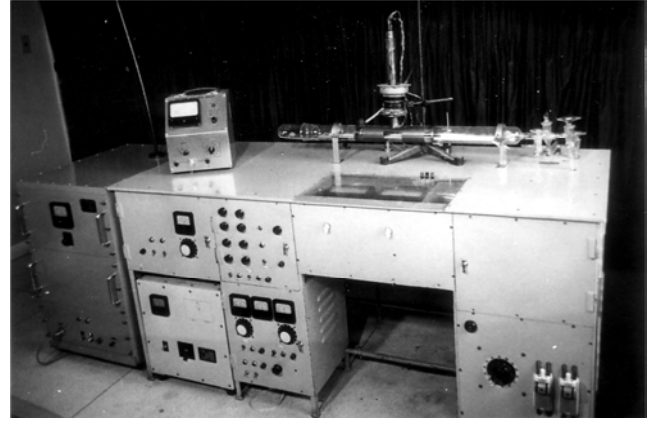

Figure 11. *Hand-made instrument of study on CL properties of phosphor screens.*

There are two kinds of the CL phosphor screens with the same chemical compound. One is for the low voltage CL phosphor screen, and other is for commercial CL phosphor screen. The difference is very clear with the voltage dependence (VD) curves of the CL. The low voltage CL phosphor screen emits the CL under the irradiation of the electron beam accelerated at low voltages. The threshold voltage for the low voltage CL phosphor screen is around 110 V, except for ZnS and ZnO phosphor screens that have the threshold voltage at around 10 V.
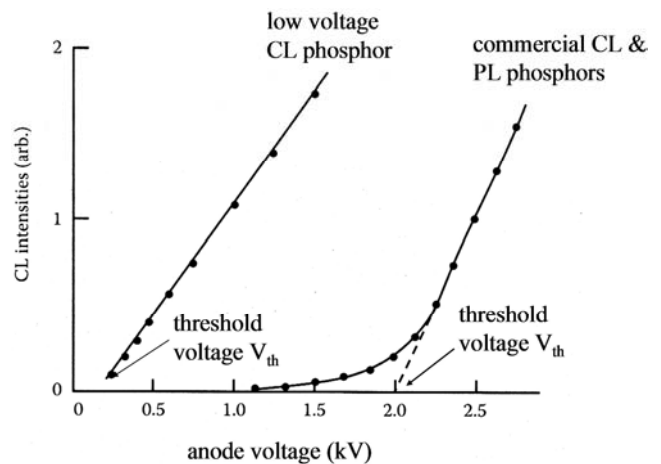

Figure 12. *Voltage dependence curves of low voltage CL phosphor screen and commercial CL and PL phosphor screens.*

The VD curves of many phosphor screens of the commercial CL phosphors (and PL phosphors) powders have the high threshold voltage at around 2000 V, even though the CL phosphor particles are the same chemical compounds with the low voltage CL phosphor screens. Figure 12 shows two VD curves. Ordinal CRT use the phosphor screens that has the

threshold voltage (V_{th}) is around 2000 V. The VD curves of those screens do not change with the screen thickness. On the other hand, the V_{th} of the low voltage CL phosphor screen sensitively changes with the thickness of the phosphor screens.
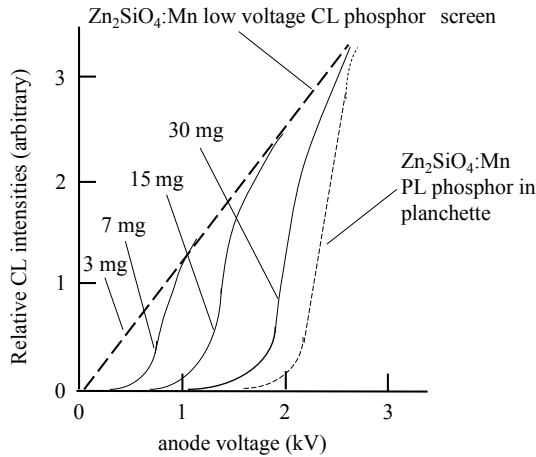

Figure 13. *Change in the voltage dependence curves with different thickness of the phosphor screens.*

Figure 13 shows the change of the VD curves of the low voltage CL phosphor screens with the thickness of the phosphor screens. The VD curves of the thick phosphor screens of the low voltage CL phosphor screen converge to the VD curve of the V_{th} = 2000 V. We take, as an example, the green emitting Zn_2SiO_4:Mn phosphor screens. The parameter of the VD curves is screening density of the phosphor powders per unit screen area (1 x 10^{-2} m = 1 cm^2). If the study on the VD curve of the phosphor screens is made with the thick screen higher than 5 mg per cm^2, we can not reveal the intrinsic lighting mechanisms in the CL phosphor screen.

The luminescence of the CL phosphor particles is not made with the direct excitation of the luminescence centers by the irradiated electron beam. The penetration depth of the irradiated electron beam into the phosphor particles is a less than 1 x 10^{-6} m from the surface of the phosphor particles. The depth of the penetration of the incident electrons to the phosphor particles change with the voltages of the incident electrons. The incident electrons into the surface volume of the phosphor particles never get in the orbital electron shells of the atoms at the lattice sites in the surface volume. The incident electrons in the surface volume may scatter with the Coulomb's repulsion from the orbital electrons in the atoms in the surface volume. The repulsed electron from the orbital electrons may take out an electron in the upper orbital shell of the atoms at the lattice sites to the narrow vacuum space between atoms at the lattice site by leaving a hole in the orbital shell of the atoms in the penetrated surface volume. The released electrons in the narrow vacuum are the secondary electrons that can move on in the narrow vacuum between atoms at lattice sites in the phosphor particles. Some secondary electrons are recombined with the holes in the electron shell of the atoms in the surface volume and disappear from the phosphor particles. Accordingly, some amount of the

electrons, equivalent numbers with the incident electrons, remains in the vacuum in the crystals. The remained electrons in the narrow vacuum are under the electric field that is generated in the deformed phosphor particles. The generation mechanisms of the electric field in the phosphor particles, without the electrodes on the phosphor particles, are followings. The phosphor particles belong to the un-symmetric crystals. The un-symmetric crystals deform the crystal structure under the irradiation of the electrons on the phosphor particles. The phosphor particles are also deformed under the lights of the energy greater than the band gap. The deformed crystals are equivalent with the polarized crystal. The polarized crystals have the electric field in the inside of the crystals. As the deformed crystals have the free electrons in the narrow vacuum between atoms at the lattice sites, the free electrons may move on in the narrow vacuum in the crystals under the generated electric field.

The moving electrons in the deformed crystals may have the chance of the excitation of the luminescence center (e.g., activators) in the crystals. The excited luminescence centers in the particles emit the CL lights. In the lighted phosphor particles, there are two critical regions, depending on the numbers of the activators. In the region that the activator concentrations are higher than the numbers of the secondary electrons, the numbers of the excited activators in the phosphor particles gradually decrease with the moving distance from the surface volume. The decrease in the excited activator in this region is caused by the loose of the kinetic energy of the moving electrons by the electric resistance, R. The R is caused by the thermal perturbation from the thermally vibrating atoms at the lattice sites. Accordingly, we may detect the electric resistance from the decrease in the CL intensity in the concentration dependence (CD) curve. In the region that the activator concentrations are lower than the generated numbers of the moving electrons in the phosphor particles, the CL intensity is linearly proportionate to the number the activator concentrations. Therefore, the CD curves of the low voltage CL phosphor screen less than 3 mg cm^{-2} may provide the experimental evidence of the described above. With an expectation, we have studied the CD curves of the Y_2O_2S:Tb phosphor screen in 3 mg cm^{-2}.
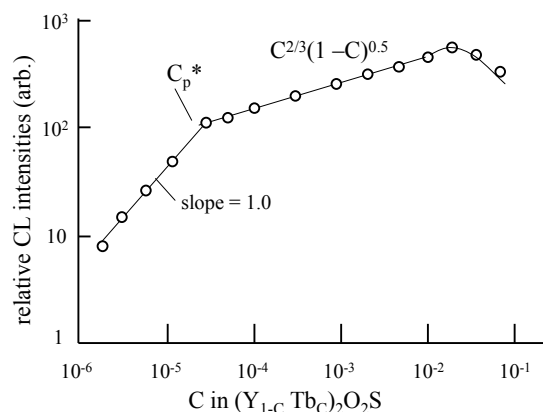

Figure 14. *Concentration dependence curve of Y_2O_2S:Tb phosphor screen.*

The following experiments are made with the CL under the 10 kV for the avoidance of the irregularity in the experiments. The phosphor screens are made with the phosphor powder, like as the phosphor screen shown in Figure 10. The tested phosphor screen is excited by the irradiation of the pulsed electron beam of 10 μ sec (10^{-5} second) with 50 Hz. Figure 14 shows the experimental results. The CD curve inflects at C_p^*. Therefore, the CD curve consists with two curves as shown in Figure 14. At the Tb concentrations higher than C_p^*, the CD curve is expressed by the $C^{2/3}(1-C)^{0.5}$. The decrease in the CL intensity is caused with the Joule Heat. Below the C_p^*, the path of some moving electrons contains only one activator, so that the some moving electron has only one chance of the excitation of the activator in the phosphor particles. Consequently, the CD curve is expressed by C.
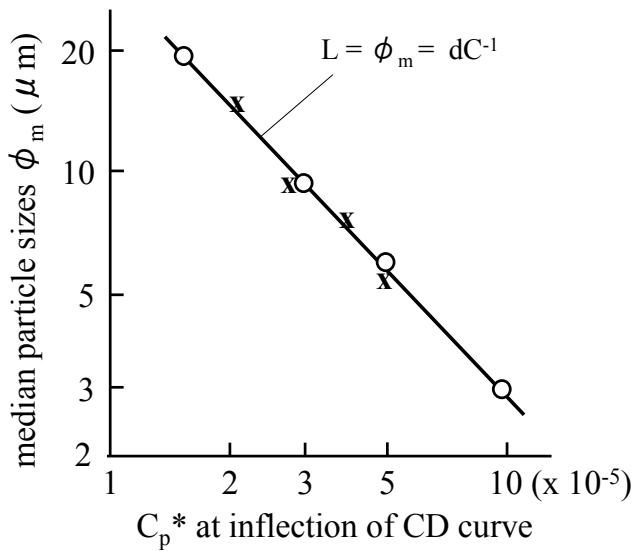

Figure 15. *Relationship of median crystal sizes ϕ_m with C_p^* of Y_2O_3:Eu (o) and Y_2O_3:Dy(x) phosphor particles.*

For the confirmation of the results in Figure 14, we have studied the C_p^* of the particle sizes from 3×10^{-6} m to 20×10^{-6} m of Y_2O_3 particles with activators of Eu or Dy. The results show in Figure 15. The results in Figure 15 have confirmed with the other phosphor particles. The same results are also obtained with the Y_2O_2S particles with Eu or Tb activators. and (b) ZnS:Ag;Cl and ZnS:Cu:Al phosphor particles. The activator concentrations of the ZnS phosphor particles are 1×10^{-4} mole. Therefore, the application of the large particles of the green ZnS:Cu:Al green phosphor to the phosphor screen in the color CRT results in the increase in the illuminance (30 %) of the color phosphor screen. We have confirmed the 30 % up of the luminance of the color CRT screen as shown in Figure 17 in later. As described above, we have studied the most fundamentals of the CL from the phosphor screens by the VD and CD curves for the improvement of the luminance of the phosphor screen of the color CRT by the theoretical analysis, rather than try and error approach.
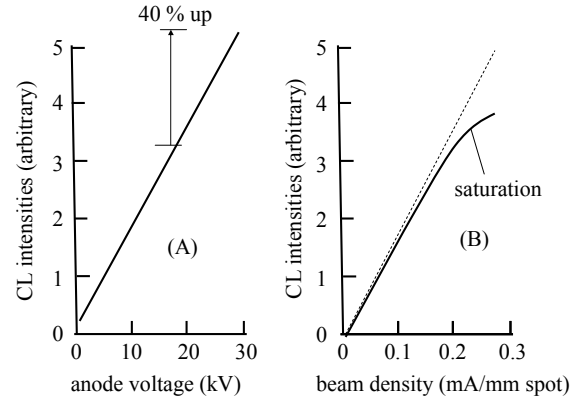

Figure 16. *CL intensities of ZnS:Cu:Al green phosphor as function of anode voltages (A) and anode electron beam density (B).*

The generation of the secondary electrons in the penetrated surface volume changes with the energy of the incident electrons in the phosphor particles. The energy of the incident electron beam is given by (V x I), where V is anode voltage and I is anode current. Figure 16 shows the CL light intensities of ZnS:Cu:Al green phosphor screen as a function of the anode voltages (kV) (A), and anode beam current densities (mA per spot of 1 mm diameter) (B). The CL intensities saturate with the high beam current densities over 0.15 mA in 1 mm spot. On the other hand, the CL intensities linearly increase with the anode voltages. Therefore, the CL intensity (brightness) of the color CRT for the TV sets increased 40 % by the application of the 30 kV anode voltages from the established anode voltage at 20 kV.

The improvement of the luminance (ft-L) of the color CRT tubes from 7 ft-L was the urgent task before 1968 for more 15 years. The improvement before 1968 was due to the try and error approach. Their efforts never increase the luminance of the color CRT. The images on the phosphor screen of color CRT were observed in the dark room before 1968, like as the movie theater. The improved luminance of color CRT tubes on 1972 is 100 ft-L that is equivalent with the daytime sceneries under the slightly overcastting sky. The images on the color TV screen can be observed in the illuminated room.
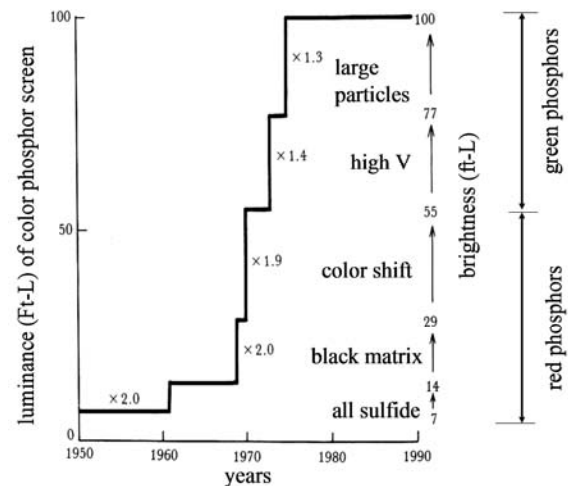

Figure 17. *Step-wise improvement of luminance (ft-L) of color TV sets.*

Figure 17 shows the stepwise improvements of the luminance (100 ft-L) of color CRT for TV sets from 1950 to 1973 [4]. The author was challenged the subject in Japan before 1967. However, he had struggles in Japan. He moved to Zenith, USA on 1998. But the CRT production was the subsidiary of the Zenith. They had the own research laboratory and engineering department. As already explained above, he did the improvement of the phosphor screen of the color CRT with the scientific study. But he could not claim it and could not apply patents with the political reasons. Zenith closed the Research Laboratory on 1978.

4. Development of Smear-Less Images on Color Phosphor Screens in CRT

After 1975, the personal computers (PC) introduce on the market. The PC used the phosphor screen of the color CRT as monitor for display of the storage information in the tiny tips. The phosphor screen of the monitor CRT project the images with the illuminance 330 lm m^{-2} that is the similar with the daytime scenery under the slightly overcastting sky. However, the users of the PC watch the image on the phosphor screen of the monitor CRT on the desk that gives the observing distance at around 0.3 m. The eyes of the PC users sensitively detect the smearing and flickering images on the phosphor screen. The removal of the smeared and flickering images on the monitor CRT became an urgent subject of the phosphor screen of the CRT. The reason of the smeared images on the phosphor screen of the CRT is a very hard subject. After the study for more than 15 years, no one figure out the reasons of the smeared and flickering images on the phosphor screen in the CRT.

The study on the smearing and flickering images on the phosphor screen under the irradiation of the electron beam involves in the solid state physics in the vacuum pressure less than 10^{-3} Pa ($< 10^{-5}$ Torr). After the extensive study on the subject, we have found that the smearing and flickering of the lighting images on the phosphor screen come from the same basis. More precisely, the smearing and flickering of the light images on the phosphor screens in CRT relates to the charge up of the lighted phosphor particles in the phosphor screens under the irradiation of the electron beam. As the phosphor screen is negatively charged up, the approaching electrons from the cathode of the CRT are disturbed by the negative electric field on the phosphor particles. The study of the charge-up of the phosphor screens steps in the study of the solid state physics in the high vacuum.
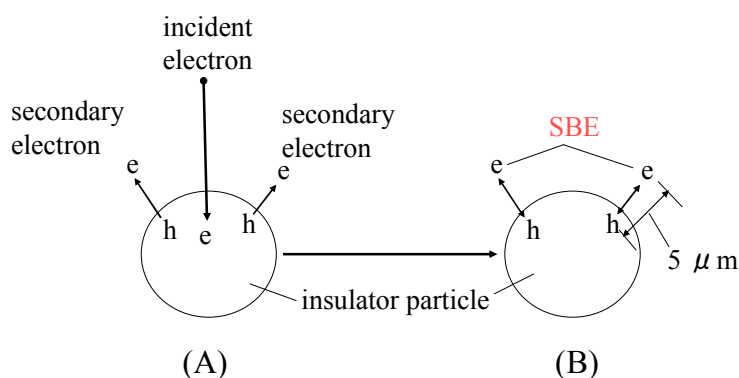

Figure 18. *Schematic explanation of formation of surface-bound-electrons (SBE) in front of surface of insulator particle; (A) generation of secondary electrons in the vacuum from surface volume of solid, and (B) formation of SBF in front of surface of solid.*

As the incident electrons from the cathode penetrate in to the thin surface volume of the solids, the incident electrons generate many secondary electrons in the penetrated surface volume in the depth of 10^{-6} m from the surface of the solid. The numbers of the secondary electrons relate with the energy of the irradiated electrons. The mean free path of the generated secondary electrons in the solid is around 10 Å (= 10^{-9} m). The secondary electrons in the surface volume shallower than 10 Å may escape from the surface of the solid to the vacuum, leaving the same numbers of the holes in the surface volume. The positive electric field of the holes in the surface volume attracts the free secondary electrons in the vacuum. But the holes in the surface volume do not give the energy that is a large enough for the penetration into the solid. The attracted secondary electrons by the holes stay in the vacuum at the front of the surface of the solid. The staying distance of the attracted secondary electrons in the vacuum is at 5 x 10^{-6} m (= 5 μ m) above the solid. Thus the secondary electron in the vacuum and the hole in the surface volume tightly bind up each other in front of the surface of the solid. The binding electrons in front of the surface of the solid are called as the surface bonding electrons (SBE). Figure 18 schematically illustrates the formation of the SBE in front of the solid.

The phosphor particles and covering materials on the phosphor particle are the solids. As shown in Figure 5, the surfaces of the phosphor particles in the screen of the commercial CRT are always covered with the SiO_2 microclusters of the electric insulator. Consequently, the phosphor screen in the commercial CRT always covered with the SBE under the irradiation of the electron beam.

Furthermore, the entire area of the surface of the phosphor particles of the commercial CL phosphor powders are uniformly covered by the very thin layer ($< 1 \times 10^{-7}$ m) of the by-products of the fluxes and phosphor particle. The thin

by-products on the phosphor particle are the electric insulators. As the consequence of the poor production process of the phosphor powders, the operating phosphor screens of the CRTs are always covered by the SBE. This is the reason that the VD curve of the phosphor screens of the commercial CL and PL phosphor powders has the V_{th} at 2000 V, as shown in Figure 12. The electron beam of the practical CRT must penetrate through SBE cloud on the surface of the phosphor particles for generation of the CL from the phosphor particles. As the incident electron beam is accelerated above 2 kV, the incident electron beam may penetrate through the SBE cloud on the phosphor screen. With this reason, the dominant CRTs on the market operate with the accelerated electron beam higher than 5 kV. As the phosphor screen is made with the commercial phosphor powder, the light images on the phosphor screen of the commercial CRT always have the smeared and flickering images. Here, we have revealed the conceal mechanisms in the study of the phosphor screen under the irradiation of the electron beam. The concealed mechanisms in the study of the CRT for 100 years are the charge up of the (a) phosphor particles and (b) the electric insulators on the phosphor particles.

As already mentioned, the incident electron beam penetrates in the surface volume of the phosphor particles, the electron beam generates many secondary electrons in the vacuum between the atoms at lattice cites, leaving the same numbers of the holes in the upper obituary shell of the atoms in the surface volume. Some amount of the secondary electrons in the thin surface volume in 10^{-9} m depth may get out from the phosphor particle to the wide vacuum between floating Ar atoms in gas phase. The generated large amount of the electron and holes in the surface volume of the phosphor particles may move on in the phosphor particles by the electric field of the polarized phosphor particles. The activators uniformly distribute throughout in the phosphor particles. As an activator in the phosphor particle captures the moving electron, the activator starts the luminescence process in the phosphor particle. The trapped electron has the localized electric field around the activator. The negative electric field from the activator attracts the hole around the activator and the activator captures the hole. Then the activator emits a photon (light). The attracted force of the hole by the trapped electrons is a function of the distance l_{trap} from the activator. The small l_{trap} strongly attracts the hole. The l_{trap} can be calculated from the mole fraction of the activator concentration and average lattice distance. The calculated l_{trap} in the phosphor particles is around 2×10^{-9} m that is much short distance as compared with the bonding distance with the $l_{SBE} = 5 \times 10^{-6}$ m. The l_{SBE} is the distance between the hole and SBE; $l_{trap} \ll l_{SBE}$. Consequently, the hole in the surface volume of the CL phosphor particles disappears in the lighted CL phosphor particles. The SBE on the phosphor particles loses the binding partner and becomes the free electrons in the vacuum. Figure 19 schematically illustrates the disappearing mechanisms of the SBE on the surface of the CL phosphor particle. As the phosphor particles have the chemically and physically clean surface, the surface of the phosphor particle may not have SBE, so that the VD
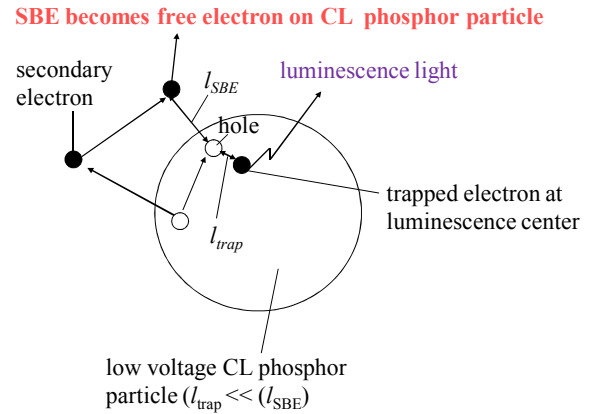
curve has the $V_{th}` = 110$ V.

Figure 19. Schematic explanation of no electric charge of SBE on clean surface of low voltage CL phosphor particle.

Here is only way to have the $V_{th} = 110$ V. The phosphor particles should have the clean surface physically and chemically. The phosphor particles must be produced by the wall wash with deionized water, and then the surface of the phosphor is etched by the acid solution for the removal of the thin by-product layer. After the rinse of the etched phosphor particles with the deionized water, the surface of the phosphor particles should be stabilized with tie H_3PO_4 solution. Then the stabilized phosphor particles dry in the headed oven at $110^{\circ}C$. The phosphor screen of CRT is prepared with the phosphor particles without the inorganic binder, such as potassium silicate. After the baking of the phosphor screens, the phosphor particles in the screen have the physically clean surface. The typical practical application of the ideal CL phosphor screen was the development of the miniature CRT. The phosphor screens in 1×10^{-4} m^2 (= 1 cm^2) of the miniature CRT may display the stable and clear images and letter with the high resolution (307,200 pixels per 1cm^2).
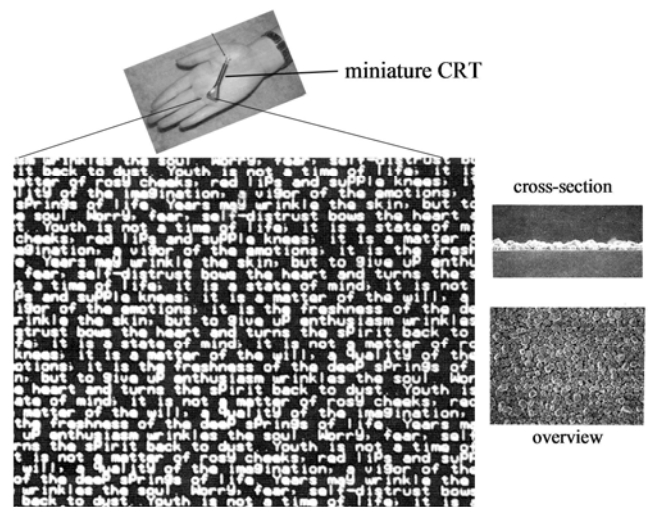

Figure 20. Developed miniatures CRT and letters on screen of miniature CRT.

Figure 20 shows the photographs of the developed miniature CRT on the palm of the hand and letters on the

phosphor screen in 1 cm^2 [6]. The photograph at right side is the cross-section and overview of` the phosphor screen. It should note that the letters on the photopicture are irregularly smeared by the position. The irregularly smeared letters in the photopicture in Figure 20 are caused by the irregular thickness of the Ag particles in the photo-film. We used the most high resolution photo-film on the market that is constructed with about 7 layers of the silver particles at around 5 x 10^{-6} m. The localized irregularities in the photo-film are caused by the irregular sizes and shapes of` the Ag particles and irregular thickness of the Ag particles. The phosphor screen on the miniature CRT displays the sharp letters on the lighted screen. Unfortunately, the developed miniature CRT was not evaluated by the poor Japanese managers who were working on the miniature CRT in the low quality for the video camera. I must apologize to someone who has had the interest and evaluate of the developed miniature CRT on the world.

We have next chance that the smear less CL phosphor screens to the color CRT for monitor of the PC and for color TV sets in Korea on 1997. As the phosphor particles fit to the lognormal distribution and each particle has the clean surface chemically and physically, the phosphor screens in the monitor CRT of the PC and TV sets display the sharp and stationary images on the color phosphor screen, like as the printed images on the photo-sheets of photograph. The eyes do not tire for the daily observation of the high resolution images on the phosphor screen of PC on the desk in the offices. The Korean company produced their color CRT for their PC and TV sets without the change of the fundamentals of their existing production lines of CRT imported from the Japan for 25 years ago. They just changed the operation manuals of the production lines with the phosphor screens by the developed phosphor particles under the instruction. They sold the produced color monitor CRT on the US market with the 3 times of the price ($ 950) of the Japanese color monitor CRT (below $350). The US customers chose the high price with the protection of their eyes. They evaluated the invention, not innovation. The Japanese companies had tried to find out the reasons of the excellent images on the color phosphor screen in the Korean CRT. However, they could not find out the reasons. Then, the Japanese Government suddenly changed the TV broadcasting system from analogue to digital system. At present, the TV sets and monitors of PC utilize the large and thin LCD panels and in some case OEL panels.

Consequently, the technologies of the color phosphor screens in CRT lost the market on the world. However, we find the large room of the new products of the developed phosphor screens as the illumination light source. At present, the illumination by the FL lamps consumes a large amount of the electricity; more than 30 % of the totally generated electric power generators on the world. We have found the power consumption (W_{qct})`of the FL lamps reduce to nearly zero level with holding the high illumination level (> 9000 lm m^{-2}) |that illuminates the room of 30 m^2 that is equivalent with the daytime scenery under slightly overcastting sky. The new FL lamps are the coil-EEFL lams. The coil-EEFL lamps will contribute to the protection of the worming up of the environment on the Earth.

5. Conclusion

We have studied the fundamentals of the production of the polycrystalline phosphor particles and the application to phosphor screens in CRTs. The ideal phosphor powders are produced with the heat program of the blended mixture in the crucibles in the right furnace, giving rise to the log-normal distribution of the phosphor particles. The next consideration is the cleanness and stabilization of the surface of the polycrystalline phosphor particles. Naturally the produced phosphor screens in CRT display the sharp and stabilized images that are equivalent with the day time scenery under the slightly overcastting sky. The basic concepts on the phosphor particles and screens can be applied to the phosphor screen in the fluorescent lamps.

Acknowledgement

Biography

The author started production of phosphor powders on 1950 in a very small factory in Japan. Then he studied all his life on the luminescence materials. First study was the possible compounds from the Periodical Table of Atoms. He obtained the certificate of the graduation of high school, master degree in science, and consultant in the applied science by the examinations of the Japanese Government. Thus, he studies the subjects by the thinking, not learn from published books by others. The review articles in Chemical Review and Royal Society London were received as the excellent reviews from the editors.

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