On the Crystal Growth of Zinc Sulfide Phosphor

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When zinc sulfide is fired, usually the flux is to be used, which 1) protects the phosphor from oxidation[1], 2) acts as the co-activator[2-4] and 3) promotes its crystallization. Concerning those functions, there have been few detailed reports on 3), the crystallization of the phosphor.

The author has made observations with an electron microscope on the process of crystallization of the phosphor, with and without flux — here, 2 wt. % of sodium chloride has been added — and, at the same time, he has determined the sizes and the forms of crystals, using a NORELCO X-ray diffractometer. It is found that, before firing, the raw material of zinc sulfide is a large aggregate of crystallites of β-form with 8% of α-form of the same material, and through firing, the process of crystal growth is much affected by the addition of flux. Also, he has discussed the effect of flux on the size of the grown crystals, the forms of crystals and their transition velocities.

Experimental Results and Discussion

The Crystal Growth and the Electron Microscope Observation.—A special replica method was used for the electron microscope observation. The phosphor powder was scattered on rock salt and Pt-Pd metal was evaporated on it obliquely from one direction. Carbon was then evaporated to cover the Pt-Pd metal and the phosphor crystal. After those procedures, rock salt was dissolved in water and zinc sulfide was dissolved in 6 N-hydrochloric acid. Thus, the Pt-Pd metal covered with carbon film was left, and was put on the mesh as a sample.

The base material of zinc sulfide phosphor was precipitated through the reaction of hydrogen sulfide gas with the solution of zinc sulfate. The precipitate was washed with de-ionized water and dried at room temperature. The precipitate was observed by the electron microscope and was found to be a large aggregate of needle-like crystallites, as is demonstrated in Fig. 1. In order to see the crystal structure of the aggregate, a NORELCO X-ray diffractometer was used and $10\bar{1}0$, 0002 and $10\bar{1}1$ patterns, the strongest patterns of α-form crystal, and 111 pattern, the strongest pattern of β-form, were checked. It was found that the raw material of zinc sulfide was not amorphous but consisted of nearly perfect crystals of β-form containing approximately 8% of α-form.

Assuming that they are perfect β-form crystals, the mean diameter of the crystals, d, is obtained from the half-peak breadth, B, of the 111 diffraction pattern, using

$$B = K\lambda / d\cos\theta \tag{1}$$

where λ is the wavelength of X-ray and θ is the angle of diffraction. For $K \approx 1$, the diameter of the unfired zinc sulfide crystal, d, is evaluated to be about 150 Å from our X-ray diffraction measurements.

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[1] K. Takagi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 959 (1958).

[2] F. A. Kröger and J. Dikhoff, *Physica* XVI, 297 (1950).

[3] F. A. Krgöer, ibid., XXII, 637 (1956).

[4] F. E. Williams, *J. Opt. Soc. Am.*, **47**, 869 (1957).

Fig. 1. Unfired ZnS: Ag.
Electron micrograph × 5,000

In Figs. 2a and 2b, the processes of crystal growth during the firing of the precipitated zinc sulfide are shown. The processes of crystalization of the samples added with or without the flux of 2 wt. % of sodium chloride were investigated with an electron microscope. In both cases, no difference is observed up to 400°C and a slight change in the crystalline state is observed at 500°C in case of a sample with 2 wt. % of sodium chloride. At 600°C, the crystallites of zinc sulfide have grown together considerably in both cases, and, at 700°C, perfectly grown crystallites were observed with 2 wt. % of sodium chloride. But without flux, the rapid crystal growth is seen at temperatures between 800 and 900°C. However, the difference between the two cases is not only in the speed of crystal growth, but also in some other aspects of growing processes. Considerations on the later aspects are given below.

For the modes of crystal growth of such sulfides, two processes are mainly considered; the one, through the screw dislocation and the other, the surface nucleation[5].

The zinc sulfide molecule, which is adsorbed on the step of the crystal, diffuses towards the kink and forms a part of the crystal lattice, pushing the step out and making the crystal larger. The diffusion length, l_d, of zinc sulfide is given by

$$l_d = \sqrt{D\tau}$$

where D is the diffusion constant and τ is the lifetime of the molecule adsorbed on the surface.

By the addition of 2 wt. % of sodium chloride the diffusion is made more active, and D becomes larger. And, through the interaction with the flux, there will be more possibilities of forming kinks at the surface of crystals, and the mean distance, l_k, between kinks will become smaller. Hence, the relationship

$$l_d \gg l_k$$

will be satisfied easily and the growth of the steps at crystal surfaces will become independent of the crystal symmetry, resulting in the circular step-wise crystals. Such cases are given in Fig. 2a; one for the sample fired at 700°C and another for that fired at 1000°C. Without flux, the diffusion of zinc sulfide molecules along the crystal surfaces is not active, and D becomes smaller. Also, the kinks at the surfaces are not formed so easily, and l_k becomes larger.

Hence, the relationship, $l_d \gg l_k$, is no longer satisfied, resulting in the considerable influence of crystal symmetries on the growth of steps at the surfaces and the anisotropic crystal growth. Some examples are given in Fig. 2b. For the firing at temperatures above 900°C, the straight step, perpendicular to the direction of crystal growth, is seen clearly. At 1100°C, the α-form crystal of zinc sulfide is observed, especially along (0001) crystal surface, which is developed as pyramids.

Relationship between the Firing Condition and the Diameter of Crystals.—The half-peak breadth of the X-ray diffraction pattern was corrected for the characteristic width of the instrument, and the crystal sizes of various zinc sulfide phosphors were obtained by using Eq. 1.

The results are given in Fig. 3. In this diagram, the solid line shows the diameter of crystals without flux and the dotted line shows that with 2 wt. % of sodium chloride as flux. For both cases, up to 400°C, little crystal growth is observed and no difference can be seen compared with the material before firing. At about 500°C, the crystal growth begins and, at 600°C, it becomes extremely rapid. When the flux is added, the growth, at temperatures around 600°C, is especially remarkable. Those results show a rather good correspondence with the behaviors of crystal growth shown in Fig. 2.

Comparison between the measured crystal diameters obtained through the X-ray diffraction method and the electron microscope is made below.

In Fig. 2b, the picture of the sample fired, without flux, at 800°C shows that the diameter of the crystal agrees with that obtained by X-ray diffraction which

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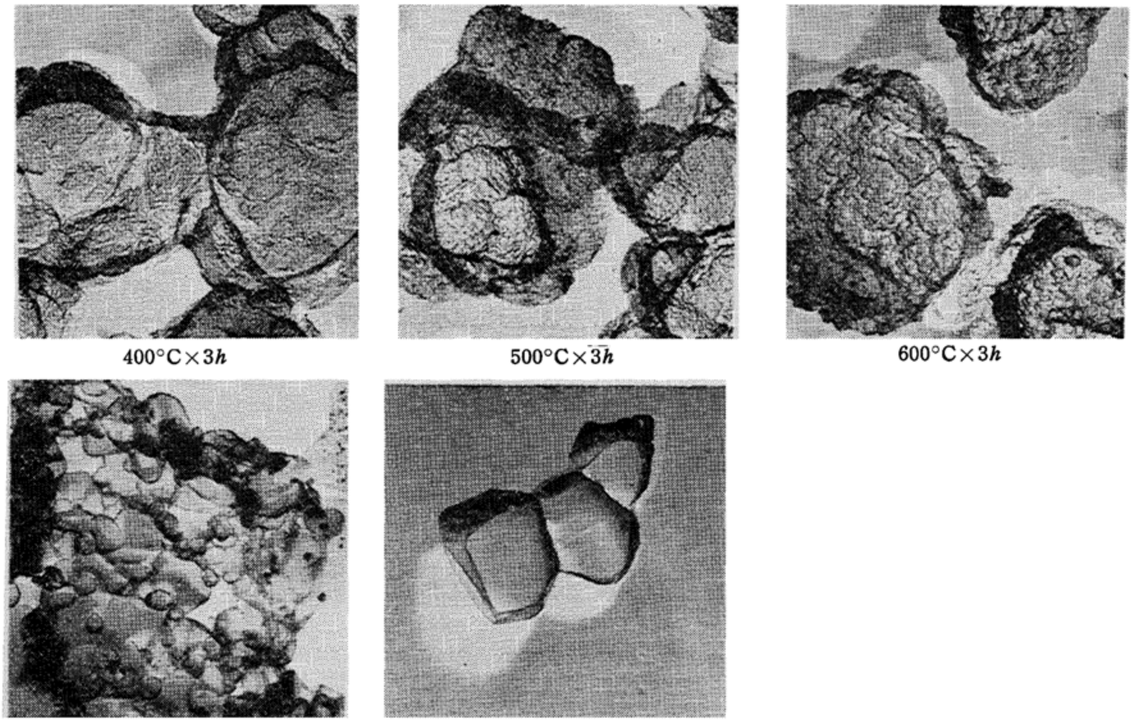
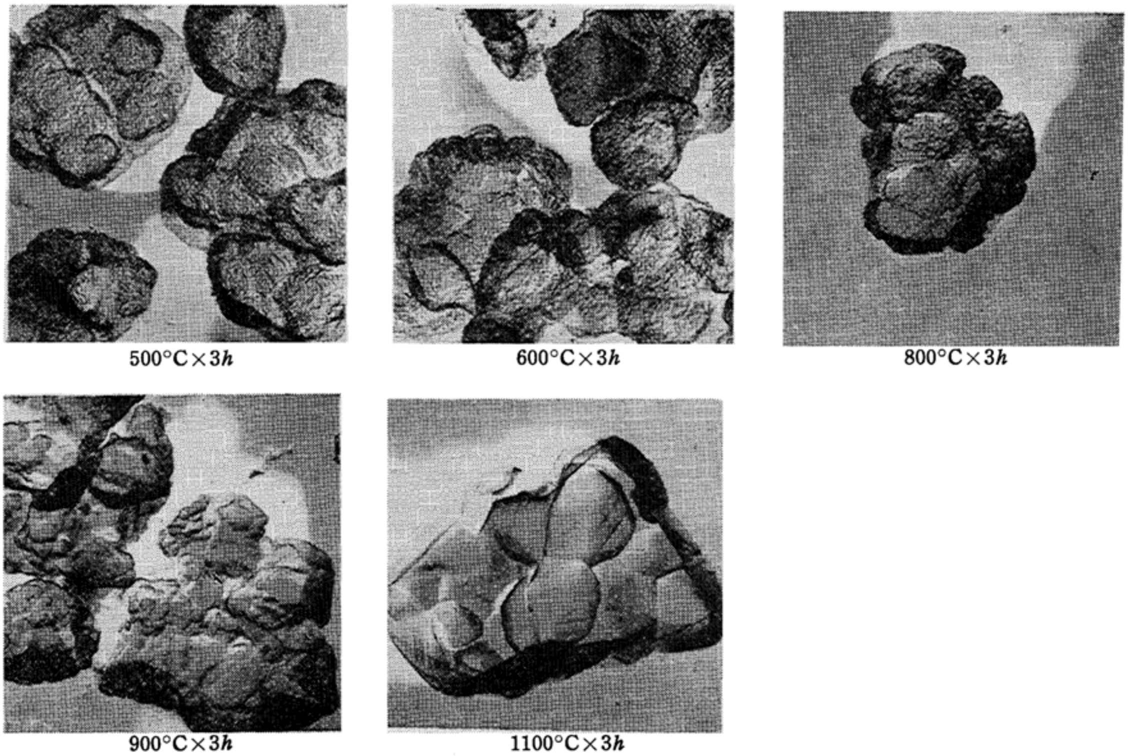
[5] D. C. Reynolds and L. C. Greene, *J. Appl. Phys.*, **29**, 559 (1958).



400°C×3*h* 500°C×3*h* 600°C×3*h*

700°C×3*h* 1000°C×3*h*

Fig. 2a. ZnS: Ag phosphor (with added 2 wt. % NaCl as flux).
Electron micrograph×5,000



500°C×3*h* 600°C×3*h* 800°C×3*h*

900°C×3*h* 1100°C×3*h*

Fig. 2b. ZnS: Ag phosphor (without flux).
Electron micrograph×5,000

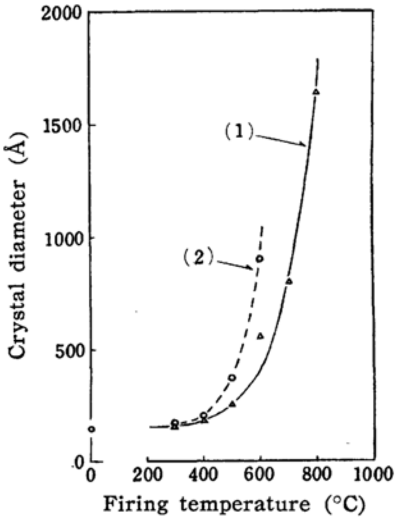


Fig. 3. Relationship between the firing temperature and the diameter of crystals;
(1) without flux, (2) with added 2 wt. % NaCl as flux.

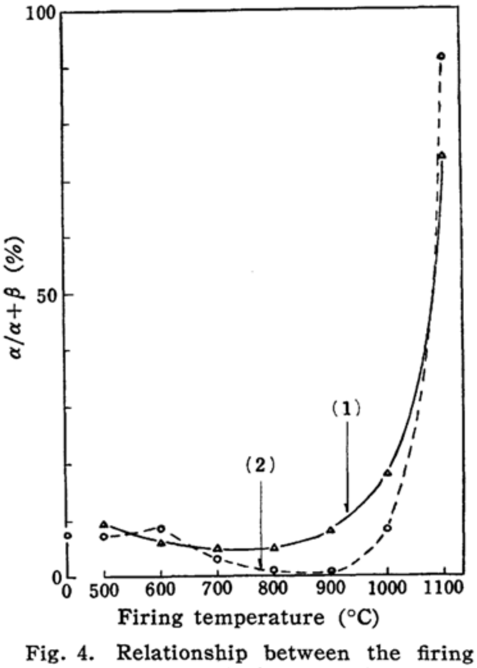


Fig. 4. Relationship between the firing temperature and the crystal form of ZnS: Ag phosphor;
(1) without flux, (2) with 2 wt.% NaCl as flux.

is about 0.2 μ. This is also true for the sample fired by 600°C. However, for the sample fired at 600°C with flux, as shown in Fig. 2a, the diameter is 0.1 μ from X-ray diffraction and is 0.3∼0.4 μ from the electron microscope experiment. The disagreement is probably due to the growth of thin plate-like crystals under this particular condition.

Relationship between the Firing Temperature and the Crystal Forms.—The transition of the crystal forms of zinc sulfide takes place at about 1020°C⁶⁾. It is known that, below 1050°C, the β-form is stable and, above 1100°C, the hexagonal α-form is stable⁷⁾. However, from our experiments the situation seems to be a little more complicated.

In Fig. 4, the ratio of the amount of α-form to that of β-form in crystal was given, which was obtained by comparing the strengths of the strongest diffraction patterns, $10\bar{1}0$, 0002 and $10\bar{1}1$ of α-form, with that of β-form, 111. The measurements were made for zinc sulfide phosphors fired for three hours at various temperatures ranging from 500°C to 1100°C, with the raw material containing 8% of α-form.

As is seen in Fig. 4, the amount of α-from in the material without flux decreases as the firing temperature increases, and the transition from α-from to β-form is observed. However, at about 900°C, the content of α-form begins to increase again and becomes 18% at 1000°C and 73% at 1100°C. For the sample with the flux of 2 wt. % of sodium chloride, the α-form begins to decrease at about 700°C. Almost all of the α-form changes into β-form at 800°C, and the amount of α-form becomes nearly equal to zero. As the temperature increases, the α-form appears again at about 1000°C and more than 90% of α-form is found at 1100°C.

The above results show the fact that the transition velocity of crystal forms is much influenced by the existence of the flux and that the transition, α-form ↔ β-form, becomes easier with 2 wt. % of sodium chloride, but is difficult without it.

The increase of α-form is observed at 600°C for the sample with 2 wt. % of sodium chloride, but the same phenomenon appears in the cases with fluxes other than sodium chloride. The explanation of this is not given yet, and the author is planning to check whether it originates from the existence of some meta-stable state which promotes the formation of α-state, because of some critical temperature to stimulate the sudden crystallization, or whether it is due to the existence of a

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6) E. T. Allen and J. L. Crenshaw, *Am. J. Science*, **34**, 341 (1912).

7) R. H. Bube, *J. Chem. Phys.*, **20**, 708 (1952).

state where the α-form is essentially stable.

Influence of Time of Firing.—Fig. 5 gives the relationships among the time of firing, the crystal forms and the intensity of luminescence. At firing temperature of 1000°C, there is not much difference in crystal forms between the sample fired for ten minutes and that fired for three hours, and the former shows a considerably better luminescence intensity. This fact implies that the crystallization has taken place during the firing for a short period. At firing temperature of 800°C, the amount of α-form decreases with the time of firing and the greater part of the crystals are of β-form after firing for thirty minutes. The intensity of luminescence shows a similar tendency and attains the limiting value in thirty minutes. Those facts imply that the complete change from α-form into β-form is finished within ten minutes when fired at 1000°C and after thirty minutes when fired at 800°C, both with 2 wt.% of sodium chloride as flux.

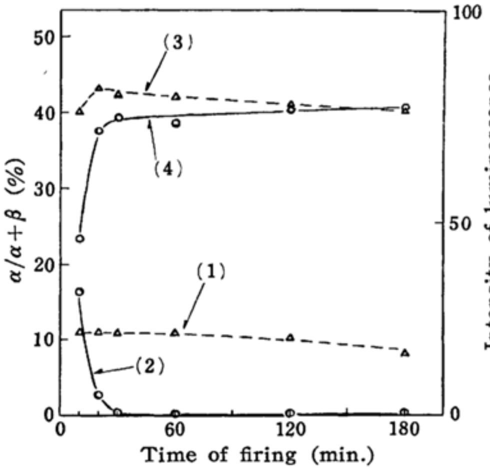

Fig. 5. Relationships among the time of firing, the crystal forms and the intensity of luminescence.
(ZnS: Ag added 2 wt. % NaCl as flux.)
(1) Content of α-form (fired at 1000°C).
(2) Content of α-form (fired at 800°C).
(3) Intensity of luminescence (fired at 1000°C; 12 kV. C.R. excitation).
(4) Intensity of luminescence (fired at 800°C; 12 kV. C.R. excitation).

Summary

(1) The zinc sulfide, before firing, is a large aggregate of crystallites with the crystal diameter of about 150 Å and contains about 8% of α-form.

(2) The crystal growth of zinc sulfide phosphor takes place at about 500°C regardless of whether there is flux or not, but the rate of the growth is much affected by the flux. Without flux, the crystal grows as step-wise piled layers, but, with flux, it grows isotropically showing no influence from the crystal symmetry. Concerning the above difference, there has been discussion, taking into account the density of kinks at the stepwise surfaces of crystals and the change of diffusion constant of zinc sulfide molecules adsorbed at the surfaces.

(3) The transition, α-form ↔ β-form, of zinc sulfide phosphor is rather easy, but becomes difficult without flux. Also, the transition is completed in thirty minutes of firing at 800°C with the flux of 2 wt.% of sodium chloride, but it is completed within ten minutes of firing at 1000°C.

(4) It is probable that there is a metastable state of α-form at about 600°C, but it requires further consideration.

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