研 究

Kinetic Analyses of the Formation of Solid
Solution in the ZnS-CdS System.*

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The formation of solid solution in the ZnS-CdS system, one of the simplest reaction which involves two or more phases, has been studied by X-ray diffraction and by the observation of ZnS or CdS phosphor in some stages of the solid solution formation.

Values of activation energy obtained from the height decrease of diffraction lines ZnS (102) are 35 kcal/mol for ZnS : CdS = 1 : 1, and 41 kcal/mol for 7 : 3. The formation process was observed by using the phosphor as one of the starting materials. It was assumed that cadmium sulfide sublimates on the first stage of solid solution formation especially when cadmium sulfide is a form of fine powder. The presence of cadmium sulfide on the outer surface of zinc sulfide was observed by EPMA, these results supporting the above assumption. Thereafter the mutual diffusion proceeded to form solid solution. The result of emission measurement coincided with those by EPMA.

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Introduction

In the previous work¹⁾ it was found that the solid solution between NaCl and KCl is formed at 300–400°C and the activation energy for this formation is estimated to be 48 kcal/mol. It was also found that the formation of solid solution between CaO and SrO proceeded between 1050°C and 1400°C with the activation energy of about 60 kcal/mol. In these cases other phenomena seem to occur than the mutual diffusion, especially in an early stage of formation. Meanwhile it was found²⁾ that the solid solution of CaO-SrO system has better anti-weathering property than calcium oxide.

In this paper it was reported that the solid solution of ZnS-CdS system is formed at 800–900°C, the process being discussed briefly.

Experimental

Starting Materials: Luminescent pure zinc sulfide and cadmium sulfide are used as starting materials, being obtained from a factory of luminescent materials. Their crystal structures were cubic forms. By the heat-treatment at 1100°C for 2 hrs. zinc sulfide transformed to hexagonal structure, while cadmium sulfide did by that at 750°C for 40 mins. When the phosphors were used as starting materials, they were prepared as follows. Zinc sulfide was mixed with silver salt and sodium chloride solutions, then, after drying, the mixture of zinc sulfide, silver salt and sodium chloride was fired in air at 1100°C for 2 hrs.. The amount of silver was 10⁻² mol% of zinc sulfide. Almost the same procedure was applied to cadmium sulfide, except that the firing temperature was 800°C.

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X-ray Diffraction Analysis: The formation process of solid solution was observed by X-ray diffraction method for the samples which were obtained by heat-treatment of the mixtures of starting materials under various conditions. X-ray apparatus was operated at 30–40 KV and 50–80 mA, the anti-cathode being copper. The height change of X-ray diffraction line (102) was observed, and the rate of solid solution formation was determined from this change by the procedure described in previous report¹⁾.

Electron Probe Microanalysis: The process of solid solution formation was observed also by EPMA for the same samples as were used for X-ray diffraction analysis. The apparatus was operated at 10–20 KV and 0.1–10 nA.

Measurement of Emission of Phosphors: When the phosphors were used as starting materials, the shift of peak wavelength of emission spectra was observed with the progress of solid solution formation. The emission spectra were measured under ultraviolet excitation by fluorescent spectrophotometer, its details being described elsewhere.

Experimental Results

Fig. 1 shows the change of X-ray diffraction pattern with heating the mixture of starting materials, the upper series being for cubic form and the lower for hexagonal ones, respectively. The rate of solid solution formation was higher in the case of cubic form than that of hexagonal ones. That is, when started from cubic sulfides, the solid solution was formed by heating at 750°C for 40 mins., while about 35% of zinc sulfide remained by heating under the same conditions when both sulfides were hexagonal forms. The heating of the cubic sulfides at 850°C for 20 mins. resulted in the formation of well-crystallized solid solution, while in the case of the hexagonal sulfides it took 50 mins. to observe the formation of the solid solution, its diffraction lines being broad.

Fig. 2 shows the first-order plot of conversion of hexagonal zinc sulfide to the solid solution between zinc and cadmium sulfides. The numbers in the coordinate mean the common logarithm of percentage of residual amount against starting one of zinc sulfide, these amount being estimated from the heights of diffraction lines (102). Fig. 3 shows the Arrhenius plot for the formation of the solid solution where values "k" were obtained from Fig. 2. Values of activation energy thus obtained are 35 kcal/mol for ZnS : CdS = 1 : 1, and 41 kcal/mol for 7 : 3.

The results of EPMA are shown in Photos. 1–6 and Figs. 4–6. From these results it was ascertained that the layer of cadmium sulfide covers zinc sulfide crystals on the beginning of heating when cadmium sulfide used was powder.

Fig. 7 and Table 1 show the results of measurement of emission from phosphors used as

Fig. 1 Change of X-ray diffraction patterns of ZnS-CdS system during the formation of solid solution.

Fig. 2 First-order plot of conversion of hexagonal zinc sulfide to the solid solution.

Fig. 3 Arrhenius plot for the formation of (Zn, Cd)S solid solution.

Table 1 The change of peak values of emission spectra during the formation of solid solution.

ZnS	CdS	Before firing	10 min.	30 min.	50 min.
Phosphor	Powder	440	635	615	605
Powder	Phosphor	700	530	560	565
Phosphor	Phosphor	440+700	610	590	585

starting materials. Fig. 7 shows the change of spectral distribution of emission from zinc sulfide phosphor which was mixed with cadmium sulfide powder, the mixture being heated at 850°C or higher temperature (those curves were plotted by dotted lines) for varying time. The curve denoted by 1100×20, which means the firing at 1100°C for 20 minutes, corresponds to the emission curve of $(\text{Zn}_{0.5}, \text{Cd}_{0.5})\text{S} : \text{Ag}$. Peak wavelength changed with the heating time from 440 nm suddenly to 650 nm, then moved to the short wavelength slowly. Such results are shown in Table 1 and the shift of peak wavelength is observed with the heating time.

Discussion

Hedvall³⁾ proposed that the reaction in the solid state would be divided into two groups, one being the reaction which starts from one phase, and other from two or more phases. In the latter reactions the reactions between two solids are very important from the industrial standpoint, however they are so complex, that it is difficult to elucidate their reaction mechanism.

The simplest one of the reactions which start from two or more phases would be the formation of solid solution and in the previous report¹⁾ the processes of this formation in the NaCl-KCl and CaO-SrO systems have been analysed by X-ray diffraction method. In the NaCl-KCl system the formation proceeds in two phases during all stages of the reaction. The rate is so high that it was difficult to analyse the kinetics of the respective reaction. The activation energy of overall reaction of the formation of solid solution is estimated to be 48 kcal/mol for the product of 1 : 1 molar ratio, and a little higher for 0.65 : 0.35 product. Meanwhile, in the system of CaO-SrO the formation proceeds in two or more phases, and it was possible to determine the value of the activation energy from the decrease of the amount of strontium oxide. The value thus obtained by means of high

temperature X-ray diffractometry was estimated to be 61 kcal/mol. From the experimental results of this research, it was clarified that the formation of solid solution proceeded by the mutual diffusion of the cations. However, the rate of formation depends on the characteristics of starting reactants as well as on the condition of the reaction.

It was published⁴⁾ in the case of solid solution of ZnS-CdS system that this solid solution obeys to Vegard's law, this fact being ascertained by the relation between lattice constant and composition. In Fig. 1 it was found that the decrease of height of zinc sulfide diffraction lines as well as the distortion of line profile of cadmium sulfide diffraction lines occurs in the process of formation of these solid solutions. As it is possible to assume that the amount of product would be proportional to the decrease of that of starting material, the rate constant "k" was calculated from Fig. 2. From Fig. 2 it is confirmed that the formation of these solid solutions proceeded according to the first-order equation. Same result was obtained in the case of CaO-SrO system¹⁾. From the Arrhenius plot shown in Fig. 3 it is possible to estimate the activation energy for the formation of this solid solution to be 35 kcal/mol or 41 kcal/mol. These values are a little smaller than NaCl-KCl or CaO-SrO system. In Fig. 3 open circles are obtained from the decrease of zinc sulfide diffraction line (101), while black points obtained from diffraction line (102), and they coincide well each other.

It is possible to clarify the formation process in detail by using the phosphor as one of the starting materials. As seen in Photos. 1-6, zinc sulfide crystal grows up during phosphor preparation⁵⁾ and its diameter is about 10 μ , while the diameter of cadmium sulfide phosphor is about 20 μ . From Fig. 4 and Photos. 1-3 it is ascertained that cadmium sulfide covers the outer surface of zinc sulfide phosphors in the early stage of solid solution formation and cadmium diffuses into phosphor crystal with the lapse of time. On the contrary such a process does not occur in the case of mixture of cadmium sulfide phosphor and zinc sulfide powder as shown in Fig. 5 and Photos. 4-6. In this case zinc and cadmium diffuse mutually to form solid solution. In the case of mixture of two kinds of phosphors the result shown in Fig. 6 is almost the same as the latter. The phenomenon in which cadmium sulfide covers the surface of zinc sulfide crystal would be initiated by the sublimation of

Fig. 4 Line analysis of ZnS crystal. The crystal was mixed with CdS powder and the mixture was heated at 850°C for 10, 20 and 50 min..

Fig. 5 Line analysis of CdS crystal. The crystal was mixed with ZnS powder and the mixture was heated at 850°C for 10, 30 and 120 min..

Photo. 1-3. EPMA Photograph.
ZnS crystal and CdS powder.
1 は 850°C 10 min.
2 は 850°C 20 min.
3 は 850°C 50 min.
×2000

Fig. 6 Line analysis of ZnS and CdS crystals.
Their mixture was heated at 850°C for 20 and 100 min..

Fig. 7 The change of emission spectra. 850×10 means the firing at 850°C for 10 min.. The coordinate of dotted curves is three times of that of solid ones.

cadmium sulfide as the sublimation temperature of cadmium sulfide is lower than that of zinc sulfide. Especially, when cadmium has a form of fine powder, the amount of sublimation would be larger than the case of large crystal.

The results shown in Fig. 7 and Table 1 support the explanation described above. It is well known that ultraviolet light penetrates into zinc or cadmium sulfide till the depth of $0.2\ \mu$, therefore the emission under ultraviolet excitation is caused by the electronic process in the neighbourhood of sulfide surface. By heating the mixture of cadmium sulfide powder and zinc sulfide phosphors whose emission has a peak at 440 nm, the emission peak changed suddenly to 650 nm, which corresponds the peak wavelength of CdS : Ag emission. This result would be explained by the fact that cadmium sulfide covers the outer surface of zinc sulfide phosphors as clarified in Fig. 4 and Photos. 1-3. Meanwhile it is explicit that silver begins to diffuse at the temperature as low as 300°C. By continuing to heat the phosphor at 850°C zinc diffuses into cadmium sulfide layer to shift the spectral distribution of emission to the short wavelength. When cadmium sulfide phosphors are used as a starting materials, the amount of sublimation decreases and the shift of emission peak is not so large as the case of cadmium sulfide powder, as shown in Table 1.

Conclusion

The simplest one of the solid state reactions which start from two or more phases would be the

formation of solid solution and this formation in the ZnS-CdS system have been kinetically analysed.

It was found by X-ray diffraction method that values of activation energy obtained from the height decrease of diffraction lines ZnS (102) are 35 kcal/mol for ZnS : CdS=1 : 1, and 41 kcal/mol for 7 : 3. These values are a little smaller than NaCl-KCl or CaO-SrO system.

The formation process was observed by using the zinc sulfide or cadmium sulfide phosphor as one of the starting materials. It was found by EPMA and the observation of emission spectra that cadmium sulfide covers the outer surface in early stage of solid solution formation. It was assumed that cadmium sulfide would sublime on the first stage of the formation especially when cadmium sulfide was fine powder. Thereafter the mutual diffusion proceeded to form solid solution.

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会 告

基礎講座「これからの生産技術」

主 催：精機学会関西支部

期 日：昭和59年11月29日(木)30日(金)，12月6日(木)7日(金)

会 場：大阪科学技術センター4階(404室)(大阪市西区靱1-8-4 電話06-443-5321)

次 第：

11月29日(木) 9:00~16:40

1. 開会の辞 岩田 一明
2. 材料学の基礎 (大阪大・工) 山田 朝治
3. 加工のための材料学 (大阪大・工) 川辺 秀昭
4. 固体の表面と検査法 (神戸大・工) 金持 徹
5. 新しい表面の制御法 (大阪大・工) 梅野 正隆

11月30日(金) 9:00~16:30

6. 精密塑性加工 (大阪府大・工) 朝倉 健二
7. 精密機械加工と加工面 (大阪大・工) 井川 直哉
8. 超精密加工 (大阪大・工) 森 勇蔵
9. 電気加工とその特質 (大阪大・工) 木本 康雄

12月6日(木) 9:00~16:30

10. 工作機械の要素技術(新日本工機株) 東本 暁美

11. 工作機械の動剛性と振動

(神戸大・工) 森脇 俊道

12. 工作精度に及ぼす熱の影響

(京都大・工) 垣野 義昭

13. 加工ふん囲気

(大阪大・工) 玉村謙太郎

12月7日(金) 9:00~16:40

14. 計測制御系におけるセンサー

(神戸大・工) 松本 治弥

15. マイクロコンピュータの計測への応用

(大阪府大・工) 川口 格

16. 生産のシステム化 (神戸大・工) 岩田 一明

17. 生産における経済性 (大阪府大・工) 橋本 文雄

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