

DISCUSSION

Iida, Y.: I want to ask you two questions about experimental procedures. (1) Was the measurement of the optical absorption made parallel or perpendicular to the C axis? (2) Did you make some reducing heat treatment of crystals, or did you use the boules as grown?

Maruyama, T.: (1) We performed the optical absorption measurements perpendicular to C axis. (2) About the heat treatment, we did not make it. And we are not sure whether the supplier of the crystal made the heat treatment or not.

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Luminescence of Doped Silver Chloride with Divalent Anions and Cations

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Several luminescence maxima of doped silver chloride crystals are obtained spectroscopically. Some of the peaks are common to more than two impurities. The peak at 520 millimicron appears with some divalent anion impurities. The peak at 545 millimicron does with some divalent cation impurities, and peaks at 485 millimicron do with both of the impurities.

Infrared quenching of the luminescence and photoconductivity at 1000c/s is measured simultaneously. It is inferred by calculation that the peaks at 485 millimicron and 520 millimicron are hole type luminescence and the peak at 545 millimicron electron type one.

Those peaks are attributed to the defects proper to silver chloride crystals which can be introduced by the impurities, *i.e.* silver vacancies are responsible for the peak at 545 millimicron and interstitial silver ions or halogen vacancies for the peak at 520 millimicron. As to the peak at 620 millimicron thermally decomposed silver atoms are responsible, and the peak at 485 millimicron may be due to the electron shallow traps accompanying other defects such as dislocations.

Doped crystals of silver chloride are obtained by Kyropoulos method with impurities of 10^{-5} – 10^{-3} in mol ratio of Ag_2O , Ag_2S , Ag_2Se , Ag_2Te , CdCl_2 , CaCl_2 , PbCl_2 and especially FeCl_3 added into the melt respectively. Many other impurities are also examined. Luminescence of these crystals is measured spectroscopically at temperatures from liquid nitrogen to room temperature. Infrared quenching and thermal quenching of the luminescence are obtained. Photoconductivity of the crystals at 1000 c/s is measured simultaneously with the luminescence, and the both are recorded. A brief result is shown in Fig. 1.

Since most of the intensity maxima of the luminescence spectra are common to more than two impurities, these peaks are attributed to defects proper to silver chloride instead of proper to impurities. For example, a peak at 485 millimicron which appears in the purest samples also appears in the crystals containing O, Se, Cd, Pb and Fe. A peak at 545 millimicron appears in the crystals containing Cd, Ca and Pb, and that at 520 millimicron does as to S, Se and Te. A peak at 620 millimicron (remarkably suppressed by the photomultiplier characteristics on recording paper for longer wave length than about 580 millimicron) appears in the crystals containing O, Se and Fe.

Anion	mol-ratio	μm	Luminescence	Photo-current
Ag ₂ O	1×10^{-4}	620	620	[Graph]
	5×10^{-4}	620		
Anneal 620, 485				
Ag ₂ Se	1×10^{-4}	620, 485	620	[Graph]
	5×10^{-4}			
Se (Metal)	1×10^{-4}	520		
	2.5×10^{-4}	(620, 485)		
Ag ₂ Te	1×10^{-4}	520	520	[Graph]
	0.5×10^{-4}	510		
Ag ₂ S	1×10^{-4}	520	520	[Graph]
	0.5×10^{-4}	520		
Cation	mol-ratio	μm	Luminescence	Photo-current
Pure		485	485	[Graph]
CdCl ₂	1×10^{-4}	545	545	[Graph]
		(485)		
CaCl ₂	1×10^{-4}	545	545	[Graph]
FeCl ₃	0.5×10^{-4}	485		
		(545)		
		620		

Fig. 1. Brief summary of the experimental results. First column shows the sort of impurities doped in silver chloride crystals. Second column shows the impurity concentrations. Third column shows the luminescence peaks obtained. Fourth and fifth columns show the infrared quenching of the luminescence and photoconductivity which undergo to be turned ultraviolet on, infrared on, infrared off, ultraviolet off, and infrared on in turn.

The peak at 545 millimicron increases with the amount of Cd ions added, and is suppressed

by co-addition of S ions. (Fig. 2) Therefore it is reasonable that the peak at 545 millimicron of luminescence depends on the amount of silver vacancies.

The peak at 520 millimicron increases with amounts of S ions and Te ions, and disappears by print out, (Fig. 3), though in the case of Te ions it has some submaxima. While the peak at 620 millimicron which once appeared disappears easily with increased amounts of O ions or Se ions indicating that the luminescence center is unstable.

It is therefore probable that the peak at 620 millimicron is due to aggregates of a few silver atoms produced by thermal decomposition of silver chloride, and that at 520 millimicron is related to interstitial silver ions or chlorine vacancies. As to the peak at 485 millimicron which is the shortest wavelength one we have obtained, it may be due to electron shallow traps associated with some defects such as dislocations.

The infrared quenching of these peaks is as follows. The peak at 485 millimicron is remarkably quenched indifferent to increase or decrease of photoconductivity by samples. That at 545 millimicron is enhanced or barely decreases together with the photoconductivity or with increasing photoconductivity. That at 520 millimicron often accompanies stimulations and then is remarkably quenched with increasing or decreasing photoconductivity. That at 620 millimicron just decreases with photoconductivity.

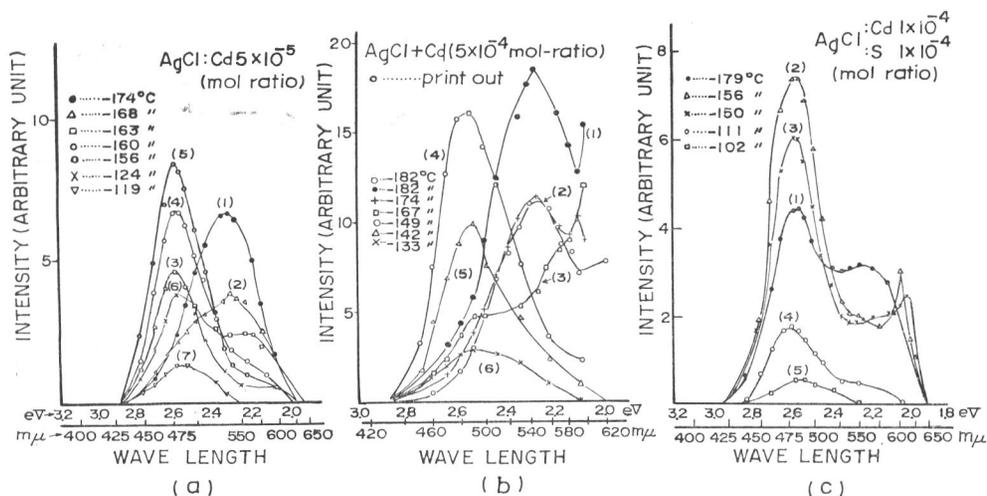


Fig. 2. Changes of luminescence peaks of silver chloride crystals by changing Cd⁺⁺ ion concentration and S⁻ ion co-addition.

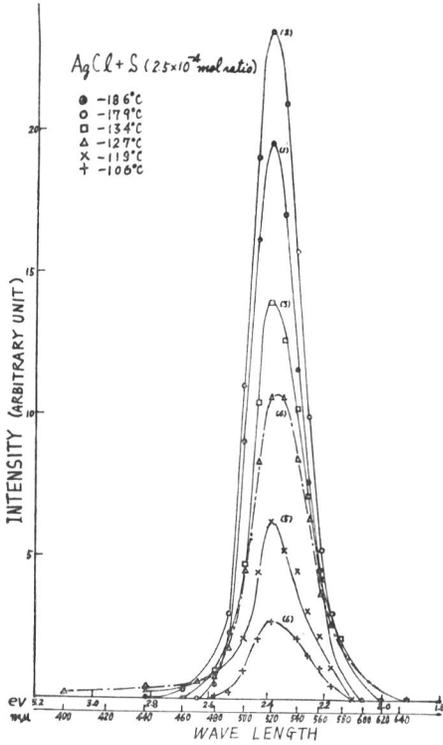


Fig. 3. The luminescence peak of the silver chloride crystal with S^{--} ions.

The above results can be explained based upon a model which contains indefinite trap levels. Let us take following symbols. (Fig. 4) L_n : Intensity of luminescence emitted by trapping of electrons. L_p : That of holes. V : Intensity of stimulating light. R : Intensity of auxiliary infrared light. N : Number of electron traps which emit the luminescence by recombination with holes. P : That of hole traps like above. γ : Excitation rate of free electrons and free holes by light. γ_n : Excitation rate of trapping electrons to conduction band by infrared light. γ_p : That of trapping holes like above. α_n, α_p : Probabili-

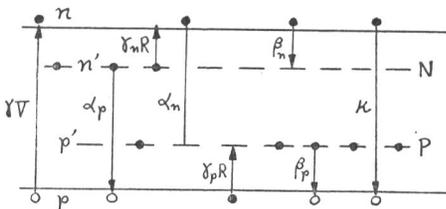


Fig. 4. A hypothetical band model of the silver chloride crystals which show the luminescence and photoconductivity with their infrared quenchings.

ties of recombinations of trapped carriers by electrons and holes. β_n, β_p : Probabilities of electron and hole trappings. n : Number of free electrons which is proportional to the photoconductivity. p : Number of free holes. n', p' : Numbers of trapped electrons and holes. κ : Probability of direct recombinations.

We assume that the Fermi level is situated in the middle of the forbidden gap, and $\alpha_n, \alpha_p, \beta_n, \beta_p$ and γ_n, γ_p nearly common in any traps. Then the recombination at any killer centers is implied as follows. When the killer centers are indifferent to the infrared light, κ contains them. When they can be excited by the infrared light, L_n or L_p is abbreviated by some factors. Thermal excitation of trapped carriers is neglected.

In equilibrium conditions,

$$L_n = \alpha_n p' n, \quad L_p = \alpha_p n' p, \quad n + n' = p + p'$$

$$\frac{dn}{dt} = \gamma V - \beta_n (N - n') n - \alpha_n p' n - \kappa p n + \gamma_n n' R = 0,$$

$$\frac{dn'}{dt} = \beta_n (N - n') n - \gamma_n n' R - \alpha_p n' p = 0,$$

$$\frac{dp'}{dt} = \beta_p (P - p') p - \gamma_p p' R - \alpha_n p' n = 0.$$

If $N \gg n'$, and $P \gg p'$,

$$\frac{\alpha_n n (\beta_p P + \kappa n)^2}{\beta_p P} \left(\frac{dL_n}{dR} \right)_{R=0} = (\gamma V - \beta_n N n) \times (\alpha_n n \gamma_n + \beta_p P \gamma_n - \kappa n \gamma_p) - (\beta_p P \alpha_n n + \kappa \alpha_n n^2) \gamma_n n - \{\beta_n N (\beta_p P \alpha_n n + \kappa \alpha_n n^2) + (\gamma V - \beta_n N n) \kappa \alpha_n n\} \frac{dn}{dR},$$

$$\frac{\alpha_p (\gamma V - \beta_n N n)}{\beta_n N} \left(\frac{dL_p}{dR} \right)_{R=0} = -(\beta_p P n + \kappa n^2) \gamma_n + \alpha_p (\gamma V - 2\beta_n N n) \frac{dn}{dR}.$$

Since $(\gamma V - \beta_n N n)$ is generally positive, the sign of dL/dR is determined by the terms in right side. If the samples which show small changes in photoconductivity by infrared light are used, in general L_n increases and L_p decreases but when κ is large L_n also decreases. And in the case of large κ , the luminescence will be faint. Therefore the peak at 620 millimicron which shows weak luminescence and decreases by infrared light is undeterminable in its nature. As to other peaks, it is plausible that the peak at 485 millimicron is L_p , that at 520 millimicron is also L_p and that at 545 millimicron is L_n .

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Reference

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