

〈Original〉 Optical Bleaching Behaviour of Neutron Irradiated KCl Single Crystal

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Abstract

Hydroxide free KCl single crystals are prepared and doped with small amounts of KSH or K_2S . The samples are subjected to neutron irradiations while keeping them under the condition of liquid nitrogen temperature in the dark. The irradiated ones are then bleached by using a U.V. lamp and analysed as four different kinds of chemical forms in ^{35}S whose valence states are -2 , 0 , $+4$ and $+6$.

It seems that the sulphide fraction of ^{35}S in doped crystals is higher than that in pure crystals. In addition, two distinct patterns in bleaching process up to 30 minutes results in a fast increase in the sulphide fraction and then the sulphide levels off to a slowly increasing region upon prolonged bleaching.

A detailed description on the distribution of ^{35}S valence states will be made in connection with point defects in the crystals.

요 약

염화카리움 단결정중 수산화물을 제거하고 이를 극미량의 음이온 불순물을 가하여 결정내에 점결함을 형성시키는 전 처리를 하였다.

이들 시료를 빛이 차단된 상태에서 액체질소 온도에서 원자로에 조사하였고 조사된 시료를 자외선으로 쬔다음 4가지 산화상태 즉 -2 , 0 , $+4$, $+6$ 가의 ^{35}S 를 화학적으로 상호분리하여 방사능을 측정하였다.

음이온 불순물로 처리된 시료는 순수한 결정에 비하여 낮은 산화상태 (-2 가)의 ^{35}S 더 많이 생성되었고, 음이온 불순물로 처리된 시료의 순수한 결정 모두를 자외선으로 쬔었을 때 30분까지는 -2 가의 ^{35}S 가 급격히 증가함을 알았다.

1. Introduction

The chemical effects of the ^{35}Cl (n,p) ^{35}S nuclear transformation has been studied by a number of authors¹⁻¹².

It is well known that radiation damage in ionic crystals results in the formation of colour centres where electrons or holes are trapped. It is also reported that the initial distributions

of the ^{35}S fractions depend upon the irradiation conditions and the pre-or post-treatment of the crystals.

Even in the pure alkali, the ^{35}S atom which has lost its initial recoil energy can be regarded as an impurity atom in the host lattice.

Adloff and Meyer⁴ have published that the ^{35}S exists in the irradiated chlorides in four

distinguishable forms, and Maddock and Kasrai¹⁰⁾ have analysed into four species such as S^- , $SCN^-(S^0)$, SO_3^- and SO_4^- .

In the present work ^{35}S atoms have been prepared hydroxide free KCl single crystals, some of which were doped with KSH or K_2S in an attempt to investigate the effects of crystalline purity and perfection upon photoannealing as determined by distribution of ^{35}S in the various valence states.

2. Experimental

1) Materials and Neutron Irradiation

Large single crystals of potassium chloride (Koch-Light) were used. All reagents used in chemical procedures were of A. R. grade.

Samples were outgassed at 2×10^{-5} mmHg and wrapped with Al foil. Irradiations were carried out in the liquid nitrogen cryostat of HERALD nuclear reactor at Aldermaston, England for 3 hours, in which a neutron flux was known to be $10^{13}n/cm^2/sec$. The fast neutron flux was varied from 1 to $3 \times 10^{12}/cm^2/sec$. After irradiation samples were kept in liquid nitrogen prior to chemical analysis.

2) Treatment of KCl Single Crystals by HCl

To remove OH^- in $KCl^{13)}$, a silica boat which had been loaded with potassium chloride single crystals was put into silica tube, 44cm long and 2.5cm wide, of which both ends were terminated by B 24 joints. The tube led into a tubular heater, while the other end was connected to a vacuum line.

The crystals were outgassed at 2×10^{-5} mmHg while the temperature was slowly raised to $450^\circ C$. The crystals were melted and kept under dry HCl for about 30 minutes.

The HCl gas above the sample was then replaced with dry nitrogen gas for a short period, and the tube was filled with these two gases alternately about thirty times.

The crystals were then cooled gradually to

room temperature in a nitrogen atmosphere, the average cooling rate being about $0.9^\circ C/min$.

3) Pre-treatment (Doping with KSH or K_2S) Two Methods were used for Doping

(1) Small amounts of dry KSH were added to some of the crystals in the dry box that were then sealed in a silica tube at 2×10^{-5} mmHg. The crystals were melted and regrown.

(2) Crystals containing small amounts of KSH or K_2S were heated at $20^\circ C$ below melting point for about 113 hours in the outgassed silica tubes. The anhydrous KSH¹⁴⁾ and K_2S ¹⁵⁾ were prepared and kept in the dry box.

After rinsing the crystals with absolute alcohol in the dry box, the amounts of SH^- or S^- in the doped crystals were estimated by spectrophotometry¹⁶⁾ which showed decreasing absorbance with increasing sulphur content as shown in Fig. 1.

4) Post-irradiation (Optical Bleaching)

The irradiated samples were warmed from liquid nitrogen temperature to room temperature for half an hour prior to bleaching them under a U. V. lamp. A medium pressure Hanover U. V. lamp was used and the distance from sample to light source was 13cm. Compressed air was blown to the sample to maintain a constant temperature.

A variation of the temperature during the bleaching was around $25^\circ C$. No optical filter was used.

5) Chemical Analysis and Counting

The irradiated samples were left at least 10 days in order that ^{42}K and ^{38}Cl might decay in liquid nitrogen dewar. They were dissolved under a safety red lamp.

Four kinds of chemical forms in ^{35}S were analysed, mainly using methods developed by Kasrai and Maddock¹⁰⁾. Because of the presence of ^{32}P impurity, however, the analysis method was slightly modified.

The ^{32}P impurity was separated as magnesium ammonium phosphate hexahydrate precipitate¹⁷⁾ and confirmed by half-life measurements.

An air oxidation effect was observed in sulphite and sulphide carrier solutions. To prevent air oxidation, the sulphite and sulphide carrier solutions were prepared in 5% mannitol¹⁸⁾ or glycerol¹⁹⁾.

To eliminate the ^{32}P in sulphate and sulphite fractions, the $\text{Ba}^{35}\text{SO}_4$ precipitate was dissolved in excess EDTA solution in concentrated ammonia and reprecipitated in hot acid medium.

Without the EDTA treatment, about 90% of radioactivity in sulphate and sulphite fractions was originated from ^{32}P in the worst case. After EDTA treatment the ^{32}P impurity was reduced to negligible amounts, only a few counts per minute.

Even for this amount, correction was made for the ^{32}P by counting twice with and without an Al absorber ($37\text{mg}/\text{cm}^2$). At least 5,000 counts were accumulated for all samples in order to get the statistically reliable result.

The density thickness was about $80\text{mg}/\text{cm}^2$ which is enough for stopping β -ray from ^{35}S .

3. Results

The results of estimating the dopant in the crystal spectrophotometry is shown in Fig. 1.

The optical bleaching behaviour of pure and doped crystals is shown in Table 1, 2, 3, and in Fig. 2.

The sulphide fraction of ^{35}S in doped crystals showed value higher than that of pure crystal and oxidised sulphur form of doped crystals was decreased gradually while that of pure crystals was showed rather irregular pattern upon U. V. photoannealing.

Two distinct stages were observed; a fast initial reduction process up to 30 minutes gives rise to a fast increase in the sulphide fraction and then the curve levels off to a slowly

Table 1. Optical Bleaching (pure KCl)

Exp. No.	Bleaching Time	^{35}S Distribution (%)			
		S^{2-}	SCN^-	SO_3^{2-}	SO_4^{2-}
1-25	0	63.8	33.7	1.7	0.8
1-22	5min	67.2	30.8	1.1	0.9
1-24	15min	72.6	25.6	0.9	0.9
1-27	30min	74.9	12.9	2.1	1.1
1-21	1hr	79.5	14.3	2.7	3.5
1-23	4hr	95.6	2.3	1.0	1.1
1-26	8hr	96.0	2.0	0.6	1.4

Table 2. Optical Bleaching (KSH doped KCl, $6.8 \times 10^{17} \text{SH}^-/\text{cc}$ of KCl)

Exp. No.	Bleaching Time	^{35}S Distribution (%)			
		S^{2-}	SCN^-	SO_3^{2-}	SO_4^{2-}
11-11	0	81.1	15.0	2.7	1.2
11-12	5min	82.6	13.9	2.5	1.0
11-13	15min	83.3	12.9	2.8	1.0
11-14	30min	85.9	11.7	1.4	1.0
11-18	1hr	87.4	9.9	1.7	1.0
11-15	2hr	88.2	9.6	1.6	0.6
11-16	4hr	89.0	8.5	1.7	0.8
11-17	8hr	90.5	6.9	1.6	1.0

Table 3. Optical Bleaching (K_2S doped KCl, $4.6 \times 10^{18} \text{S}^{2-}/\text{cc}$ of KCl)

Exp. No.	Bleaching Time	^{35}S Distribution (%)			
		S^{2-}	SCN^-	SO_3^{2-}	SO_4^{2-}
111-15	0	72.5	23.5	2.8	1.2
111-12	5min	75.5	21.3	2.0	1.2
111-14	15min	82.0	15.0	1.8	1.2
111-17	30min	83.8	12.8	1.4	2.0
111-18	2hr	87.5	9.6	1.7	1.2
111-13	4hr	87.7	10.1	1.2	1.0
111-16	8hr	92.7	5.8	0.4	1.0

increasing region upon prolonged photoannealing.

In the fast initial stage, the bleaching times may be plotted against $\frac{1}{1-R(S^=)}$ as shown in Fig. 3 in which $R(S^=)$ is the fraction of sulphide. The best curve fittings were made by a least squares method, and straight lines constructed.

4. Discussion

The nascent ^{35}S atom becomes thermallised among or near point defects that are produced along its recoil path as well as these present in the crystal due to the pile neutron irradiation. The recoiled energy is 31 Kev²⁰⁾.

The nascent ^{35}S from the (n, p) reaction is formally a singly charged negative ion, but this charge will generally be lost by shake-off and in a few events a positively charged ion may even be produced¹²⁾.

As suggested by Maddock and Mirsky¹⁾ it is most likely that the reduced or oxidised sulphur fractions compete with F and V centres. The reduction or oxidation takes place after the recombination of F and V centres. The reduction or oxidation takes place after the recombination of F and V centres, because the number of defects centres is at least 10^7 times more than the ^{35}S atoms produced by a nuclear reaction. Thus reduction only proceeds rapidly when the closely associated pairs of F and V centres have discharged each other.

The valence distribution should be determined only by the nature of the trapping sites and the availability of electrons or holes from the surroundings.

As expected, the KSH or K_2S doped crystals showed a marked increase in the sulphide precursor due to the enhancement of F centres by anion impurities.

Both $\text{S}^=$ and S^- can be introduced or produced substitutionally in alkali chloride lattices^{21, 22)}.

In this work, any possible contribution to the yield of ^{35}S from the dopant by the $^{34}\text{S}(n, \gamma)^{35}\text{S}$ reaction is ruled out, because the number of ^{35}S atoms from the (n, γ) reaction is 10^5 times less than those from $^{35}\text{Cl}(n, p)^{35}\text{S}$.

It seems to be effective that electrons from vacancies or dislocations in the crystals are continuously supplied for stabilizing the ^{35}S atoms.

The sulphide precursor appears to be sulphide, but it could conceivably be S^- .

A number of authors predicted^{1, 2)} the existence of S^0 species in the irradiated alkali chlorided crystals. Chiotan *et al*⁵⁾ have confirmed this S^0 species by extractions with trichloroethylene.

The properties of the thiocyanate producing species determine this to be S^0 .

The results show that at least some of sulphate or sulphite precursors do not contain S-O bonds because these would preclude the possibility of reduction by optical bleaching. The sulphite or sulphate precursor can hardly exist as preformed S-O bonds in the crystals; the oxygen content of the crystal is too low for the randomly produced ^{35}S to acquire three or four oxygen atoms.

Maddock and Kasrai¹⁰⁾ have postulated that the most likely entities seem to be SCl , SCl^- and SCl^2 which are analogous to Cl_2 and Cl_3^- (V type centres). These precursors do not themselves contain quadri or sexivalent sulphur; which must be produced in an oxidative hydrolysis.

Summing up the above, it may be drawn that upon bleaching the sulphide precursor is formed by $\text{S}^0 + \text{F}$ centres and their derivatives $\rightarrow \text{S}^=$, and the sulphite or sulphate precursor is produced by S^0 or $\text{S}^- + \text{V}$ centres and their derivatives $\rightarrow \text{SCl}$ or SCl^- in the crystal.

Comins and Wedepohl²³⁾ have reported that the F centres can be produced by X-irradia

tion of KCl at 77°K, the bleaching mechanism is due to the mutual destruction of interstitials and vacancies, and kinetics are more nearly second order.

It is known that equal number of F centres and interstitials are produced by irradiation in alkali halides at any temperatures²⁴⁾. In the irradiated alkali halide, the interstitial halogens are mobile at room temperature²⁵⁾.

According to this work, it may be concluded that the photoannealing mechanism is mutual destruction of F centres and interstitials within the bleaching time of 30 minutes as shown in Fig. 3.

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