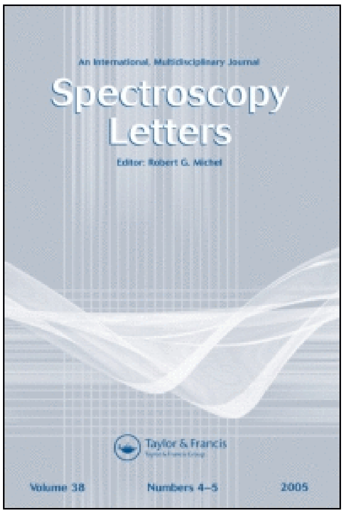

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Optical Absorption Study on the Annealing Behavior of Alkali Colloids in KCl:Na Crystals

Chao-Zhong Zhao[a]; Yun-Cheng Ge[a]; Wei-Guo Gao[b]
[a] Physics Department of Harbin, Normal University, Harbin, P. R. China [b] Agarian Teacher's College of Heilongjiang Province, Heilongjiang Province, P. R. China

To cite this Article Zhao, Chao-Zhong , Ge, Yun-Cheng and Gao, Wei-Guo(1997) 'Optical Absorption Study on the Annealing Behavior of Alkali Colloids in KCl:Na Crystals', Spectroscopy Letters, 30: 1, 163 — 171
To link to this Article: DOI: 10.1080/00387019708002597
URL: http://dx.doi.org/10.1080/00387019708002597

PLEASE SCROLL DOWN FOR ARTICLE

SPECTROSCOPY LETTERS, 30(1), 163-171 (1997)

OPTICAL ABSORPTION STUDY ON THE ANNEALING BEHAVIOR OF ALKALI COLLOIDS IN KCl:Na CRYSTALS

Key Words: optical absorption, alkali colloids, KCl:Na crystals

Chao-Zhong Zhao Yun-Cheng Ge* Wei-Guo Gao+
Physics Department of Harbin Normal University, Harbin 150080, P.R.China.
+Agarian Teacher's College of Heilongjiang Province, Archeng 150301, Heilongjiang Province, P.R.China

ABSTRACT

In this paper the results of optical absorption study on the annealing behaviour of alkali colloids in KCl:Na crystals were presented. It is found that the sodium colloids were formed in the crystals during the annealing treatment, instead of the potassium colloids. The absorption properties of these sodium colloids were observed, and show that the states of the colloids are dependent on the annealing treatment that include three factors: (a)the time of annealing treatment, (b)the temperature of annealing treatment

and (c)the process of annealing treatment. To discriminate the F-band and colloids-band, the emission spectra were also measured in some cases.

INTRODUCTION

Alkali halide crystals coloured by an excess of alkali metal may exhibit a great variety of optical absorption spectra, depending upon the manner of preparation and subsequent treatment of the sample. The absorption bands are in turn attributed to various colour centres in the crystal arising from the presence of the excess metal. Two classes maybe distinguished. In the first class are all the familiar electron centres which have been dignified by names: F, $R(F_3)$, $M(F_2)$, $N(F_4)$ etc. These centres have the common features that each consists of an electron which has become detached from its parent alkali metal atom and has been trapped at a lattice defect. It is the nature of the trap which determines the optical properties of the resultant center. Another class of colour centres exists. This class consists of electrons trapped on alkali ions to form neutral metal. An enormous variety of possible centres of this type exists, ranging from single atoms of alkali metal lodged at irregularities in the lattice, upto actual macroscopic pieces of included metal. The entire class is grouped together and referred to as colloid. No exact particle size is implied. It is a remarkable fact that the colloidal centres as a whole do possess a well-defined and regular absorption band. The present paper is devoted to a study of these bands in KCl crystals. The early literature concerning colloids in alkali halides has been reviewed by Seitz[1] and Przibram[2]. Renewed attention to these systems[3-7] may be expected as well in view of the current renewed interest in 'mesoscopic system' , i.e. systems of intermediate size between the single atom and the bulk solid size.

Although significant efforts have been invested in the research on the colloids in alkali halides, the formation of metallic colloids is not yet completely understood. In particular, the process of its formation, the changes of colloidal particles with annealing temperature, time, or other external conditions should be investigated closely. In this paper the KCl:Na single crystals that coloured additively were studied by optical absorption measurement. The samples were annealed treated at various temperature for various intervals, and were then measured time by time. It was found that the colloidal particles formed during the annealing treatment, but they are sodium colloids, not potassium colloids. And it is shown that the states of these sodium colloids are dependent on the annealing treatment, such as the temperature, time and process of the annealing treatment. The potassium colloids had not been observed during various treatments.

EXPERIMENTAL

Single crystals of KCl were grown in air by Kyropoulos method from spectroscopically pure KCl and NaCl powder. The NaCl concentration was 5mol.% in the melt solution. These contain less than 1ppm of background divalent cation impurities. The crystal were cleaved into blocks of approximate dimension $1cm^3$. The cleaved blocks were then additively colored by heating in potassium vapour at 970K for more than 8 hours. Care was taken to keep the crystals in dark during the colouring and cleaving process and during subsequent measurements. Samples used in this work were cleaved from the interior portions of the additively coloured KCl single crystals. The absorption spectra were measured by a Hitachi-UV--3100 spectrophotometer. Before annealing treatment, the samples contain primarily F-centres, the position of the F, M, R and N bands are in agreement with those reported in the literature[1]. When the sample was annealed for 30s at 800K, all absorption peaks of aggregative centres vanish while the F-band grows stronger, i.e. the aggregative centres have transformed to F-centres. Using Smakula relation[8], the F-centres concentration N in the sample can be calculated as follows:

for Lorentz type band $Nf=1.29\times10^{17}\dfrac{n}{(n^2+2)^2}KH$

for Guassian type band $Nf=0.87\times10^{17}\dfrac{n}{(n^2+2)^2}KH$

Here N is the concentration of the colour centres, n is the refractive index of the medium. K is the absorption coefficient at the center of the band, H is the width at half maximum of the band(ev), f is the oscillator strength of the F centres. Generally speaking the shape of measured F band is between the two ideal line type. For KCl the equation maybe placed in the form

$$Nf=1.08\times10^{16}\,\frac{\ln(T_0/T)}{l}\,(1.24/l_2-1.24/l_1)$$

Here l is the thickness of the crystal, l_1 , l_2 are the wavelengths at half-maximum of the absorption band, T_0/T is the transmission ratio of the absorption band. The concentration of F-centres in the sample used was calculated to be $4.46\times10^{-16}cm^{-3}$.

The sample was then annealed at various temperatures in an electrically heated oven, which was controlled by a DWT702 type temperature controlling apparatus (made in China), the temperature errors were maintained within 1K.

RESULTS AND DISCUSSION

The samples was first annealed at 250°C, the treated time were 2 minutes, 5 minutes, 15 minutes and 30 minutes, respectively. The results are represented in Fig.1. It is shown that the aggregative centres disappear with the annealing treatment at 250°C for 2 minutes and only the F-band was measured in this case(Fig.1(b)). Further treated for 3 minutes, the F-band weakened largely, as shown in Fig.1(c). Implying the decreasing of the amount of F-centres. Then the sample was annealed at 250°C again for another 10 minutes. The measured spectrum is given as Fig.2.

It should be noted that the absorption band in Fig.2(b) is different from that in Fig.2(a)First, the position of the absorption band moves to long wavelength, i.e. from 550nm moves to about 590nm. Second, the width of the band broadened and its intensity became higher. Third, a "shoulder" appeared at short-wavelength side of the absorption band, its position is about 400nm. With succeeding annealing treatment for 15 minutes, the measured absorption spectrum changes little except the intensity of the

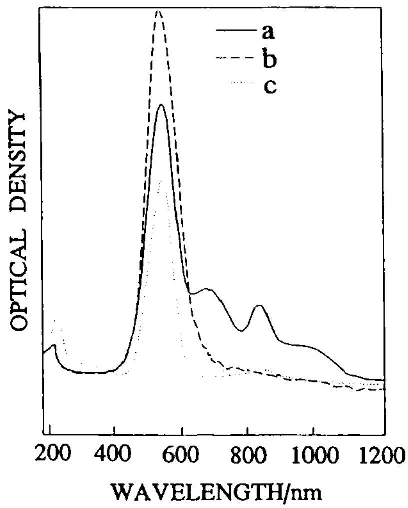

Figure 1. Optical absorption spectra of additively colored KCl:Na crystal, a: untreated; b: annealing treated at 250°C for 2 minutes; c: annealing treated at 250°C for 5 minutes.

590nm-band decreases a little. From the facts above, and the knowledge that F-centres could not persist at this temperature, we can conclude that the absorption band must be colloids band and not F-band. To verify the conclusion, the emission spectrum of F-centres was measured and observed essentially no F-centres' emission band. It is known that the potassium colloids band located at about 780nm[1], and the sodium colloids band located at about 580nm[4,5]. So we can draw the conclusion that the 590nm-band is sodium colloids band. And it implies that the sodium colloids are easier to be formed than potassium colloids in the doped samples. We should also note the existence of

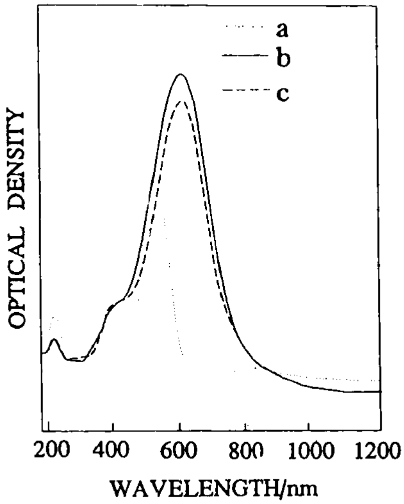

Figure 2. Optical absorption spectra of additively colored KCl:Na crystal, a: annealing treated at 250°C for 7 minutes; b: annealing treated at 250°C for 15 minutes; c: annealing treated at 250°C for 30 minutes.

400nm-band. In all spectra where the 590nm-plasmon-band is present, there is a peak at about 400 nm. The 400nm-band is much weaker than the 590nm-plasmon-band, and scales roughly with the colloid band.This band has also been observed in the literatures[9-12]. Different models were proposed[11,12], but none of these model is accepted. We think that the 400nm-band is due to sodium colloids. Perhaps the 400nm-band can be explained by the optical properties of the conduction electrons in the sodium particles in the crystals.

REFERENCES

1. F. Seitz, Revs. Modern Phys., vol.**26**, 7, (1954).
2. K. Przibram, Irradiation Colors and Lumine-science(Pergamon Press, London, 1956),p.85.
3. J. R. W. Weerkamp, J. C. Groote, J. Seinen, and H. W. Hartog, Phys. Rev. B, vol.**50,** No.14, 9781, (1994).
4. J. Seinen, J. C. Groote, J. R. W. Weerkamp, and H. W. Hartog, Phys. Rev. B, vol.**50,** No.14, 9787, (1994).
5. J. Seinen, J. R. W. Weerkamp, J. C. Groote, and H. W. Hartog, Phys. Rev. B, vol.**50,** No.14, 9793, (1994).
6. J. C. Groote, J. R. W. Weerkamp, J. Seinen, and H. W. Hartog, Phys. Rev. B, vol.**50,** No.14, 9798, (1994).
7. R.Ramfrez et al., Solid State Communication, vol.**80**, No.8, 549, (1991).
8. A. Smakula, Z. Phys. vol.**59**, 603, (1930).
9. Z. Gyulai, Z. Phys. **35,** 411 (1926).
10. Z. Gyulai, Z. Phys. **37,** 889 (1926).
11. P. Thevernad, J. Phys. (Paris) Colloq. **37,** C7-526(1976).

12. J. C. Groote, J. R. W. Weerkamp, and H. W. den Hartog, Cryst. Latt. Defects Amorph. Mater. **17**, 83 (1987).

Received: June 19, 1996
Accepted: July 31, 1996