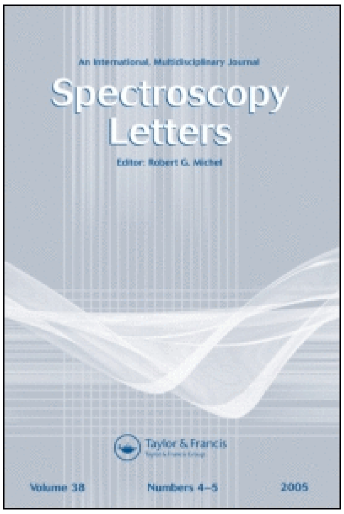

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Optical Absorption Study on the Annealing Behaviour of Metallic Colloids in KCl: K Crystals

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OPTICAL ABSORPTION STUDY ON THE ANNEALING BEHAVIOUR OF METALLIC COLLOIDS IN KCl:K CRYSTALS

Keywords: Optical Absorption, Annealing, Metallic colloids, KCl:K crystals

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ABSTRACT

The results of optical absorption measurements on potassium colloids in KCl crystals have been presented in this paper. The samples were annealed at various temperatures with different time. It is found that the colloids band is dependent on the annealing temperature and annealing time. The transformation process between F-centers and colloidal centers were observed. The colloids band shows complex structures for the samples which did not attained equilibrium, indicating that there are different kinds of colloidal centers in such samples. Also we found that in

these samples(which is in the nonequilibrium state), the transformation process from F-centers to colloidal centers does not stop even at room temperature.

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. The results of optical absorption measurements on potassium colloids in KCl crystals have been presented in this paper. The samples were annealed at various temperatures with different time. It is found that the colloids band is dependent on the annealing temperature and annealing time. The colloids band shows complex structures for the samples which did not attained equilibrium, indicating that there are different kinds of colloidal centers in such samples. Also we found that in these samples(which is in the nonequilibrium state), the transformation process from F-centers to colloidal centers does not stop even at room temperature.

EXPERIMENTAL

Single crystals of KCl were grown in air by Kyropoulos method from spectroscopically pure KCl powder. These contain less than 1ppm of background divalent cation impurities. The crystal were cleaved into blocks of approximate dimension 1.5x1.0x0.6cm^3. The cleaved blocks were then additively colored by heating in potassium vapour at 960K for more than 10 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 60s at 650K, 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

$$Nf = 1.29 * 10^{17} \frac{n}{(n^2+2)^2} KH$$

for Guassian type band
$$Nf=0.87*10^{17}\frac{n}{(n^2+2)^2}KH$$

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

$$Nf=1.08*10^{16}\frac{\ln(T_0/T)}{l}(1.24/l_2-1.24/l_1)$$

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 $6.56\text{x}10^{-16}\text{cm}^{-3}$.

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 DISCUSSIONS

The absorption spectra were measured from time to time. Fig.1 shows the typical transformation between F-centers and C-

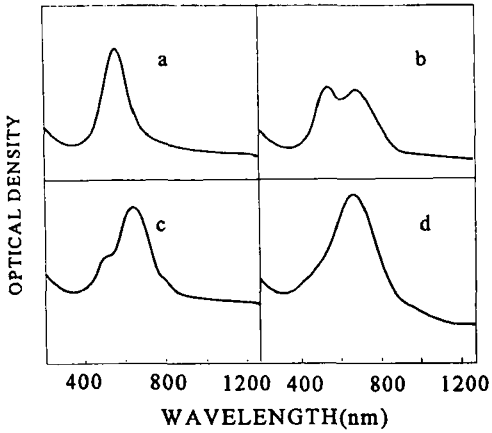

Fig.1 Optical absorption spectra of additional colored KCl crystals annealed at 500K. The annealing treatments time are: (a) 0 min.; (b) 10 min.; (c) 20 min.; (d) 30 min.,respectively.

centers(i.e. colloidal centers). The important feature of Fig.1 is the peak position of the colloids band in curve (d), which located at 670nm, it is much shorter in wave length than the results of the literatures. The difference is about 100nm.We may conclude that very small colloidal particles had formed during the annealing treatments. According to the theory of Doyle[9], the diameter of the colloidal particles is about 1nm in magnitude. Another feature of Fig.1 is that the F-band is almost invisible, and the C-band is very strong, which indicate that the F-canters have mostly converted to colloidal centers. It also worth noting that the total area under the F-band and the C-bands is not constant. In fact, the aggregated

phase is much more effective in attenuating the incident light beam than the dispersed F-centers are.

When the samples are treated at 650K, the C-band moves to long wavelength, as shown in Fig.2, the position and shape of it change with the time of annealing treatments. In measurements on subsequently treated samples, we found that the intensity of the C-band decreases with the time of treatment while the position of it moves to long wavelength, and the width of the band enlarges. In order to interpret the changes of position, line width and intensity in terms of particles' size, we can use collective dipole model of Doyle[9] for the optical absorption of small metallic particles. In contrast with the macroscopic electrodynamic approach of Mie theory, the metal particles here are regarded as large Thompson atoms and simply as individual atomic dipoles. According to the results of Doyle with the increasing of the particle size, the electric-dipole excitation coefficient moves to long wavelength, the extinction band become broadened, the intensity of the band undertakes the process of increasing first and then decreasing gradually. So we can conclude that the size of colloids particles in our sample increase with the time of annealing treatment until the equilibrium value has been acquired for certain temperature. The intensity, position and bandwidth changing process here, is also in agreement with Doyle's theory, the particles formed at certain temperature between C and C exhibiting the strongest extinction,

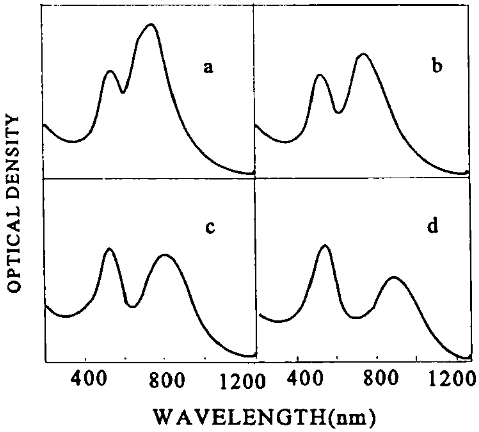

Fig.2 Optical absorption spectra of additional colored KCl crystals annealed at 650K. The annealing treatments time are: (a) 5 min.; (b) 10 min.; (c) 20 min.; (d) 30 min., respectively.

that can be seen from Fig.2. Another point should noted is the irregular shape of the colloids band in Fig.2(a), which implies that there may be colloidal particles of different sizes, at least two kinds of particles exist. This results admit a simple explanation that the colloidal particles of different sizes may appeared in the formation process of larger colloidal particles until the equilibrium state attained, as we can see in Fig.2(d), the shape of colloids band is normal after a nonequilibrium process. However, if we stop further annealing before the system attaining its equilibrium state, the nonequilibrium state may be partially cold as presented in Fig.3. After annealed at 650K for 10 min., the

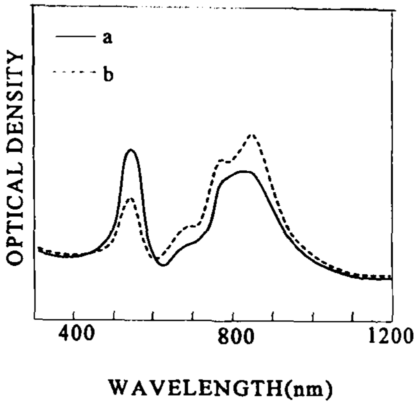

Fig.3 Optical absorption spectra of additional colored KCl crystals annealed at 650K for 10 minutes and 600K for 10 minutes; solid curve, measured just after the sample was annealed; dashed curve, measured 12 hours after it is annealed.

sample was retreated at C for 10 min.(the system had not attained its equilibrium state). It is found that the colloids band shows irregular shape, implying that there are particles of multiple sizes. And then we stopped annealing, i.e. before attaining the equilibrium state, the system is cold in the nonequilibrium state. The sample was stayed in dark at room temperature for 12 hours. Then it is re-measured, the results seems rather surprising, that the spectrum shows large changes comparing to the one measured 12 hours ago. First , the relative intensity of F-band and colloids band changed, i.e. the F-band decreased and the C-band

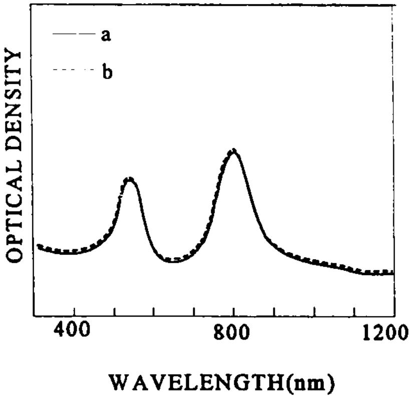

Fig.4 Optical absorption spectra of additional colored KCl crystals annealed at 650K for 10 minutes and 600K for 30 minutes; solid curve, measured just after the sample was annealed; dashed curve, measured 12 hours after it is annealed.

increased; second, the C-band shows consisting of multiple peaks; finally, a week peak appeared at about 680nm, which may be one part of the extinction band of large colloidal particles as given by the theory of Doyle. All these phenomena show that the diffusion of F-centers do not stop even at room temperature, especially for the system in nonequilibrium state, so that the composition of the colloidal particles become more complex and resulted in the multiple structures appeared in the C-band, as represented in Fig3(b). The facts above indicate that the transformation process between F-centers and C-centers is dependent on the annealing treatment. For comparison, another sample cleaved from the same crystal was annealing treated as the former, the only difference is that it attained equilibrium state at C before staying in dark at room temperature. The results are shown in Fig.4. It can be seen that the spectrum measured just after annealing and that measured 12 hours later, are almost the same. Indicating that the sequence of annealing treatment affect the C-centers in the crystal.

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