Ruby Laser Induced Changes in the Absorption Spectra of Sodium Decorated Sodium Chloride Crystals

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The effects of intense Q-switched ruby laser light on the absorption spectra of NaCl crystals, additively coloured by colloidal sodium were investigated at different depths along the laser beam path as well as after being subjected to different annealing conditions. A strong general increase in absorption was observed in the region where the laser light entered the crystal, while a strong decrease in absorption occurred in the colloid band, especially around the laser wavelength. This bleaching was accompanied by the generation of a new absorption band at ~ 1200 nm (~ 1.0 eV) in the infrared, which, according to its sensitivity to temperature treatment, is not of colloidal origin. The energy density necessary for its generation was found to be about 400 mJ/cm². It is suggested that the bleaching of the colloid band could be used for the storage of holograms.

1. Introduction

In recent years the interaction of laser light with crystals exhibiting special absorption bands has received considerable attention [1–7]. Apart from being of purely scientific interest, there is also the possibility that the interaction of colour centres with laser light might be used for storing information in thick holograms [7, 8]. Storage materials which have been investigated so far and which operate on this mechanism suffer the big disadvantage of relatively fast bleaching with time, temperature and light intensity, especially in the reconstruction process. There is the possibility that this disadvantage might be overcome by the use of colloidal absorption bands, since they are known to have a good resistance to light and temperature effects [9].

The absorption of laser light in NaCl additively coloured by colloidal Na has already been described briefly [5]. The present paper gives a more detailed description of the observed effects as well as some quantitative results.

2. Experimental Procedure

NaCl crystals of the Harshaw Chemical Company were additively coloured with sodium metal by the method of AMELINCKX [10, 11]. After heating the NaCl-Na system for 15 hours at 700 °C it was quenched to room temperature. This resulted in the precipitation of Na colloids along dislocation lines and small angle grain boundaries. A determination of the excess sodium by the method of KLEINSCHROD [12] gave a concentration of about 25 ppm.

Smal slices of about 2 × 4 × 7 mm³ were cleaved from the decorated NaCl crystals and were used as samples for absorption measurements and laser irradiation. As radiation source a Technical Research Group, Inc. model 104 ruby laser with a rotating prism Q-switch was used. The output energy was measured with a Technical Research Group, Inc. model 101 calibrated thermopile and the pulse width was monitored with a fast Tektronix oscilloscope.

The single laser pulse, with half-intensity width of about 40 nsec and energies up to 400 mJ, were focused onto the sample surface by means of a modified metallurgical microscope. An $f/3.7$ objective with focal length of 26 mm was used. The focal spot area was found experimentally to be about 1 mm² (for details see Ref. [6]).

The power density on the sample surface is given for the present experimental arangement by the expression

$$P \approx 10^6 \cdot I \text{ Watt/cm}^2 \qquad (1)$$

where I is the laser energy in millijoule incident during the pulse as measured with the thermopile.

All spectroscopic absorption measurements were made with a Beckman DK-1 spectrophotometer. In the

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case of laser irradiated crystals, transmission measurements were usually carried out perpendicular to the laser beam path and a 0.5×1 mm^2 diaphragm was used to select unirradiated from irradiated crystal areas. Spectra were taken at different depths D from the surface of laser light incidence, before and after laser irradiation.

From the observed transmission measurements the absorption coefficients were deduced by means of the following expressions:

$$I_\text{b} = I_0 \, e^{-k_\text{b} d}\,, \tag{2 a}$$

$$I_\text{a} = I_0 \, e^{-k_\text{b} d} \, 2\,r(D) \int_0^{1/2r(D)} \cdot \exp\{-2\,r(D)\,\sqrt{1-u^2}\,(k_\text{a}-k_\text{b})\}\,\text{d}u \tag{2 b}$$

where I_0 is the intensity of the incident spectrophotometer light beam and I_b and I_a are the transmitted intensities before and after laser irradiation, respectively; d is the thickness of the sample; k_b and k_a are the absorption coefficients; and $2\,r(D)$ is the diameter of the laser beam path cone at a distance D from the surface of incidence. In the present case the function $2\,r(D)$ is equal $(1+0{,}17\,D)$. Eq. (2 b) takes into account the fact that for transmission measurements after laser irradiation the spectrophotometer beam passes through a conically shaped irradiated volume with absorption coefficient k_a and an unirradiated portion on each side with absorption coefficient k_b. In Fig. 1 the ratio $I = I_\text{a}/I_\text{b}$ of the transmitted energy after and before laser irradiation is plotted as a function of $(k_\text{a}-k_\text{b})$ for different values of D. From this plot k_a can be obtained immediately for different distances if the ratio I_a/I_b is measured. All absorption values k_a in the following were deduced in this manner.

3. Experimental Results

3.1. Absorption Spectra of Na-decorated NaCl

The absorption spectra of Na-decorated NaCl crystals show a strong dependence on the quenching conditions. Fig. 2 gives some typical spectra for different samples. Though the bands overlap quite strongly, they can be ascribed to well-known absorption centres: the F-band which is not very well developed at ~460 nm (2.72 eV), the Scott-band at ~550 nm (2.25 eV) (also known as the X- or Δ-band) and the Mie-bands (colloid bands) at longer wavelengths.

Depending on the quenching conditions the Mie-bands occurred at variable positions. In the present investigation crystals with Mie-bands at 690 nm (1.8 eV) were arbitrarily designated as type 1, and those with Mie-bands at 760 nm (1.63 eV) as type 2.

The different samples showed only a weak dichroism. This indicated that the colloids were fairly closely spherical in shape [13, 14]. Furthermore, except

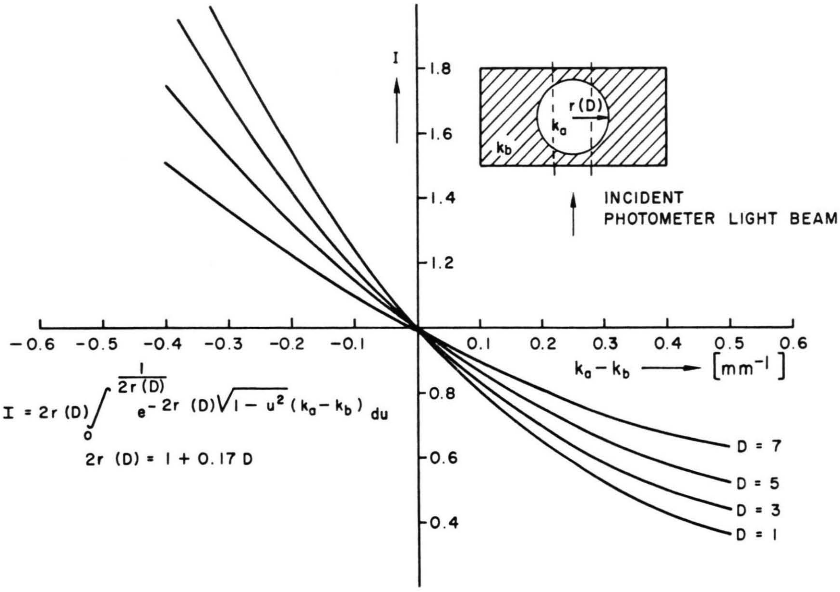

Fig. 1. Ratio of transmitted intensity before and after laser irradiation (I) as a function of the difference in absorption coefficient. The curves are calculated according to Eq. (2 b) for the distances indicated. The values of D are given in mm.

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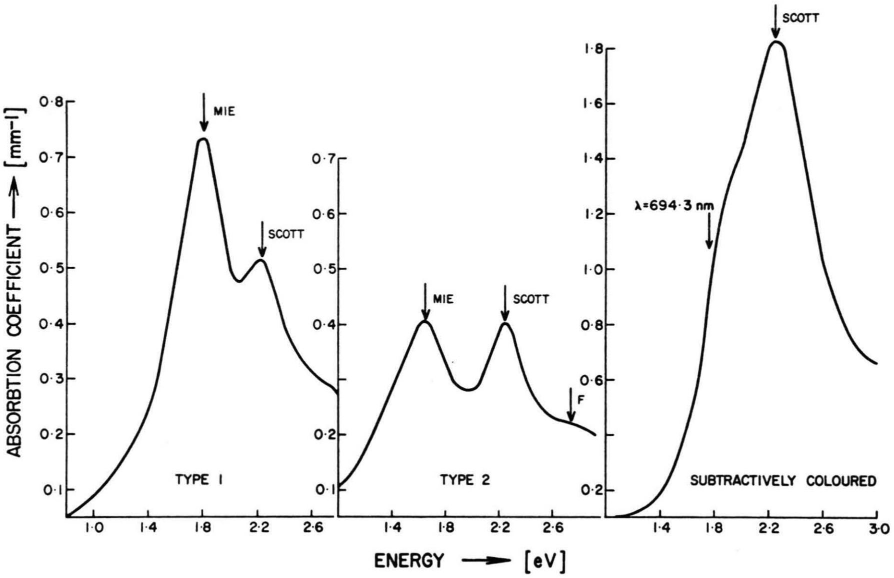

Fig. 2. Absorption spectra of coloured NaCl. The first two curves were taken after additive coloration under different quenching conditions; the third after subtractive coloration and subsequent bleaching with white light.

for changes in the F- and Scott-bands, no further changes in the spectra were observed at liquid nitrogen temperatures, which confirm their colloidal origin. Good resistance to elevated temperatures (up to 200 °C) and to bleaching by ordinary light was also observed.

Colour centres in the NaCl[Na] colloidal system have already been discussed by SOVASTIANOVA[15] on the basis of MIE's theory[16]. The relationship between colloidal absorption bands and colloidal size was shown explicitly. By extrapolation of Sovastianova's results, an estimate of the diameter of the colloids could be obtained in the present case. Thus the maximum absorption at 1.8 eV in type 1 crystals, for example, led to a colloidal diameter of $2\,\varrho = 90$ nm.

The absorption spectrum of a sample of subtractively coloured NaCl is also shown in Fig. 2, for comparison. It was obtained from an x-ray irradiated crystal which was subsequently bleached with intense white light. Though the general shape of the spectrum is somewhat similar to that of type 1 crystals, it originates from completely different absorption centres, namely an overlapping of Scott,- M-, F- and R-bands[17, 18].

3.2. Changes by Laser Irradiation and Subsequent Annealing

3.2.1. General Features

Fig. 3 shows a sequence of absorption spectra at different depths from the surface of laser light incidence before and after a type 2 crystal was laser irradiated. A single laser pulse with an energy of 390 mJ was used. As can be seen, close to the surface laser irradiation causes a very strong increase in background absorption throughout the whole spectral region, especially on the high energy side, which decreases rapidly with depth. This was a characteristic feature of all the irradiated NaCl[Na] samples investigated. At $D = 1$ mm a bleaching of the Mie-band at ~1.63 eV is already noticeably, which at this depth, however, is still strongly overlapped by the enhanced general background absorption. At depths between 2.5 and 4.0 mm this background has disappeared almost completely and consequently the bleaching of the Mie-band itself is even more pronounced, while the Scott-band at 2.25 eV appears broadened and slightly shifted towards lower energies. In addition a new infrared band which usually occurred between 1.0 and 1.2 eV – designated IRB

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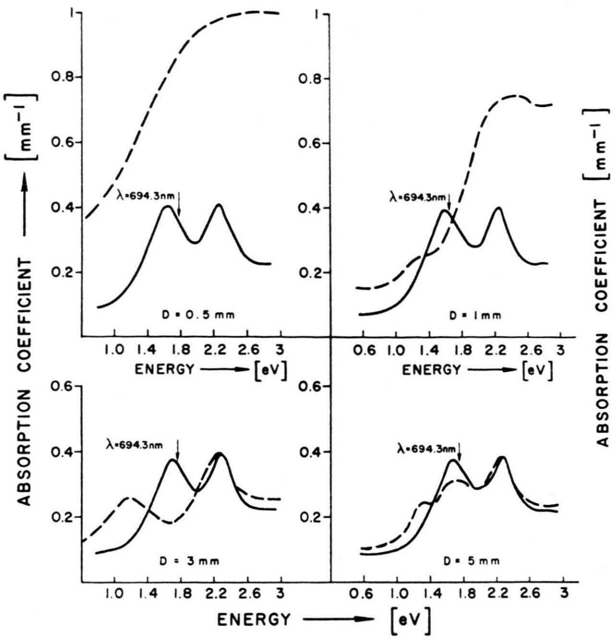

Fig. 3. Absorption spectra of type 2 crystals before (full line) and after laser irradiation (broken line). The spectra were taken at different distances, *D*, from the surface of incidence. Arrows indicate the laser line position.

in the following – is generated. Going deeper into the crystal these effects diminish and after about 7 mm no change in the spectrum is observed.

Similar results were obtained for type 1 crystals whilst the subtractively coloured samples showed only a general increase in absorption (see Fig. 4).

3.2.2. *Changes in Absorption with Depth*

The behaviour of the different absorption centres as a function of depth was studied in some detail. Fig. 5 shows the relative change in absorption coefficient at the band positions with increasing depth for a type 1 crystal. In this case the irradiating laser energy was 180 mJ. Whilst the curve for the F-band position shows an almost exponential behaviour, the one for the Scott-band position already reaches negative values, i. e. it is bleached, at a depth of ~2.25 mm. For the Mie-band region around 1.8 eV the bleaching is even more pronounced, reaching values of more than -50% at depths between 2.5 and 3.0 mm. The minimum in this curve may be caused by the "true" bleaching curve of the Mie-band being superimposed on the enhanced general background absorption. The IRB, on the other hand, has a very pronounced maximum which appears at a depth of ~2.75 mm under the particular experimental conditions.

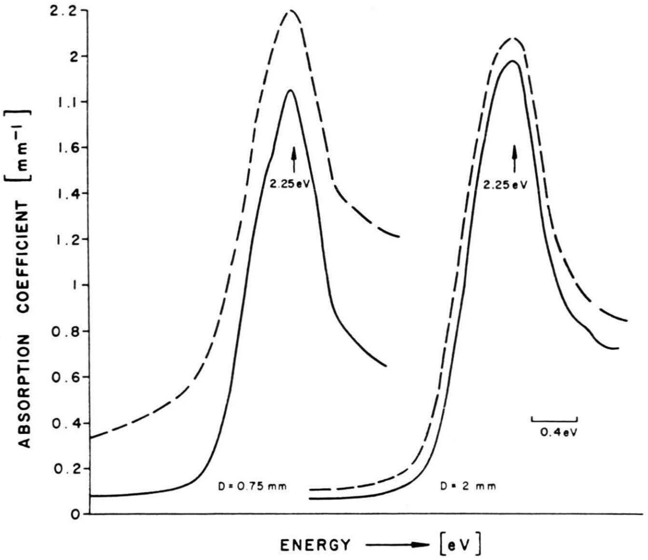

Fig. 4. Absorption spectra of subtractively coloured NaCl before (full line) and after laser irradiation (broken line) at a distance $D = 0.75$ mm and $D = 2$ mm from the surface of incidence.

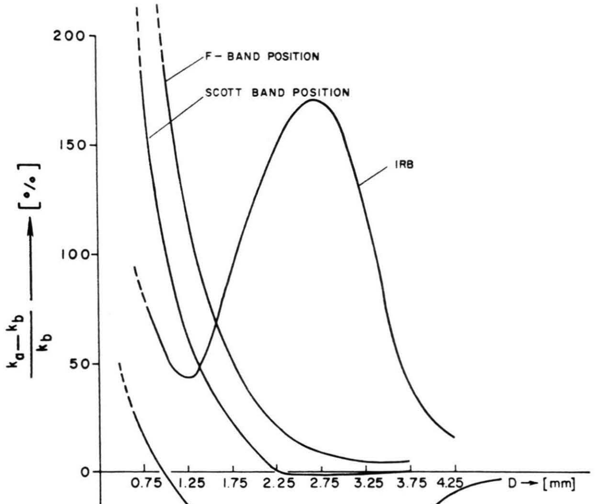

Fig. 5. The relative change in absorption coefficient at the different band positions in decorated NaCl (type 1) as a function of depth after laser irradiation with 180 mJ.

Since all the bands overlap to a lesser or greater extent an exact analysis of these curves was not attempted.

If one replots the curve for the F-band position in Fig. 5 on a logarithmic scale an approximate straight line is obtained (curve I, Fig. 6). If the rather obvious assumption that the effect which is responsible for the enhanced background absorption is proportional to the laser energy at that particular depth is made now, then curve I is equivalent to a laser light absorption curve, the slope of which is the apparent absorption coefficient k^*. This curve should be compared with the absorption behaviour of ordinary light at 694.3 nm in the unirradiated coloured sample which is indicated in Fig. 6 as a broken line (curve II). It follows that under the experimental conditions of Fig. 5 the absorption coefficient for ruby laser light ($k^* = 1.65\ \mathrm{mm}^{-1}$) is twice that of ordinary light ($k^{694.3} = 0.83\ \mathrm{mm}^{-1}$). The same ratio was also found when other laser energies were used.

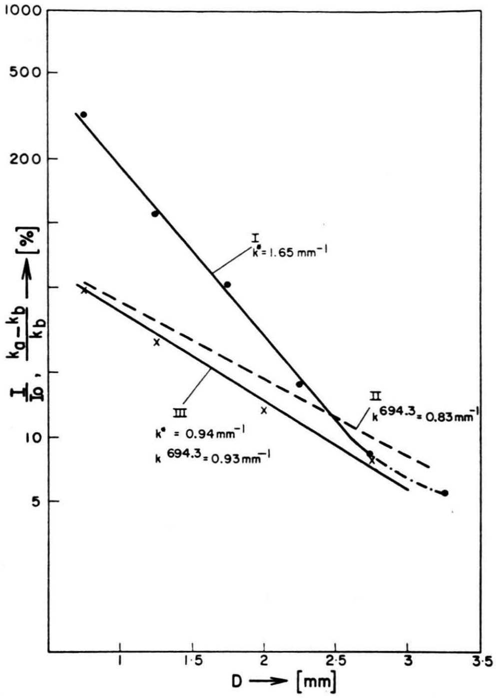

Fig. 6. Laser light absorption and ordinary light absorption in coloured NaCl. The full lines represent the change of the increased absorption at 460 nm with penetration depth for decorated and subtractively coloured NaCl, respectively, whilst the broken line gives the absorption for ordinary light in decorated NaCl.

Similar results were obtained for crystals of type 2, whilst the subtractively coloured NaCl did not show a marked difference in absorption between laser light ($k^* = 0.94\ \mathrm{mm}^{-1}$) and ordinary light at 694.3 nm ($k^{694.3} = 0.93\ \mathrm{mm}^{-1}$) (see curve III in Fig. 6).

A different absorption behaviour for laser light and for ordinary light has already been observed for transparent crystals and coloured liquids [19–22], and has thus far been ascribed to nonlinear phenomena liked stimulated Mandelstam-Brillouin scattering, multiphoton excitation, selffocussing, etc.

3.2.3. Annealing Behaviour of the Infrared Band (IRB)

Annealing experiments were carried out at temperatures between ambient and 150 °C in an attempt to obtain more information on the nature and possibly the origin of the IRB. Fig. 7 gives as an example the results for type 1 crystals which have been annealed at 40 °C for different time intervals after laser irradiation with 180 mJ. At this temperature the IRB bleaches almost completely after about 25 hours. At 120 °C the same bleaching takes only

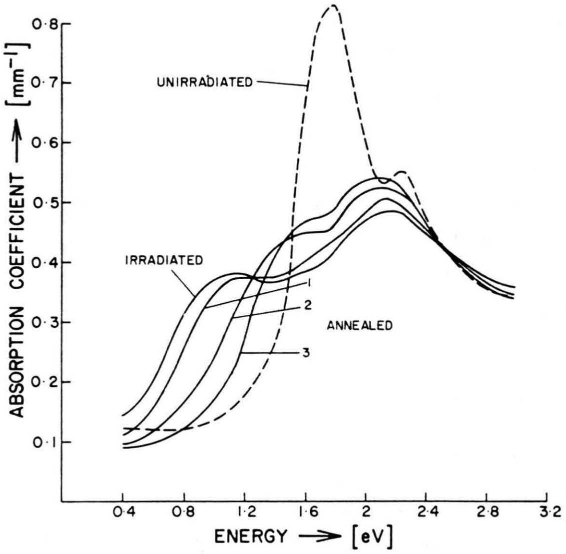

Fig. 7. Annealing of decorated NaCl (type 1) after laser irradiation with 180 mJ: curve 1 after 30 minutes, curve 2 after 9 hours and curve 3 after 25 hours at 40 °C. (The spectra were taken at a depth of about 2.8 mm.)

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half an hour. It can also be noted from the figure that during annealing the absorption between 1.3 and 1.5 eV increases at first and then decreases again. This implies that in the annealing process several intermediate stages are involved. Finally, the figure indicates that in the region of the Mie-band (1.5 – 2.2 eV) a general increase in absorption took place during annealing, but that even after 25 hours the original spectrum was not re-established.

Since the newly observed IRB is strongly overlapped by the colloid band, the absorption coefficient at the maximum was the only property which could conveniently be measured quantitatively. In the following the relative change in absorption coefficient at the IRB (~ 1.1 eV) is therefore used to characterize its magnitude. Fig. 8 shows the annealing behaviour of this band with time for two different temperatures. Here k_t refers to the absorption coefficient after heat treatment. The reasonably straight lines on the logarithmic plot indicate that the thermal bleaching process is governed by a temperature dependent decay constant α. The values obtained in Fig. 8 would lead to a thermal activation energy of 0.5 eV.

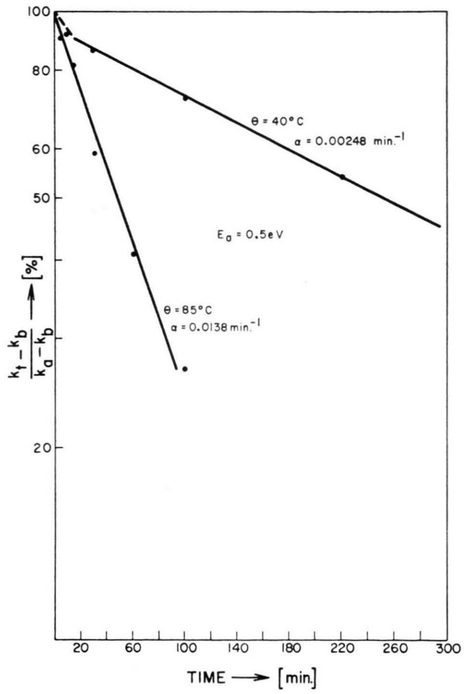

Fig. 8. Change of the infrared band with time during annealing at different temperatures.

3.2.4. *Influence of Laser Light Intensity on the Generation of the Infrared Band (IRB)*

In Fig. 9 a the relative change in absorption at the IRB is plotted as a function of the laser energy used. Despite a large scatter of the experimental points, it is clear that the absorption increase is practically independent of the laser energy and has an average value of about 150%. On the other hand, the depth at which the maximum absorption in the IRB occurs, D_{IRB}, is found to increase with increasing laser energy. It seems that the IRB is generated whenever the laser energy density reaches a certain critical value. This value can be deduced from the exponential absorption law, which under the present experimental conditions is given by

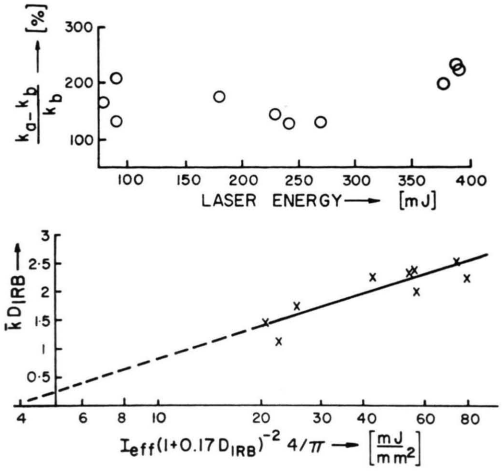

Fig. 9. Behaviour of the infrared band after irradiation of type 1 crystals with different laser intensities. (a) Relative change of absorption as a function of the laser energy. (b) Position of the infrared band expressed in terms of optical density $\bar{k}\cdot D_{\mathrm{IRB}}$ as a function of the effective intensity of the laser light.

$$\frac{I_{\mathrm{eff}}\cdot A}{\pi/4\,(1+0.17\,D_{\mathrm{IRB}})^2}\cdot e^{-\bar{k}D_{\mathrm{IRB}}} = I_{\mathrm{crit}}\,. \tag{3}$$

In this expression I_{eff} represents the effective laser intensity incident on the sample surface in millijoule/cm^2 and can be calculated from Eq. (1); A is the focal spot area which in this case is ~ 1 mm^2; the denominator gives the cross sectional area of the laser beam cone at the depth D_{IRB} in mm^2; and $\bar{k}$ is the average absorption coefficient along the distance D_{IRB}.

Eq. (3) suggests that if the total optical density, $\bar{k}\,D_{\mathrm{IRB}}$, is plotted against the quantitity

$$I_{\mathrm{eff}}\cdot 4/\pi(1+0.17\,D_{\mathrm{IRB}})^{-2}$$

on a logarithmic scale, a straight line should result. As can be seen from Fig. 9 b this is indeed the case, even though the scatter of the experimental points is again rather large. From this curve the value of approximately 400 mJ/cm^2 is obtained for the critical energy density.

The large scatter of the experimental points in Fig. 9 a and 9 b may be due, amongst others, to variations in the absorption properties of the samples themselves and to variations in the laser output energy. The sample surface condition also has been observed to have a pronounced effect on the propagation of the light through the crystal.

3.3. *Experiments with Unfocused Laser Light*

The results in the foregoing section imply that a 400 mJ unfocused laser beam with a cross sectional area of 1 cm^2, such as can be obtained from the laser used in the present investigations, should also be capable of generating the IRB — but then only very close to the surface of incidence. In order to check this a thin (0.4 mm) sample of type 1 crystal was irradiated with 400 mJ/cm^2 unfocused ruby laser radiation. The absorption spectra of the unirradiated, the irradiated and the subsequently annealed crystal (25 min at 85 °C) are shown in Fig. 10. In this case the transmission measurements were carried out parallel to the direction of irradiation which meant that no correction to the absorption coefficient such as considered in Eq. (2 b) was necessary. As can be seen, the spectra are very similar to those of Fig. 6, thus confirming, amongst others, the essential correctness of the interpretation concerning the critical energy required for generation of the IRB. The relative changes in absorption coefficient after irradiation are ~ 120% for the IRB at ~ 1.0 eV (1200 nm) and — 40% for the colloid band at ~ 1.8 eV (~ 700 nm), which are also — even quantitatively — in good agreement with the results of Fig. 5. The annealing experiment confirmed that the absorption spectrum after laser irradiation was of the same nature and origin as those previously considered.

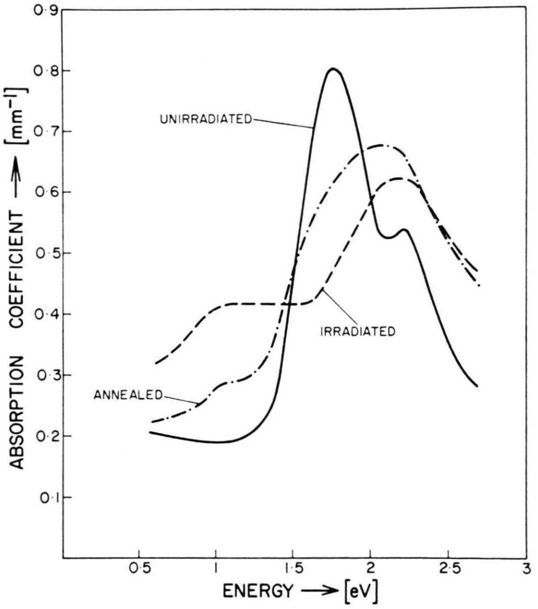

Fig. 10. Change of absorption of type 1 crystals after irradiation with unfocused laser light (390 mJ) and subsequent annealing for 25 minutes at 85 °C.

4. Discussion und Conclusions

4.1. *Laser Produced Changes in the Mie-, Scott- and F-Bands*

A considerable amount of the incident laser light will be absorbed by the colloids. SOVASTIANOVA [15] found the absolute values for the absorption coefficients of the colloids to be of the order of 5×10^5 mm^{-1}. This means that even for 10 nm particles nearly al the energy is absorbed and the rate of absorption per unit volume of the colloid is given by the expression

$$Q = 0.24\, \varrho^2\, \pi\, P\, V_c^{-1} \quad [\text{cal cm}^{-3}\,\text{sec}^{-1}] \qquad (4)$$

where ϱ is the radius, V_c the volume of the colloid, and P is calculated from Eq. (1). Formula (4) leads to Q values of the order 10^{12} cal cm^{-3} sec^{-1}, which, of course, will result in very high colloid temperatures.

For an estimate of the temperature the exact heat conductivity problem of a constant rate of heat flow involving a sphere of medium 1 embedded in an infinite medium 2 has to be considered. By using the same expressions as in Ref. [6] a value of 5200 °C was found for a laser pulse energy of 400 mJ.

Due to the thermal expansion of the colloids and their immediate surroundings at these high temperatures macro and micro defects will be generated. Indeed, ultra-microscope investigations [5] have revealed the presence of such defects in the form of cracks and cubical cavities in the laser beam path close to the surface of incidence. These are most probably responsible, by scattering, for the increase in general background, especially in the F-band region, which is observed close to the surface of incidence. This mechanism is more probable than the generation of new F centres, especially since, contrary to DOYLE's [9] observation that F centres coagulate quite rapidly into Scott centres at ~ 180 °C, no change in absorption could be observed in the F-band region when irradiated samples were annealed for prolonged periods at this temperature.

Deeper inside the crystal the thermal expansion will be less severe and therefore less defects will be generated. The temperature increase of the colloids may, however, still be high enough to cause a partial redistribution of the colloidal metal into the surrounding matrix. This explains the bleaching of the Mie-band and the observed broadening and shift of the Scott-band towards lower energies since new smaller colloids are generated.

4.2. *The Origin of the Infrared Band (IRB)*

The most surprising effect – and also the most difficult to explain – is the appearance of the IRB at ~1200 nm (~1.0 eV). Temperature treatment showed that it is not of colloidal origin and that it has an activation energy of ~0.5 eV for thermal bleaching. The only known intrinsic bands in this region are those of the *N* centres (from ~827 to 1219 nm) and ionized higher aggregates of the F centre such as F_3^+ (860 nm), F_2^+ (1306 nm), M^+ (1306 nm), R^+ (1549 nm), R′ (1380 nm) and M′ (1720 nm) [23, 24]. However, most of these bands have been observed only at very low temperatures and then only for KCl and LiF. The numbers in brackets in the foregoing refer to the zero phonon positions of the particular bands, should they occur in NaCl. They were calculated from the available experimental data for KCl and LiF by means of a Mollwo-Ivey relation. The band peak positions should occur at slightly longer wavelengths.

Apart from these centres any rearrangement of excess sodium around a semi-redistributed colloid could also be responsible for the IRB.

To obtain more information on the nature of this band laser irradiation at very low temperatures followed by subsequent annealing may prove useful.

4.3. *Possible Holographic Application*

As reported by BOSOMWORTH [7] a change in absorption coefficient of $0.05-0.3\ \mathrm{mm}^{-1}$ in doped CaF_2 crystals is sufficient to enable such crystals to be used for storing holographic information. According to Fig. 7 the change in absorption coefficient at 700 nm in the Mie-band of a Na-doped NaCl crystal upon laser irradiation is quite large and even after annealing still has a value of $\sim 0.4\ \mathrm{mm}^{-1}$. Furthermore, the spectrum is very stable to temperature and to bleaching by ordinary light.

Since changes in absorption of similar magnitude can be produced in the Mie-band even with unfocused laser light, the use of such Na-doped NaCl crystals for storing holographic information should be possible.

Acknowledgements

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