Surface damage during the colouration of laser-quality alkali halide crystals

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The cause of alkali metal loss and surface damage which take place during additive-colouration, using a simple heat-pipe, have been investigated. It has been found that both effects have their origin in the outgassing of the colouration tube and can be easily minimized, thus allowing the attainment of laser-quality coloured crystals.

1. Introduction

Colour-centre lasers can now operate over the spectral region between 0.85–4.0 µm. This has been possible because of the discovery of efficient laser action in different alkali halides using a variety of colour centres [1, 2].

The active laser centres are produced preferentially by additive colouration because in this way the stability of the centres is increased [3].

To ensure a sufficiently high density of the desired centres, avoiding at the same time the formation of other unwanted products (i.e., colloids), the colouration conditions (pressure and temperature) have to be carefully controlled. In order to do that, reducing surface damage, the Mollenauer [4] version of the Van Doorn [5] heat-pipe has been adopted in the most recent works.

The principal innovations of Mollenauer's design are the incorporation of a fine stainless-steel wick, which holds and disperses the melted alkali metal, and the addition of a valve which provides for an air lock to isolate the wick from the upper part of the tube [4]. The main advantages of this design are: (1) It allows loading and retrieval of the crystals without loosing the metal charge, (2) preserves the crystal surface from contamination of alkali metal. Pre-polished crystals can be used with only a brief repolishing, (3) there is no loss of alkali metal, allowing operation for arbitrarily long times.

Although the first feature is perhaps not essential, except for industrial applications, the other two characteristics are necessary for the clean, precise and controlled colouration required to obtain laser-quality crystals. Nevertheless the wick is a delicate and vulnerable part of the apparatus which requires a thorough deoxidizing treatment (1 h at 1000 °C in a flowing hydrogen atmosphere) [4], thus it looses the simplicity of the Van Doorn system, particularly the feasibility of easy change from a colouring metal to another.

In order to preserve this versatility, which is sometimes interesting from the research point of view, the origin of the alkali metal loss and surface damage, and the possibility of obtaining laser-quality crystals with the traditional Van Doorn system, have been studied.

2. Experimental details

The colouration apparatus used in this work (Fig. 1) is based in the traditional Van Doorn heat-pipe [5] and consisted of a stainless steel tube (length 350 mm, outer diameter 35 mm and wall thickness 3 mm). Stabilized 347-type stainless steel was used to prevent corrosion in the bottom (welded zone) of the tube [4]. A water cooling coil and a conic condenser were used to confine the metal vapour. The upper part of the tube is a standard NW-20 KF flange connection through which the tube is either evacuated or filled with nitrogen at the desired pressure, also providing space for the thermocouple feedthrough and the crystal container fixing.

Crystals of either NaCl or KCl have been coloured using the corresponding alkali metal. The samples, $1 \times 1 \times 2$ cm³ in size, were cut from boules, supplied by the Crystals Growth Laboratory (Applied Physics Department of the Universidad Autónoma de Madrid), grown in inert atmosphere from Suprapure (Merck) starting material.

Optical microscopy was performed using a Ultraphot Zeiss microscope. Scanning electron microscopy (SEM) was carried out using a Philips scanning electron microscope (SEM 500) linked with an EDAX system (model 711). The samples were attached to the SEM specimen mount by graphite paint and the whole set was covered with gold, evaporated by sputtering in an Edwards evaporator.

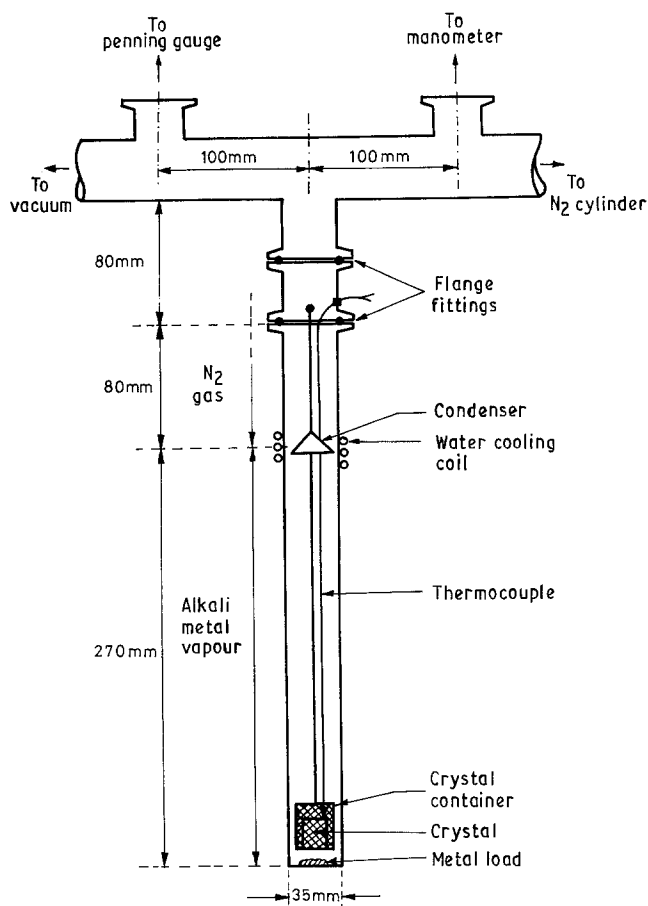* Permanent address: Physics Department, University of Joensuu, Joensuu, Finland.
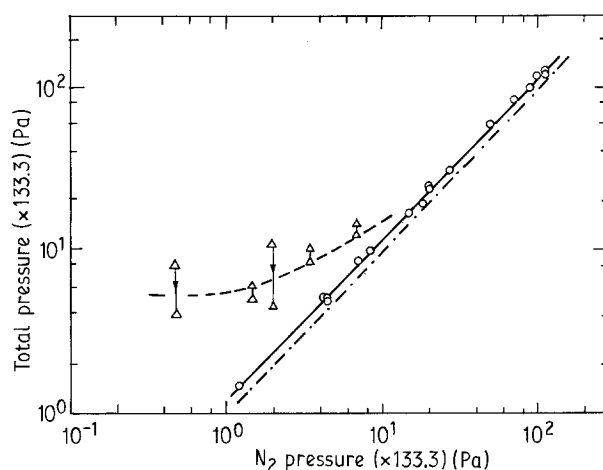
Figure 1 Diagram of the colouration apparatus.

Figure 2 Total pressure during additive-colouration as function of the initial pressure of the N_2 buffer. The triangles indicate the upper and lower limits reached when the colouration tube has been evacuated, before colouration, at room temperature, whereas the circles correspond to high temperature evacuation. The bar-dotted line represents a hypothetical line of zero pressure increase.

3. Results and discussion

Our first experimental observations are related to the search of the laser active $(F_2^+)_H$ centres in sodium and potassium chlorides. The optimum conditions to produce these centres have been reported [6, 7] as starting from oxygen doped samples and adding colouring at moderately low pressures ($\leq 5.33 \times 10^3$ Pa).

Above a colouration pressure of $\simeq 2.66 \times 10^3$ Pa we have obtained good reproducibility during colouration but such a reproducibility is lost when colouring at lower pressures. Simultaneously, it becomes apparent that a sizeable pressure increase takes place during the colouration process. This increase also happens at high colouration pressures but represents a small percentage of the total value, whereas at low colouration pressures it approaches a ten-fold increase in the total pressure.

This situation is illustrated in Fig. 2 where the total pressure reached during the colouration process is represented as a function of the initial value determined by nitrogen gas. It can be seen (triangles) that at low colouration pressures the value reached by the total pressure clearly exceeds that initially chosen by the N_2 buffer. This effect becomes more apparent as the initial pressure decreases. The black arrows indicate the slow decrease between the upper and lower limits, which take place during the colouration time.

As the colouration tube is heated, the alkali metal evaporates from the bottom, being condensed as soon as it reaches the refrigerated upper part of the tube (Fig. 1). In this way, the metal vapour circulates be-

tween these two boundaries and the N_2 gas is compressed to the upper part of the colouration system. A pressure increase $\Delta P/P = -\Delta V/V \simeq 10\text{-}15\%$ is expected, taking into account the dimensions of our colouration system. Therefore, this process cannot explain by itself the observed pressure increase, which reaches a ten-fold factor, thus it becomes necessary to look for an alternative reason to account for the pressure change.

After a thorough check of the system, in order to discard the possibility of a vacuum leak, the only candidate to produce the observed pressure increase is the incorporation of extra molecules to the colouration apparatus due to the outgassing of the colouration tube walls. Such an effect should obviously be occurring but, surprisingly after many years of practicing additive colouration, its incidence on the quality of the coloured crystals has not been analysed in detail.

This effect can be confirmed after examining the behaviour of the system when the colouration tube has been thoroughly cleaned before colouration. The circles in Fig. 2 represent the final pressure reached during colouration when the tube has been previously outgassed under vacuum ($P \simeq 6.66 \times 10^{-4}$ Pa) at the colouration temperature for four h. It is evident that in this case the pressure increase corresponds to the 10-15% expected from the evaporation of the alkali metal. The bar-dotted line gives, for comparison purposes, the hypothetical line of zero pressure increase.

Further confirmation of this explanation can be obtained after the study of the time evolution of the total pressure with the colouration time, which can be observed in Fig. 3. The data corresponds to three situations beginning with the same N_2 pressure (5.99 $\times 10^2$ Pa), but with different outgassing treatments being performed before loading the alkali metal and subsequent colouration. The squares correspond to observations after evacuation of the tube at $\simeq 6.66 \times 10^{-4}$ Pa over four h at colouration temperature,
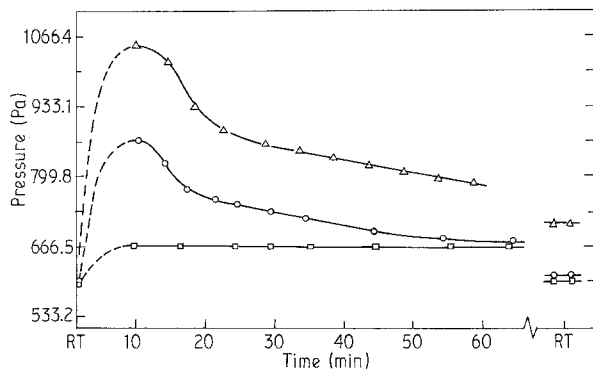
Figure 3 Time evolution of the total pressure during colouration when the tube has been evacuated at room temperature over 4 and 24 h (triangles and circles, respectively), or at the colouration temperature (squares). The final pressure, after colouration, when the tube has been cooled to room temperature (RT) is also represented.

whereas the triangles and circles correspond to observations after room temperature evacuation (4 and 24 h, respectively).

In the first case (squares) only a slight pressure increase is observed during heating and after that, it remains constant during colouration time, finally, recovering the initial value when the system is cooled to room temperature.

In the other situations, when the previous outgassing has been only partial (circles and triangles) the pressure increase is much higher, being the highest for the less pre-cleaned conditions (triangles). In addition, when the crystal is cooled to room temperature after colouration, the pressure does not return to the initial value but shows a residual increase which is also correlated with the evacuation conditions. These results prove the incorporation of extra molecules to the colouration tube which remain in the tube after the process has finished.

With regard to the origin of these spurious molecules, it seems that water vapour absorbed into the colouration tube walls is the more likely candidate. It is well known [8] that even a short contact of clean stainless steel with the open atmosphere produces a strong absorption of water vapour. In fact, a period of 1 h with the tube in open atmosphere followed by evacuation at room temperature below 6.66

$\times 10^{-3}$ Pa produces, when heated to colouration temperature, several pascal of final pressure.

The monotonous pressure decrease during colouration time can then be easily understood. The water molecules will obviously react with the evaporated alkali metal producing the corresponding hydroxide, with a much lower vapour pressure [9], which is deposited at the bottom of the tube with the corresponding pressure decrease.

These processes obviously produce a loss of metal vapour which seems to be the origin of some of the observed problems when using the traditional Van Doorn system. The complex dependence of this loss on the previous outgassing process and on the metal load would explain the irreproducible results obtained during the low pressure colourations.

Although the Van Doorn system always produces additional metal losses because of explosive boiling of metal droplets [4], which sends, irreversibly, some material to the uppermost region of the tube, the main metal loss is produced because of the reaction with the desorbed water molecules, which can be suppressed with the adequate treatment.

When the colouration tube is previously outgassed at the colouration temperature, metal vapour circulation is easily sustained over many hours, avoiding one of the main drawbacks of the Van Doorn system, that is, the critical loss of metal vapour.

In addition to the above mentioned effects, there are some others, also related to the appearance of water vapour, which affect the production of laser-quality additively-coloured alkali halides. These are surface attack and contamination which damage pre-polished surfaces.

The differences in surface quality obtained after a thorough or only partial outgassing before colouration can be appreciated in Fig. 4, where optical microscopy of the surfaces are given. The state of the surface when water vapour has been produced during colouration (Fig. 4b) presents clear evidence of surface attack, showing irregular (rounded) figures, which can be compared (Fig. 4a) with the excellent surface quality obtained after a clean colouration. Both surfaces correspond to freshly cleaved crystals immediately before colouration. This surface attack is presented
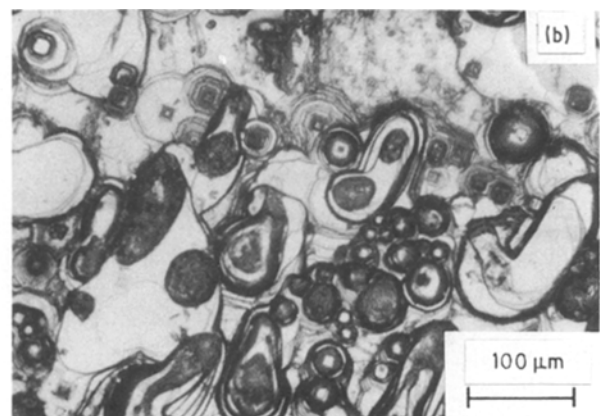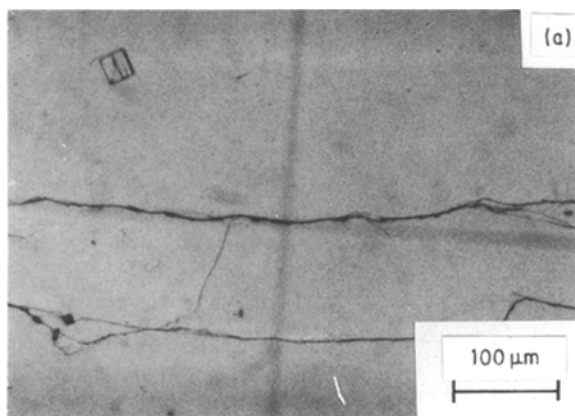

Figure 4 Optical microscopy of the crystal surface after colouration when the system has been previously outgassed at (a) colouration or (b) room temperature.
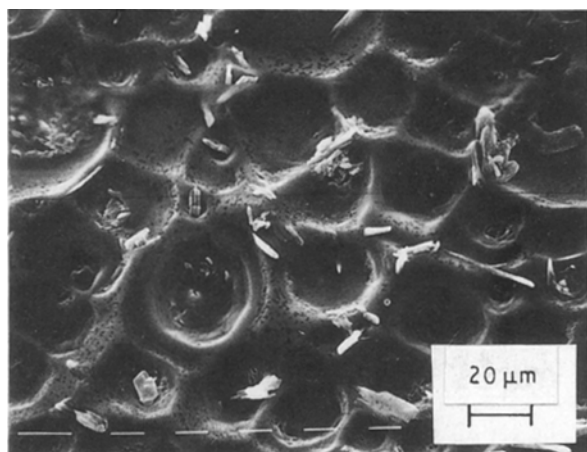
Figure 5 Image, using scanning electron microscopy, of a crystal surface after additive-colouration. In addition to the erosion of the surface a number of irregular shaped precipitates are also observed.
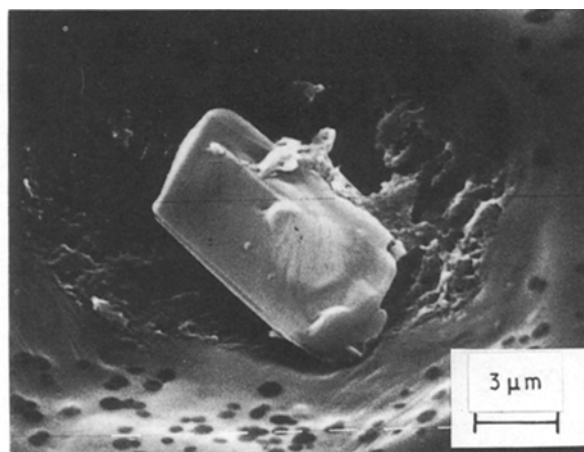

Figure 6 Image, by scanning electron microscopy, of a metal-rich precipitate (77% K) on the surface of a coloured KCl crystal.

with greater detail in Fig. 5, by using scanning electron microscopy. In addition to the evident erosion of the surface, there can also be distinguished a number of irregular shaped depositions, one of which is shown in Fig. 6 at a bigger magnification.

The composition of such microprecipitates, obtained by energy dispersive analysis of X-rays proves that they are metal-rich precipitates. The analysis of the area depicted in Fig. 6, which corresponds to an additively-coloured KCl crystal, reveals a large excess of K (77%) with respect to Cl (23%). Similar compositions are obtained in different microprecipitates.

It has sometimes been assumed that surface contamination during colouration is mainly due to deposition of metal particles [4]. Nevertheless, as we have observed such contamination does not appear when the colouration tube has been previously baked at colouration temperature to avoid the production of water vapour, it seems that such contamination is either enhanced because of the previous surface attack or, more likely, the contaminant is the reaction product (metal hydroxide). As both sodium and potassium hydroxides have much lower vapour pressures than the pure metals [9], they can be deposited onto the attacked surface from where it is not removed by evaporation.

It then seems reasonable to conclude that surface deterioration during additive-colouration of alkali halides, as well as the metal losses, are mainly due to the incorporation of water vapour from outgassing of the tube walls. Such harmful effects are obviously suppressed by using the Mollenauer design, where after the first deoxidizing treatment the alkali metal region is continuously isolated from the atmosphere, but they can also be easily suppressed in the Van Doorn system. If the colouration set up is routinely

subjected to a simple outgassing treatment (evacuation at $P \le 6.66 \times 10^{-4}$ Pa at colouration temperature) before each colouration, negligible loss of metal or surface damage are observed, and then the traditional Van Doorn method can be used to produce laser-quality crystals, taking advantage of its versatility to change from a colouring metal to one another.

Acknowledgements

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