Journal of Luminescence 134 (2013) 576–579

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Electrolytic coloration and spectral properties of hydroxyl-doped potassium bromide single crystals

Lan Qi [a,*], Cuiying Song [b], Hongen Gu [c]

[a] Department of Hydroelectricity, Tianjin University, Tianjin 300072, PR China
[b] School of Science, Tianjin University of Commerce, Tianjin 300134, PR China
[c] Department of Physics, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form
3 July 2012
Accepted 25 July 2012
Available online 1 August 2012

Keywords:
Potassium bromide single crystal
Electrolytic coloration
Color center

ABSTRACT

Hydroxyl-doped potassium bromide single crystals are colored electrolytically at various temperatures and voltages by using a pointed cathode and a flat anode. The characteristic OH^- spectral band is observed in absorption spectrum of uncolored single crystal. The characteristic O^-, OH^-, U, V_2, $O^{2-}-V_a^+$, M_{L1}, F and M spectral bands are observed simultaneously in absorption spectra of colored single crystals. Current–time curve for electrolytic coloration of hydroxyl-doped potassium bromide single crystal and its relationship with electrolytic coloration processes are given. Production and conversion of color centers are explained.

1. Introduction

Pure alkali halide single crystals are very good optical materials. Some of alkali halide single crystals with appropriate color centers or impurities are well-known optoelectronic materials [1–4]. Colored potassium bromide single crystals have very good optical and spectral features, in particular to impurity-doped ones. They have been paid recently a deal of attention to their applications in laser [5], hologram [6], optical storage [7] and spectral holeburning [8] etc. Hydroxyl impurity ions can be introduced into alkali-halide single crystals for stabilizing F_2^+ laser active centers. A color-center laser using hydroxyl-doped potassium bromide single crystal has been realized [5].

Hydroxyl-doped potassium bromide single crystals can be colored by additive coloration and ionizing radiation [9,10], while various color centers are produced in the colored single crystal. As is well known, also electrolytic coloration is an effective and convenient coloration method for producing structural defects in some single crystals such as alkali-halide and alkaline earth halide single crystals. Among advantages of electrolysis is its speed, possibility for visual observation and thus real-time monitoring and control, as well as selectivity with respect to radicals or color centers. Moreover, experimental set up for electrolysis is much simpler than in other coloration methods such as high-energy electromagnetic irradiation or high-energy particle bombardment. Heretofore, no electrolytic coloration for hydroxyl-doped potassium bromide single crystals has been performed because it was believed impossible in anion-doped single crystal in the past research. That is because hydroxyl impurity ions or their dissociated products, such as oxygen-related impurities, can prevent the formation of the secondary alkali cathode. The formation of the secondary alkali cathode is a very necessary condition to start traditional electrolytic coloration through electron injection by using a pointed cathode and a flat anode. However, our recent researches have proved that hydroxyl-doped potassium bromide polycrystals can be colored electrolytically at various temperatures and voltages by using our homemade electrolysis apparatus [11]. Our present results show that hydroxyl-doped potassium bromide single crystals can be colored electrolytically with the same electrolysis apparatus by using a pointed cathode and a flat anode. Useful oxygen-related impurities and various intense F and F-aggregate color centers are produced simultaneously in the colored single crystals. These impurities and color centers can hardly be derived simultaneously from other coloration methods, especially the additive coloration method.

2. Research details

All used potassium bromide single crystals were doped with potassium hydroxide of $5 \times 10^{-4}\,\mathrm{mol}^{-1}$ and supplied commercially. Samples of dimension $8 \times 6 \times 4\,\mathrm{mm}^3$ were cut from the single crystals and polished optically. The samples were colored electrolytically at various temperatures $(200-600\,^\circ\mathrm{C})$ and DC

---

* Corresponding author. Tel.: +086 022 27402970; fax: +086 022 27401284.
E-mail address: lqipaper@eyou.com (L. Qi).

0022-2313/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2012.07.027

voltages (300–3000 V) with the same electrolysis apparatus as the previously used one [12], by using a pointed tungsten cathode and a flat stainless steel anode. Some coarse graphite powders damped with alcohol are used between the sample and anode to ensure good contact. The coarse graphite grains become a graphite anode matrix. The sample is held in slowly flowed dry and pure nitrogen during the electrolytic coloration to protect the electrodes against oxidation. The sample is put on a large copper bulk for quenching to room temperature (RT) after the electrolytic coloration. Absorption spectra of the hydroxyl-doped potassium bromide single crystals before and after electrolytic coloration are measured with a spectrophotometer model UV-240 at RT.

3. Main results

The typical absorption spectrum of a hydroxyl-doped potassium bromide single crystal before electrolytic coloration is shown in Fig. 1. The 197 and 215 nm absorption bands correspond to the O^- and OH^- absorption bands, respectively [13].

Fig. 2 depicts the typical absorption spectrum of a hydroxyl-doped potassium bromide single crystal colored electrolytically at 405 °C and 1500 V for 24 min. The 198, 214, 260, 285 and 620 nm absorption bands correspond to the O^-, OH^-, V_2, $O^{2-}-V_a^+$ and F absorption bands, respectively [11,14,15]. The 363 nm absorption band and the incomplete absorption band near 900 nm may correspond to M_{L1} absorption band and M absorption band peaked at 900 nm, respectively [16].

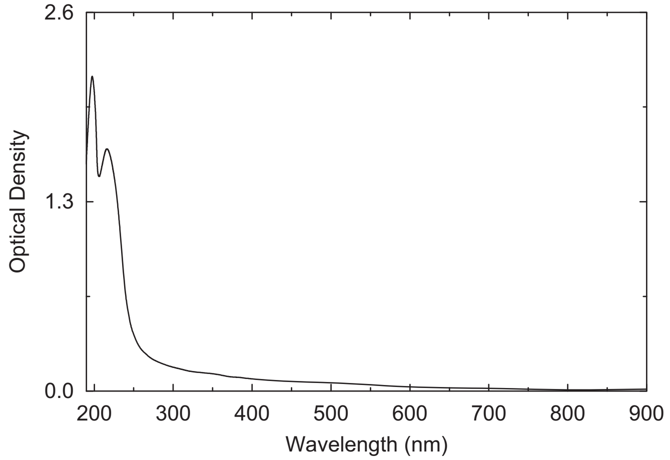

Fig. 1. Absorption spectrum of a hydroxyl-doped potassium bromide single crystal before electrolytic coloration.

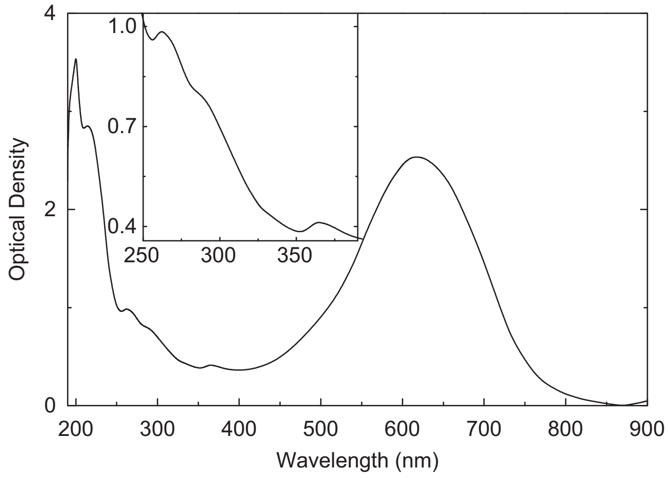

Fig. 2. Absorption spectrum of a hydroxyl-doped potassium bromide single crystal colored electrolytically at 405 °C and 1500 V for 24 min. Inset shows a local enlarged spectrum.

Fig. 3 shows the typical absorption spectrum of a hydroxyl-doped potassium bromide single crystal colored electrolytically at 405 °C and 600 V for 20 min. The 199, 214, 259, 285, 363 and 900 nm absorption bands correspond to the O^-, OH^-, V_2, $O^{2-}-V_a^+$, M_{L1} and M absorption bands, respectively. The intense and broad absorption band corresponds to the F absorption band. The 312 nm absorption band does not correspond to any known color centers and absorption bands.

The typical current-time curve for electrolytic coloration of the hydroxyl-doped potassium bromide single crystal by using a pointed cathode and a flat anode at 410 °C and 1500 V is presented in Fig. 4. The current–time curve of the single crystal is very similar to that of the hydroxyl-doped sodium chloride single crystal [17], and displays two different zone-regimes, which will be discussed in the following chapter.

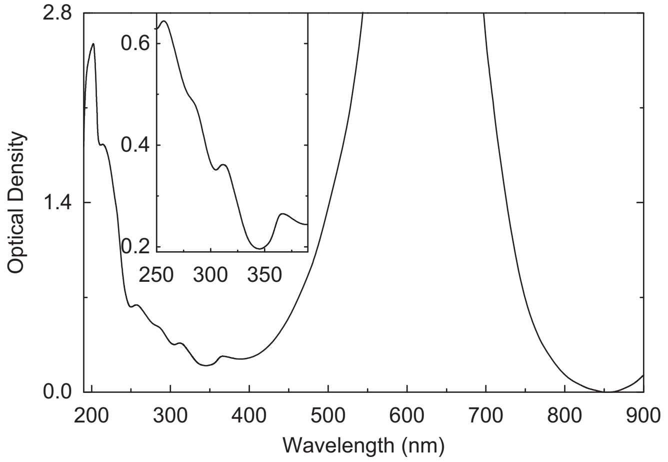

Fig. 3. Absorption spectrum of a hydroxyl-doped potassium bromide single crystal colored electrolytically at 405 °C and 600 V for 20 min. Inset shows a local enlarged spectrum.

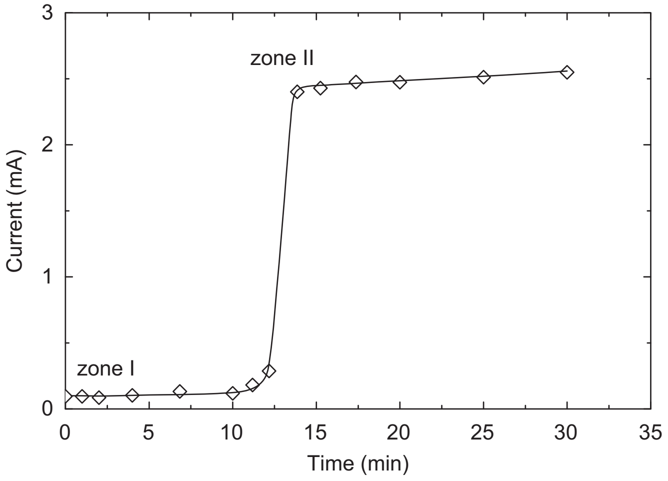

Fig. 4. Current – time curve for electrolytic coloration of a hydroxyl-doped potassium bromide single crystal by using a pointed cathode and a flat anode at 410 °C and 1500 V.