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Electrolytic coloration of air-grown sodium fluoride crystals

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Abstract

Air-grown sodium fluoride crystals were colored electrolytically by using a pointed cathode at various temperatures and electric field strengths, which should mainly benefit appropriate coloration temperatures and electric field strengths. O_2^-, F, M, N_1, N_2 color centers and O^{2-}–F^+ complexes were produced in the colored crystals. Current–time curves for the electrolytic colorations were given, and activation energy for the V color center migration was determined. The formation of the color centers was explained.

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Keywords: Air-grown sodium fluoride crystal; Electrolytic coloration; Color center

1. Introduction

Sodium fluoride hosts with color centers are good optoelectronic materials and have been paid much attention to [1–3]. The color centers in colored sodium fluoride crystals have very good spectral properties in the ultraviolet, visible and near-infrared wavelengths, especially in the colored sodium fluoride crystals containing impurities such as hydroxyl and oxygen impurities. The hydroxyl and oxygen impurities were introduced into sodium fluoride crystals to stabilize laser-active F_2^+ color centers [4], and the pure or impurity-containing sodium fluoride crystals can be easily colored by high-energy ray or particle irradiation. As is well known, electrolysis is a very convenient and efficient method for producing color centers in some crystals. However, the sodium fluoride crystals were difficultly colored using the electrolysis method. According to the literature, only two electrolytic colorations used the pure sodium fluoride crystals with substantial elimination of the hydroxyl impurity or the hydroxyl-free and the mercury-doped ones with hydroxyl neutralization by the divalent mercury ions were successfully performed up to now [5,6]. In the past electrolysis research, it was believed impossible to color electrolytically directly anion-doped crystal such as hydroxyl- or oxygen-containing one because the anions result in electrolytic coloration not to start. However, in our recent work, it is proved that the hydroxyl-doped sodium chloride crystals and lithium-doped strontium fluoride crystals can be colored electrolytically using our homemade electrolysis apparatus at appropriate coloration temperatures and electric field strengths [7,8]. In this work, it is shown that the air-grown sodium fluoride crystals containing more hydroxyl and oxygen impurities also can be colored electrolytically using the same apparatus with a pointed cathode at various temperatures and electric field strengths.

2. Research details

All used sodium fluoride crystals were grown in air atmosphere in our laboratory. Samples of dimension $10 \times 8 \times 7\,mm^3$ were cleaved from the crystal block. The samples were polished optically with waterless abrasive, and then stored in a desiccator with drier until electrolytic coloration due to hygroscopicity of the sodium fluoride crystal. The samples were colored electrolytically at various temperatures and DC electric field strengths using the same

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electrolysis apparatus as the previously used one [7,8], using a pointed tungsten cathode and a flat stainless steel anode. Some graphite powders damped with alcohol were filled between the sample and anode in order to ensure good contact. The sample was held in slowly flowing dry and pure nitrogen during the electrolytic coloration, put on a copper bulk for quenching to room temperature and stored in the desiccator after the electrolytic coloration. Absorption spectra of the samples were measured with a UV-240 spectrophotometer at room temperature and the hygroscopic influence of the samples was not observed obviously during the spectral measurements.

3. Main results

A typical absorption spectrum (solid curve) of an air-grown sodium fluoride crystal colored electrolytically at temperature 703 K and electric field strength $3.15\times10^3\,\mathrm{V\,cm^{-1}}$ for a period of 2.5 h is shown in Fig. 1. There are six obvious absorption bands peaked at 196, 255, 363, 410, 501 and 575 nm in the spectrum. The spectrum can be roughly decomposed into eleven Gaussian type absorption peaks (dashed curves) at 193.0 (peak 1), 220.0 (peak 2), 255.0 (peak 3), 280.0 (peak 4), 342.4 (peak 5), 355.2 (peak 6), 380.0 (peak 7), 414.4 (peak 8), 504.1 (peak 9), 575.5 (peak 10) and 639.2 nm (peak 11), and the corresponding widths are 0.711, 0.640, 0.600, 0.400, 0.600, 0.300, 0.230, 0.246, 0.494, 0.450 and 0.350 eV, respectively. The peaks 1–4 and 6 are due to oxygen impurities, among which the peak 1 associates to O^{2-} color centers [9], the peaks 2 and 4 to O^{2-}–V_a^+ complexes, the peak 3 to O_2^- color centers and the peak 6 was observed previously but unidentified [10]; the peaks 7 and 8 associate probably to remanent magnesium impurities [11]; the peaks 5 and 9–11 associate to F, M, N_1 and N_2 color centers [12], respectively.

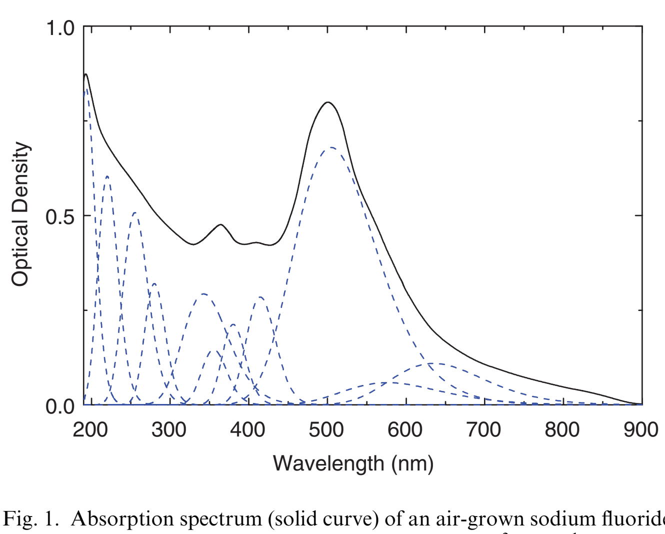

Fig. 1. Absorption spectrum (solid curve) of an air-grown sodium fluoride crystal colored electrolytically at 703 K and $3.15\times10^3\,\mathrm{V\,cm^{-1}}$ for 2.5 h. Dashed curves show resolved peaks.

Fig. 2 presents a typical absorption spectrum (solid curve) of an air-grown sodium fluoride crystal colored electrolytically at temperature 743 K and electric field strength $3.39\times10^3\,\mathrm{V\,cm^{-1}}$ for a period of 4.0 h. It is obvious that the spectrum features are quite similar to those in Fig. 1. The spectrum can be roughly decomposed into eleven Gaussian type absorption peaks (dashed curves) with the same wavelength positions and widths as those of the above peaks, and only relative intensities have some changes.

Current–time curves for the electrolytic coloration of the air-grown sodium fluoride crystals by using a pointed cathode are shown in Fig. 3. These current–time curves are similar to those of the hydroxyl-doped sodium chloride crystals [7] and offer three obvious zones.

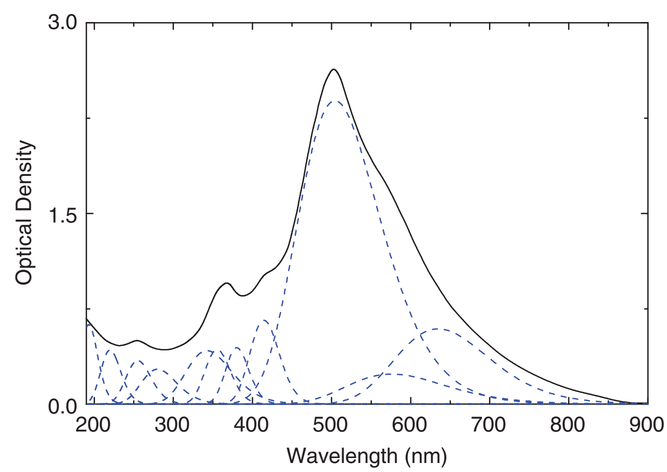

Fig. 2. Absorption spectrum (solid curve) of an air-grown sodium fluoride crystal colored electrolytically at 743 K and $3.39\times10^3\,\mathrm{V\,cm^{-1}}$ for 4.0 h. Dashed curves show resolved peaks.

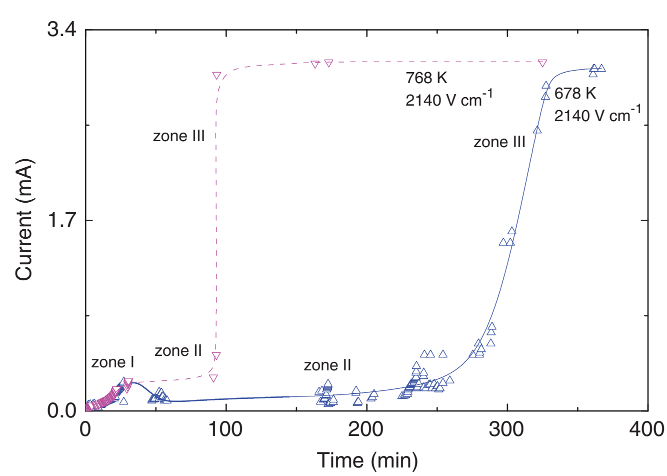

Fig. 3. Current–time curves for electrolytic coloration of air-grown sodium fluoride crystals by using a pointed cathode. The solid curve shows that the crystal was subject to temperature 678 K and electric field strength $2140\,\mathrm{V\,cm^{-1}}$, and the dashed one to temperature 768 K and electric field strength $2140\,\mathrm{V\,cm^{-1}}$.