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Electrolytic coloration of O_2^{2-}-doped NaCl crystals

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Abstract

O_2^{2-}-doped NaCl crystals are colored electrolytically by using a pointed cathode and a flat anode at various temperatures and voltages, which mainly benefit from appropriate coloration temperatures and voltages as well as anode structure of used electrolysis apparatus. Characteristic OH^-, U, V_2^m, U_A, V_2, V_3, O^{2-}–V_a^+ complex, F, R_1, R_2 and M absorption bands are observed in absorption spectra of the colored crystals. Production and conversion of color centers in electrolytic coloration is explained. Current–time curves for electrolytic colorations and their relationships with electrolytic colorations were given.

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Keywords: O_2^{2-}-doped NaCl crystal; Electrolytic coloration; Color center

1. Introduction

Today, it is well known that $(F_2^+)_H$ color center in NaCl crystal host is a very good active center and can be produced by photo- and thermal-treating colored NaCl crystal doped with O_2^{2-} or OH^- impurities [1–3]. A necessary condition for producing the $(F_2^+)_H$ color center is that there is O^{2-}–V_a^+ dipole or its complex in the crystal. Many O^{2-}–V_a^+ dipoles were produced in O_2^{2-}-doped NaCl crystal after crystal growth [4]. O_2^{2-}-doped crystal can be easily colored by additive coloration and high-energy ray or particle irradiation. As well known, an electrolytic coloration is one of traditional coloration methods and has more substantial advantages as compared with other coloration methods such as additive coloration and ionizing radiation ones. The main advantages of the electrolytic coloration include simple apparatus, quick speed, safety, visual, real-time monitor and control and environment protection, in particular to interconversions of impurity ions and productions of electron color centers in some crystals doped with impurity ions, such as the O_2^{2-}-doped NaCl crystal. The O_2^{2-}-doped NaCl crystal contains more negative oxygen and hydroxyl impurity ions, and the impurity ions and their conversion products pay an important role in the applications of the O_2^{2-}-doped NaCl crystal. It will be very significant to simultaneously produce the useful impurity ions and various intense electron color centers such as F and F-aggregate ones if only one simple coloration method is used, and the electrolytic coloration is such a very employable candidate. Unfortunately, no electrolytic coloration for the NaCl crystal doped with O_2^{2-} impurities has been performed heretofore because it was believed impossible to color electrolytically directly anion-doped crystals such as O_2^{2-} or OH^--doped ones in the past electrolysis researches. That is because oxygen impurities prevented formation of secondary alkali cathode that is very necessary to start electrolytic coloration by electron injection. However, our recent researches have proved that OH^--doped NaCl, air-grown NaF and O^{2-}-doped LiF crystals and OH^--doped KI polycrystals are colored electrolytically with our homemade electrolysis apparatus at various temperatures and voltages [5–9]. Our present results show that O_2^{2-}-doped NaCl crystals can be colored electrolytically with the same electrolysis apparatus by using a pointed cathode and a flat anode, and useful

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oxygen-related impurity ions and various intense F and F-aggregate color centers are quickly and efficiently produced simultaneously in the colored crystals, which can hardly be derived from other traditional coloration methods, especially the additive coloration method.

2. Research details

All used NaCl crystals were doped with Na_2O_2 of $3\times10^{-4}\,mol^{-1}$ and supplied commercially. Samples of dimension $10\times5\times5\,mm^3$ were cut from the crystals and polished optically. The samples were, then, electrolytically colored at various temperatures (400–620 °C) and DC voltages (600–1500 V) with the same electrolysis apparatus as the previously used one [10], by 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. The sample was put on a copper bulk for quenching to room temperature after the electrolytic coloration. Absorption spectra of the samples were measured with a UV-240 spectrophotometer at room temperature.

3. Main results

A typical absorption spectrum (solid curve) of an O_2^{2-}-doped NaCl crystal before electrolytic coloration is presented in Fig. 1. The spectrum can be decomposed into 5 Gaussian-type characteristic absorption peaks at 185, 192, 201, 220 and 275 nm, and the corresponding widths are 0.717, 0.300, 0.340, 0.340 and 0.280 eV, respectively. The 220 and 275 nm peaks correspond to O^{2-}–V_a^+ dipoles [4]. The 185 and 192 nm peaks correspond to OH^- ions and U color centers, respectively [11]. The 201 nm peak corresponds probably to U_A color centers (U color centers perturbed with remanent monovalent metal ions such as magnesium ions). In case of KCl:OH^-, Na^+ crystal [12], absorption band of U_A color centers had a red shift to that of U color centers. Therefore, we conjecture that the red shift of the U absorption band of the O_2^{2-}-doped NaCl crystal results probably from existence of U_A color centers.

Fig. 2 shows a typical absorption spectrum of an O_2^{2-}-doped NaCl crystal colored electrolytically at temperature 460 °C and voltage 600 V for 43 min. The absorption band peaked at 200 nm corresponds to the U and U_A color centers, the 210 nm shoulder absorption band to the V_3 color centers [13], the 268 nm absorption band to the O^{2-}–V_a^+ complexes, and the 451 and 547 nm absorption bands to the known F and F_3 color centers [5], respectively. The absorption platform from 300 to 400 nm most probably consists of overlapping absorption bands of Mg-related color centers [14], and the Mg impurities derive from the Mg remnant in the original NaCl material.

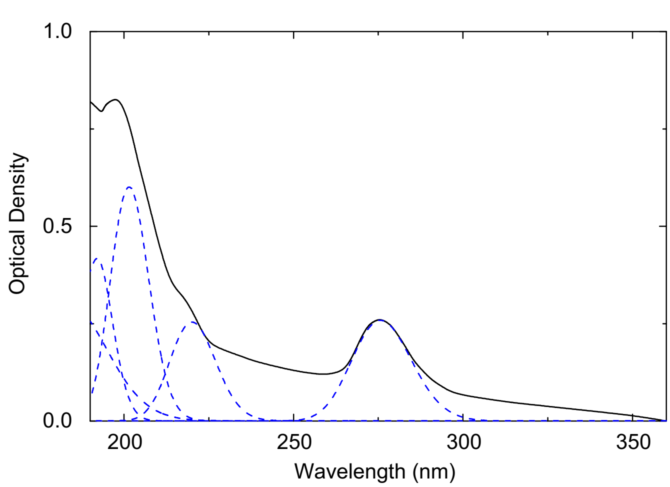

Fig. 1. Absorption spectrum (solid curve) of an O_2^{2-}-doped NaCl crystal before electrolytic coloration. Dashed curves show resolved peaks.

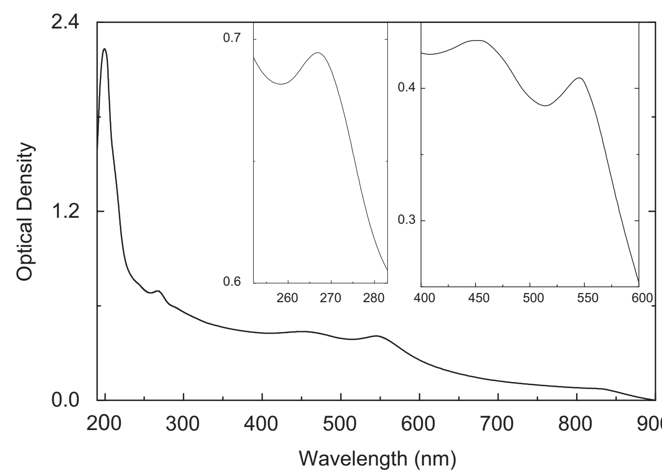

Fig. 2. Absorption spectrum of an O_2^{2-}-doped NaCl crystal colored electrolytically at temperature 460 °C and voltage 600 V for 43 min.

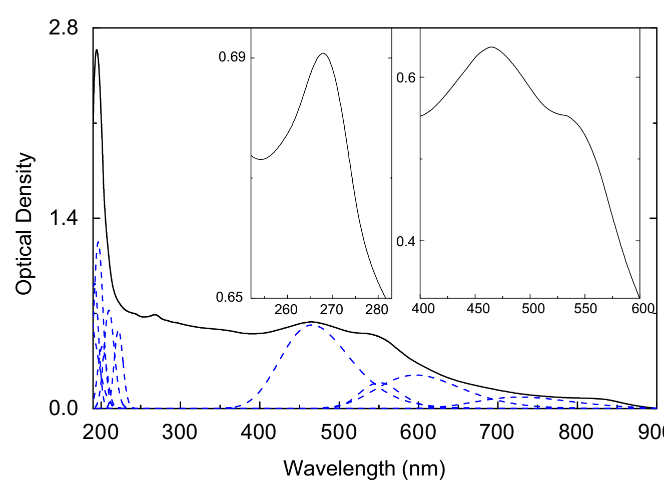

Fig. 3. Absorption spectrum of an O_2^{2-}-doped NaCl crystal after electrolytic coloration at temperature 508 °C and voltage 900 V for 60 min. Dashed curves show resolved peaks.