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Annealing effects on optical properties of natural alexandrite

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Abstract

Natural alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) crystals are investigated as regards the effects of annealing on their optical properties. Optical absorption spectra are measured from the ultraviolet (190 nm) to the near infrared (900 nm), for a sample subjected to consecutive annealing processes, where time and temperature are varied. Besides this, luminescence spectra are simultaneously obtained for this sample, excited with a Kr^+ laser source, tuned on an ultraviolet multi-line mode (337.5, 350.7 and 356.4 nm). We observe from absorption as well as from emission data that annealing mainly influences the distribution of Cr^{3+} and Fe^{3+} ions, located on sites of a mirror plane (C_s symmetry), which are responsible for the optical properties of alexandrite. The results obtained lead to the conclusion that annealing induces a modification of the population of Cr^{3+} on C_s sites as well as on sites located on an inversion plane (C_i). Annealing could improve the optical properties of this material, as regards its application as a tunable laser.

1. Introduction

Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) has technological importance as a material capable of generation of continuous tunable laser output in the range 700–800 nm [1]. It belongs to orthorhombic crystalline system and spatial group $Pnma$ [2]. Its structure is a distorted hexagonal close-packed (hcp) lattice of oxygen ions, where Al^{3+} and Be^{2+} occupy octahedral and tetrahedral sites, respectively. Distortion of a regular hcp lattice of oxygen ions, which are shifted with respect to the c axis, causes the existence of two octahedrally coordinated sites: Al_1 , located at inversion sites (C_i symmetry), and Al_2 , located at mirror sites (C_s symmetry) [3, 4]. It is well known that the larger Al_2 mirror sites are preferentially occupied by Cr^{3+} ions, which dominate absorption and emission properties [1, 5] and, in other words, are responsible for lasing. Alexandrite emission and absorption spectra have been investigated under different conditions, with or without polarization light along the crystallographic axis [6], as functions

of applied pressure or varying temperature [7], or as functions of the pumping wavelength [1]. However, the correct distribution of Cr³⁺ in Al₁ and Al₂ sites is still unknown.

In this paper we present optical absorption and luminescence spectra, which are obtained through consecutive annealing processes for natural alexandrite samples, coming from Minas Gerais state, Brazil. Characteristics of optical spectra and modifications of the curve shape induced by annealing provide information on the interaction between optically active ions and the host lattice [8]. These interactions affect the optical behaviour and decay dynamics, which are very relevant for alexandrite laser operation. For comparison we also present luminescence spectra of a synthetic alexandrite sample, grown by the Czochralski technique.

2. Experimental set-up

The natural sample is 1.16 mm thick and the synthetic sample is 2.32 mm thick. The chemical composition of the natural sample was determined by x-ray spectroscopy of the wavelength dispersion (WDX). Three distinct phases were found: chrysoberyl itself (BeAl₂O₃), quartz and mica, as confirmed by x-ray diffraction [9]. As regards the atomic composition, besides Cr (0.073 at.%), there is also a large concentration of Fe (0.130 at.%) as an impurity in the chrysoberyl matrix. Smaller amounts of other impurities, such as Ti, K, Si, Mg and Ca, have also been found. Only the impurity Cr has been identified in synthetic alexandrite, which makes this sample suitable as a reference for comparative analysis of optical results as regards the Fe activity in natural alexandrite.

We have used an Innova Coherent 200 Kr⁺ laser, tuned on ultraviolet multi-lines (MLUV: 337.5, 350.7 and 356.4 nm), with output power of 0.43 W, as the excitation source in our luminescence set-up. The irradiation of alexandrite with this laser induces a colour change from green to red in the samples, which means the excitation of an absorption band of Cr³⁺. The laser beam is guided by mirrors and lenses and laser pumping is carried out such that the laser beam irradiates the sample in a direction parallel to the monochromator entrance slit, which means that the emitted signal is collected perpendicularly to the laser illumination direction. The luminescence signal is focused by an objective lens and modulated by a chopper placed just before a Jarrel-Ash monochromator. The monochromator works with a diffraction grating of 1200 g mm⁻¹ and blazed at 500 nm. The scanning range goes from 380 to 900 nm and the resulting signal is detected by a Hamamatsu R446 photomultiplier. Data acquisition is done using a lock-in amplifier coupled to a computer that also controls the scanning speed and motor step. The slit width is 10 μm and the resulting resolution is 0.20 nm.

For optical absorption measurements we have used a Cary 17 spectrophotometer, with the scanning range from 185 to 2500 nm. Data acquisition was done at room temperature as well as at 77 K, with 0.5 nm resolution.

The natural alexandrite sample was subjected to annealing in a muffle oven, at room temperature, for varying times and temperatures of annealing. The thermal combinations used are: 700 °C—15 min (TT1); 800 °C—15 min (TT2); 900 °C—15 min (TT3); 1000 °C—15 min (TT4); and 1000 °C—5 h (TT5). Cooling down was done by removing the sample from the oven always at 700 °C and placing it on an aluminium foil, located over a glass plate kept at room temperature. This procedure represents an attempt to achieve slow cooling, avoiding thermal shocks that could leave the sample fragile.

3. Spectroscopy of Cr³⁺ in natural alexandrite

The optical properties of Cr³⁺ in alexandrite are similar to those of Cr³⁺ in other hosts with octahedral symmetry such as Al₂O₃ and YAlO₃. All of these compounds present two well

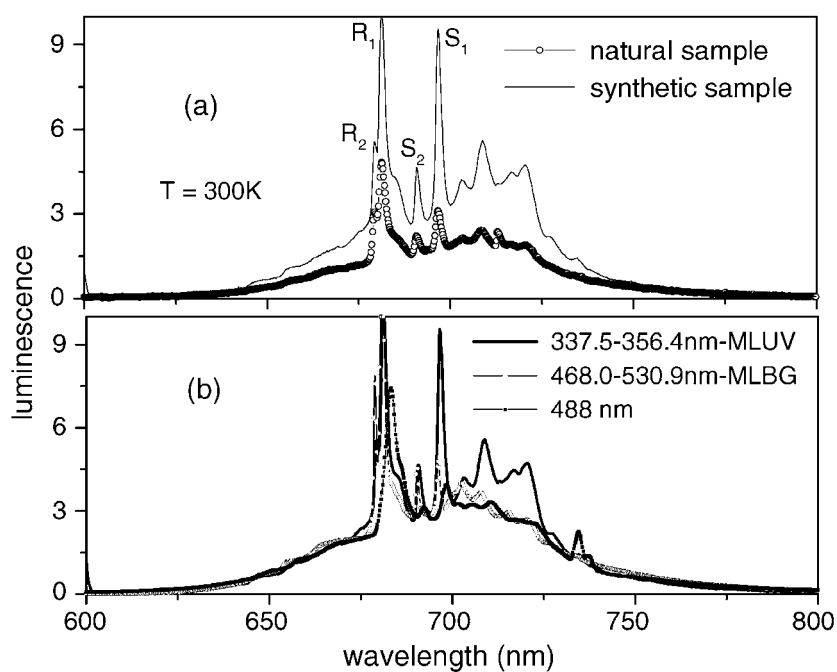


Figure 1. (a) Luminescence spectra of natural and synthetic alexandrite at 300 K, prior to any annealing. Excitation is done with MLUV from a Kr⁺ laser. (b) Luminescence spectra of a synthetic sample as a function of the pumping wavelength.

defined lines, for ${}^4A \leftrightarrow {}^2E$ (R lines), and two broad absorption bands. However, the intensity and relative position of these transitions vary from host to host [10]. In the case of alexandrite these broad bands are associated with transitions from the ground state 4A_2 to the excited state 4T_2 (called band A and centred at 590 nm) and 4T_1 (called band B and centred around 420 nm). These transitions are related to changes in the crystal field orbitals of electrons and are highly sensitive to the crystal field in the neighbourhood of the ion sites. Vibrational modulations of the field strength produce such broadenings of bands [8]. As regards the R lines, they come from the transition from the ground state to the degenerate 2E level and are related to small modifications of the electron wavefunction due to spin, without changes in the crystalline field and, thus, they show up as narrow lines [8]. These lines are attributed to Cr³⁺ ions in sites located on a mirror-like plane (R₁ and R₂ lines) and appear at precisely the same wavelengths, 680.4 and 678.5 nm respectively, in spectra of absorption and emission at room temperature. In the emission spectra, the lines S₁ and S₂ at about 695.8 and 689.9 nm are from the zero-phonon transition ${}^2T_1 \leftrightarrow {}^4A_2$. Zero-phonon lines should also appear in exactly the same position in the emission and absorption spectra whereas vibronic transitions appear as mirror images about the zero-phonon line [11].

In figure 1(a) we present the luminescence spectra of natural and synthetic samples, prior to any kind of annealing. In this case, the relative intensities of the R₁ and R₂ lines, due to Cr³⁺ in Al₁ sites, present the same behaviour, with the intensity of the R₁ lines higher than that of the R₂ ones. Figure 1(b) shows luminescence spectra for the synthetic sample using a distinct pumping wavelength. Although it shows variation in intensity, the laser pumping wavelength does not shift the line position. To our knowledge, luminescence spectra obtained with multi-line ultraviolet (MLUV) (337.5–356.4 nm) have never been reported before.

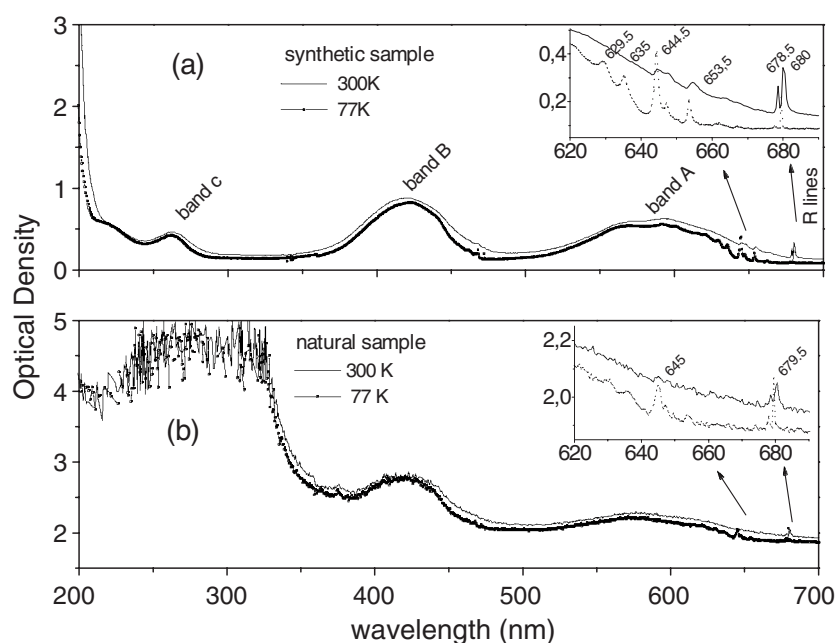


Figure 2. (a) Optical densities of synthetic alexandrite at different temperatures. (b) The optical density of natural alexandrite. Inset (in both figures): details of the region between 620 and 690 nm showing R lines and vibronic transition lines. The labels indicate the lines observed at 77 K.

Figure 2 shows absorption spectra for a natural sample as well as for a synthetic sample, measured at two temperatures: 77 and 300 K. In this figure, the same behaviour as in the luminescence spectra is observed for the R lines. In the optical absorption spectra of the synthetic sample, besides bands A and B, centred around 576.5 and 424.5 nm, there is also a third band [9], less intense, at about 265 nm (band C), which relates to a third transition allowed by spin: ${}^4A_{2g} \leftrightarrow {}^4T_{1g}$. Although band C can be predicted [12], it is hardly found experimentally, since Cr^{3+} spectra in the ultraviolet region are masked by the presence of Fe^{3+} traces. For the synthetic sample (figure 2(a)), band C is observed, but for the natural sample the Fe^{3+} concentration higher than that of Cr^{3+} , making it impossible to observe band C. In the right tail of band A and B, vibronic transition lines are present, at about 650 and 470 nm respectively, weakly visible in the absorption spectra at room temperature, at about 655.7, 649.3 and 645.2 nm. S lines are not identified in the absorption spectra shown in figure 2. At 77 K, the presence of the vibronic transition lines at 629.5, 635, 644.5, 647 and 653.5 nm is clearly evident. Besides this, lines at 468 and 472 nm which are attributed to Cr^{3+} ions located at mirror sites are also seen.

For Cr^{3+} lines relating to Al_1 , S_1 and S_2 sites, it is seen in the luminescence spectra that for the synthetic as well as the natural sample, the S_1 line is more intense than the S_2 line. We believe that this behaviour is related to a variation of population rates. This effect has also been observed for optical absorption data, since the widths and intensities of these peaks change slightly between natural and synthetic samples.

Luminescence spectra as a function of thermal annealing are shown in figure 3(a). All of them have been obtained by pumping the sample with a Kr^+ laser tuned to the MLUV. For the sake of clarity, the curves obtained after TT2 and TT4 are not shown. The spectra show that lines S_1 and S_2 present distinctive intensities when compared to those for the synthetic sample,

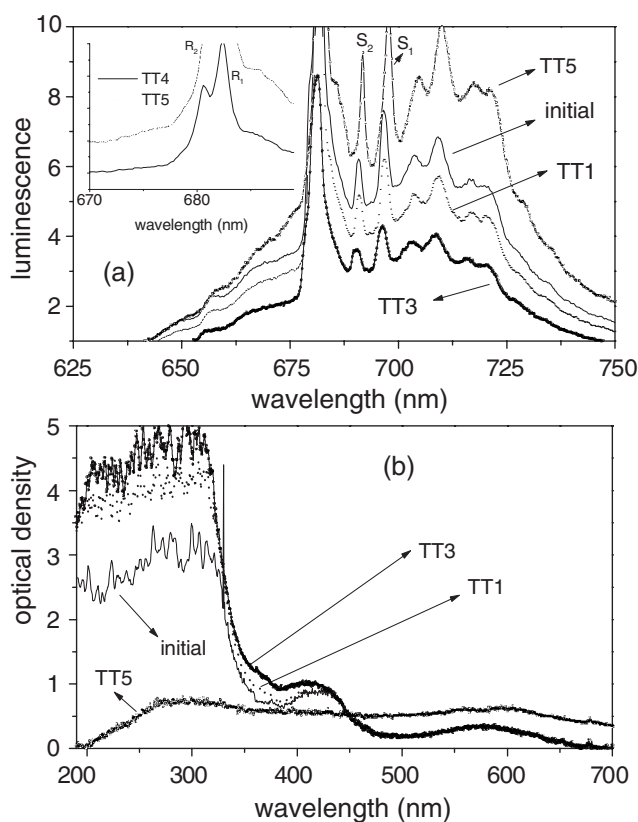


Figure 3. (a) Normalized luminescence spectra of natural alexandrite as a function of consecutive annealings. Inset: detail of the R_1 and R_2 separation after TT4. (b) Normalized optical density of natural alexandrite as a function of consecutive annealings. TT1: 700 °C—15 min; TT2: 800 °C—15 min (curve not shown); TT3: 900 °C—15 min; TT4: 1000 °C—15 min (curve not shown); TT5: 1000 °C—5 h.

similar to what happens before annealing. As mentioned previously, lines S_1 and S_2 , at about 696.9 and 690.8 nm respectively, are related to Cr^{3+} located on inversion sites. We notice that after annealing for a short time (15 min) at different temperatures (700, 800 and 900 °C, respectively), these lines show an intensity decrease, resulting in a reduction of about 50% after the third annealing (900 °C—15 min). After the fourth annealing (1000 °C—15 min), the S lines have their intensity increased again, becoming practically identical to the original data, prior to any annealing. After the fifth annealing (1000 °C—5 h), the intensity shows a sharp increase. Besides this, bands become higher and narrower after the TT4 and TT5 annealing, with better defined peaks related to their position. Then, we can notice that S lines suffer a slight shift towards lower energy, of about 1 nm. On the other hand, R_1 and R_2 lines present intensities much higher than those of S lines before annealing and the separation of these lines becomes harder to observe. These lines are originally located at 681.2 and 679.4 nm respectively and are attributed to Cr^{3+} ions located on mirror sites, responsible for the optical properties of alexandrite. The positions of the R lines are also shifted to lower energy after TT4 and TT5, similarly to the S line behaviour. The fourth annealing also seems to influence the R_1 and R_2 separation: it becomes possible to distinguish them after TT4—at 682.4 and 680.6 nm

respectively. Again, for the sake of clarity, this separation of the R lines in the luminescence spectra after TT4 is shown in the inset of figure 3(a). However, after the fifth annealing, the emission intensity increases very much and it becomes hard to observe the R line separation.

This S and R line behaviour after this sequence of annealings indicates that variation of the Cr^{3+} population rate occurs and also that such variation is possibly related to higher Fe^{3+} concentration compared to that of Cr^{3+} , as obtained from compositional analysis of natural samples. This hypothesis is reinforced by the observation of optical absorption spectra in figure 3(b), where it is shown that after TT5 (1000 °C for 5 h) a dramatic modification in the absorption spectra is seen. In figure 3(b), for the sake of clarity once more, the curves obtained after TT2 and TT4 are not shown. Band B, attributed to overlap of the bands of Cr^{3+} and Fe^{3+} distributed on inversion and mirror sites, practically vanishes. Besides this, band C shows up in the UV region. These effects support the hypothesis that annealing promotes Fe^{3+} ion migration to other sites as well as a redistribution of Cr^{3+} ions throughout the alexandrite structure. However, modifications of the positions and intensities of the emission lines and absorption bands do not affect the optical properties of alexandrite. The change in colour of this material when exposed to artificial light is preserved. Besides this, the R lines, responsible for the optical properties, remain present in the luminescence spectra as well as in the absorption spectra. These effects mean that the potential of alexandrite for continuous tunable emission output is preserved in the range 650–750 nm, a very desirable laser requirement [1].

At present, we are carrying out annealing under controlled partial pressure of oxygen, since it has been observed [13] that the presence of oxygen vacancies may cause the formation of electric dipoles of impurity–vacancy (IV) type [14]. With these new annealing experiments we should get more details on Cr^{3+} and Fe^{3+} migration and, thus, give new contributions to a better understanding of the site occupation, which could lead to an improvement of the attractive optical properties of this material.

4. Conclusions

Luminescence spectra of natural alexandrite show an increase in intensity when the sample is subjected to a rather long annealing, improving the peak resolution of the S lines. Optical absorption data are substantially modified by a series of annealings, in agreement with our hypothesis of Fe^{3+} ion migration as well as Cr^{3+} ion redistribution throughout the sample. X-ray diffraction results show no alteration of the alexandrite crystalline structure.

Our data show that the optical properties of alexandrite are essentially preserved no matter what time and temperature of annealing are chosen. However, the redistribution of Cr^{3+} and Fe^{3+} ions between inversion and mirror sites in natural samples may lead to improved emission efficiency, if the time and temperature of annealing are appropriately selected.

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