

Cr³⁺ Distribution in Al₁ and Al₂ Sites of Alexandrite (BeAl₂O₄: Cr³⁺) Induced by Annealing, Investigated by Optical Spectroscopy

Neilo M. TRINDADE¹, Rosa M. F. SCALVI², Luis V. A. SCALVI^{2*}

¹Programa de Pós-Graduação em Ciência e Tecnologia de Materiais (POSMAT)-FC, UNESP, C. P. 473, Bauru, SP, Brazil

²Physics Department-FC-State University of São Paulo—UNESP, CP 473, CEP 17033-360, Bauru, SP, Brazil
Email: scalvi@fc.unesp.br

Abstract: In order to investigate optical properties of alexandrite, the present work deals with the influence of thermal annealing on optical absorption and luminescence spectra of natural samples. The exposure time to heat treatment at 1000°C is taken into account. Possible migration of Cr³⁺ ions from Al₁ (inversion site) to Al₂ (reflection site) is detected. Sample composition is obtained through Scanning Electron Microscopy (SEM) measurements and points to a rearrangement of Cr³⁺ and Fe³⁺ ions in the alexandrite crystalline structure, under thermal annealing influence. This feature may be used to control the optical properties of natural alexandrite, which can be associated to the observed laser emission effect.

Keywords: A. oxides, D. optical properties, D. defects

1. Introduction

Alexandrite is a rather rare and precious mineral and the interest on its production goes from gemological to laser technology. Alexandrite structure is of chrysoberyl type with the incorporation of chrome in its lattice, according to the chemical formula: BeAl₂O₄:Cr³⁺. This material became technologically important from 1974, when its utilization as an active media for laser action became known, through the utilization in a synthetic form [1]. Alexandrite emission can be tuned in the range 700-800nm [2]. There is a great interest for the alexandrite laser in the present days since it has been vastly used for medical purposes, presenting superior performance compared to other lasers [3–5]. The combination of the chromium doping and chrysoberyl matrix leads to very favorable properties. The alexandrite crystal is mechanically rigid and presents a fair thermal conduction. The alexandrite laser is able to resist to higher repetition rates, and emit a higher average output power, when compared to other Cr³⁺ lasers [6]. Although its utilization has been widely spread, the laser effect, which is related to its optical properties, is not completely understood. This issue has motivated very recent research on this subject [7]. Besides, Brazil is one of the largest producers of natural alexandrite, which possess a high gemological value, related to the alexandrite effect. This effect means a color change from green, under exposition to sunlight, to red, on illumination by an

incandescent lamp [8].

The alexandrite unit cell can be visualized as approximately hexagonal close packed (hcp) and composed of four molecules, with eight Al³⁺ ions, occupying distorted octahedral sites, and four Be²⁺ ions, located at tetrahedral distorted sites, besides oxygen ions located in plans perpendicular to c axis [9]. Distortions from a precise hcp structure of oxygen ions originate two sites of distinct symmetries: one is called Al₁, located at an inversion site and the other is called Al₂, located at a reflection site [10]. Both Al sites are octahedrally coordinated. The Al₂ coordination octahedron has a larger Al-O average bond length (1.938 Å) when compared to the Al₁ octahedron (1.890 Å) resulting in a larger polyhedral volume [7]. It is known that Al₂, due to its larger size, is preferentially occupied by the Cr³⁺ ions and it is the main responsible for the optical properties of alexandrite [11]. A recently reported work [8] shows the importance of the doping with chromium ions in alexandrite, and claims that the saturation of the green and the red color is virtually determined only by the relative amount of chromium ions replacing aluminum in Al₁ and Al₂ sites. Besides, the color depends on the relative concentration of other impurities, such as titanium and iron [8].

In order to investigate optical properties of this material, the optical absorption technique has demonstrated as very appropriate to analysis of the impurities effect [12]. Previous published data [13] show that spectroscopic properties of Cr³⁺ ion in alexandrite are similar to

Table 1. Composition of natural alexandrite obtained through EDS analysis for two samples

Element	Composition (wt%)	
	<i>Sample I</i>	<i>Sample II</i>
C	0.74	1.54
Na	0.14	-
Mg	0.07	0.30
Al	76.45	77.47
Si	13.33	8.74
Cl	0.10	0.55
K	0.37	1.37
Ca	0.15	0.90
Ti	0.12	0.24
Cr	0.09	0.17
Fe	0.44	1.93

Table 2. Compositional analysis, particularly for Fe and Cr of natural alexandrite obtained by WDS

Sample	Wt%Cr	Wt%Fe
<i>I</i>	0.13	0.61
<i>II</i>	0.41	0.37

Cr^{3+} ion effect in other oxide hosts with octahedral symmetry such as Al_2O_3 and YAlO_3 . In all of them, the spectra present two well defined lines ${}^4\text{A}_{2g} \leftrightarrow {}^2\text{E}_g$ (R lines) and two wide absorption bands. However, the intensity and relative position of the lines related to these transitions depend on the host nature [14]. In the case of alexandrite, these wide bands are associated with the transition from ground state ${}^4\text{A}_{2g}$ to excited states ${}^4\text{T}_{2g}$ (band A, centered at 590nm) and ${}^4\text{T}_{1g}$ (band B, centered at 420 nm). These A and B bands are attributed to Cr^{3+} and Fe^{3+} ions, which may be present in the two sites of distinct symmetries. A third band has been reported [15], and has been related either to a charge transfer transition or to a transition terminating in one of highest levels of the $3d^3$ configuration, such as the ${}^4\text{T}_{1g}$ levels [16,17]. This band is generally called C, located in the UV region, being hardly observed in the optical absorption spectra, because this range is strongly influenced by Fe^{3+} traces [18].

In this paper, we present results of optical absorption measurements on natural alexandrite samples, along with results obtained for a synthetic sample, for comparison. These data allow identifying an Ultraviolet (UV) band, besides broad bands in the visible (VIS) range. The influence of thermal annealing at 1000°C is taken into account. Previous results of X-Ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) corroborate

to the obtained conclusions.

2. Experimental

All the natural samples used in this paper come from the same mine, in the Minas Gerais state, Brazil. The synthetic sample was grown by the Czochralski method, and has been initiated by a high-quality crystalline seed. This sample has been described elsewhere [19]. Optical absorption measurements were carried out in the range 200 to 700nm (UV-VIS), using a spectrophotometer Cary 1G of Varian. For absorption data obtained at 77K, a liquid nitrogen cryostat was used, which was placed close to the spectrophotometer excitation slit. Luminescence data was obtained through excitation with an Argon laser from Spectra Physics, model 2017, with main excitation energy of 2.51eV. The laser beam excites the sample located inside a He closed-cycle Janis Research cryostat, model CS-150, which uses a Cryogenics compressor, model 8200. The emitted light is acquired by a Jobin Yvon T6400 spectrophotometer and the signal is detected by CCD (Charge Coupled Device) also from Jobin Yvon.

Thermal annealing was accomplished by varying time, with the temperature fixed at 1000°C , under room pressure conditions. Natural alexandrite samples were annealed according to the following procedure: the oven temperature was raised until 1000°C with $20^\circ\text{C}/\text{min}$ of rate and kept at this temperature by the desired time. The cooling down is done using the same temperature rate. Samples were submitted to consecutive annealing whereas the optical absorption spectra are recorded between each annealing.

Chemical composition of these samples was measured by EDS (Energy Dispersive Spectroscopy) and WDS (Wavelength Dispersive Spectroscopy), particularly Al, Cr and Fe concentration. Table 1 presents composition obtained through EDS from the analysis of two natural alexandrite samples coming from the same source, and Table 2 presents the compositional analysis, particularly for Fe and Cr present in these samples, obtained by WDS. The Fe composition is very relevant in the alexandrite sample, because a high amount of this impurity may mask the identification of optical absorption bands attributed to Cr^{3+} in the host matrix. As can be verified in Tables 1 and 2, Fe has higher concentration compared to Cr in natural alexandrite. EDS analysis was performed in order to determine the presence of the most concentrated elements in the material and these results are semiquantitative, since the oxygen determination is not reliable and beryllium is not detected by this technique. On the other hand, the Fe and Cr composition determined by WDS are practically quantitative, since it is possible to determine the oxygen concentration. Results are as expected since natural materials present several types of

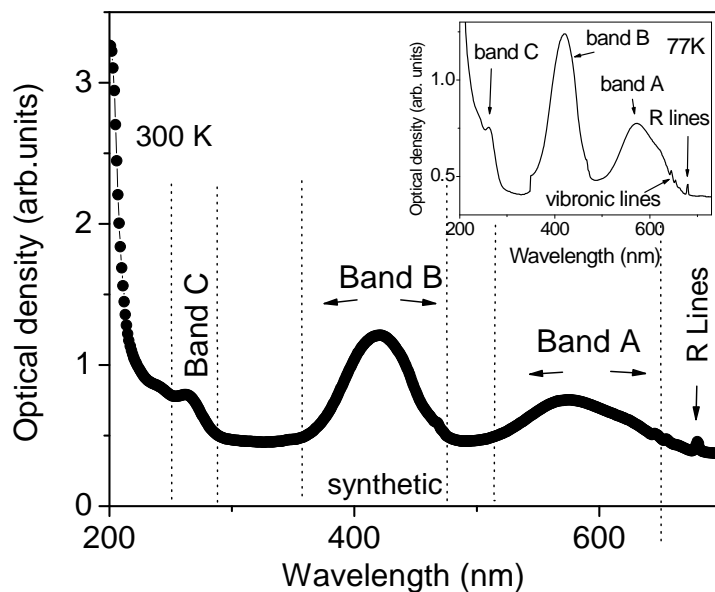


Figure 1. Optical absorption spectra of synthetic alexandrite samples, measured at room temperature (300K). Inset-optical absorption spectra of synthetic alexandrite, measured at liquid nitrogen temperature (77K).

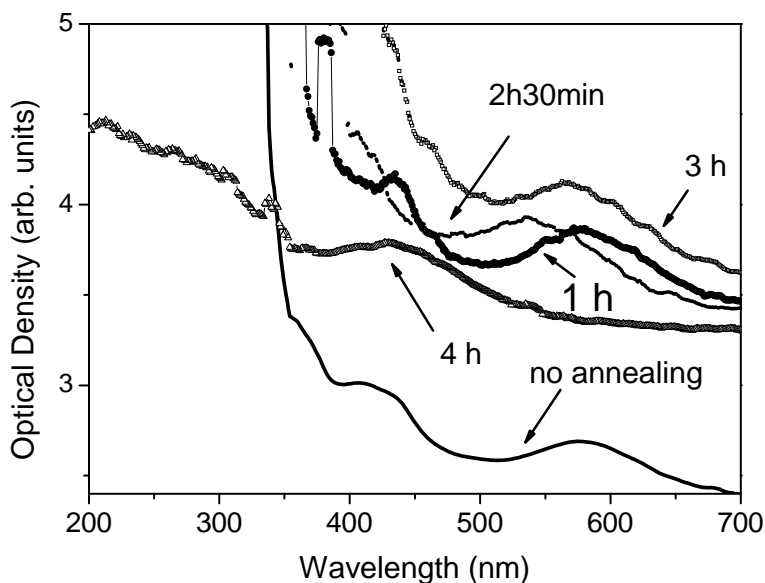


Figure 2. Optical absorption spectra of natural alexandrite as function of consecutive annealing

impurities incorporated in the original stone. Moreover, these data confirm that the presence of Fe in these samples is high, surmounting the presence of Cr in the material.

3. Results and Discussion

Figure 1 shows optical absorption spectra for synthetic alexandrite, measured at 300K. The inset in Figure 1 represents the absorption spectra for the same synthetic sample, measured at 77K. Bands A and B are clearly

identified. Band C is also identified, which becomes possible due to the absence of iron in the synthetic sample composition. The lines R in alexandrite are attributed to Cr^{3+} located at Al_2 sites on a reflection plane (lines R_1 and R_2), and show up precisely at same wavelength either in the emission as well as in the absorption spectra, at 680.4 and 678.5nm, respectively [20]. The lines R are responsible by optical properties of alexandrite.

Band A represents overlapping of two absorption bands of Cr^{3+} ions in two distinct sites Al_1 and Al_2 . Band B represents Cr^{3+} and Fe^{3+} also incorporated at different

sites. Relevant parameters for the synthetic sample are obtained from Figure 1, such as band wavelength position, absorption coefficient and the full width a half maximum ($\Delta\lambda$), and are presented in Table 3. As can be verified, the results of optical absorption at room temperature and at liquid nitrogen temperature, in synthetic alexandrite, show agreement in the position of absorption bands, absorption coefficients and $\Delta\lambda$, with no significant variations. This sample is used as a reference in this paper, due to its outstanding optical quality. The measurement carried out at 77 K (inset of Figure 1) shows clearly the vibronic transition lines at 645, 654 and 663 nm [21].

The influence of consecutive thermal annealing on optical absorption bands of natural alexandrite is shown in Figure 2. The analysis of variation in the spectra allows investigation of the possible migration of Cr^{3+} between Al_1 and Al_2 sites. Relevant parameters for this material, such as $\Delta\lambda$ and absorption coefficient are obtained from Figure 2, and are presented in Table 4.

With the help of Tables 3 and 4, bands A and B of natural alexandrite samples without thermal annealing and the bands due to synthetic sample, recorded at room temperature, can be compared. It is easily verified that their central position (λ) shows a short shift. A larger difference occurs between their absorption coefficients, where the synthetic sample presents lower values than the natural alexandrite. Natural sample shows an absorption coefficient 12 times higher for band A and 5 times higher for band B compared to the values of corresponding bands for the synthetic sample. That can be explained by the Cr concentration, which is higher for natural material and also due to the Fe concentration, which is present only in the natural samples. This is in good agreement with the lower optical density and higher transparency of synthetic sample.

Concerning the natural sample, the absorption spectra present large bands centered about 580 and 585nm (band A) and 425 and 435 nm (band B), besides the R lines, close to 680nm. Thermal annealing causes a consecutive and discrete increase in the optical absorp-

tion coefficients and a broadened band, which must be related to the increase of Cr^{3+} population in sites Al_1 and Al_2 . This statement is reinforced by decomposition of this band, as shown in Figure 3. Band A vanishes with thermal annealing during 4 h, when the noise in the UV starts to disappear and band C begins to gain shape. This band had previously been found only with 5h of thermal annealing [21]. It shows that thermal treatment is an efficient method of refining the optical absorption data. Then, the emerging of band C can be related to the disappearing of band A. It is known that band A is an absorption band from Cr^{3+} ions in sites Al_1 and Al_2 and band C is also related with presence of Cr^{3+} [15]. Then, one may conclude that thermal annealing leads to diffusion of Cr^{3+} through the alexandrite lattice. An increase of absorption coefficient of band B is taking place, presenting a maximum with 2h of annealing time, vanishing with 2 and a half hours and showing up back, but with lower absorption coefficient with 4 h of thermal treatment. These modifications indicate migrations of Cr^{3+} and/or Fe^{3+} ions throughout the materials structure, revealed by the variation of $\Delta\lambda$. The lines R, either can be observed in a sole line, or separated in two lines, called R_1 and R_2 . The line R_1 is located around 680- 682nm and R_2 around 678-680nm.

The analysis of optical absorption bands behavior of natural alexandrite sample submitted to thermal annealing can be done by comparing with synthetic sample (Figure 1). In our approach, the band A is decomposed in two Gaussian curves, in order to estimate the relative amount of Cr^{3+} ions between Al_1 and Al_2 sites [14] and the migration caused by thermal annealing. The data fitting for the synthetic sample, shown in Figure 3, leads to the best fitting of band A, when a regression of two Gaussian curves is used. Band A corresponds to overlapping of optical absorption bands from Cr^{3+} located in sites Al_1 and Al_2 , as already mentioned. Al_2 is larger than Al_1 , and then, it is preferentially occupied by Cr^{3+} ions. There is a dependency on color shift and other optical properties with Cr^{3+} distribution among these sites,

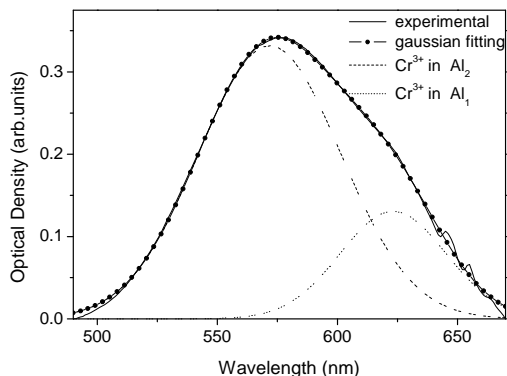
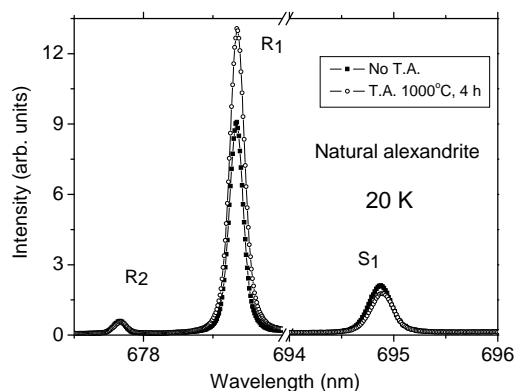
Table 3. Parameters obtained from optical Absorption data for synthetic alexandrite, at 300 and 77 K. λ means the position of maxima. α is the optical absorption coefficient and $\Delta\lambda$ is full width a half maximum

T (K)	Optical Absorption bands – Synthetic sample									Absorption Lines of Cr^{3+}
	Band A (Cr^{3+})			Band B (Cr^{3+} , Fe^{3+})			Band C (Cr^{3+})			
	λ (nm)	α (cm^{-1})	$\Delta\lambda$ (nm)	λ (nm)	α (cm^{-1})	$\Delta\lambda$ (nm)	λ (nm)	α (cm^{-1})	$\Delta\lambda$ (nm)	
300	583	0.31	91.5	420	0.75	59.5	267	0.11	16.8	680
77	582	0.32	90	419	0.76	56.6	265	0.11	15.8	680

Table 4. Parameters obtained from optical Absorption data (UV-Vis) for natural alexandrite sample after thermal annealing. λ means the position of maxima. α is the optical absorption coefficient and $\Delta\lambda$ is full width a half maximum

	Absorption bands of natural alexandrite									Absorption Lines of Cr ³⁺
	Banda A (Cr ³⁺)			Banda B (Cr ³⁺ , Fe ³⁺)			Banda C (Cr ³⁺)			
	λ	α	$\Delta\lambda$	λ	α	$\Delta\lambda$	λ	α	$\Delta\lambda$	
	(nm)	(cm ⁻¹)	(nm)	(nm)	(cm ⁻¹)	(nm)	(nm)	(cm ⁻¹)	(nm)	(nm)
STT	585	3.71	85	426	3.9	47.8	-	-	-	680
TT1000°C/ 1h	585	5.76	93.8	429	4.36	46.2	-	-	-	680 and 682
TT1000°C/ 1h 30min	583	4.24	84	428	6.08	48.9	-	-	-	679
TT1000°C/ 2h	585	5.71	89.7	432	8.11	46.9	-	-	-	679 and 681
TT1000°C/ 2h30min	563	4.9	89.64	-	-	-	-	-	-	-
TT1000°C/ 3h	577	7.2	96.98	-	-	-	-	-	-	-
TT1000°C/ 4h	-	-	-	429	1.8	57.67	276	6.4	57.4	680

which was determined by Electron Paramagnetic Resonance (EPR) [11,22], and indicates that Cr³⁺ in BeAl₂O₄ enters in a average ratio of 75% in Al₂ and 25% in Al₁, either in natural sample as well as synthetic alexandrite sample. Based on this ratio, the analysis of Figure 3 was performed and the results are shown in Table 5. With the help of Figures 1 and 2, it may be concluded from Table 5 that in the synthetic sample, we have the 1:3 ratio in agreement with previous mentioned reported data [11, 22]. The addition of two Gaussian curves leads to a perfect fitting of the experimental curve. Then, they can be used to the analysis of the absorption band of natural sample. In this case, the fitting by Gaussian curves is hard to be done, which is caused by the experimental noise. In the cases where a data fitting of band A became possible, it was observed that an increase of thermal annealing time leads to decrease of Cr³⁺ in Al₁ sites and thus, an increase in the occupation of Al₂ sites. Besides, there is an increase of the Gaussian curves area, which

**Figure 3. Decomposition of band A of optical absorption spectra in two Gaussian curves for synthetic alexandrite****Figure 4. Photoluminescence spectra of natural alexandrite, measured at 20 K, before any thermal annealing and after the final annealing at 1000°C, 4 hour****Table 5. Analysis of bands A, B and C of natural and synthetic alexandrite samples, obtained from decomposition of optical absorption bands**

Thermal annealing temperature/time	Band A		Average total area (a. u.)		
	Al ₁ (%)	Al ₂ (%)	Band A	Band B	Band C
STT	33.5	66.5	15.7	20.4	-
1000°C/5min	22.1	77.9	24.2	15.4	-
1000°C/15min	14.5	85.5	24.7	17.5	-
1000°C/30min	15	85	28.1	44.8	-
1000°C/2h	-	-	29.0	79.3	-
1000°C/2h30min	18.2	81.8	35.6	-	-
1000°C/3h	4.8	95.2	41.4	-	-
1000°C/4h	-	-	-	14.1	35.7
Synthetic sample	22.7	77.3	31.8	50.4	3.1

means an increase of Cr³⁺ concentration, responsible for the optical absorption in the sample. Cr³⁺ ions in Al₂ sites are responsible for laser emission, which are characterized by electric dipole transitions of high-probability,

whereas Cr^{3+} ions in Al_1 do not contribute significantly to the optical absorption. The excitation of Cr^{3+} located in Al_1 ions are magnetic dipole transitions, and do not participate in the laser emission process. Besides, this transition contributes for decreasing the excitation energy of Cr^{3+} in Al_2 [23].

As expected from the absorption coefficient data, the area under band B also increases until 2 h of annealing time, however band B vanishes for longer times, as already mentioned. This band shows up again with 4 h of annealing along with band C. On the other hand, band A resists to the thermal annealing, vanishing only with 4 h of annealing time, when band C shows up. In summary, the analysis of bands A, B and C leads to the conclusion that bands A and B present increased area with longer thermal treatment.

In alexandrite luminescence spectra, the Cr^{+3} lines, due to the ion located in the reflection site, are the R_1 and R_2 lines and the lines due to Cr^{3+} located in the inversion site are S_1 and S_2 . As previously mentioned, the R lines show up precisely at the same wavelength, 680.4 nm and 678.5 nm, either in the absorption spectra as well as in the emission spectra. Lines S_1 and S_2 show up at 695.8 and 689.9 nm, respectively in the emission spectra and as narrow lines at 655.7 nm, 649.3 nm and 645.2 nm in the absorption spectra [16]. In order to assure the hypothesis of ion migration, photoluminescence measurements on natural samples were carried out at low temperature (20K), before any thermal annealing and after the last annealing (1000°C, 4 hour). This measurement temperature was chosen in order to have a very well defined spectrum, not influenced by phonon emission. These results are shown in Figure 4, where lines R_1 , R_2 and S_1 are easily observed, whereas S_2 line is not observed. The most relevant information for this work is that the R_1 line has its intensity increased by the thermal annealing, whereas S_1 presents lower intensity. This behavior reinforces the possibility of ion migration from the inversion site, Al_1 , to the reflection site, Al_2 , in good agreement with our absorption data fitting procedure.

Previously reported X-ray diffraction data for alexandrite sample before and after thermal annealing [24] show that the characteristic peaks occur at the same positions. Thermal annealing does not cause modifications on alexandrite structure, which is a very interesting result, since our main goal is to study its optical properties related to Al_1 and Al_2 occupation by Cr^{3+} ions, and the variations on optical properties induced by thermal annealing.

4. Conclusions

We summarize the conclusions that we have drawn in this paper as follows: thermal annealing has allowed the observation of meaningful variation on the optical absorption bands of natural alexandrite in the visible and ultraviolet ranges. Depending on time of thermal anneal-

ing at 1000°C the bands A, B and C have its shape completely changed. The annealing favors the presence of Cr^{3+} in Al_2 sites, which was verified by alteration in the specific areas of the decomposed absorption bands and variation of relative emission intensity. This may also explains why, unlike other tunable lasers, alexandrite lasers emit with fair efficiency even at room temperature. Chemical composition shows that the iron concentration is high in the natural alexandrite, which does not ruin the conclusion on Cr^{3+} optical absorption properties drawn in this paper, because although the Fe ions present strong influence in the ultraviolet range, the analyzed bands related to Cr ions are in the visible range.

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