

Temperature Dependent Luminescence Spectra of Synthetic and Natural Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$)

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ABSTRACT

Results of photoluminescence measurements for natural and synthetic alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) are presented, where the samples are excited by the 488 nm line of an Ar^+ laser, at different temperatures. The main issue is the analysis of the Cr^{3+} transition in the chrysoberyl matrix (BeAl_2O_4), with major technological application as active media for laser action. Results indicate anomalous behavior of Cr^{3+} transition depending on the measurement temperature. A simple model to explain the phenomena is suggested.

Keywords: Alexandrite, Luminescence, Cr^{3+} Transitions, Optical Absorption

1. Introduction

The use of alexandrite as an active media for laser action, with emission in the range 700 - 800 nm [1], has appeared for the first time in 1978 [2]. Since then, this material became technologically important. Recently, many reports show wide application of the alexandrite laser, in medicine as well as for atmospheric studies [3,4].

Alexandrite structure may be visualized as approximately hexagonal close packed (hcp), with unit cell of four molecules, with eight Al^{3+} ions, occupying distorted octahedral sites and four Be^{2+} ions, occupying distorted tetrahedral sites, formed by oxygen located at plans perpendicular to c axis. The distortion from a perfect hcp structure of oxygen ions give birth to the appearing of two sites of distinct symmetries: Al_1 , located at inversion sites and Al_2 , located at mirror sites [5,6]. Cr^{3+} ions are incorporated in the octahedral of reflection and inversion symmetries and may be denoted by Cr_s^{3+} and Cr_i^{3+} , respectively.

The octahedrally coordinated Al_2 site is supposed to be larger when compared to Al_1 , which can be explained by the length of the bond Al-O (1.938 Å), which is longer than for Al_1 (1.890 Å), resulting on a larger polyhedral volume [7]. The Al_2 site, due to its larger size, is preferentially occupied by Cr^{3+} ions, and then it is responsible for the optical properties of alexandrite [8]. Then, Cr_s^{3+} ions are characterized by a high probability of electric dipole

transition. The magnetic dipole transitions of the Cr_i^{3+} do not contribute significantly to the optical absorption and emission of this material. Besides, they are excluded from the laser process, equilibrating or reducing the excitation energy of Cr_s^{3+} ions [5]. Then, the ratio of Cr_s^{3+} and Cr_i^{3+} concentrations become a determinant parameter for the alexandrite optical efficiency. EPR measurements indicate that, in general, the Cr^{3+} ion enters in the BeAl_2O_4 lattice in a ratio of about 75% of Al_2 and 25% of Al_1 , for the natural sample as well as for synthetic material, showing variations depending on the relative quantity of Cr_2O_3 in the sample [9].

In the luminescence spectra, the Cr_s^{3+} lines are called R_1 and R_2 , and the lines of Cr_i^{3+} are called S_1 and S_2 . As experimentally observed [6], the R lines show up precisely in the same wavelength, 680.4 and 678.5 nm, respectively, at room temperature, in both spectra: optical absorption and emission. In the emission spectra, the lines S_1 and S_2 show up around 695.8 and 689.9 nm and in the absorption spectra they are seen as narrow lines at 655.7, 649.3 and 645.2 nm [10,11].

2. Experimental

Alexandrite stones come from Minas Gerais state in Brazil, and show a dark green color, due to the presence of clusters. Samples have been cut such that parallel plans between the faces were provided, leading to an average

thickness of 1.5 mm. The synthetic sample has been grown by H. P. Jenssen and R. Morris (from Allied Signal Inc, U.S.A.), by the Czochralsky method as mentioned elsewhere [6]. The thickness is 2.3 mm and show perfectly parallel faces.

For luminescence excitation it is used an Ar^+ laser tuned at $h\nu = 2.51$ eV. In the excitation system, the laser beam is irradiated through a chopper, being redirected to the sample, which is placed inside a closed cycle He cryostat. The emitted light from the sample (photoluminescence) is sent to a spectrophotometer coupled to a germanium detector, where the electrical signal is amplified by a lock-in amplifier, linked to a computer which controls the spectrophotometer and collects the obtained data.

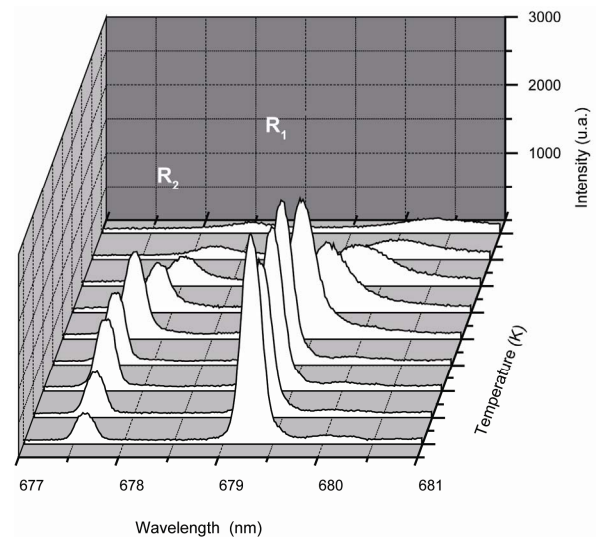
3. Results and Discussion

Figure 1 shows the Luminescence spectra for the synthetic alexandrite sample measured at several temperatures. **Figure 1(a)** evidences the lines R, and **Figure 1(b)**, lines S. Below room temperature, the luminescence spectra is dominated by the R lines of individual Cr ions and the S lines, originated from exchange-coupled pairs of chromium ions [11].

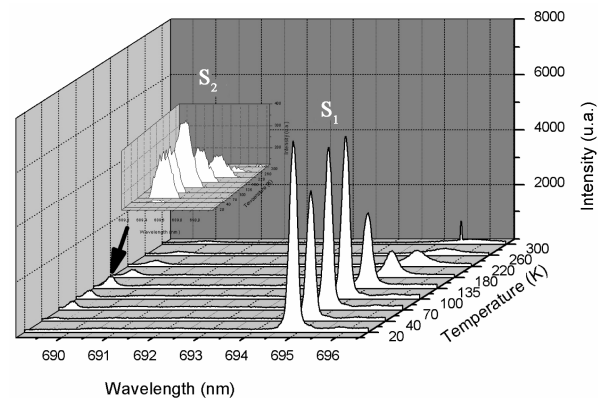
The luminescence of R and S lines points towards a dependency with the measurement temperature, as can be observed in **Figures 1(a)** and **1(b)**, for the synthetic sample.

In **Figure 1(a)**, the relative intensity of Cr_s^{3+} lines, R_1 and R_2 , present always the same behavior, with the intensity of line R_1 being higher than for line R_2 , and the difference between them decreases with temperature. As the temperature is raised, the line R_1 has an intensity decrease, whereas the line R_2 show intensity increase until 135 K. Above this temperature, this line also shows a gradual intensity decrease. For the Cr_i^{3+} lines, S_1 and S_2 , shown in **Figure 1(b)**, the line S_1 is more intense than line S_2 . The variation in the intensities of these lines is explained as an indicative that more than one type of carrier relaxation mechanism is present [12]. **Figure 1(b)** shows that line S_1 decreases, whereas line S_2 has a slight intensity increase until about 135 K, and above that a regular intensity decrease.

The variation in intensities of R lines as well as S lines for natural alexandrite is shown in **Figure 2**. The variation of both lines occurs in a similar way for this sample, as shown in the photoluminescence spectra of **Figures 2(a)** and **2(b)**. In the spectra, it is also possible to observe that the lines R and S change position, starting from 135 K, shifting to higher wavelengths (lower energy), followed by a wavelength broadening of these lines. Moreover, in a comparison of synthetic and natural samples, it can be noticed that the lines position is practically in the



(a)



(b)

Figure 1. Luminescence spectra for the synthetic alexandrite sample as function of temperature. (a) Lines R, (b) Lines S.

same wavelength.

Considering that either the natural as the synthetic sample shows the same effect in the intensity of emission lines measured at different temperatures, the explanation concerning the behavior of lines R and S, can be done by analogy. A simple model is proposed and is shown in **Figure 3**, where the electron and hole ground states are represented. Vertical lines stand for radiative transition and oblique lines represent the electron transfer from an electronic level to another. t represents the lifetime of the carrier in the level and is associated with the transition probability between two levels.

In this model, it is supposed that initially there is no interaction between electronic levels R and S. Free carriers of a site probably do not interact with the carriers from another level, and with the associated levels of Cr^{3+} clusters. Then, the probability that carriers from level R

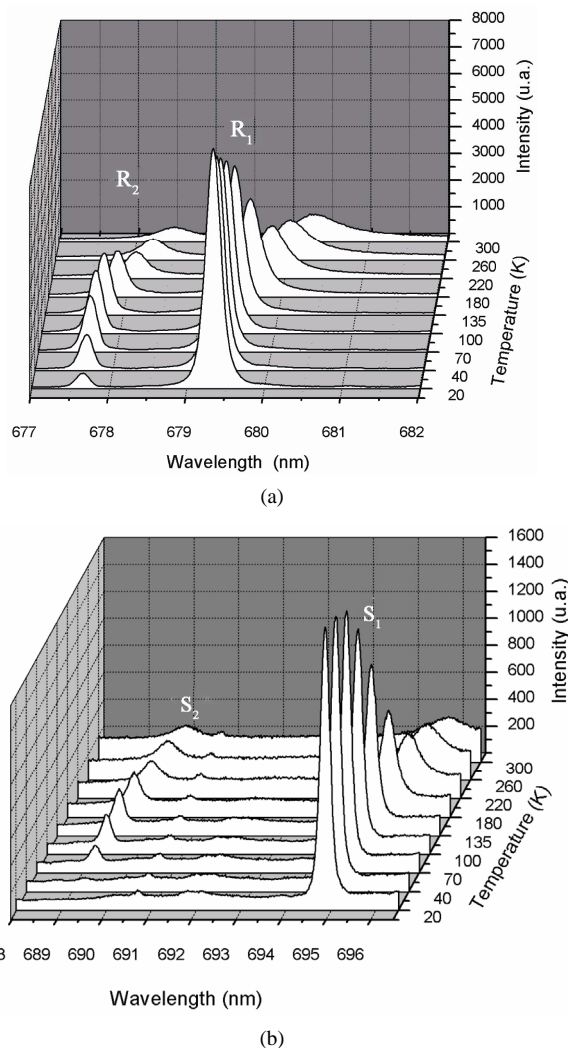


Figure 2. Luminescence spectra for natural sample as function of temperature (a) Lines R and (b) Lines S.

are transferred to level S and vice-versa is very low, as well as from levels R or S to the levels associated with Cr^{3+} clusters.

Then, at low temperature, electrons excited by optical pumping lose energy by phonon emission (lattice vibration) and are trapped by levels R and S. Then, they recombine with holes from the ground state, generating the lines R_1 , R_2 , S_1 and S_2 . With the temperature increase, as the intensity of lines R_1 and S_1 decrease due to interaction between electrons and phonons, the emission associated to lines R_2 and S_2 show inverse behavior, and present intensity increase. This behavior is observed until 135 K. Above that temperature, the intensities decrease due to the electron-phonon coupling. This behavior is explained as follows: as the temperature is increased, some R_1 carriers are excited back to R_2 . This is possible if the lifetime t_{21} is long enough for the excitation or at

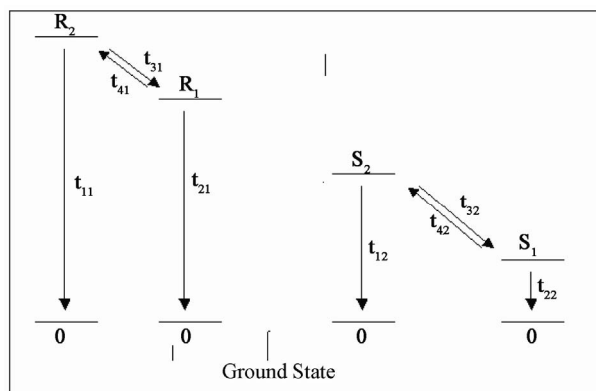


Figure 3. Diagram representing the transfer ratio between emission levels and lifetime (t).

least of the same order of magnitude of t_{41} , the lifetime for excitation back of carriers from R_1 to R_2 . On the other hand, if the lifetime t_{31} is longer than t_{11} , the carriers in R_2 tend to recombine radiatively with holes in the ground state instead of finishing in the R_1 level, making the emission intensity associated with R_2 to increase. With higher temperature increase, more carriers in R_1 will gain energy to populate R_2 , and then, the intensity grows with the temperature increase. However, above 135 K, the electron-phonon coupling becomes very strong and the relaxation via phonons (non-radiative) becomes dominant. In this case, the intensity of lines R_1 in the photoluminescence spectra decreases. The same process may be applied to the transition involving S levels.

We have observed that it leads to some interesting variation in the luminescence dependency with temperature. Lines R and S remains fixed at their wavelengths until about 135 K, where a peak shift takes place to higher wavelengths (lower energy), followed by a wavelength broadening of these lines, shown in the emission spectra. This peak shift is associated with the increase of the alexandrite unit cell with temperature.

The luminescence spectra also allow analyzing the difference between wavelengths of emission lines in these samples, as can be seen in **Table 1**.

It can be verified in **Table 1** that the wavelength separation between S lines is about three times larger than the

Table 1. R_1 , R_2 , S_1 and S_2 lines position and separation ($\Delta\lambda$) between these lines at room temperature, for synthetic and natural alexandrite samples.

Sample	R_2 (nm)	R_1 (nm)	S_2 (nm)	S_1 (nm)
Synthetic	678.5	680.3	689.9	695.7
	$\Delta\lambda = 1.8$		$\Delta\lambda = 5.8$	
Natural	678.5	680.3	689.9	695.8
	$\Delta\lambda = 1.8$		$\Delta\lambda = 5.9$	

separation between R lines. This behavior indicates a stronger low symmetry component of the crystalline field for ions located in a inversion center [13].

4. Conclusions

Photoluminescence measurements carried out at several temperatures for alexandrite samples have shown up as very relevant to the analysis of Cr³⁺ transition in this material, because it is related to its potentiality to laser activity. The temperature dependency of the emission spectra exhibits an anomalous behavior for natural samples as well as for the synthetic one, compared to most materials, for instance, semiconductors. Then, a simple model is proposed, based on electronic transitions of levels R and S, characteristic of Cr³⁺ transitions.

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