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Red-Emitting Cr³⁺ on α -Al₂O₃:Cr Spheres Obtained in Seconds Using Laser Processing

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Abstract: Cr-doped Al₂O₃ spheres with strong red emission were produced using a simple laser processing approach with a 50 W continuous CO₂ laser. Structural characterization revealed that the produced spheres were monophasic, comprising the α -Al₂O₃ phase. Photoluminescence (PL) studies indicated that the observed red emission originates from multiple Cr³⁺ optical centers being dominated by the ²E → ⁴A₂ transition (R-lines), with a further contribution from the parity and spin forbidden ²T₁ → ⁴A₂ transition (R'-lines). The identification of additional radiative recombination from chromium ion pairs (N-lines) evidences that the produced samples are heavily doped. As such, energy transfer processes between the different chromium optical centers are seen to take place, as suggested by the lifetime decay analysis. PL excitation revealed that the room temperature luminescence is preferentially populated via the spin-allowed ⁴A₂ → ⁴T₂, ⁴T₁ transitions and by the parity and spin-forbidden ⁴A₂ → ²T₂ (B-lines), ²T₁ (R'-lines), ²E (R-lines). Such results demonstrate that the present synthesis method is able to deliver high-optical-quality Al₂O₃:Cr crystals in a fast and simple way, with potential interest for optical, sensing, or lasing applications.

Keywords: Al₂O₃; spheres; Cr³⁺ doping; laser processing; photoluminescence



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1. Introduction

The optical properties of trivalent chromium (Cr) ions in bulk alumina (Al₂O₃) have been extensively studied in the past and resulted in the development of the ruby laser, as reported by Maiman et al. [1,2], which emits in the red region of the electromagnetic spectrum. Sugano and Tanabe [3–6] studied the electronic energy levels of Cr³⁺ in Al₂O₃ both from the theoretical and experimental points of view. Under diluted doping conditions, Cr³⁺ ions are known to substitute Al³⁺ in the Al₂O₃ lattice forming a trigonal distorted octahedron [3–6]. As such, the levels of the ion in the cubic field are further split by the interplay of the trigonal field strength and the spin–orbit interaction [3–6]. Accordingly, in octahedral symmetry, and for a measured crystal field and Racah parameters of Dq/B = 2.8 (obtained from absorption spectroscopy measurements), the electronic states of the ion correspond to the ⁴A₂(t₂³) ground state and ²E(t₂³), ²T₁(t₂³), ⁴T₂(t₂²e), ²T₂(t₂³), ⁴T₁(t₂²e) excited states (excluding the ones of higher energy) [3–10], where the lowest excited state is the ²E, as expected for the ion under a strong crystalline field [6,10]. The ²E states are further split into two Kramers doublets and the main emission is due to the parity and spin-forbidden ²E → ⁴A₂ transition, resulting in two sharp zero phonon lines (ZPL) at ~1.79 eV in the red region, the so-called R-lines [1–10]. The absorption is dominated by the broad bands corresponding to the spin-allowed ⁴A₂ → ⁴T₂, ⁴T₁ transitions with maxima near 2.2 eV and 3.1 eV, respectively [9,10].

Recently, the remarkable optical properties of α -Al₂O₃:Cr have been exploited in a myriad of applications such as temperature, pressure, and stress sensors [11–14], dosimeters in ionizing radiation therapy [15–17], red-emitting phosphors for plant growth [18,19],

or fluorescent probes for biological applications [20], among others. In addition, doped polycrystalline alumina is a material of excellence in high-power phosphor color converters or laser gain media [21,22]. The doping is typically attained during the growth [17,21,23] but there are some works reporting on ex situ doping, for instance by ion implantation [24]. Particularly, micrometer-sized crystalline spheres are known to be suitable for application in non-linear optical devices, quantum optics, sensing, and lasing [25–27]. Indeed, microspheres are amongst the most common microresonators that sustain whispering gallery modes (WGM), providing the highest quality factor (Q factor) values when compared with structures like microdisks and Fabry–Perot cavities [25,26]. The use of WGM microresonators as microlasers is one of the most interesting possibilities, given the high Q factor and small volumes of the modes, which allow for obtaining an ultralow lasing threshold [26,27]. Additionally, biosensors based on microcavities are especially valuable for exploiting the effects generated by the evanescent electromagnetic field in the surroundings of the surface, allowing the detection of analytes linked to the surface by monitoring the changes in the resonance frequency that they promote [26]. Likewise, among other sensor types (e.g., gas, humidity), they can also be used as temperature sensors, since temperature leads to deviations in the resonance frequency of the microcavity [26]. Nevertheless, producing high sphericity particles with dimensions in the micrometer range, mandatory for highly efficient lasing, remains a challenge [25]. The main fabrication approaches typically involve the melting of glass materials or the sol-gel process [26]. Other methods to produce crystalline spheres of different sizes (from nano to some millimeters) have been reported and include laser ablation [25,28–30], spray pyrolysis [31,32], microfluidic synthesis strategies [33], hydrolysis-precipitation methods [34], hydrothermal [35], and even other laser sintering approaches [36].

Although Al_2O_3 is a very well-known material, there is still plenty of room to improve its fabrication methods toward simplicity, low-cost, and eco-friendly approaches [21,27,37]. Therefore, there is a growing interest in finding new strategies to attain Cr-doped Al_2O_3 crystals with excellent optical properties, including high transparency [21,38,39]. To achieve such properties, densification of the material is usually required in order to minimize the residual porosity at the same time preserving a fine microstructure, i.e., small grain size [21,38]. Most of the currently employed methods involve high-temperature synthesis and/or controlled sintering approaches such as vacuum, pressure-assisted, or field-assisted sintering techniques [21,23,38,40,41]. Nowadays, the use of laser processing as a synthesis method is of particular relevance in additive manufacturing, enabling the production of several types of ceramic materials from precursor powders in a fast way. For instance, laser ablation in fluids, which relies on ultrahigh pressure and ultrahigh temperature, has been used to produce crystalline microspheres with high sphericity, presenting very interesting results in the synthesis of materials such as zinc oxide (ZnO), cadmium selenide (CdSe), zinc selenide (ZnSe), or cerium oxide (CeO_2) [25].

In this context, the use of fast and inexpensive synthesis methods, together with the incorporation of dopants in inorganic matrices that allow optical pumping tuning for laser action, has assumed particular relevance [27]. Hence, the purpose of the present work can be divided into two main goals: (1) to demonstrate that laser technology can be used to process Al_2O_3 and Cr_2O_3 powders to obtain chromium-doped crystalline $\alpha\text{-Al}_2\text{O}_3$ spheres in air atmosphere simply and promptly, without the need of expensive equipment or post-sintering heat treatments to obtain $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$ with strong red emission; and (2) to investigate the optical properties of the doped spheres using photoluminescence (PL), PL excitation (PLE), time-resolved PL (TRPL), and Raman spectroscopies. Temperature and excitation energy-dependent PL and lifetime measurements were also performed to establish the recombination models and clarify the Cr^{3+} optical signatures on the laser-processed $\alpha\text{-Al}_2\text{O}_3$ spheres.

2. Materials and Methods

Material synthesis was carried out using a commercial CO₂ 50 W laser marking system (Redsail M500) with air-assist off and the XY motion disabled. Al₂O₃ (Sigma-Aldrich, St. Louis, MO, USA, activated, basic, Brockmann I, powder $\geq 99.5\%$) and Cr₂O₃ (Sigma-Aldrich, St. Louis, MO, USA, powder $\geq 98\%$) powders were mixed in an agate mortar in a 97:3 (*w/w*) proportion, according to reference [42], to lead to the formation of Cr-doped Al₂O₃. Then, the powders were inserted in a $\varnothing$ 6 mm $\times$ 6 mm graphite crucible. The crucible was then placed into the laser system with the top of the powder set at 4 cm below the focal point of the system. This process is performed out-of-focus to minimize thermal gradients and allow the production of larger spheres. Also, if the laser was focused on the powder surface, a violent ejection of material would occur at the ~ 100 μ m irradiated region. After five 1-second bursts at 5 W to sinter the surface of the powder and prevent the ejection of powder during temperature ramp-up, the laser was set at 50 W for 20 s. The sample was then left to cool, and the produced sphere was removed from the crucible. One sphere was produced each time. Figure 1 displays a schematic representation of the experimental setup used to synthesize the Al₂O₃:Cr spheres.

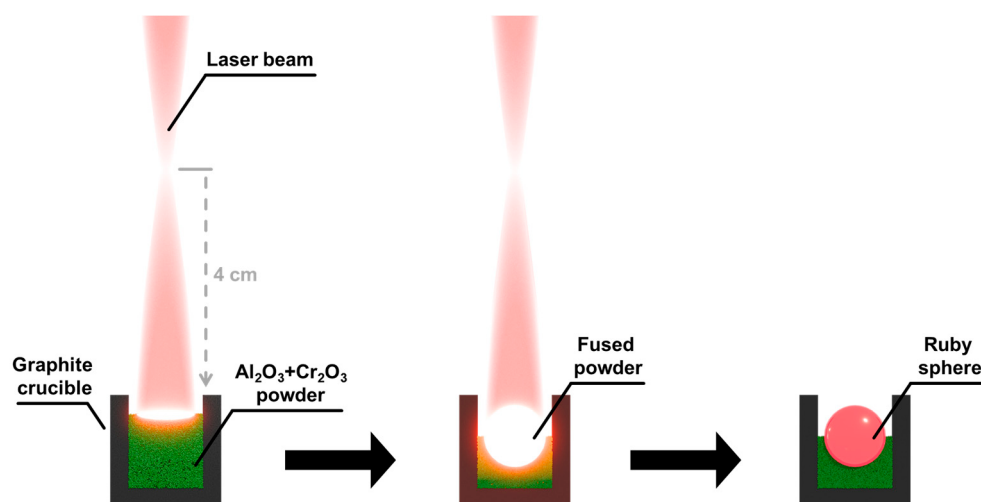


Figure 1. Schematic representation of the experimental setup used to synthesize the spheres.

Sample morphology was evaluated using secondary-electron scanning electron microscopy (SEM) on a TESCAN VEGA3 microscope with a working distance of 15 mm and a 10 keV electron beam. A carbon coating was applied to reduce the charge effect. Additionally, energy dispersive X-ray (EDS) spectra were acquired with a Bruker XFlash Detector 410-M to assess the doping levels. X-ray diffraction (XRD) analysis was employed to identify the crystalline structure of the prepared samples using a PANalytical X'Pert PRO diffractometer operating in the Bragg-Brentano configuration and with CuK α radiation ($\lambda = 1.54056$ Å). Raman spectroscopy measurements were performed at room temperature (RT) in a backscattering configuration on a Horiba HR800 micro-Raman spectrometer equipped with a 600 grooves mm^{−1} grating and using the 441.6 nm laser line from a HeCd laser (Kimmon IK Series, Fukushima, Japan) and a 50 $\times$ objective (spot size ~ 2 μ m, NA = 0.7, Olympus). A neutral density filter OD = 1 was used to attenuate the laser power to prevent the luminescence from saturating the detector.

Steady-state PL was carried out by exciting the samples with the 325 nm (~ 3.81 eV) line from a cw He-Cd laser (Kimmon IK Series, excitation power density ~ 0.6 W cm^{−2}). The samples were placed in a cold finger of a closed-cycle helium cryostat and the temperature was controlled in the range between 14 K and RT. A dispersive system SPEX 1704 monochromator (equipped with a 1200 grooves mm^{−1} diffraction grating) coupled to a cooled Hamamatsu R928 photomultiplier tube was used to measure the luminescence of the produced spheres. Further RT energy excitation-dependent PL and PLE experiments

were performed in a Fluorolog-3 Horiba Scientific modular system, equipped with a double additive grating Gemini 180 scanning monochromator (with 1200 grooves mm^{-1} diffraction grating) for excitation, and an iHR550 spectrometer (1200 grooves mm^{-1} diffraction grating blazed at 500 nm) for the emission. This system is also fitted with an R928P photomultiplier detector. A 450 W Xe arc lamp was used as the excitation source. The PLE measurements were conducted by setting the emission monochromator at the maxima of the Cr^{3+} emission lines and the excitation wavelengths being scanned to higher energies. RT TRPL spectra were acquired with the same Fluorolog-3 system using a pulsed Xe lamp (operating at up to 25 Hz) coupled to the same excitation monochromator and with the excitation fixed at either 372 nm (~ 3.333 eV) or 520 nm (~ 2.385 eV), matching the Cr^{3+} absorption bands. The full width at half maximum (FWHM) of each lamp pulse is 3 μs , so that lamp interference during the acquisition of decay curves is minimized. The measurement conditions were set to a sample window of 5 ms, with 20 ms of time per flash and a flash count of 100. Several time delays after flash were employed from 0.05 to 20 ms. Lifetime decays were also recorded in this time range and under similar experimental conditions (sample window, number of flashes, and time per flash). In this case, three wavelengths were used for the excitation, 372 nm (~ 3.333 eV), 520 nm (~ 2.385 eV), and 550 nm (~ 2.273 eV), and the PL intensity was monitored at either 692 nm (~ 1.792 eV) or 704 nm (~ 1.761 eV).

3. Results and Discussion

3.1. Morphological and Structural Characterization

Figure 2a shows an optical photograph of the macroscopic appearance of one of the produced spheres when illuminated with a UV hand lamp ($\lambda_{\text{exc}} = 365$ nm), exhibiting the strong red luminescence typical of ruby crystals. Although spherical in shape, some irregularities are present at the surface, which can be seen in detail in the SEM micrograph of Figure 2b. The spherical shape probably results from the solidification process that follows melting induced by the local heating of the Gaussian-profile laser beam. This behavior explains the bubble-shaped irregularities at the sphere surface. At a higher magnification (Figure 2c) it is possible to observe a small roughness that comes from the polycrystalline nature of the outer sphere. The microcrystals at the surface exhibit polyhedral shapes dominated by a cubic geometry with dimensions ranging from 5 to 30 μm . EDS analysis revealed an average of 0.47 at.% and 1.19 wt.% for chromium, showing an effective doping with high homogeneity, with a maximum variation between the three probed points of 0.17 wt.%. XRD analysis (Figure 3a) of the powdered sample puts in evidence its monophasic constitution, corresponding to 100% of the $\alpha\text{-Al}_2\text{O}_3$ crystalline phase, according to ICDD Ref. 04-005-4505 data. The Raman characterization (Figure 3b) corroborates the XRD results. $\alpha\text{-Al}_2\text{O}_3$ possesses a rhombohedral crystal structure, with two Al_2O_3 units per unit cell, belonging to the D_{3d} space group. The optical modes of such structure can be described by the irreducible representation $\Gamma = 2A_{1g} + 2A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 4E_u$, among which the A_{1g} and E_g modes are Raman active. Hence, seven modes were predicted in the Raman spectrum of the prepared crystal [43,44]. Indeed, Figure 3b evidences the presence of the typical main set of peaks assigned to the vibration modes of $\alpha\text{-Al}_2\text{O}_3$. In fact, as shown in Figure 3b, the expected Raman features were all observed in spectra taken from the samples' surface, namely five modes with E_g symmetry at 380, 432, 450, 578, and 752 cm^{-1} and two others with A_{1g} symmetry at 418 and 646 cm^{-1} [43].

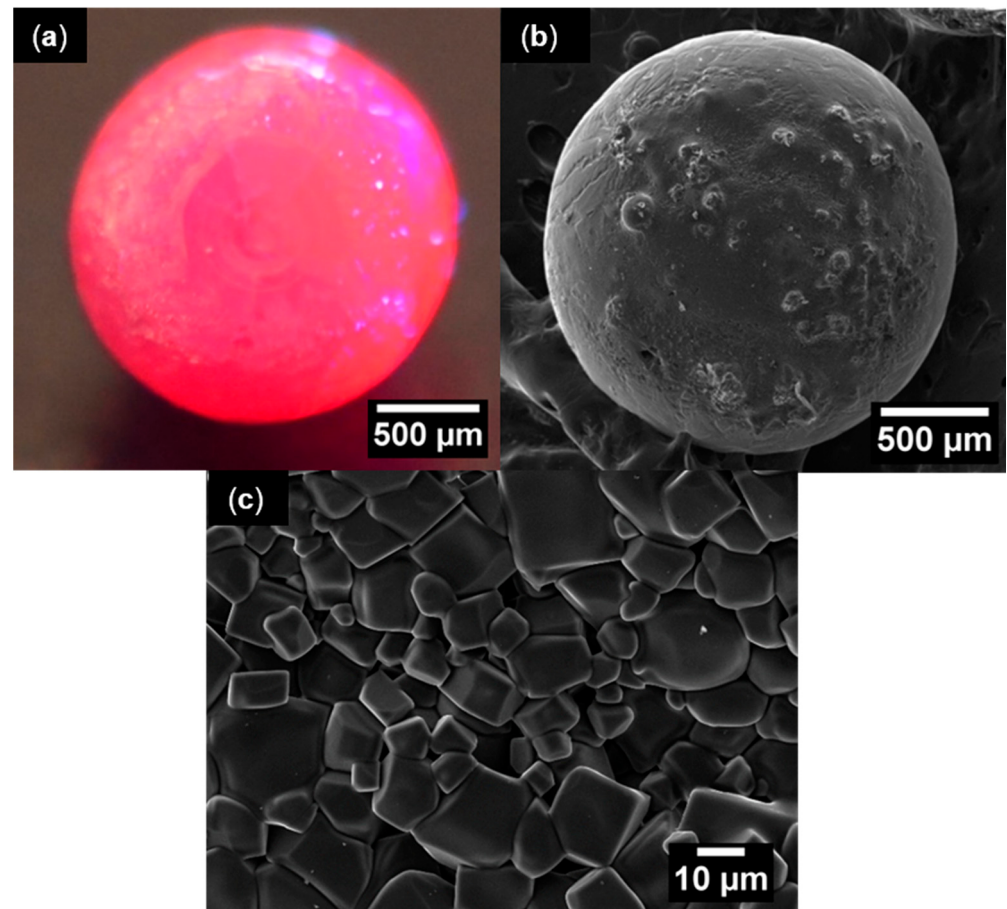


Figure 2. (a) Optical photograph of the ruby sphere when illuminated with a UV lamp (365 nm); (b) electron microscopy image of the α -Al₂O₃ sphere surface; (c) high-magnification SEM image evidencing the polycrystalline nature at the outer sphere.

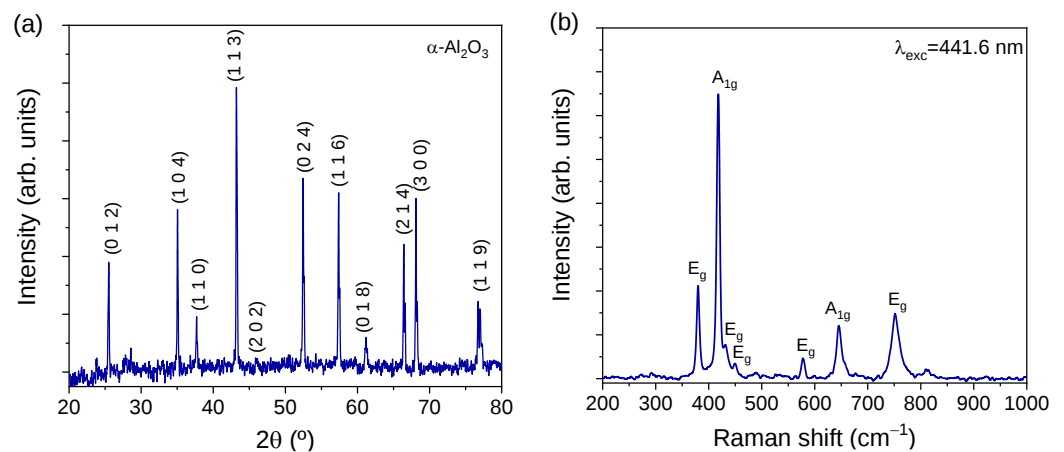


Figure 3. (a) XRD diffractogram of the powdered sample demonstrating its monophasic nature; (b) Raman spectrum performed with 441.6 nm laser line of a HeCd laser.

3.2. Photoluminescence Analysis

RT PLE and selectively excited PL spectra of the α -Al₂O₃:Cr spheres are shown in Figure 4. The PL spectra are dominated by two narrow lines (the above-mentioned R-lines) in the red spectral region, which are due to the ${}^2E \rightarrow {}^4A_2$ transition (see the Tanabe–Sugano diagram in Figure 4c and energy level scheme in Figure 4b). These lines appear with a separation of 3.6 meV from each other, the first one placed at 1.792 eV (R₂) and the other at

1.788 eV (R_1). This observation agrees well with the values reported for individual Cr^{3+} in Al substitutional sites identified in dilute doped samples [3,7,8]. As above-mentioned, the observation of the two R-lines indicates that, in the studied samples, the trivalent chromium ions are in distorted octahedral sites and their energy levels are split by a low symmetry trigonal component of the crystal field and spin-orbit coupling. At RT, the FWHM of the R-lines is about 2.5 meV. On the lower and higher energies sides of the zero phonon R-lines, a vibrationally assisted structure can be identified, corresponding to the Stokes and anti-Stokes emission, respectively. In addition, on the low energy side of the R-lines, sharp features can be discerned at ca. 1.77 eV and 1.76 eV, assigned to the presence of chromium ion pairs and/or Cr^{3+} -complex defects, the so-called, N-lines (N_2 and N_1 , respectively, due to fourth-nearest neighbor and second-nearest neighbor pairs, respectively), whose intensity ratio to the R-lines is known to be dependent on the chromium concentration [45–49]. On the high-energy side of the R-lines, two zero-phonon lines separated by ca. 27 meV and located at 1.882 eV and 1.855 eV, respectively, are well-resolved. These, called R' -lines, are assigned to the ${}^2T_1 \rightarrow {}^4A_2$ transition due to the partial relaxation of the spin multiplicity rule [6,8]. All these transitions are schematized in the diagram of Figure 4d.

By monitoring the luminescence at the maximum of the intra-ionic Cr^{3+} lines, it was verified that the main populating mechanisms in the studied spectral range correspond to the spin-allowed ${}^4A_2 \rightarrow {}^4T_2$, 4T_1 transitions, giving rise to asymmetric broad excitation bands (FWHM of ca. 450 meV) with maxima around 3.1 eV and 2.2 eV. The asymmetrical band shape is in accordance with the splitting of the excited states into three Kramers doublets. However, the FWHM is wider than the ones reported for a single Cr^{3+} center, which is about 250 meV [2]. Therefore, the broad asymmetric excitation bands likely correspond to a spectral overlap of several excitation bands due to multiple optical centers of Cr^{3+} . Besides the R-lines, a set of other narrow lines overlapped on the onset of the broad excitation bands were identified. In particular, the excitation lines corresponding to the parity and spin-forbidden ${}^4A_2 \rightarrow {}^2T_1$ R' -lines were seen to be a mirror image (without Stokes shift) of the ones observed in the PL spectra. Moreover, additional sharp lines are seen 50 meV apart in the blue region of the electromagnetic spectrum, at 2.66 eV and 2.61 eV, respectively, assigned to the ${}^4A_2 \rightarrow {}^2T_2$ transitions (B-lines). The R-, R' -, and B-lines result from the spin-orbit admixture of the 4T_1 and 4T_2 electronic states with the 2E , 2T_1 , and 2T_2 levels [4,50]. According to the measured spectra, the highest emission intensity occurs for the blue and green photon excitation. As such, the data are consistent with the fact that at RT, after excitation to any of the Cr^{3+} higher excited states, the system efficiently relaxes to the 2T_1 and 2E levels, from which emission to the ground 4A_2 state occurs. Simultaneously, the used excitation also promotes the recombination of the chromium ion pairs (N-lines, as observed in the PL spectra of Figure 4b). Nevertheless, the presence of other Cr^{3+} -complex defects emitting in the same spectral region cannot be discarded [45–49,51].

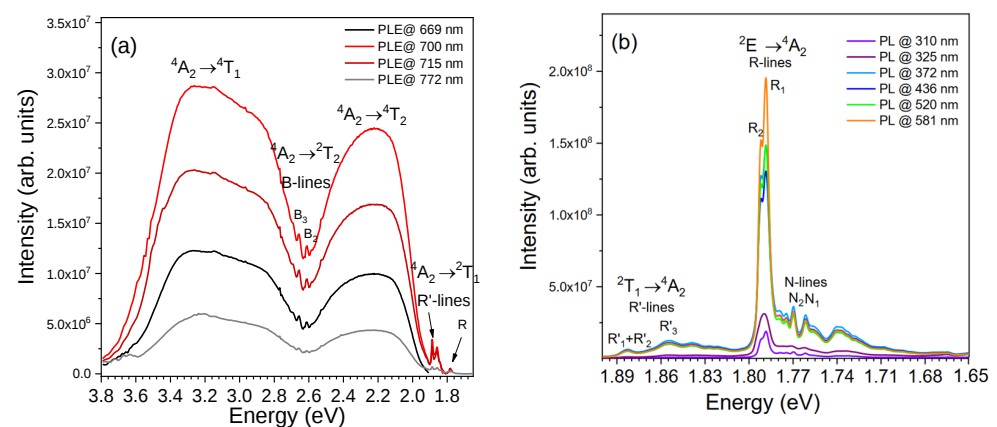


Figure 4. Cont.

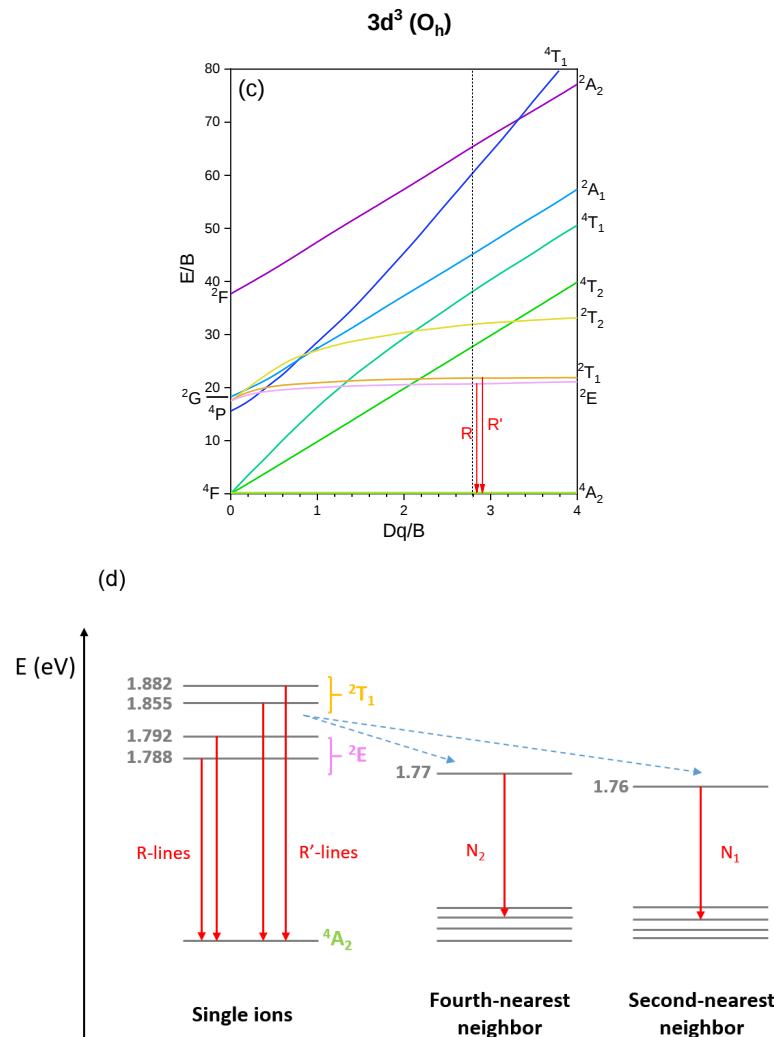


Figure 4. RT (a) PLE and (b) PL spectra of the analyzed α - Al_2O_3 :Cr sphere; (c) Tanabe–Sugano diagram for the single Cr^{3+} ions ($3d^3$ electronic configuration) in octahedral symmetry (O_h). The dashed line corresponds to $Dq/B = 2.8$, as reported for isolated Cr^{3+} in Al^{3+} substitutional sites [3–6]; (d) schematic representation of the split emitting levels under trigonal distortion for a single Cr^{3+} and their nonradiative transfer to the N pairs, namely second- (N_1) and fourth- (N_2) nearest neighbors. The energy values correspond to the ones measured in the present samples. The levels' energy positions are not at scale. The vertical full arrows denote the observed radiative transitions (R-, R'-, and N-lines), while the dashed arrows represent energy transfer. Scheme based on reference [47].

To acquire additional information on the spectral features of the Cr-doped α - Al_2O_3 spheres, the temperature of the samples was lowered down to 14 K. Figure 5 shows a highly resolved PL spectrum obtained at 14 K with 3.81 eV photon excitation. The low-temperature spectrum exhibits additional spectral complexity, with the presence of several lines at lower energies than the R ones, which are absent at high temperatures. At 14 K, the R-lines are peaked at 1.793 eV (R_2) and 1.789 eV (R_1). Besides the appearance of new lines on the low energy side of the R ones, on the high energy side, the R'-lines are observed, meaning that the emission from the 2T_1 level to the ground state occurs even at 14 K. Additionally, new doublet lines emerge at 14 K, with maxima at 1.809 eV and 1.805 eV, here assigned as R_2'' - and R_1'' -lines, respectively. Analogously to the R-lines, the two R''-lines are 4 meV apart and are likely to be due to a $^2E \rightarrow ^4A_2$ transition from a distinct trivalent charged chromium optical center, thus justifying a model corresponding to multi-non-equivalent Cr^{3+} optical centers.

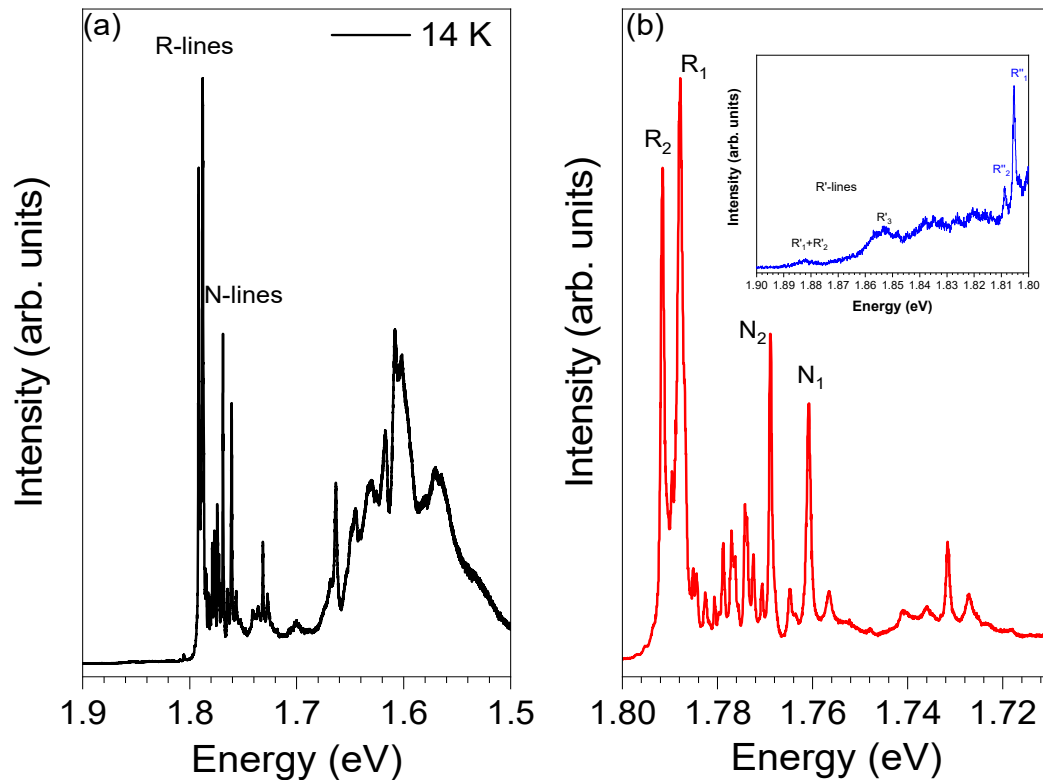


Figure 5. (a) The 14 K PL spectrum of α -Al₂O₃:Cr spheres obtained with 3.81 eV photon excitation; (b) enlarged spectrum in the region of the R- and N-lines. In the inset, the high-energy side of the R-lines is displayed.

Figure 6 depicts the PL spectra obtained at several temperatures under 3.81 eV photon excitation. As seen, between 14 K and RT, the overall luminescence intensity decreases with increasing temperatures. The PL intensity of the distinct Cr³⁺ optical centers exhibits distinct sensitivities to the temperature rise. It was verified that the peak position of the R'-lines slightly shifts toward lower energies with increasing temperature. This deviation is accompanied by an increase in the PL intensity of the lines from 14 K to RT, suggesting the existence of a thermal population process of the ²T₁ electronic state. For the case of the R₂''- and R₁''-lines, it is seen that the intensity of the R₂''-line decreases rapidly for temperatures above 70 K, while it is possible to observe the R₁''-line up to the RT, with a shift of its maximum toward lower energies. The R-lines show an analogous behavior, exhibiting a decrease in their PL intensity. This is more pronounced for temperatures above 90 K, accompanied by a redshift of the line peak position along with an enlargement of its width with increasing temperature (please note that each R-line is a multi-component line, as shown in Figure 6c). It was also observed that the intensity of the N₂- and N₁-lines dropped more rapidly than that of the R-lines for temperatures above 14 K. Their emission maxima also show a shift to lower energies, which is also accompanied by an increase in their FWHM.

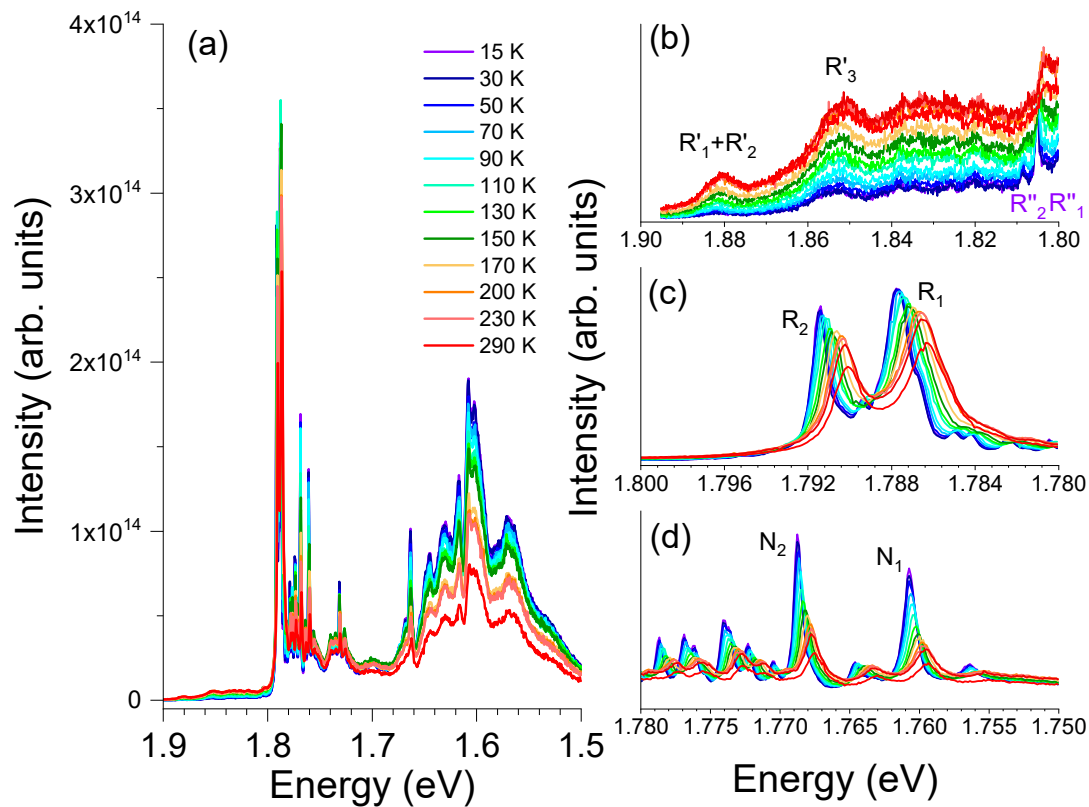


Figure 6. (a) Temperature dependence PL spectra of the α - Al_2O_3 :Cr spheres obtained with 3.81 eV photon excitation. Enlarged spectra in the region of (b) the R' - and R'' -lines, (c) R_2 - and R_1 -lines, and (d) the N_2 - and N_1 -lines.

Figure 7 shows the temperature dependence of the peak position for the R'' -, R -, and N -lines and the dependence of the FWHM for the R - and N -lines. The linewidth and temperature shift of the R - and N -lines in dilute and heavily chromium-doped Al_2O_3 can be explained based on the contributions of the microscopic strains and impurity-phonon interactions [8,46]. For the case of samples doped with 2.1 at.% and 0.94 at.% Cr, Powell et al. [46] measured a redshift of about 2–2.5 meV for the peak position and a line broadening of about 1–2 meV for both the R - and N -lines when inspected between 13 K and RT. Considering a simplified model where the energy shift is proportional to the phonon population number, the temperature dependence of the peak position, $E(T)$, can be expressed by [52],

$$E(T) = E_0 - \frac{A}{\exp(\hbar\bar{\omega}/k_B T) - 1} \quad (1)$$

where E_0 is the line energy at 0 K, A corresponds to a proportionality factor, $\hbar\bar{\omega}$ is the energy of the phonons involved, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and T is the absolute temperature. The best fits to Equation (1) to the temperature dependence of the lines' peak position are shown by the solid lines in Figure 7. The E_0 values of 1.809 eV, 1.805 eV, 1.793 eV, 1.789 eV, 1.769 eV, and 1.761 eV were found for the R_2'' , R_1'' , R_2 , R_1 , N_2 , and N_1 lines, respectively. Constant factors of 2.7×10^{-3} eV, 0.7×10^{-3} eV, and 0.6×10^{-3} eV were determined for the (R_2'' , R_1''), (R_2 , R_1), and (N_2 , N_1) lines, and about 10 meV was obtained for the $\hbar\bar{\omega}$ of the R_1'' , R_2 , R_1 , N_2 , and N_1 lines.

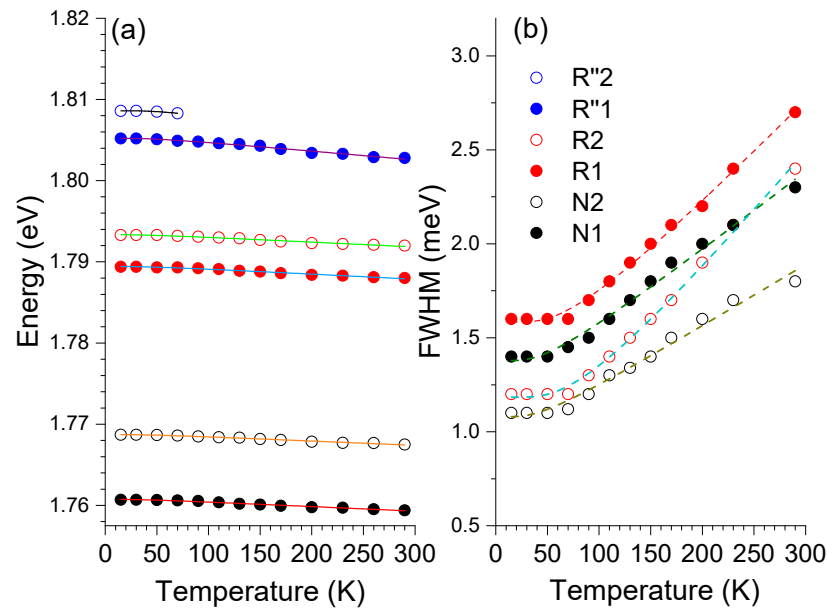


Figure 7. Temperature dependence of the (a) peak position of the R'', R-, and N-lines obtained with 3.81 eV photon excitation and (b) full width at half maximum of the R- and N-lines. Symbols denote the experimental values while full and dashed lines correspond to the theoretical fits of Equations (1) and (2), respectively.

Similarly, using the simplified model, the temperature dependence of the lines FWHM, $\Gamma(T)$, can be determined by [52],

$$\Gamma(T) = \Gamma_0 + \frac{B}{\exp(\hbar\bar{\omega}/k_B T) - 1} \quad (2)$$

where Γ_0 is the lines' FWHM at 0 K and B corresponds to a proportionality factor. The best fit to Equation (2) was reached for Γ_0 equal to 1.18 meV, 1.58 meV, 1.08 meV, and 1.38 meV for the R₂, R₁, N₂, and N₁ lines, respectively, B constants of 0.6 meV, 1.2 meV, 0.4 meV, and 0.6 meV, and values of 19 meV (R₂, R₁) and 11 meV (N₂, N₁) for the $\hbar\bar{\omega}$.

The temperature dependence of the R- and N-lines PL intensity has been previously studied by Powell et al. [46] and Fonger et al. [53], allowing the identification of the location of the energy diagrams, transitions from isolated Cr³⁺ ions (R-lines), and Cr³⁺ complexes (N₁ and N₂ lines), as well as the energy transfer processes between the different chromium optical centres present in the samples. The energy transfer process between single and exchange-coupled pairs of chromium ions (R and N lines) was also previously studied by Imbusch [47] via lifetime measurements in low, intermediate, and highly doped samples. Imbusch [47] proved that the energy transfer from single ions to pairs occurs nonradiatively with a fast transfer of excitation between the single ions until they are close enough for the energy to be transferred to the pairs. In addition, following the model proposed by Dexter [54] and Forster [55], the author was able to identify that the nonradiative energy transfer is driven by electric quadrupole–quadrupole interaction, rather than exchange and magnetic dipole–dipole interactions, or electric dipole–dipole interaction, which are all weaker than the former [47]. In his studies, Imbusch [47] found that the radiative decay of the R-lines is distinct from the N-lines, being slower in the former. Even for low-doped samples, the decay measured at 77 K for the R-lines (8.8 ms) was higher than that detected by Nelson et al. [9] for single chromium ions (4.2 ms) as a consequence of the luminescence-trapping dependence of the radiative recombination on the chromium concentration. Additionally, the N-lines evidenced a non-exponential lifetime at this temperature (77 K), described by a fast component in the order of 1.0 ms and a slow component with the same decay rate as the R-lines, showing that energy transfer occurs from the single chromium ions to chromium pairs [47]. Figure 8 shows the time-resolved

spectra and decay times measured at RT in the present $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$ samples. Considering the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2, {}^4\text{T}_1$ excitation, it was possible to notice that the emission intensity of the R-lines decreases at $1/e$ from its initial value at about 3.0 ms, following the measured single average exponential decay of 3.2 ms shown in Figure 6b. Additionally, the decay times measured at the N₂ line (the N-one with the highest intensity at RT) can be fitted to a multi-exponential model, with a fast lifetime of less than 0.5 ms, an intermediate one of 1.5 ms, and a slow lifetime similar to that of R-lines (~ 3.1 ms). It is worth mentioning that, as depicted in Figure 6b, different excitation wavelengths were employed to assess the lifetime of the mentioned emissions and all led to similar values. As above-mentioned, and in line with what was previously reported, this behavior suggests that there is energy transfer between the different chromium optical centres [47].

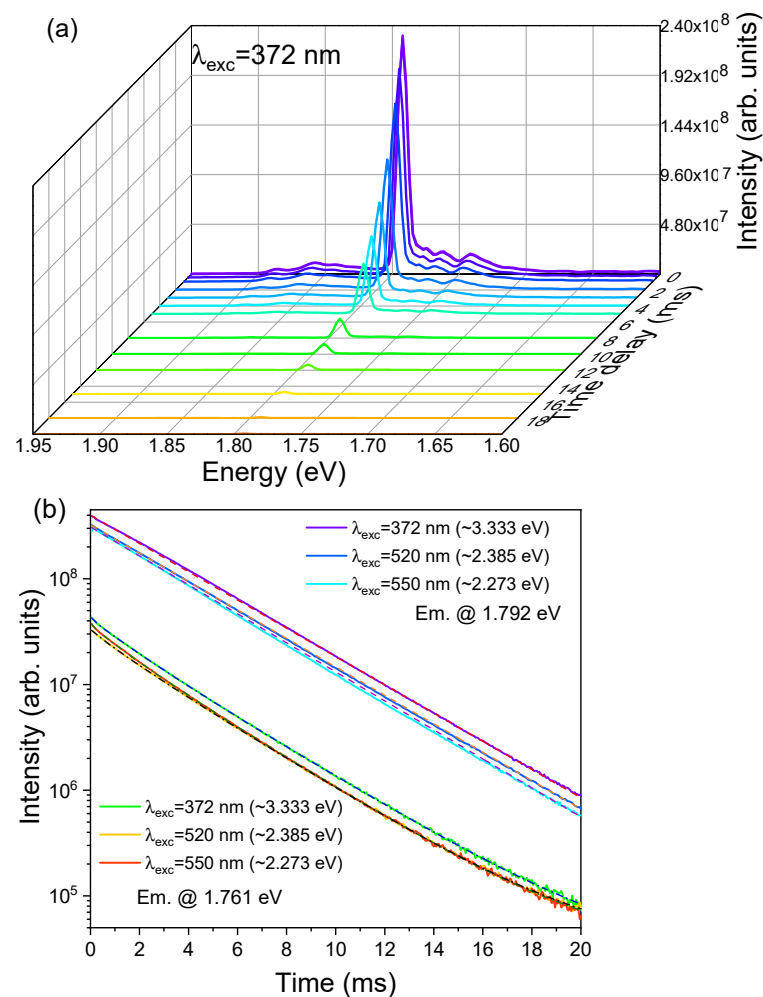


Figure 8. RT (a) TRPL spectra obtained with ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ excitation (similar spectra were obtained with ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ excitation) and (b) decay times measured at R- and N₂-lines with different excitation wavelengths. Broken lines: experimental fits to a single (R-lines, emission @ 1.792 eV)- and multi-exponential (N-lines, emission @ 1.761 eV) decay.

4. Conclusions

Crystalline $\alpha\text{-Al}_2\text{O}_3\text{:Cr}$ spheres were easily and quickly produced using laser synthesis under air atmosphere conditions with Al_2O_3 and Cr_2O_3 mixture powders as precursor materials, which can be extended to a large-scale process. The spheres were seen to be monophasic and with a polycrystalline nature and average doping of 0.47 at.% and 1.19 wt.% of Cr. Photoluminescence and photoluminescence excitation revealed that the main red luminescence is due to the single Cr^{3+} ions in trigonal distorted Al^{3+} octahedral sites, as identified by the dominant split R-lines due to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition. Additionally,

emission from the parity and spin-forbidden ${}^2T_1 \rightarrow {}^4A_2$ transition (R'-lines) was also observed. Besides the recombination from single Cr^{3+} ions, the synthesis conditions favor the observation of the radiative recombination from chromium ion pairs (N-lines), meaning that the produced samples are heavily doped. The presence of multiple Cr^{3+} optical centers is corroborated by the presence of a new doublet of lines (R''-lines) at low temperature and by the FWHM of the excitation bands, which are wider than those expected for the case of single Cr^{3+} ions. At room temperature, the R-lines exhibit a single exponential decay of about 3.2 ms, while the N-lines can be well-fitted to a multi-exponential model with a fast decay time of less than 0.5 ms, an intermediate one of about 1.5 ms, and a slow lifetime similar to that of R-lines, suggesting that energy transfer processes between the different chromium optical centers are taking place.

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