

Investigation of the Structural and Luminescent Properties and the Chromium Ion Valence of $\text{Li}_2\text{CaGeO}_4$ Crystals Doped with Cr^{4+} Ions

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Abstract: Herein, we report on the growth of Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystals by the flux growth method from the flux of LiCl , as well as on the effect of doping $\text{Li}_2\text{CaGeO}_4$ with Cr^{4+} ions on the NIR region spectral properties and crystal structure. The results quantified the occupancy of Cr^{4+} in Ge^{4+} sites. The emission spectrum presented broad bands in the NIR region, i.e., 1000–1500 nm excited by 980 nm, with maximum peaks at 1200 nm at room temperature caused by the transition of ${}^3\text{T}_2 \rightarrow {}^3\text{A}_2$ in Cr^{4+} ions. The lifetime decreased with the Cr^{4+} ion doping concentration, specifically from 14.038 to 12.224 ms. The chemical composition and the valence state of chromium in $\text{Li}_2\text{CaGeO}_4$ were analyzed using X-ray photoelectron spectroscopy, which showed that the chromium in $\text{Li}_2\text{CaGeO}_4$ was tetravalent and no trivalent chromium was found. Therefore, the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystal has a great potential and future in optical applications.

Keywords: Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$; crystal growth; NIR luminescence property; XPS

1. Introduction

Since the first demonstration of the tetrahedral laser action in coordinated tetravalent chromium at the end of the 1980s [1–3], Cr^{4+} -doped media have attracted significant attention in femtosecond [4,5] and tunable solid-state lasers [6–8] because they emit very important wavelengths at 1.1–1.6 μm . Cr^{4+} -doped materials have many advantages, including a simple energy level structure, allowing continuous-wave and pulse operation with low threshold pump power, and a broad absorption band overlapping the working wavelengths of several commercial pump lasers [9]. Lasers emitting in this range have increasingly been used in medicine [10], spectroscopy [11], telecommunications systems [12], etc. These lasers possess a number of unique properties, including a broad tuning range, the possibility for direct diode pumping and producing femtosecond pulses, the fact that the transmission maximum of fused silica optical fibers is located within the wavelength range of these lasers, and the fact that radiation of this wavelength range is safe for the eyes [13].

However, due to the lack of truly effective ion hosts, the adoption of Cr^{4+} lasers has been limited. Currently, the most widely used Cr^{4+} -doped media are $\text{Y}_3\text{Al}_5\text{O}_{12}$ (garnet) [1] and Mg_2SiO_4 (forsterite) [2]. In addition, according to reports, other hosts also have laser effects, including Cr^{4+} - Y_2SiO_5 [14],

$\text{Cr}^{4+}\text{-Ca}_2\text{M}_2\text{SiO}_7$ ($\text{M} = \text{Al, Ga}$) [15], $\text{Cr}^{4+}\text{-CaSnOSiO}_4$ [16], $\text{Cr}^{4+}\text{-LiMO}_2$ ($\text{M} = \text{Al, Ga}$) [17], $\text{Cr}^{4+}\text{-GSGG}$ [18], $\text{Cr}^{4+}\text{-Y}_3\text{Sc}_{0.5}\text{Al}_{4.5}\text{O}_{12}$ [19], $\text{Cr}^{4+}\text{-Ca}_2\text{GeO}_4$ [20], and $\text{Cr}^{4+}\text{-LuAG}$ [21]. However, these media have several disadvantages. The fluorescent quantum yield of these media is quite low due to the nonradiative transition of Cr^{4+} ions; as a result, the quantum efficiency amounts to approximately 9% for Mg_2SiO_4 and 14–22% for YAG [22]. Another disadvantage is the presence of Cr^{3+} ions in the Cr^{4+} ions [23]. Due to the problems mentioned, finding an appropriate medium to perform Cr^{4+} ion doping is still an active area of research. Currently, the germanate materials are promising candidates due to their tetrahedral environment preferred by Cr^{4+} [24].

$\text{Li}_2\text{CaGeO}_4$ is a tetragonal system with a spatial structure and lattice constants $a = b = 5.14 \text{ \AA}$ and $c = 6.59 \text{ \AA}$ [25]. As the ionic radius of Cr^{4+} ($\text{CN} = 4$, $0.39 \text{ \AA}$) is very close to the ionic radius of Ge^{4+} ($\text{CN} = 4$, $0.41 \text{ \AA}$), Cr ions can enter germanate crystals, Cr^{4+} can replace the tetrahedral position of Ge^{4+} , and Cr^{4+} is thus more compatible in the structure. The appearance of Cr^{3+} in citrate crystals is avoided, and there is no introduction of Cr^{3+} impurities in forsterite crystals. In this paper, $\text{Cr}^{4+}\text{-Li}_2\text{CaGeO}_4$ crystals were grown using the flux growth method from the flux of LiCl, and the properties of the $\text{Cr}^{4+}\text{-Li}_2\text{CaGeO}_4$ crystals were studied.

2. Experimental Procedure

2.1. Sample Preparation

In this paper, in order to reduce the volatilization of the raw materials during the crystal growth process, segregation and other crystals were avoided. First, $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ polycrystalline material was prepared by the high-temperature solid-phase synthesis method. A series of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ samples ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) were prepared using CaCO_3 (AR), Li_2CO_3 (AR), GeO_2 (99.999%), and Cr_2O_3 (99.999%) as starting materials, mixed in stoichiometric amounts and sintered at $900 \text{ }^\circ\text{C}$ for 5 h in an air atmosphere. This prepared polycrystalline material was used as the initial material for the subsequent crystal growth process and some measurements.

$\text{Cr}^{4+}\text{-Li}_2\text{CaGeO}_4$ crystals were grown by the flux growth method from the flux of LiCl. The initial solution contained 70 wt% LiCl and 30 wt% $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$. The experiments were performed in platinum crucibles of 70 mm height and 70 mm diameter, and the total amount of the initial solution was 300 g. The crystallization parameters were as follows: Crystal growth temperature range of $700\text{--}900 \text{ }^\circ\text{C}$. After complete melting of the raw materials, the solution was homogenized at $900 \text{ }^\circ\text{C}$ for 5 h and the saturation temperature of the melt was measured by the test seed crystal method; crystallization began at $5\text{--}10 \text{ }^\circ\text{C}$ above the saturation temperature, and then dropped to the saturation temperature after 3 h. After constant temperature growth, the drawing rate was $0.1\text{--}0.2 \text{ mm/h}$; the seed rotation speed was $18\text{--}22 \text{ rpm}$; and the growth cycle was approximately 25 days. Crystals were extracted from the liquid surface and then cooled to room temperature at a rate of $20 \text{ }^\circ\text{C/hour}$ to obtain crystals. Finally, the completely transparent, dark-green $\text{Cr}^{4+}\text{-Li}_2\text{CaGeO}_4$ crystals were grown under the crystallization parameters.

2.2. Characterizations

Differential scanning calorimetry (DSC)/thermogravimetry (TG) for the determination of the synthesis temperature was measured using a Netzsch STA449C at a heating rate of 10 K/min from room temperature to $1400 \text{ }^\circ\text{C}$. The crystal structures of all of the samples were checked with X-ray powder diffraction (XRD) (Ultima IV-X) with $\text{CuK}\alpha$ radiation at 40 kV and 20 mA at room temperature. The data were collected in the 2θ range of $10\text{--}80^\circ$. The infrared absorption spectrum of the samples was measured using the PerkinElmer Frontier infrared spectrometer, while the Raman spectrum was measured using the MKI-1000 Raman spectrometer. The luminescence characteristics of the samples were investigated using a steady-state Fluorolog-III spectrofluorometer with a high spectral resolution at room temperature. The fluorescence lifetime of the different doping concentrations of the crystals was measured by Fluorolog-III fluorescence spectroscopy. X-ray photoelectron spectroscopy (XPS) analyses were performed using the EP13-002 electron analyzer. The C (1s) signal (284.6 eV) was employed as a reference for the calibration of the binding energies of

different elements to correct for the charge effect. All of the measurements, in addition to the DSC/TG, were performed at room temperature.

3. Results and Discussion

3.1. The Phase Formation Temperature

Figure 1 shows a $\text{Li}_2\text{CaGaO}_4$ crystal with a mass of 2.9090 g, while Figure 2 illustrates the DSC/TG curve of the heating process for $\text{Li}_2\text{CaGaO}_4$. The TG curve indicates that the mass loss occurred in three main steps. The first step (from 285 to 600 °C) yielded a weight loss of approximately 4–5%, which was mainly caused by the adsorption of water in the precursor and the adsorption of CO_2 on the surface in the form of carbonic acid. This phenomenon can be verified by the DSC curve, where exothermal processes occurred over this temperature range. The second weight loss step was approximately 30–31%, occurring in the temperature range of 600–750 °C and attributed to the decomposition and volatilization of metal carbonates or metal oxides. The DSC curve diagram at 649.1 °C has a sharp endothermic peak in this temperature range, which is also the phase-forming temperature of $\text{Li}_2\text{CaGeO}_4$. The third step yielded a weight loss of approximately 2–3% after 800 °C. The mass loss after 800 °C was mainly due to the volatilization of GeO_2 . There is a large, sharp endothermic peak at 1134.1 °C, and according to Ref. [24], 1134 °C may be the melting temperature of $\text{Li}_2\text{CaGeO}_4$.



Figure 1. $\text{Li}_2\text{CaGaO}_4$.

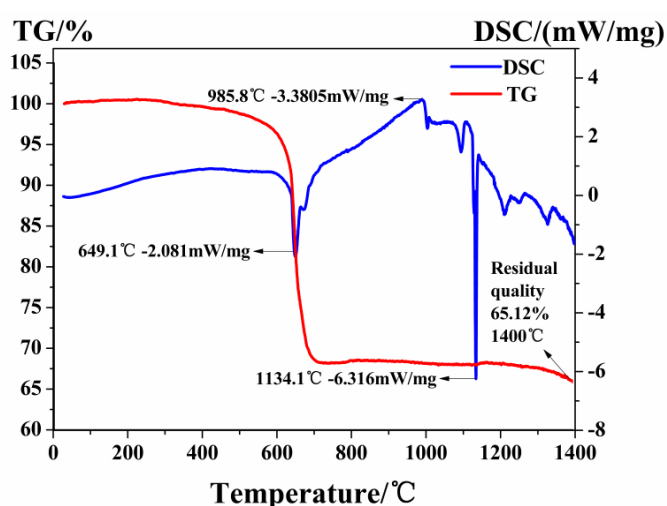


Figure 2. Differential scanning calorimetry (DSC)/thermogravimetry (TG) curve of $\text{Li}_2\text{CaGaO}_4$.

3.2. Crystal Structure Analysis

According to the literature (Table 1) $\text{Li}_2\text{CaGeO}_4$ is a tetragonal crystal system with space group $I4_2m$ and lattice parameters $a = b = 5.141 \text{ \AA}$, $c = 6.595 \text{ \AA}$, $c/a = 1.2828$, $V = 174.31 \text{ \AA}^3$, and $Z = 2$. The $\text{Li}_2\text{CaGeO}_4$ crystal structure consists of $[\text{LiO}_4]$ and $[\text{GeO}_4]$ tetrahedra and a $[\text{CaO}_6]$ octahedron [25]. In the structure of $\text{Li}_2\text{CaGeO}_4$, Ca is in a dodecahedral position, Ge has four types of tetrahedra, and the

other tetrahedron is occupied by Li [26]. According to the work reported by Shannon [27], we know the connection between the coordination number and the ionic radius, so we can determine the ionic radii of cations with Li⁺ ions (CN = 4, ion radius = 0.59 Å), Ca²⁺ ions (CN = 8, ion radius = 1.12 Å), Ge⁴⁺ ions (CN = 4, ion radius = 0.39 Å), and Cr⁴⁺ ions (CN = 4, ion radius = 0.41 Å). As the Cr⁴⁺ ionic radius is similar to that of Ge⁴⁺, Cr⁴⁺ ions can replace the cation site Ge⁴⁺ in the tetrahedron symmetry.

Table 1. The structural parameters of Li₂CaGeO₄ derived from X-ray diffraction data.

Atom	Wyckoff Position	x/a	y/b	z/c	Chemical Valence
Li	4d	0	1/2	1/4	1
Ca	2b	0	0	1/2	2
Ge	2a	0	0	0	4
O	8i	0.199	0.199	0.149	−2

Figure 3a shows the representative XRD patterns of Li₂CaGe_{1-x}Cr_xO₄ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1), along with the corresponding standard XRD pattern of Li₂CaGeO₄. All of the diffraction peaks of the as-prepared samples can be matched well with the data of pure Li₂CaGeO₄ (JCPDS 027-0289). According to the XRD analysis, the upping of Cr⁴⁺ ions in the studied concentration did not cause any phase transition or a new phase of the crystal structure. However, the XRD patterns of the Cr⁴⁺-doped samples showed regular changes, as evidenced in Figure 3b. With the increase in the Cr⁴⁺ doping concentrations, the leading peak compared to the peak of doped Li₂CaGeO₄ gradually shifted to a low 2θ angle. This change is due to an increase in the number of Cr⁴⁺ ions to replace the Ge⁴⁺ sites. This phenomenon also confirms that the Cr⁴⁺ ions successfully entered the crystal lattice of Li₂CaGeO₄ and substituted the Ge⁴⁺ ions. According to the Bragg equation (Equation (1)):

$$2d \sin \theta = n\lambda \quad (1)$$

where d is the spacing between the planes in the atomic lattice, θ is the angle between the incident ray and the scattering planes, n is an integer, and λ is the wavelength of the incident X-ray, the expansion of lattice cells due to the replacement of smaller ionic radii (r) of Cr⁴⁺ substituted for Ge⁴⁺.

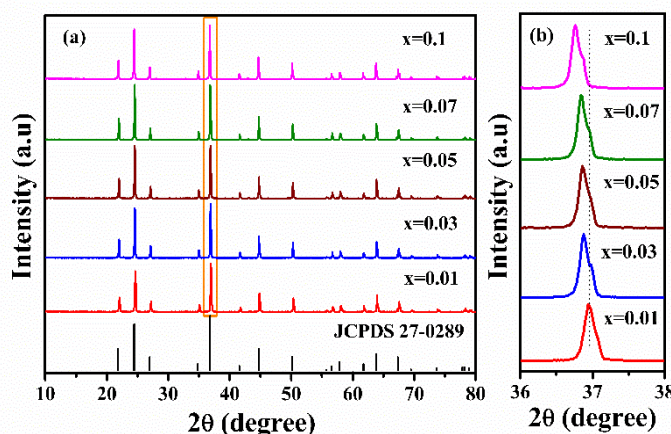


Figure 3. (a) X-ray powder diffraction (XRD) patterns of Li₂CaGe_{1-x}Cr_xO₄ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) and the standard data of the Li₂CaGeO₄ phase as a reference; (b) the magnified XRD curves in the range of 36°–38°.

3.3. Fourier Infrared Spectrum Spectroscopy Analysis

The Fourier infrared spectra of Li₂CaGe_{1-x}Cr_xO₄ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) are shown in Figure 4. Figure 4a shows the FT-IR spectra in the range of 4000–400 cm^{−1}. It can be seen from the figure that the vibration absorption bands of all samples are basically the same, which proves that the main lattice structure of the doped crystals did not change, which corresponds to the XRD analysis of the Li₂CaGe_{1-x}Cr_xO₄ crystals. The main vibration absorption bands of the sample were concentrated in the range of 1000–400 cm^{−1}, and in the range of 4000–1000 cm^{−1}, there were mainly

two absorption peaks at 3445 and 1443 cm^{-1} ; the vibration absorption band at 3445 cm^{-1} is a typical characteristic of hydroxyl stretching ($\gamma\text{-OH}$), while the absorption band at 1443 cm^{-1} is the absorption band of the OH vibration absorption of water and CO_3^{2-} of CO_2 in the air [28]. Figure 4b shows the FT-IR spectra of the absorption bands in the range of 1000–400 cm^{-1} . In this range, the $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ crystals showed four main vibration absorption bands: 878, 746, 512, and 425 cm^{-1} . The two absorption bands located at 878 cm^{-1} were caused by the stretching vibration of Ge–O bonds (terminal groups); the absorption band detected at 746 cm^{-1} can be attributed to the asymmetrical stretching vibration of Ge–O–Ge bonds; the absorption band at 512 cm^{-1} was caused by the symmetrical stretching vibration of Ge–O–Ge bonds; the absorption band around 425 cm^{-1} can be attributed to the deformation vibration of O–Cr–O bonds, which also shows that the Cr ions were indeed doped into the $\text{Li}_2\text{CaGeO}_4$ crystals [29–31]. In addition, the absorption band of the symmetrical stretching vibration of the Ge–O–Ge bonds moved in the low-wavenumber direction as the Cr^{4+} ion doping concentration increased from 512 to 500 cm^{-1} , which means that the energy required for the vibration became lower and the Ge–O–Ge bonds became more unstable. Meanwhile, as the Cr^{4+} ion doping concentration increased, the Ge–O bond vibration increased, thereby increasing the absorption band at 878 cm^{-1} . This is because when Cr ions occupy the tetrahedral position of Ge ions in $\text{Li}_2\text{CaGeO}_4$ crystals, the Cr ions combine with O ions to form O–Cr–O bonds that break the Ge–O–Ge bonds, resulting in some Ge–O–Ge bonds becoming Ge–O bonds.

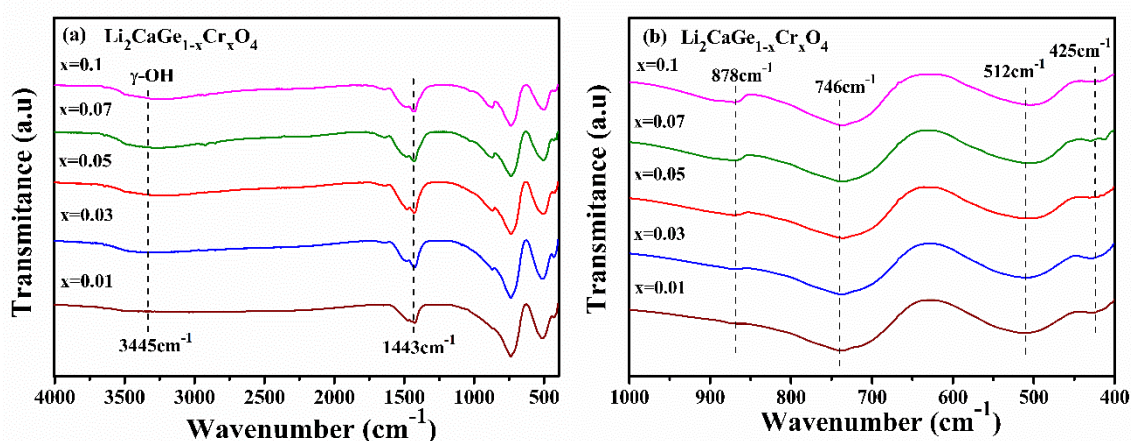


Figure 4. Fourier infrared spectra of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1): (a) FT-IR spectrum in the range of 4000–400 cm^{-1} ; (b) FT-IR spectrum in the range of 1000–400 cm^{-1} .

3.4. Raman Spectrum Analysis

Figure 5 shows the Raman spectra of the $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) crystals, consisting of seven Raman peaks: 321, 373, 730, 741, 856, 882, and 907 cm^{-1} . The first four Raman peaks (i.e., 321, 373, 730, and 741 cm^{-1}) remained basically consistent and did not change with the increase in Cr^{4+} concentration. The two Raman peaks at 730 and 741 cm^{-1} were caused by the $(\text{GeO}_4)^{4-}$ tetrahedral n_3 and n_1 stretching modes. The peak located around 373 cm^{-1} was caused by the bending vibration of O–Ge–O bonds, while the peak at 321 cm^{-1} can be attributed to the tetrahedral GeO_4 vibrations [32,33]. In addition, the intensity of the other three Raman peaks (i.e., 856, 882, and 907 cm^{-1}) gradually increased as the Cr^{4+} ion doping concentration increased, showing that these three Raman peaks are related to Cr ions. The two Raman peaks located around 856 and 882 cm^{-1} correspond to the n_1 and n_3 vibration modes of the CrO_4 , which also proves that Cr^{4+} ions preferentially occupy the Ge^{4+} tetrahedron position in $\text{Li}_2\text{CaGeO}_4$ crystals. Finally, the Raman peak at 907 cm^{-1} belongs to the symmetric stretching vibration of CrO_3 [34,35].

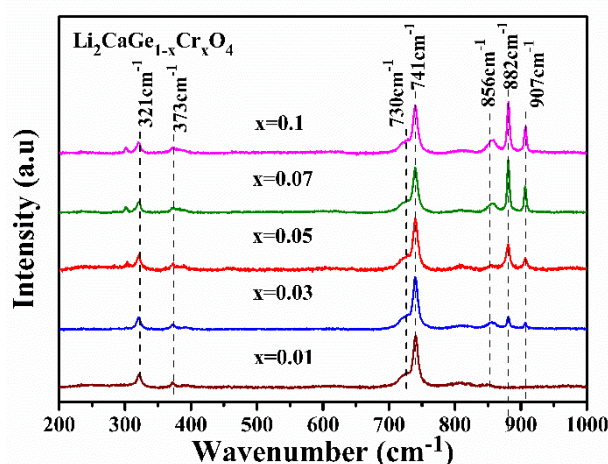


Figure 5. Raman spectra of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1).

3.5. Luminescence Properties and Analysis

Figure 6 shows the PLE and PL spectra of the $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$ sample at room temperature. Figure 6a shows the excitation spectra of the sample, where the excitation spectrum monitored at 1200 nm covers a broad spectral region from 800 to 1000 nm, which contains nine excitation bands derived from the $^3\text{A}_2 \rightarrow ^3\text{T}_2$ transitions of the Cr^{4+} ion, with the strongest stimulated peak located at 993 nm. The emission spectra are shown in Figure 6b for the 980 nm excitations at room temperature. The emission spectrum of the $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$ sample appeared between 1500 and 1000 nm, with luminescence resulting from the phonon-coupled $^3\text{T}_2 \rightarrow ^3\text{A}_2$ transition of the Cr^{4+} ions [36]. The single band with peaks at 1200 nm ($\lambda_{\text{ex}} = 980$ nm) can be attributed to the Cr^{4+} ions. Figure 6c illustrates the Gaussian fits of the emission spectra for $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$. We obtained three different fitted peaks located at 1200, 1302, and 1492 nm ($\lambda_{\text{ex}} = 980$ nm), specified as the transitions of three different orbital components from the $3t_2$ excited state to the $^3\text{A}_2$ ground state [37] ($^3\text{A}''(1) \rightarrow ^3\text{A}_2$, $^3\text{A}'(2) \rightarrow ^3\text{A}_2$, $^3\text{A}'(3) \rightarrow ^3\text{A}_2$).

The crystal absorption spectra at room temperature, as shown in Figure 7a, of the Cr^{4+} doping concentration, crystals, and test range of 200–900 nm, in addition to the absorption peak intensity, rose as the Cr^{4+} ion doping concentration increased, and the location and shape of the absorption peaks did not change. Three main absorption peaks at 280, 370, and 420 nm and an absorption band in the range of 550–850 nm can be observed in the absorption spectra. The absorption peaks at 280 and 370 nm were caused by the charge transfer transition from oxygen to Cr^{6+} , the absorption peak at 420 nm was caused by the $^3\text{A}_2 \rightarrow ^3\text{T}_1$ (3P) energy level of Cr^{4+} , and the absorption band between 550 and 850 nm was caused by the $^3\text{A}_2 \rightarrow ^3\text{T}_1$ (3F) energy level of Cr^{4+} at the tetrahedral position. Between 550 and 850 nm in the absorption spectrum absorption band of the Gaussian fitting, the Gaussian curve, as shown in Figure 7b, can be seen from the diagram inside the absorption band to have three absorption peaks: 628, 674, and 724 nm. This is because the Cr^{4+} ions of the excited states $^3\text{T}_1$ have three different transition tracks for $^3\text{A}_4$, $^3\text{A}_5$, and $^3\text{A}_6$ respectively. The three absorption peaks in the absorption band correspond to three different electron-polarized transition orbitals from the ground-state energy level $^3\text{A}_2$ of Cr^{4+} ions to the excited-state level $^3\text{T}_1$. Besides these three main absorption peaks, the other weak absorption peaks were caused by the vibration side band transition of the zero phonon line. The absorption band in the range of 750–900 nm was caused by the transition from the Cr^{4+} ions' ground-state level $^3\text{A}_2$ to the excited-state level $^3\text{T}_2$.

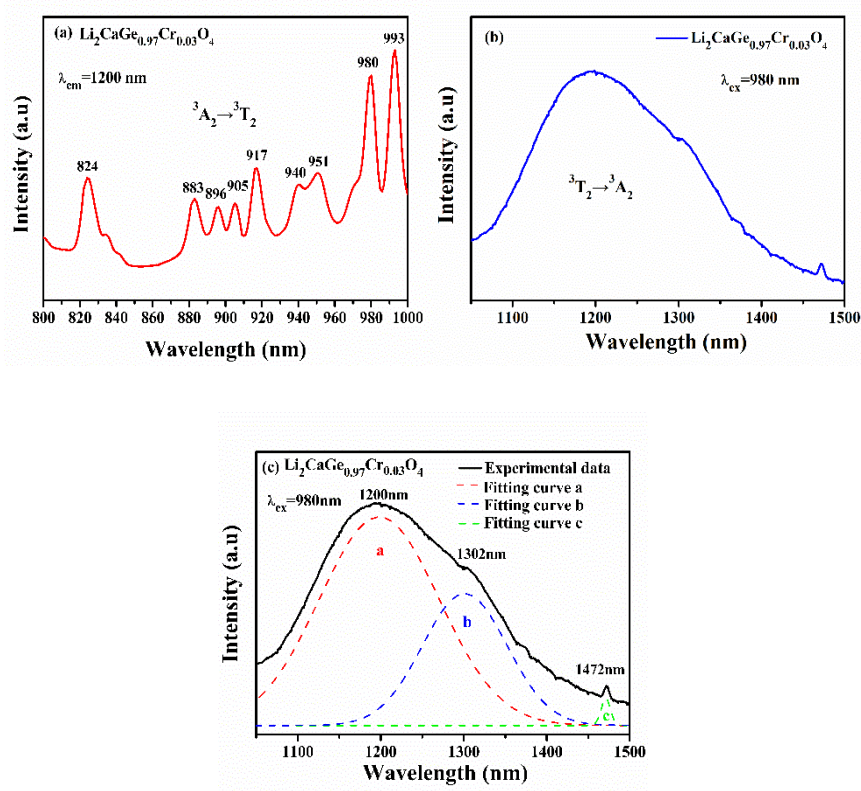


Figure 6. (a) Excitation spectra of $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$ ($\lambda_{\text{em}} = 1200$ nm); (b) emission spectra of $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$ ($\lambda_{\text{ex}} = 980$ nm); (c) Gaussian-fitted spectrum of the emission spectra of $\text{Li}_2\text{CaGe}_{0.97}\text{Cr}_{0.03}\text{O}_4$ ($\lambda_{\text{ex}} = 980$ nm).

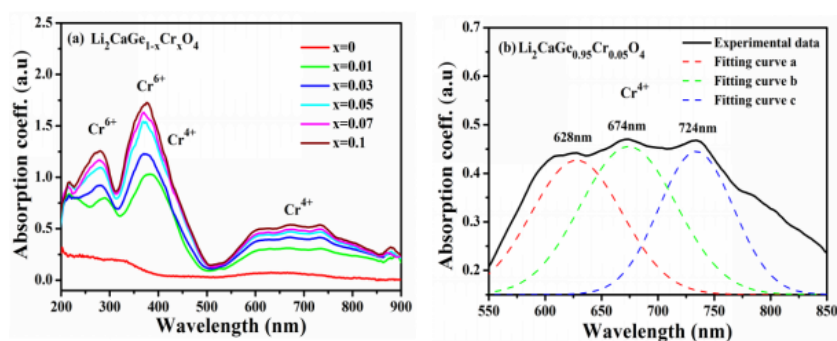


Figure 7. $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ crystal absorption spectra: (a) Absorption spectra of crystals with different doping concentrations (200–900 nm); (b) the Gaussian of $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ (550–850 nm).

Figure 8 illustrates the energy level diagram of the Cr^{4+} ions for the two lowest high-spin terms, namely, ${}^3\text{T}_1$ and ${}^3\text{T}_2$. According to the Tanabe–Sugano diagram of the Cr^{4+} ions, in the ideal tetrahedral position of T_d symmetry, the lowest free-ion level of the $d^2\text{--Cr}^{4+}$ ions is ${}^3\text{F}$. Due to the splitting of the crystal field, the free-ion level is split as follows: ${}^3\text{F} \rightarrow {}^3\text{A}_2 + {}^3\text{T}_2 + {}^3\text{T}_1$. The energy order of these levels is as follows: ${}^3\text{T}_1 > {}^3\text{T}_2 > {}^3\text{A}_2$. Generally, the ${}^3\text{A}_2$ energy level can be considered to be a ground state and the ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1$ transition is an allowed electric dipole (spin-allowed), while ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$ is an allowed magnetic dipole. Based on the structure of $\text{Li}_2\text{CaGeO}_4$, the local environmental symmetry is less than the T_d symmetry, and the tetrahedron is distorted along the two axes, which splits the ${}^3\text{T}_1$ and ${}^3\text{T}_2$ bands into three components. The most probable chain of descent of symmetry is $T_d \rightarrow C_{3v} \rightarrow C_s$.

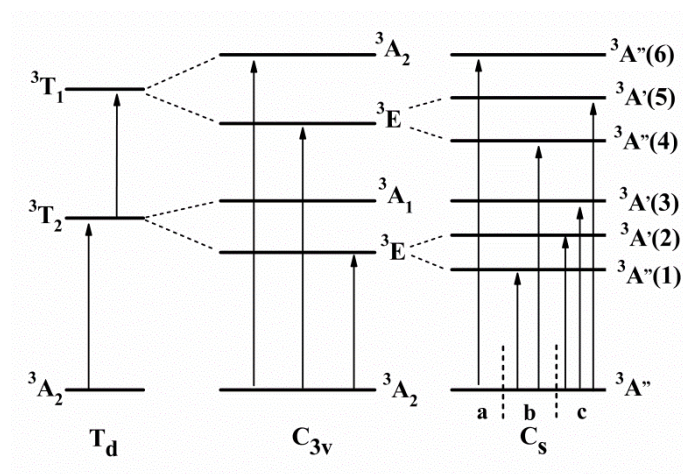


Figure 8. Energy level of the Cr⁴⁺ ions.

The dependence of the emission spectra on the Cr⁴⁺ doping concentration was investigated, and the results are shown in Figure 9. Here, the emission spectra of Li₂CaGe_{1-x}Cr_xO₄ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) with excitations of 980 nm at room temperature are characterized. When the Cr doping concentration increased from 1 to 5 mol%, the emission intensity monotonically also increased, reaching a maximum at $x = 5$ mol%. However, a further increase in the Cr⁴⁺ concentration (9 and 12 mol%) resulted in a reduction in emission intensity due to concentration quenching, which was caused by energy transfer between the Cr⁴⁺ ions. The experimental results indicate that the optimal Cr⁴⁺ ion concentration is 5 mol% in Cr⁴⁺-Li₂CaGeO₄. Generally, the energy transfer rate between luminescent centers increases with the number of active ions, and so does the energy transfer rate from the luminescent center to the traps nearby. The critical energy transfer distance (R_c) between the neighboring donors (activators) and acceptors (quenching site) can be expressed by Dexter's theory [38] (Equation (2)):

$$R_c = 2 \times (3V / 4\pi X_c N)^{1/3} \quad (2)$$

where V is the unit cell volume of the host lattice, X_c is the critical concentration, and N is the number of sites available for the dopant in the unit cell. In the case of Li₂CaGeO₄, $N = 2$, $V = 174.3 \text{ \AA}^3$ [39], and X_c was experimentally determined to be 0.05. As a result, the critical R_c value of the Cr⁴⁺ ions in Li₂CaGeO₄ was calculated to be approximately 14.93 Å. In general, nonradiated electron transfer from the excitation agent to the activator may be the result of exchange and multipolar electrical interactions. Here, the critical R_c value is 14.93 Å; the value of R_c is much larger than the typical distance ($R_c < 5 \text{ \AA}$) that is required for an exchange interaction, inferring that the concentration quenching mainly takes place via electric multipolar interactions between the Cr⁴⁺ ions. The type of multipolar energy transfer mechanism between the Cr⁴⁺ ions can be determined by the following formula (Equation (3)) [40]:

$$\frac{I}{x} = K[1 + \beta(x)^{\theta/3}]^{-1} \quad (3)$$

where I is the emission intensity at the concentration of the activator (x), K and β are the constants for each type of interaction in a specific host lattice, and the values of $\theta = 6, 8$, and 10 correspond to the dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q) interactions [41], respectively. According to Equation (3), the dependence of $\lg(I/x)$ on $\lg(x)$ is plotted in Figure 10. The fit result appears to be linear with a slope of -0.529 ; therefore, the calculated value is approximately 6, indicating that the d–d interaction mechanism acts as the leader in the excitation process of the Cr⁴⁺ center in the Li₂CaGeO₄ body.

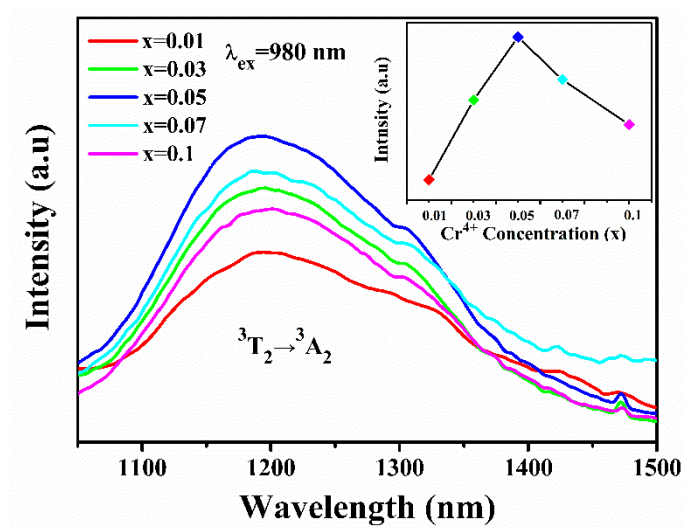


Figure 9. The persistent luminescence spectra of the $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ samples ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1). Inset: Plot of the emission intensity vs. Cr-doping content.

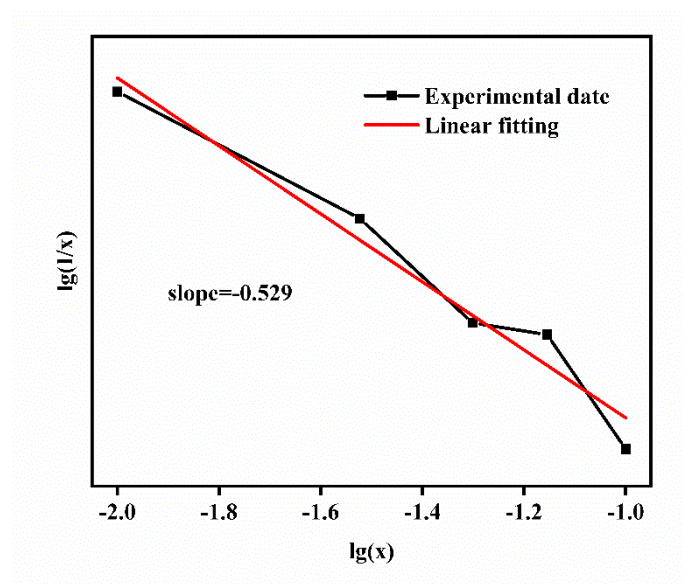


Figure 10. The dependence of $\lg(I/x)$ on $\lg(x)$ according to Equation (3).

3.6. Fluorescence Lifetime Analysis

The data are normalized, and Figure 11a shows the fluorescence decay curves of the $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ crystals ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) by monitoring the 1200 nm emission with excitation at 980 nm. The decay curves measured for all samples can be fitted well by an exponential function expressed by the following equation [42]:

$$I = A \exp\left(-\frac{t}{\tau}\right) + I_0 \quad (4)$$

where I and I_0 are the luminescence intensities with time t and 0, respectively, A is a constant, t is time, and τ is the decay time for the exponential components. According to the above fitting equation, the decay time of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1) is 13.895, 12.672, 12.268, 11.961, and 11.828 ms, respectively. The function of the lifetime of the Cr^{4+} ions at 1200 nm (${}^3\text{T}_2 \rightarrow {}^3\text{A}_2$) and the concentration in $\text{Li}_2\text{CaGeO}_4$ is shown in Figure 11b. As the Cr^{4+} ion doping concentration increased, the fluorescence lifetime of the samples gradually decreased. This may be due to the

increase in the doping concentration of the Cr^{4+} ions itself, which leads to an increase in the cross-relaxation between two adjacent Cr^{4+} ions. Generally, there are a number of reasons that can cause decay kinetics behavior, including the number of luminescent centers, energy transfer, and defect types. If the Cr^{4+} ions occupy different positions in the host lattice, different luminescent centers will be generated, resulting in multi-exponential behavior [43]. However, the fluorescence decay curve in the $\text{Li}_2\text{CaGeO}_4$ host is consistent with a single exponential behavior. This indicates that the Cr^{4+} ions have only one luminescence center in $\text{Li}_2\text{CaGeO}_4$ with the Cr^{4+} ions only occupying the position of the Ge^{4+} ions.

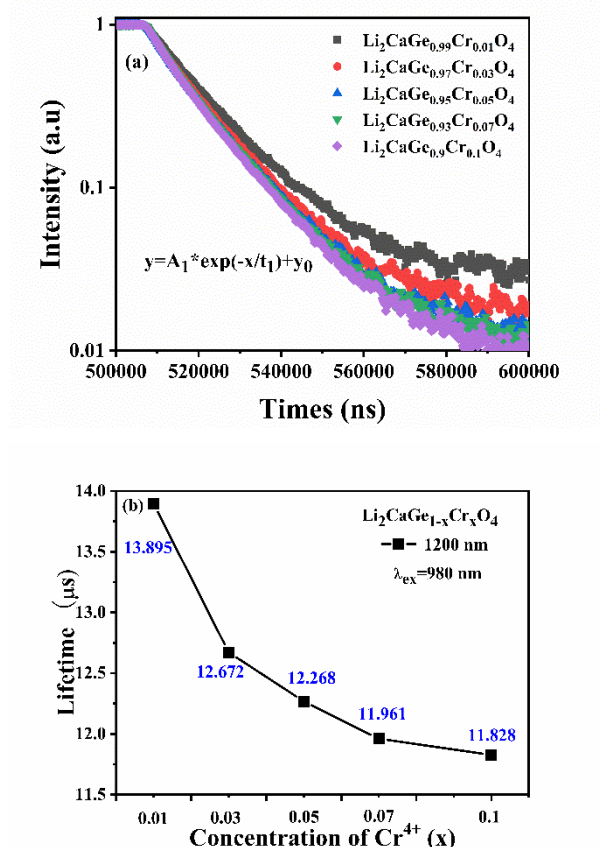


Figure 11. (a) Fluorescence lifetime curve of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.1); (b) dependence of the decay time of $\text{Li}_2\text{CaGe}_{1-x}\text{Cr}_x\text{O}_4$ on the Cr^{4+} doping concentration.

3.7. XPS Analysis of the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ Crystals

Figure 12 shows the XPS survey spectra of the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ crystals, and Figure 10 shows that the signals of calcium (Ca), germanium (Ge), oxygen (O), and carbon (C) elements are clear. Simultaneously, relatively weak chromium (Cr) signals can also be observed. In the case where the carbon (C) element was not an intrinsic component in the crystals, the role of carbon was used to calibrate the binding energy. The peak binding energies of the elements in the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ crystals are shown in Table 2.

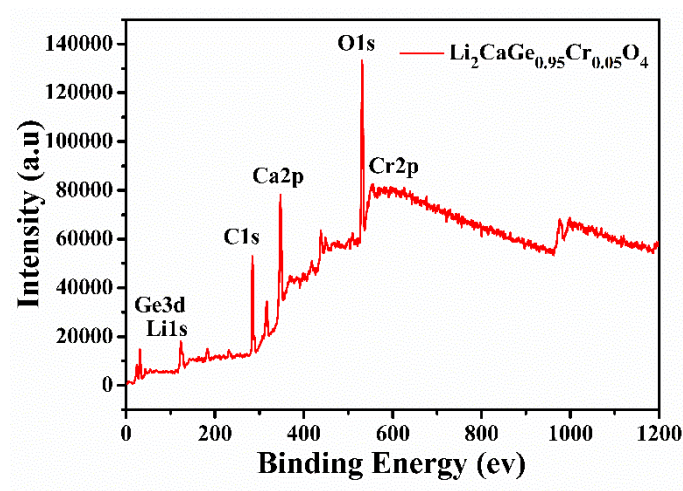


Figure 12. X-ray photoelectron spectroscopy (XPS) survey spectra of the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ crystal.

Table 2. The peak banding energy of the elements of the $\text{Li}_2\text{Ca}_{0.95}\text{Cr}_{0.05}\text{GeO}_4$ crystals.

Element	Peak BE
C1s	284
Cr2p	579
Ca2p	346
Ge3d	31
Li1s	54
O1s	531

Figure 13 shows the narrow-scan XPS spectra of $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ for the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ sample around the Cr2p core region. The narrow-scan spectra of XPS were fitted using Gaussian equations with two peaks centered at 575.6 and 584.4 eV due to $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$, respectively, corresponding to the Cr^{4+} ions. In the Gaussian fitting curves, we did not find peaks of the Cr^{3+} ions, of which the two peaks centered at 577.0 and 586.7 eV were ascribed to $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ of the Cr^{3+} ions, respectively [44,45]. Therefore, the $\text{Li}_2\text{CaGeO}_4$ sample contained only Cr^{4+} ions without the presence of Cr^{3+} ions, which is consistent with the results of the fluorescence spectroscopy analysis. However, in the Gaussian fitting curve, we found two peaks centered at 579.5 and 588.9 eV from $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$, respectively, corresponding to the Cr^{6+} ions [45]. This phenomenon occurred because Cr^{3+} ions can be oxidized not only into Cr^{4+} ions but also into Cr^{6+} ions at high temperatures, and Cr^{6+} ions exist in the form of CrO_3 and are stable at room temperature.

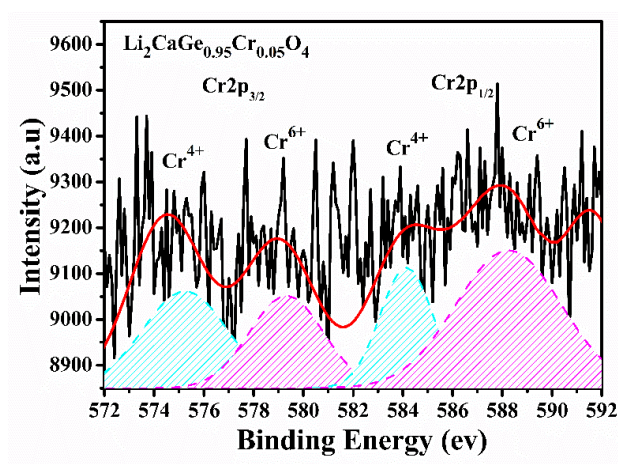


Figure 13. Narrow scanning spectra of XPS for Cr2p.

In the synthesis of the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ polycrystalline material using the solid-phase method, the Cr^{4+} ions were received by oxidization of Cr^{3+} from the raw material of Cr_2O_3 in the oxygen atmosphere. This involved the conversion mechanism from Cr^{3+} to Cr^{4+} . The XPS survey spectra and the fluorescence spectroscopy results indicate that the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ sample contains Cr^{4+} ions. At the same time, the results of the XPS analysis prove that the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ sample also contains Cr^{6+} ions. When synthesizing samples in an air atmosphere at high temperatures, Cr_2O_3 reacts with the oxygen in the air, converting Cr^{3+} to Cr^{4+} ions, and Cr^{4+} ions continue to react with oxygen at high temperatures to form Cr^{6+} ions [46].

Figure 14 shows the XPS narrow-scan spectra of the other elements in the $\text{Li}_2\text{CaGe}_{0.95}\text{Cr}_{0.05}\text{O}_4$ crystals, where Figure 14a is the narrow-scan spectrum of the Li1s peak, Figure 14b is the narrow-scan spectrum of the Ca2p peak, and Figure 14c is the narrow-scan spectrum of the Ge3d peak. Meanwhile, the narrow-scan spectrum of Figure 14d is that of the O1s peak. As can be seen from Figure 12, there is only one broad peak at 55.3 eV in the narrow-scan spectrum of the Li1s peak, corresponding to the (+1) valence of Li ions, which is mainly formed by the Li–O bonds in the crystals. As can be seen from Figure 14b, in the narrow-scan spectrum of the Ca2p peak, there are two main peaks, namely, 347.2 and 350.3 eV, which belong to the Ca ions $\text{Ca}2p_{3/2}$ and $\text{Ca}2p_{1/2}$, respectively, corresponding to the (+2) valence of Ca ions mainly formed by the Ca–O bonds. It can be seen from Figure 14c that in the narrow-scan spectrum of the Ge3d peak, only the peak at 33.4 eV exists in the crystals, which belongs to the GeO_4 structure; meanwhile, no peak of GeO_2 can be found in the crystals, and so it can be inferred that the Ge element only exists in the form of GeO_4 in the crystals. Figure 14d shows the main three fitted peaks of the O1s peak, located at 531.7, 532.7, and 533.5 eV, which belong to the Li–O, Ca–O, and Ge–O bonds, respectively [47–50].

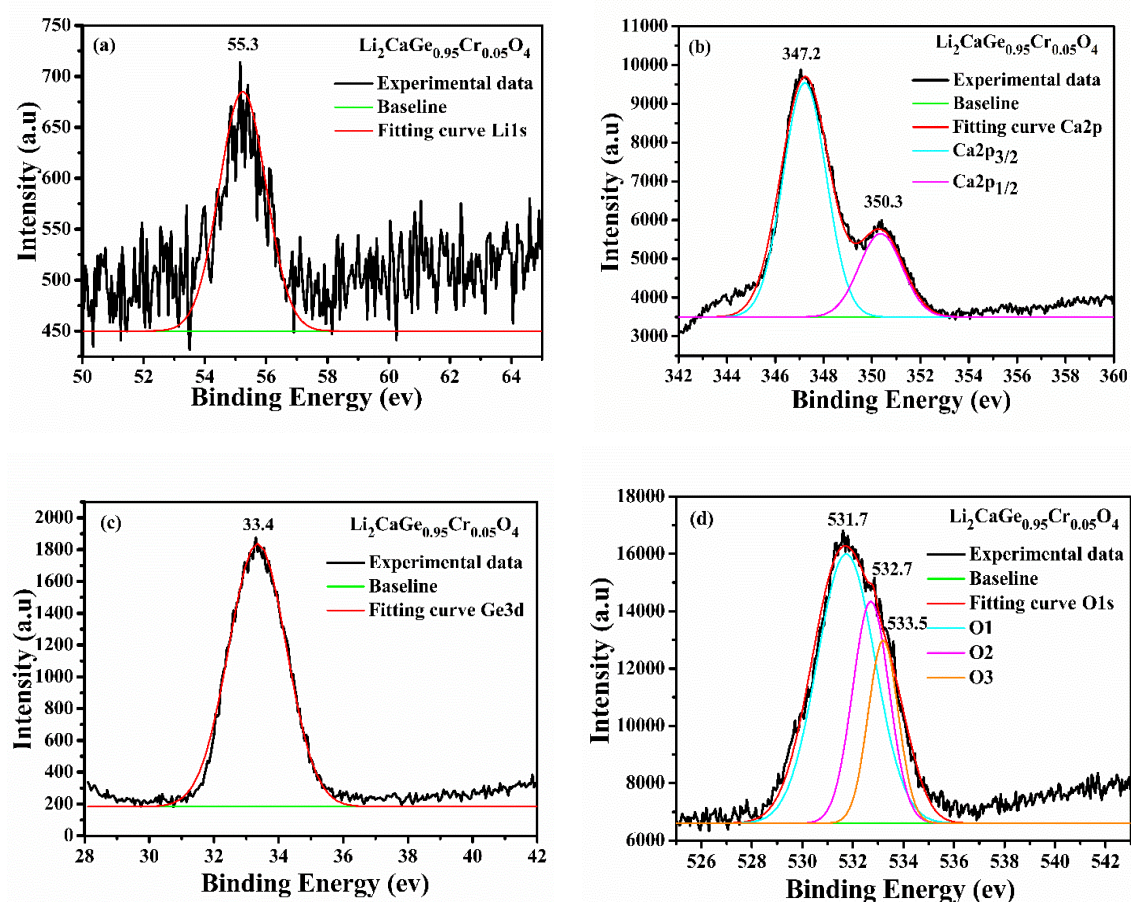


Figure 14. Narrow scanning spectra of XPS for the other elements: (a) Li1s, (b) Ca2p, (c) Ge3d, and (d) O1s.

4. Conclusions

In conclusion, polycrystalline synthesis, crystal growth, and the structure and spectral properties of the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystals were described in this paper. The Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystal was grown by the flux growth method from the flux of LiCl. The $\text{Li}_2\text{CaGeO}_4$ crystal structure was characterized, indicating the site occupancy preferences of the Cr^{4+} in Ge^{4+} sites. The Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystals showed strongly NIR regional spectra typical for Cr^{4+} located in tetrahedral positions. The emission spectra presented in the range of 1000–1500 nm were excited by 980 nm, with the maximum peaks at 1200 nm at room temperature, caused by the transition of ${}^3\text{T}_2 \rightarrow {}^3\text{A}_2$ in the Cr^{4+} ions. The optimal Cr^{4+} ion concentration was shown to be 5 mol% in Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$, beyond which the d–d interaction-based energy transfer between adjacent Cr^{4+} ions caused concentration quenching. The fluorescence spectroscopy and XPS analysis indicated that only Cr^{4+} ion substitution occurred in the Cr-doped $\text{Li}_2\text{CaGeO}_4$, and no Cr^{3+} ions were found in the samples. Therefore, the Cr^{4+} - $\text{Li}_2\text{CaGeO}_4$ crystal has a great potential and future in optical applications.

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