

Article

Infrared and Raman Investigations of Cr-Doped Glasses and Glass–Ceramics Containing $\text{Li}_2\text{CaGeO}_4$ Nanophase

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Abstract

IR and Raman spectra of pure and chromium doped glasses and glass–ceramics from the system $\text{Li}_2\text{O}-\text{CaO}-\text{GeO}_2-\text{B}_2\text{O}_3$ are investigated and analyzed. The IR spectra of the pure and chromium doped glass samples contain bands typical of germanate and borate glasses. The amorphous network in the undoped glass is built by deformed GeO_4 tetrahedra, BO_3 groups and LiO_4 tetrahedra. Doping with 0.5 at% Cr_2O_3 leads to the appearance of BO_4 groups and an increase in the symmetry of the GeO_4 groups. The bands associated with chromium are not observed. The comparison between glass and glass–ceramic IR spectra shows the more intensive bands in the latter. Raman spectra of pure glass–ceramic samples show an increase in the number of Raman bands compared with glass samples. The shoulder at 850 cm^{-1} is associated with internal stretching vibrations of the CrO_4 tetrahedron, so Cr^{4+} ions occupy the Ge^{4+} tetrahedron position in the $\text{Li}_2\text{CaGeO}_4$ crystal phase in glass–ceramic samples. A change in the symmetry of the GeO_4 units after doping with Cr_2O_3 in the glass–ceramic is also observed. Results from IR and Raman studies of non-doped and Cr-doped glass, and glass–ceramics containing the crystal phase of $\text{Li}_2\text{CaGeO}_4$, show that the IR spectra clearly show the change in the local environment of Li, Ge, and B group, but the detection of CrO_4 is questionable. In contrast, Raman spectroscopy is a more suitable method for the detection of CrO_4 units in the glass–ceramic samples. Raman analysis of the glass–ceramic confirmed the formation of CrO_4 units.

Keywords: glasses; glass–ceramics; IR; Raman; structural units



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1. Introduction

Cr^{4+} -doped media are widely used in femtosecond lasers [1,2], passively Q-switched lasers [3] and tunable solid-state lasers [4–7]. Their emission in the range 1.1–1.6 μm allows continuous-wave and a broad absorption band, which makes them attractive for using as several commercial pump lasers [8]. Lasers emitting in this wavelength range find increasing applications in medicine [9], spectroscopy [10], telecommunications systems [11], etc. The optical characteristics of Cr_2O_3 -doped materials are dependent on the structure of the host matrix and Cr ion coordination and concentration.

However, all of the known media doped with Cr^{4+} have several disadvantages. The fluorescent quantum yield of these media is quite low due to the nonradiative transition of Cr^{4+} ions and the quantum efficiency is low. The presence of Cr^{3+} ions together with Cr^{4+} ions into the matrix is another drawback. The mentioned problems encourage scientists

to search for appropriate media for doping with Cr^{4+} . As Cr^{4+} prefers a tetrahedral environment, silicate and germanate phases are promising matrices due to their tetrahedral environment of Si^{4+} or Ge^{4+} [12,13]. Unfortunately, many of the compounds with tetrahedral structural units possess polymorph transition or melt incongruently; thus, growth of single crystals is impossible or problematic [14–17]. An alternative way is synthesizing a glass–ceramic with a desired compound phase with the same laser characteristic like a corresponding single crystal. One of the perspective media for Cr^{4+} doped is $\text{Li}_2\text{CaGeO}_4$. The $\text{Li}_2\text{CaGeO}_4$ structure consists of columns of alternating, edge-sharing (GeO_4) tetrahedra and (CaO_8) dodecahedra. These columns are linked by their corners to neighboring columns and form a three-dimensional network with the Li ions located at the twisted LiO_4 tetrahedron units. Thus, channels are formed that contain the lithium atoms. Ca–O bond distances can be separated into two different groups: four oxygens at 2.74 Å form the common (110) edges of two (GeO_4) tetrahedra and one (CaO_8) dodecahedron; the other four at 2.39 Å directly link neighboring (CaO_8) dodecahedra [18]. Figure 1 presents the $\text{Li}_2\text{CaGeO}_4$ structure.

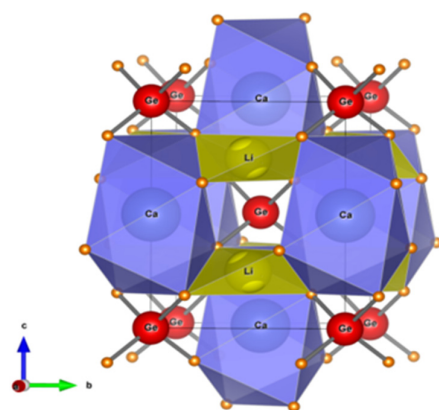


Figure 1. Structure of $\text{Li}_2\text{CaGeO}_4$.

So, from a structural point of view, $\text{Li}_2\text{CaGeO}_4$ meets the requirements for doping with Cr^{4+} . However, this compound also melts incongruently and the preparation of single crystals from it is possible only from high-temperature solutions. This growth technique is associated with a number of problems, mainly the growth conditions and the very low growth rates [19].

In our previous investigations, we found the optimal composition for obtaining transparent $\text{Li}_2\text{CaGeO}_4$ containing nano glass–ceramics doped with Cr^{4+} (Li_2O – CaO – GeO_2 in 1:1:1 mol% with 5 mol% B_2O_3) [20]. The choice was made in accordance with the basic requirements for the glasses for preparing the glass–ceramics: obtaining the parent glass in the simplest possible way, maximum amount of the crystallizing phase, absence or minimal amount of unwanted crystallizing phases, etc. The optimal thermal treatment regime for glass processing was experimentally established based on DSC curves and XRD analysis. Thus, after experiments for choosing the optimal composition of the parent glass and applying different treatment regimes, a temperature of 490 °C and a time of 2 h were chosen. The nanoparticles obtained in this way have no more than 30 nm sizes. We investigated the optical properties of selected glass–ceramics. The glass–ceramics with chromium concentrations of 0.5, 1.0, 1.5 and 2.0 at% in place for germanium possess absorption in two regions, 900–1100 nm and 550–900 nm. The first is due to the presence of Cr^{4+} in a tetrahedral environment and the latter one is due to the overlapping of both Cr^{3+} absorption in an octahedral environment and Cr^{4+} absorption in a tetrahedral environment. On the other hand, $\text{Li}_2\text{CaGeO}_4$ glass–ceramic contains 0.2 at.% Cr ions exhibits a broad area of luminescence from 1000 to 1500 nm with center at 1220 nm and 36 ms lifetime [20].

These characteristics are fully comparable with that received for $\text{Li}_2\text{CaGeO}_4$ single crystal grown by the flux method [19] as well as with $\text{Li}_2\text{MgSiO}_4$ and $\text{Li}_2\text{ZnSiO}_4$ glass–ceramic the synthesis of which is difficult because of the high temperature required for homogenization of the used parent glass [17,21].

The low chromium concentration in glass–ceramics and the presence of Cr^{3+} together with Cr^{4+} prompted us to explore some of the obtained samples by IR and Raman spectroscopy analysis to study the glass and glass–ceramics structures and their changes with increasing chromium concentration. On the other side, the presence of Cr^{3+} and Cr^{4+} would also have an impact on the spectral lines.

In this article, we present the infrared (IR) and Raman spectroscopy analysis of the chosen glasses and glass–ceramics obtained by thermal treatment at 490 °C for 2 h, both in their pure form and doped with different at.% Cr in place of Ge ions.

2. Materials and Methods

2.1. Synthesis of Glass and Glass–Ceramics

The preparation, structural, and optical characterization of pure glass, Cr-doped glasses, and glass–ceramic materials was already published in our previous article [20].

2.2. Characterization

The amorphous structure and the structural changes that occurred after doping with Cr were examined using IR and Raman techniques. A Nicolet-320 FTIR spectrometer (Waltham, MA, USA) was used for IR analysis of the obtained glass and glass–ceramics. All transmittance spectra were recorded at room temperature in the range of 1200–400 cm^{-1} with a spectral resolution of 2 cm^{-1} and 64 scans per spectrum.

The Raman spectra were recorded at room temperature by a Via Qontor Raman Confocal Microscope (Renishaw plc, New Mill, Wotton-under-Edge, UK) at a laser wavelength of 532 nm (Nd:YAG laser). The laser power on the sample was kept up to 1% of the nominal power, so no heating effects on the powder sample could be observed. The excitation light was focused and collected using a 50× LWD objective lens (Renishaw plc, New Mill, Wotton-under-Edge, UK).

3. Results and Discussion

The glass and glass–ceramics structure of Cr-doped samples were analyzed using infrared (IR) and Raman spectroscopy, which together confirm the presence of the germanate and borate units, their transformation as well as the presence of CrO_4 groups. The effect of thermal treatment of the undoped and doped samples is also investigated and the obtained results are compared. The IR spectra of the glass samples without and with Cr_2O_3 contain shows the bands typical for of the germanate and borate base glasses (Figure 2). Most absorption bands are broader with low intensity, apart from of this at 760 cm^{-1} . This stronger band is designated to the asymmetric vibration of the Ge–O band in GeO_4 tetrahedra, building the amorphous network [22]. The presence of two shoulders at 810 and 735 cm^{-1} around the strong band (760 cm^{-1}) can be explained by the formation of the deformation GeO_4 groups. The weak absorption band at 500 cm^{-1} is assigned to the asymmetric vibration of the same structural units [22]. The vibration bands at 1420, 1380, 1280 and 1210 cm^{-1} , typical of the asymmetrical B–O bond from BO_3 groups, are observed in the undoped glass. The intensity of these bands is lower, which relates to the low concentration of these groups as compare with GeO_4 ones. It is well known that the vibrational modes of the B_2O_3 glass network are active in three infrared spectral areas- from 1200 to 1600 cm^{-1} , which is attributed to the asymmetric stretching of the B–O band in BO_3 units; from 800 to 1200 cm^{-1} , typical of the stretching of the B–O bonds in BO_4 units and the

last ones from 600 to 800 cm^{-1} , which is due to the bending vibrations of B–O–B linkages of both BO_3 units [23,24]. The weak band at 410 cm^{-1} is due to the vibration of Li–O from the formed LiO_4 entity [25]. Having in mind the above spectral features, we conclude that the main structural units in the undoped glass are BO_3 , GeO_4 and LiO_4 tetrahedra. A slight change in the IR spectrum of the 0.5 at% Cr-doped glass was observed. Doping with 0.5 at% Cr_2O_3 led to the appearance of an additional shoulder at 880 cm^{-1} and a band at 1045 cm^{-1} . The high frequency band at 1045 cm^{-1} is due to the vibration of B–O from BO_4 groups, which means new BO_4 units are formed in the doped glass sample [26]. On the other hand, the shoulders at 810 and 735 cm^{-1} are disappearance as well as the band at 760 cm^{-1} become narrow and indicate that GeO_4 groups become more symmetrical. The band at 500 cm^{-1} vanishes after doping with Cr_2O_3 . According to the literature data the absorption band at 880 cm^{-1} can be attributed to vibration of the Ge–O or B–O bond from GeO_4 and BO_4 units, respectively [23,26,27]. But some authors consider that vibration in the IR range from 865 to 890 cm^{-1} can be associated with vibration of CrO_4 units in the glass materials [28], glass–ceramics [29] and crystal phases [30].

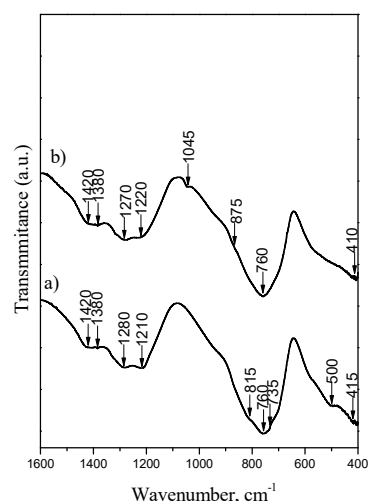


Figure 2. IR spectra of (a) non-doped glass and (b) 0.5 at% Cr_2O_3 -doped glass with Li_2O – CaO – GeO_2 content, with a stoichiometric ratio for $\text{Li}_2\text{CaGeO}_4$ equal to 1:1:1 and 5 mol% B_2O_3 .

Recently, in the literature, data have been reported for the vibration of CrO_4 units around 425 cm^{-1} in the IR spectra of the crystal phases and crystals [19,31]. In our study, the bands are not observable within the range of 865–890 cm^{-1} and at 425 cm^{-1} . We can conclude that a change in the mainly structural units BO_n and GeO_4 was observed after doping with Cr_2O_3 . The dominant absorption bands at 1420, 1380, 1270, 1210, 750 and 410 cm^{-1} remain unaffected.

Figure 3 shows the IR spectra of the glass–ceramics samples obtained after thermal treatment at 490 °C for 2 h without and doped with Cr_2O_3 . In comparison to the IR spectra of glass, the spectra of glass–ceramics display more intense bands are related to additional thermal treatment and the formation of the $\text{Li}_2\text{CaGeO}_4$ phase. The heat treatment on the undoped sample led to a shift in the band positions from 760 to 730 cm^{-1} [32]. The new vibration bands at 1510, 1175, 1085 and 490 cm^{-1} appeared due to the network reorganization induced by the crystallization process. The bands at 1510, 1175, and 1085 cm^{-1} are connected to vibration of BO_3 and BO_4 units, respectively. The following change we observation after doping with 0.5at.% Cr_2O_3 in the IR spectrum of the glass–ceramic sample:

- (i) Strong absorption band at 1510 cm^{-1} disappeared.
- (ii) Appearance of new weak bands at 1380, 1045, and 575 cm^{-1} .

- (iii) Shift in position from 1175 to 1220 cm^{-1} .
- (iv) The band at 870 cm^{-1} is transformed into a shoulder at 880 cm^{-1} , and the band at 490 cm^{-1} is transformed into a shoulder at 510 cm^{-1} .

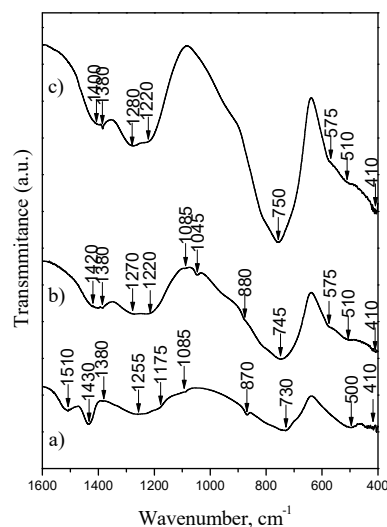


Figure 3. IR spectra of (a) non-doped glass-ceramic, (b) 0.5 at% Cr_2O_3 - and (c) 1.5 at% Cr_2O_3 -doped glass-ceramic samples with $\text{Li}_2\text{O}-\text{CaO}-\text{GeO}_2$ content in a stoichiometric ratio for $\text{Li}_2\text{CaGeO}_4$ equal to 1:1:1 and 5 mol% B_2O_3 .

When the content of Cr_2O_3 increase to 1.5 at% the absorption bands at 1085, 1045 and 870 cm^{-1} vanished, indicating a reduction in BO_3 and GeO_4 units within the glass-ceramic structure. But the intensity of the IR bands is higher due to a higher amount of Cr_2O_3 . Even after doping with 1.5 at% Cr_2O_3 we do not detect the absorption bands typical for vibration of the Cr-O bond. In conclusion, IR analysis does not provide evidence of the existence of Cr^{4+} ions in doped glass and glass-ceramics samples. Moreover, infrared spectroscopy distinguishes the various borate and germanate structural units present in the investigated glasses and glass-ceramics.

Raman spectroscopy is an additional effective technique for examining the structure of the glass and glass-ceramic samples. Raman spectrum of non-doped and doped glasses is shown in Figure 4. Three weak intense bands at 340, 560 and 925 cm^{-1} , and one strongly intense and broad band with a maximum at 785 cm^{-1} was observed. The mode at 340 cm^{-1} is assigned as Li-O stretching motion from LiO_4 units [33]. The Raman band at 560 cm^{-1} is due to the bending vibrations of GeO_4 building the amorphous structure of the investigated samples [34]. The intensity band at 785 cm^{-1} corresponds to the asymmetric vibrations of the Ge-O bond in GeO_4 units [19]. The band at 920 cm^{-1} is super position and corresponds to the symmetric vibrations of both GeO_4 and to vibrations of BO_4 groups [35,36]. The Raman spectrum of glass doped with 0.5at% Cr_2O_3 is very close to that of the non-doped glass. The shift in the Raman peaks is not observed; the main structural units in both glasses (non-doped and doped with Cr_2O_3) are almost the same. According to the literature data the Raman peak in the range from 840 to 885 cm^{-1} is due to the asymmetric stretching vibration of Cr-O bonds in CrO_4 tetrahedral units [37,38]. The absence of the peaks in above mentioned range indicated that Raman spectroscopy is not sensitive enough to determine the presence of vibration of CrO_4 at low concentration in the structure of glass samples. By analyzing the glass samples using IR spectroscopy, the same tendency was found.

Raman spectra of the undoped and Cr-doped glass-ceramic samples are presented in Figure 5. The thermal treatment at 490°C of the non-doped sample led to an increase in the number of Raman bands at 153, 193 and 328 cm^{-1} . The band at 785 cm^{-1} splits two bands at 745 and 783 cm^{-1} is observed corresponding to ν_3 and ν_1 of the stretching

vibrations of GeO_4 groups [19,28]. After doping with 0.5 at% Cr_2O_3 the shoulder at 850 cm^{-1} was observed, which is associated with internal stretching vibrations of the CrO_4 tetrahedron [37–39]. This demonstrates that Cr^{4+} ions occupy reside in the Ge^{4+} tetrahedron position in formed $\text{Li}_2\text{CaGeO}_4$ crystal phase in glass–ceramic samples. In our case the Raman peaks typical of vibration of the CrO_4 group are the only ones in comparison with the peaks typical of the same groups in the Cr^{4+} – $\text{Li}_2\text{CaGeO}_4$ crystals obtained by the flux growth method [19]. The low frequency peaks at 153 and 193 cm^{-1} were disappearance. When the amount of Cr_2O_3 increases up to 1.5at% this shoulder is transformed into a well resolution peak (Figure 5c). R. Vijay et al. reported only one active Raman mode of CrO_4 units at the same frequency in the glass samples containing Li_2O – Sb_2O_3 – PbO – GeO_2 [40]. The Raman vibration of these groups was found above 850 cm^{-1} in the glass–ceramics based on the Li_2O – CaF_2 – P_2O_5 system [41]. The other Raman modes of the CrO_4 groups were not identified in our spectra [42]. All Raman lines show a higher intensity as one strong peak at 784 cm^{-1} was observed after doped with 1.5at.% Cr_2O_3 . These changes indicate that to change the symmetry of the GeO_4 units after doping with Cr_2O_3 in the glass–ceramic structure. On the other hand, the changes in the local germanium structure in crystalline phases depending on the amount of Cr_2O_3 is monitored by Raman analysis.

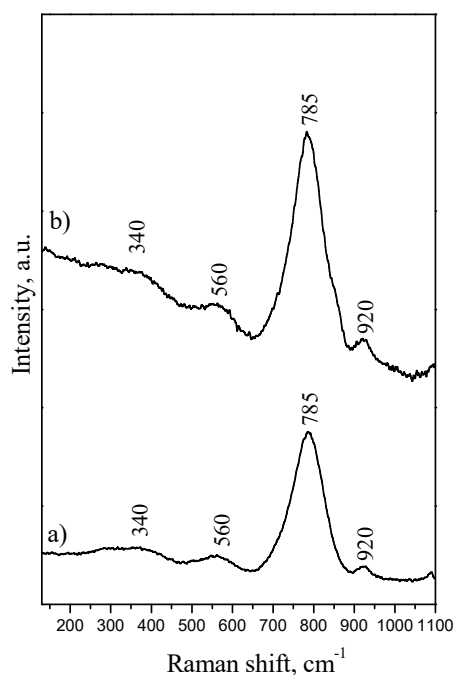


Figure 4. Raman spectra of (a) undoped and (b) 0.5 at% Cr_2O_3 -doped glass with a Li_2O – CaO – GeO_2 composition having a stoichiometric ratio for $\text{Li}_2\text{CaGeO}_4$ equal to 1:1:1 and 5 mol% B_2O_3 added.

In summary, we can conclude that only Raman spectroscopy confirms the incorporation of Cr ions into the glass–ceramics samples in GrO_4 groups at a higher concentration. Raman spectra indicate that the intensities of the vibration bands associated with the GeO_4 units increase with the presence of Cr_2O_3 .

As a results from IR and Raman studies of non-doped and Cr-doped glass, and the glass–ceramics containing the crystal phase of $\text{Li}_2\text{CaGeO}_4$, are that the IR spectra clearly show the change in the local environment of Ge and B group, but the detection of CrO_4 is questionable. This is probably due to the low concentration of Cr (0.5 and 1.5 at% relative to the Ge content in the samples investigated). The selected Cr concentrations, although that it is higher than the optimal Cr concentration for maximum laser emission intensity in the 1.1 – $1.6\text{ }\mu\text{m}$ range, still appear to be too low to be detected through IR spectroscopy. In contrast Raman spectroscopy is a more suitable method for detecting CrO_4 units in the

glass–ceramic samples at Cr concentrations of 0.5 and 1.5 at.%. In addition to the typical Cr^{4+} emission in a wide range from 1.1 to 1.6 μm , this is further evidence for the successful obtaining of $\text{Li}_2\text{CaGeO}_4$ glass–ceramics doped with Cr^{4+} ions.

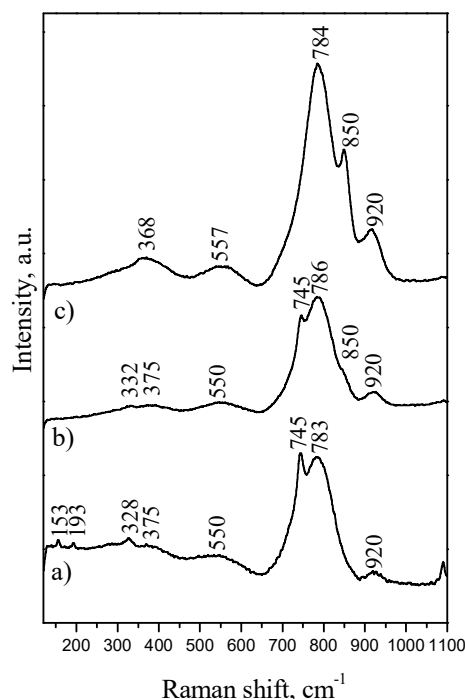


Figure 5. Raman spectra of (a) non-doped, (b) 0.5 at% Cr_2O_3 -, and (c) 1.5 at% Cr_2O_3 -doped glass–ceramic samples with Li_2O – CaO – GeO_2 content in a stoichiometric ratio for $\text{Li}_2\text{CaGeO}_4$ equal to 1:1:1 and 5 mol% B_2O_3 .

4. Conclusions

IR and Raman spectra of pure and chromium doped glasses and glass–ceramics from the system Li_2O – CaO – GeO_2 – B_2O_3 are investigated and discussed. The amorphous network in the undoped glass is built by following structural units such as deformed GeO_4 , BO_3 and LiO_4 groups. Doping with 0.5 at% Cr_2O_3 leads to the appearance of BO_4 entities and the GeO_4 groups become more symmetrical. The IR absorption bands are more intensive of the glass–ceramic samples. New vibration bands appear due to the crystallization process. Increasing the content of chromium to 1.5 at% leads to a reduction in BO_3 and GeO_4 units within the glass–ceramic structure.

Comparison between Raman spectra of pure glass and glass–ceramic samples show an increase in the number of Raman bands in the latter. The shoulder at 850 cm^{-1} is associated with internal stretching vibrations of the CrO_4 tetrahedron, so Cr^{4+} ions occupy the Ge^{4+} tetrahedron position in the $\text{Li}_2\text{CaGeO}_4$ crystal phase in glass–ceramic samples. A change in the symmetry of the GeO_4 units after doping with Cr_2O_3 in the glass–ceramic is also observed.

Results from IR and Raman studies of non-doped and Cr-doped glass and the glass–ceramics containing the crystal phase of $\text{Li}_2\text{CaGeO}_4$ show that the IR spectra clearly show the change in the local environment of Li, Ge, and B ions, but the detection of CrO_4 is questionable. This is probably due to the low concentration of Cr (0.5 and 1.5 at% relative to the Ge content in the samples investigated). The selected Cr concentrations, although that it is higher than the optimal Cr concentration for maximum laser emission intensity in the 1.1–1.6 μm range, still appear to be too low to be detected through IR spectroscopy. In contrast, Raman spectroscopy is a more suitable method for detection of CrO_4 units in the glass–ceramic samples at Cr concentration of 0.5 and 1.5 at.%.

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References

- Spälter, S.; Böhm, M.; Burk, M.; Mikulla, B.; Fluck, R.; Jung, I.; Zhang, G.; Keller, U.; Sizmann, A.; Leuchs, G. Self-starting soliton-modelocked femtosecond Cr^{4+} :YAG laser using an antiresonant Fabry-Pérot saturable absorber. *Appl. Phys. A* **1997**, *65*, 335–338. [\[CrossRef\]](#)
- Sennaroglu, A.; Carrig, T.J.; Pollock, C.R. Femtosecond pulse generation by using an additive-pulsemode-locked chromium-doped forsterite laser operated at 77 K. *Opt. Lett.* **1992**, *17*, 1216–1218. [\[CrossRef\]](#)
- Tang, J.; Bai, Z.; Zhang, D.; Qi, Y.; Ding, J.; Wang, Y.; Lu, Z. Advances in all solid state passively Q-switched laser based on Cr^{4+} YAG saturable absorber. *Photonics* **2021**, *8*, 93. [\[CrossRef\]](#)
- Kück, S. Laser-related spectroscopy of ion-doped crystals for tunable solid-state lasers. *Appl. Phys. A* **2001**, *72*, 515–562. [\[CrossRef\]](#)
- Moncorge, R.; Manaa, H.; Boulon, G. Cr^{4+} and Mn^{5+} active centers for new solid state laser materials. *Opt. Mater.* **1994**, *4*, 139–151. [\[CrossRef\]](#)
- Kuo, Y.-K.; Huang, M.-F.; Birnbaum, M. Tunable Cr^{4+} :YVO₄ Q-switched Cr^{4+} :LiCAF laser. *IEEE J. Quantum Electron.* **1995**, *31*, 657–663. [\[CrossRef\]](#)
- Moncorge, R. Laser materials based on transition metal ions. *Opt. Mater.* **2017**, *63*, 105–117. [\[CrossRef\]](#)
- Sennaroglu, A. Broadly tunable Cr^{4+} -doped solid-state lasers in the near infrared and visible. *Prog. Quantum Electron.* **2002**, *26*, 287–352. [\[CrossRef\]](#)
- Mukhopadhyay, P.K.; Alsous, M.B.; Ranganathan, K.; Sharma, S.K.; Gupta, P.K.; George, J.; Nathan, T.P.S. Simultaneous Q-switching and mode-locking in an intracavity frequency doubled diode-pumped Nd:YVO₄/KTP green laser with Cr^{4+} :YAG. *Opt. Commun.* **2003**, *222*, 399–404. [\[CrossRef\]](#)
- Gilmore, D.A.; Cvijin, P.V.; Atkinson, G.H. Intracavity laser spectroscopy in the 1.38–1.55 μm spectral region using a multimode Cr^{4+} :YAG laser. *Opt. Commun.* **1993**, *103*, 370–374. [\[CrossRef\]](#)
- Chai, Y.; Leburn, C.G.; Lagatsky, A.A.; Brown, C.T.A.; Pentty, R.; White, I.; Sibbett, W. 1.36-Tb/s spectral slicing source based on a Cr^{4+} :YAG femtosecond laser. *J. Light. Technol.* **2005**, *23*, 1319–1324. [\[CrossRef\]](#)
- Zhang, J.; Kalisky, Y.; Atkinson, G.; Kokta, M. *Advances Solid State Lasers Technical Digest*; Optical Society of America: Washington, DC, USA, 1995; Paper TuC10; p. 182.
- Devi, P.S.; Gafney, H.D.; Petricevic, V.; Alfano, R.R.; He, D.; Miyano, K.E. Sol-gel syntheses and spectroscopic characterization of chromium-doped silicates and germanates. *Chem. Mater.* **2000**, *12*, 1378–1384. [\[CrossRef\]](#)
- Petricevic, V. Laser and Spectroscopic Parameters of Cr^{4+} Doped Laser Crystals. In Proceedings of the 7th International Workshop on Laser Physics, (LPHYS'98), Berlin, Germany, 6–10 July 1998; Volume 2.
- Subbotin, K.A.; Zharikov, E.V.; Smirnov, V.A.; Shcherbakov, I.A. Growth and luminescent properties of single-crystal monticellite doped with chromium. *Bull. Lebedev Phys. Inst.* **1977**, *11*, 12–17.
- Hartung, S.; Kück, S.; Danger, T.; Petermann, K.; Huber, G. ESA Measurements of Cr^{4+} -doped crystals with wurtzite-like structure. In *Advanced Solid State Lasers*; Optica Publishing Group: Washington, DC, USA, 1996; paper TL8.
- Anino, C.; Théry, J.; Vivien, D. $(\text{CrO}_4)^{4-}$: $\text{Li}_2\text{MgSiO}_4$, a near IR broad-band emitting material with very long fluorescence lifetime. In *Advanced Solid State Lasers*; Optica Publishing Group: Washington, DC, USA, 1997; p. SC6.

18. Gard, J.A.; West, A.R. Preparation and crystal structure of $\text{Li}_2\text{CaSiO}_4$ and isostructural $\text{Li}_2\text{CaGeO}_4$. *J. Solid State Chem.* **1973**, *7*, 422–427. [\[CrossRef\]](#)
19. Wang, D.; Zhang, X.; Wang, X.; Leng, Z.; Yang, Q.; Ji, W.; Lin, H.; Zeng, F.; Li, C.; Su, Z. 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. *Crystals* **2020**, *10*, 1019. [\[CrossRef\]](#)
20. Nikolov, V.; Solé, R.M.; Koseva, I.; Mateos, X.; Marsal, G.; Díaz, F. Synthesis and optical characterization of Cr^{4+} doped $\text{Li}_2\text{CaGeO}_4$ transparent glass-ceramic. *Cer. Int.* **2025**, *51*, 42717–42724. [\[CrossRef\]](#)
21. Zhuang, Y.; Tanabe, S.; Qiu, J. Wavelength tailorability of broadband near-infrared luminescence in Cr^{4+} -activated transparent glass-ceramics. *J. Am. Ceram. Soc.* **2014**, *97*, 3519–3523. [\[CrossRef\]](#)
22. Mansour, E.; Damrawi, G.E.; Fetoh, R.E.; Doweidar, H. Structure-properties changes in ZnO-PbO-GeO_2 glasses. *Eur. Phys. J. B* **2011**, *83*, 133–141. [\[CrossRef\]](#)
23. Moustafa, F.A.; Fayad, A.M.; Ezz-Eldin, F.M.; Kashif, I.E. Effect of gamma radiation on ultraviolet, visible and infrared studies of NiO , Cr_2O_3 and Fe_2O_3 -doped alkali borate glasses. *J. Non-Cryst. Sol.* **2013**, *376*, 18–25. [\[CrossRef\]](#)
24. Liu, T.; Li, C.; Huang, Q.; Liu, C.; Lin, C.; Zhang, Q.; Luo, Z.; Zhu, L.; Lu, A. Characterization of structure and properties of $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-Cr}_2\text{O}_3$ glass-ceramics. *J. Non-Cryst. Sol.* **2020**, *543*, 120154–120162. [\[CrossRef\]](#)
25. Tarte, P. Identification of Li-O bands in the infra-red spectra of simple lithium compounds containing LiO_4 tetrahedra. *Spectrochim. Acta* **1964**, *20*, 238–240. [\[CrossRef\]](#)
26. Dong, X.; Hai, L.; Weiling, Y.; Chun, L.; Lina, L.; Shasha, L.; Fanming, Z. From structure to luminescence investigation of $\text{B}_2\text{O}_3\text{-GeO}_2\text{-BaO-ZnO}$ glass doped with Dy^{3+} . *J. Non-Cryst. Sol.* **2024**, *634*, 122965–122978. [\[CrossRef\]](#)
27. Sudhakar, B.K.; Chand, N.R.K.; Prasanna, H.N.L.; Rao, S.G.; Rao, K.V.; Dhand, V. Vibrational spectral analysis of structural modifications of Cr_2O_3 containing oxyfluoroborate glasses. *J. Non-Cryst. Sol.* **2010**, *356*, 2211–2217. [\[CrossRef\]](#)
28. Ram, S.; Ram, K. IR and Raman studies and effect of γ radiation on crystallization of some lead borate glasses containing Al_2O_3 . *J. Mater. Sci.* **1988**, *23*, 4541–4546. [\[CrossRef\]](#)
29. Suresh, S.; Narendrudu, T.; Yusub, S.; Kumar, A.S.; Kumar, V.R.; Veeraiah, N.; Rao, D.K. Influence of local structural disorders on spectroscopic properties of multi-component $\text{CaF}_2\text{-Bi}_2\text{O}_3\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ glass ceramics with Cr_2O_3 as nucleating agent. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2016**, *153*, 281–288. [\[CrossRef\]](#)
30. Akbar, N.; Javed, M.; Khan, A.A.; Masood, A.; Ahmed, N.A.; Mehmood, R.Y.; Khisro, S.N.; Abdul, M.A.S.A.; Haniff, M.A.S.M.; Shah, A. Zircon-Type CaCrO_4 Chromite Nanoparticles: Synthesis, characterization, and photocatalytic application for sunlight induced degradation of rhodamine B. *ACS Omega* **2023**, *8*, 30095–30108. [\[CrossRef\]](#)
31. Wang, D.; Leng, Z.; Jiang, X.; Wang, X.; Yang, W.; Zhang, T.; Shi, X.; Zhang, X.; Zeng, F.; Li, C.; et al. Study and applicability of photoluminescence properties of Cr^{4+} : LiInGeO_4 . *Phys. B Phys. Cond. Matt.* **2022**, *628*, 413312–413319. [\[CrossRef\]](#)
32. Yang, W.; Yang, Y.; Chen, R.; Liu, H.; Leng, Z.; Jiang, X.; Zhang, Z.; Zuo, C.; Zhou, L.; Lin, H.; et al. First principles calculations of structure, vacancy defects, thermodynamic and mechanical properties and near-infrared luminescence properties of $\text{Li}_2\text{CaGeO}_4$ and Er^{3+} : $\text{Li}_2\text{CaGeO}_4$ crystals. *J. Lumin.* **2024**, *270*, 120541. [\[CrossRef\]](#)
33. Hu, Q.; Lei, L.; Jiang, X.; Feng, Z.C.; Tang, M.; He, D. Li ion diffusion in LiAlO_2 investigated by Raman spectroscopy. *Solid State Sci.* **2014**, *37*, 103–107. [\[CrossRef\]](#)
34. Wan, S.; Zhang, S.; Gong, X.; Zeng, Y.; Jiang, S.; You, J. Structural investigations on two typical lithium germanate melts by in situ Raman spectroscopy and density functional theory calculations. *Cryst. Eng. Comm.* **2020**, *22*, 701–707. [\[CrossRef\]](#)
35. Kaky, K.M.; Sayyed, M.I.; Mhareb, M.H.A.; Abbas, H.H.; Baki, S.O. Physical, structural, mechanical, and various radiation shielding properties of $\text{TeO}_2\text{-GeO}_2\text{-ZnO-Al}_2\text{O}_3\text{-Li}_2\text{O-M}$ ($\text{M} = \text{WO}_3, \text{MoO}_3, \text{PbO}, \text{and CuO}$) glasses. *Opt. Mater.* **2023**, *143*, 114370–114378. [\[CrossRef\]](#)
36. Maniu, D.; Iliescu, T.; Ardelean, I.; Cinta-Pinzaru, S.; Tarcea, N.; Kiefer, W. Raman study on $\text{B}_2\text{O}_3\text{-CaO}$ glasses. *J. Mol. Str.* **2003**, *485*, 651–653.
37. Hakeem, M.A.; Jackson, D.E.; Hamlin, J.J.; Errandonea, D.J.; Proctor, E.; Bettinelli, M. High pressure Raman, optical absorption and resistivity study of SrCrO_4 . *Inorg. Chem.* **2018**, *57*, 7550–7557. [\[CrossRef\]](#)
38. Xu, R.; Wang, Z.; Xu, H. Viscosities and structures of $\text{SiO}_2\text{-CaO-3 wt\% MgO-10 wt\% Fe}_2\text{O}_3\text{-10 wt\% Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ coal slags. *J. Non-Cryst. Sol.* **2024**, *646*, 123253–123261.
39. Agrawal, A.K.; Jaiswal, S.K. Emergence of perovskite and hashemite-type phases in chromium doped $(\text{Ba}_{0.90}\text{Sr}_{0.10})(\text{Fe}_{1-x}\text{Cr}_x)\text{O}_3 \pm \delta$ oxides: Formation, Rietveld refinement and Raman spectra. *J. Alloys Compd.* **2024**, *996*, 174715–174725. [\[CrossRef\]](#)
40. Vijay, R.; Ramesh Babu, P.; Ravi Kumar, V.; Piasecki, M.; Krishna Rao, D.; Veeraiah, N. Dielectric dispersion and ac conduction phenomena of $\text{Li}_2\text{O-Sb}_2\text{O}_3\text{-PbO-GeO}_2\text{:Cr}_2\text{O}_3$ glass system. *Mater. Sci. Semicond. Process.* **2015**, *35*, 96–108. [\[CrossRef\]](#)

41. Krishna, G.M.; Gandhi, Y.; Venkatesan, R.; Veeraiah, N. Features of the local structural disorder in $\text{Li}_2\text{O}-\text{CaF}_2-\text{P}_2\text{O}_5$ glass–ceramics with Cr_2O_3 as nucleating agent. *Physica B* **2008**, *403*, 702–710. [[CrossRef](#)]
42. Heyns, A.M.; Hardena, P.M. The temperature dependence of the Raman spectra of chromium-doped titanite (CaTiOSiO_4). *J. Raman Spectrosc.* **2013**, *44*, 1615–1624. [[CrossRef](#)]

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