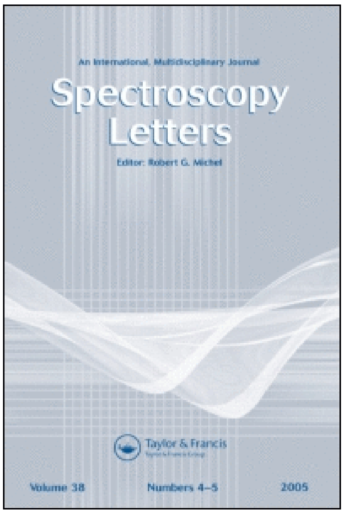

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Spectroscopic Study of Optical Property and Structural State of Vanadium Ions in Lithium Aluminosilicate Glass-Ceramics

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ABSTRACT The optical property and the structural states of vanadium ions were studied by multiple spectra (UV-visible, IR, Raman, and electron paramagnetic resonance (EPR)) in LAS glass and glass-ceramics. The color of glasses changed drastically from light yellow-green to claret during crystallization, the optical absorption in visible range is the characteristic absorption of V^{4+}, and the variation of absorption region is mainly attributed to the change of vanadium ions' coordination polyhedron during crystallization process. The V^{4+} ions, formed by reduction of V^{5+} ions, existed as the VO^{2+} complex in octahedral coordination with a tetragonal compression with C_{4v} symmetry. Additionally, the V^{4+} ions partially replaced Li^+ and occupied tetrahedral sites in beta-quartz solid solution.

KEYWORDS EPR, glass-ceramics, IR, optical property, Raman, spectroscopy, structural state, vanadium

INTRODUCTION

The transition metal ions and the rare earth metal ions are good coloring agents, and transition metal ions[1–10] such as Co, Cr, and Ni and rare earth metal ions[11–14] such as Nd, Eu, and Er have been studied in various glass system. It is widely recognized that the doping ions occupy either octahedral sites or tetrahedral sites in glasses and crystals, and the color of glasses are associated with the valence, structural state, and surrounding ligand field of the doping ions. In view of their outer-shell electron orbital functions with rather broad radial distributions and their sensitive responses to surroundings ions, these ions can also be used to probe the host glass structure.

The Li_2O-Al_2O_3-SiO_2 (LAS) glass-ceramics are of interest as hosts for transition metal ions or rare earth metal ions in preparation of colored transparent glass-ceramics. The LAS glass system has been studied for many years and continues to attract attention in the view of both science and economy due to low thermal expansion coefficient and high visible transparency. Various studies[15–18] have been done to discuss the crystallization mechanism and microstructure by using the thermal analysis (DTA), X-ray

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diffraction analysis (XRD), and scanning electron microscopy (SEM) technologies. The LAS system glass implanted with chromium ions was prepared and studied by EI-Diasty et al.,[6,7] the different oxidation states adopted by the chromium ions into the glass network were identified by the optical data, and the relationship between optical property and the composition of glass was also determined by the IR spectroscopy. Different colored LAS glass-ceramics were prepared by doping of Ni^{2+}, and it was found that Ni^{2+} ions moved from trigonal bipyramid five-fold sites in the as-cast glass to octahedral sites in glass-ceramics, and then to distorted octahedral sites with increasing temperature.[9] The similar behaviors of Ni^{2+} ions were also found in ZnO-Al_2O_3-SiO_2 system glass-ceramics.[10] Additionally, some rare earth metal ions such as Eu, Er were also incorporated into LAS glass-ceramics, and the optical-absorption fluorescence spectra were evaluated.[13,14] O. S. Dymshits and A. A. Zhinlin et al. have carried out a series of studies about LAS glass system containing Co^{2+}, Ni^{2+}, and Nd^{2+} in the past 30 years.[2–4,11,12] Moreover, they have used the Raman spectroscopy successfully to investigate the phase decomposition process and quantitatively analyze beta-quartz derivative phase in LAS glass-ceramics.[19–22]

Vanadium is one common coloring agent exhibiting green or pink in glass. The valence of vanadium ions is +3, +4, or +5, and their spin-orbit coupling could be changed sensitively in different coordination polyhedron. In the phosphate,[23] borate[24–27] and calcium alumina silicate[28,29] glasses doped with V_2O_5, V^{4+} has been found as a tetragonally distorted octahedral VO^{2+} complex. However, there is no study devoted to vanadium-doped LAS glass-ceramics. In this study, V_2O_5 was introduced into the LAS glass system, and colorized transparent glass-ceramics were prepared. Glass experience revealed that the color changed from light yellowish-green drastically to claret and even to beta-spodumene solid solution (s.s)-based opaque glass-ceramics after crystallization. Since the crystallization occurs upon reheating process, this simple phenomenon is much more interesting and complicated.

The objective of this research was to understand the behaviors of vanadium ions in LAS glass-ceramics. Different spectra (such as UV-Visible, IR, and Raman) of the glass and glass-ceramics were used to investigate the optical properties and to obtain structural states of vanadium ions. The electron paramagnetic resonance (EPR) was used to grasp information about the coordination polygon around vanadium ions. The traditional materials characterization techniques such as DTA and XRD were used also to analyze the influence of V_2O_5 on crystallization.

MATERIALS AND METHODS

The studied glass and glass-ceramics were derived from the LAS system ($Li_2O:Al_2O_3:SiO_2 = 1:1:4$). Li_2O was partially substituted by MgO and ZnO in order to improve the property and reduce the melting temperature. Analytical reagents of Li_2CO_3, SiO_2, Al_2O_3, MgO, and ZnO were selected as raw materials. TiO_2 and ZrO_2 were added as nucleating agents. The alterations of color in glass and glass-ceramics caused by 0.25-wt% V_2O_5 were already visible. Furthermore, the LAS glass with 2-wt% and 5-wt% V_2O_5 were also prepared in order to investigate the structural states of the vanadium ions and their effect on the structure and crystallization of glass. The mixtures were melted in alumina crucibles at 1600°C for 4 hr using electric muffle furnace, and the melt was then quenched by pouring onto steel plate and annealed at 600°C for 2 hr. Glass-ceramics were prepared by subjecting the glass to heat treatments at temperatures between 700°C and 900°C.

The DTA and XRD were used firstly to determine the crystallization temperature and to analysis the effect of V_2O_5 on nucleation and crystallization. All parameters were determined on a different thermal analyzer (Diamond TG/DTA, PE) with a heating rate of 15°C/min. The XRD patterns were obtained by an X-ray diffractometer (Model D/Max 2500, Rigaku) in the range of 10° to 80° with a scanning rate of $5° \min^{-1}$, with the CuKα radiation produced at 40 kV and 200 mA. The Electron Paramagnetic Resonance spectra were recorded at room temperature on an EPR spectrometer (ESR300E, Bruker) operating at the band frequency of about 9.8 GHz with a field modulation frequency of 100 KHz. The modulation width was set at 0.1 mT, and the microwave power was 10 mW. A powdered specimen equal-weighed was taken in a quartz tube for EPR measurements. The transmission spectra of the original glass and the glass-ceramics were measured using a spectrophotometer (Unicam UV-500, Backman) in the range of 200–800 nm, and Infrared absorption spectra were measured by infrared spectrometer (Spectrum GX, PerkinElmer) in the range from 2000 cm^{-1} to 400 cm^{-1}. Raman spectra were also excited by using Microscopic Confocal Raman Spectrometer (RM2000, Renishaw) with a wavelength of 514.5 nm. The glass and glass-ceramics samples were polished to 2 mm under optical quality requirement before optical measurement.

RESULTS

Crystallization of LAS Glass

DTA and XRD analysis are usually combined to study the crystallization of glass ceramic. Figure 1 shows the results of DTA runs of glasses with different content of V_2O_5 additives, and the observed exothermic peaks correspond to the crystallization of a beta-quartz structured solid solution phase (indentified by XRD and discussed subsequently). As shown in Fig. 1, the crystallization temperature decreases from approximately 861°C in the undoped glass to 822°C in the glass with 5-wt% V_2O_5, with an increasing amount of V_2O_5. Furthermore, the crystallization temperature decreases weakly when the V_2O_5 is more than 2 wt%.

Figure 2 shows the XRD patterns of the samples heat-treated at various temperatures. All samples heat-treated at 750°C belonged to the amorphous glass, and then the diffraction peaks of beta-quartz s.s were indentified in samples doped by V_2O_5 at 800°C, while the undoped glass remained amorphous. The peak at about 25°C (2θ) with low intensity indicates the lower crystallinity at this temperature. The main crystalline phase, beta-quartz s.s (50–100 nm in size), precipitates from 750°C and up to 850°C. We also find few beta-spodumene s.s phases

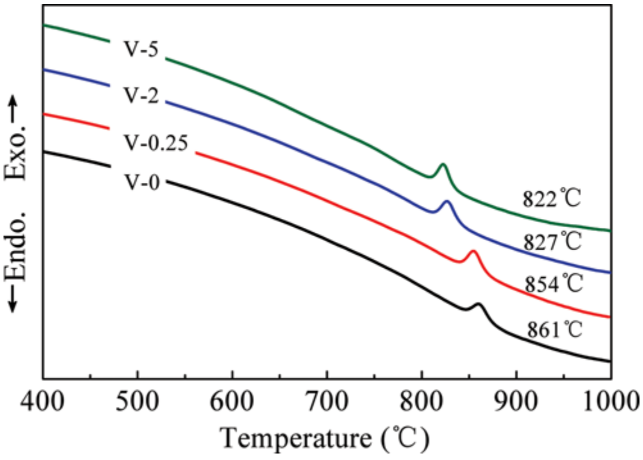


FIGURE 1 DTA curves of the LAS glasses with different V_2O_5.

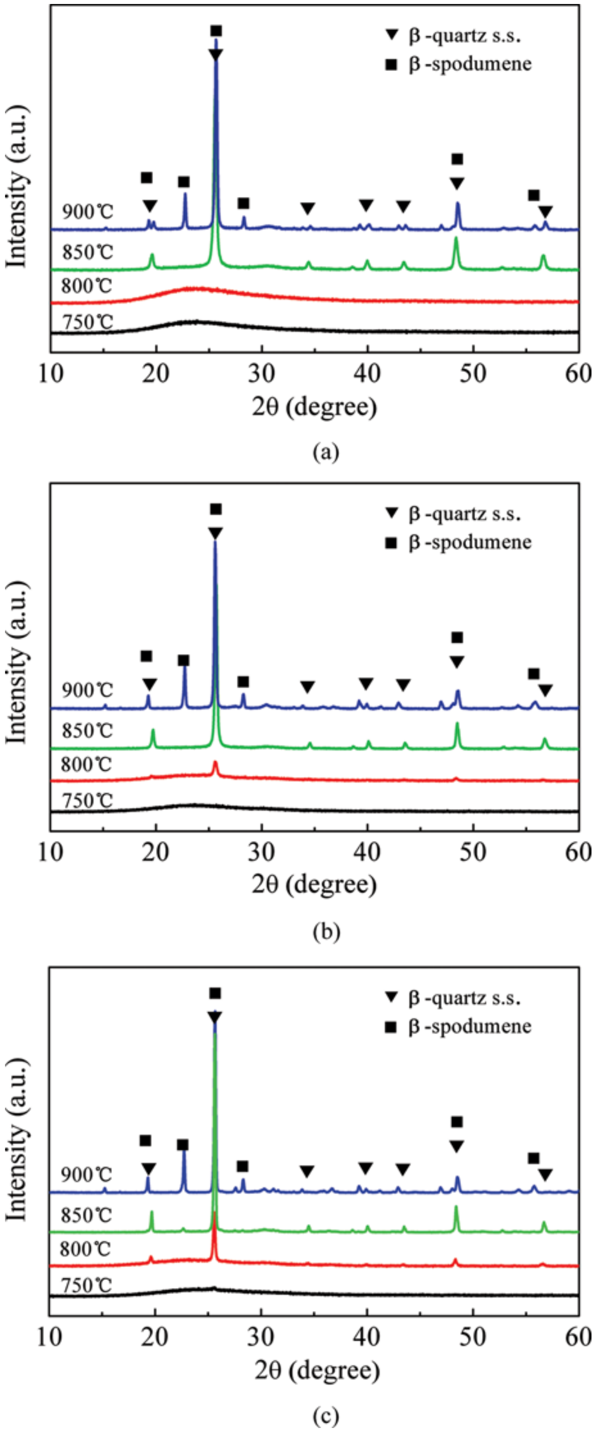
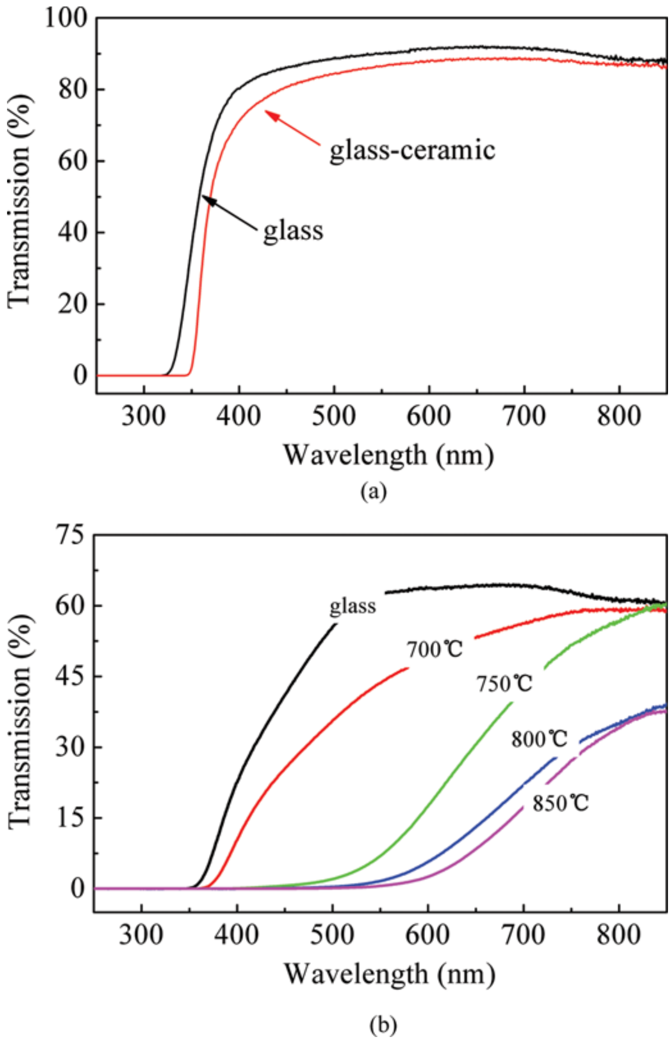


FIGURE 2 X-ray diffraction patterns of the LAS glass heat treated at different temperatures for 30 min for (a) undoped glasses; (b) 2-wt% V_2O_5; (c) 5-wt% V_2O_5.

formed at 850°C in LAS glasses doped with 5-wt% V_2O_5. Due to the DTA and XRD analysis, the main phases of the series of LAS glass studied in this research were acknowledged for further measurement. In conclusion, it was found that the addition of V_2O_5 affects the crystallization process of LAS glass by decreasing the crystallization temperature and promoting the phase transition from beta-quartz s.s to beta-spodumene s.s at lower temperature.

UV-Visible Absorption Spectroscopy

Firstly, the undoped glass samples were transparent, which can be recognized through the high transmission in visible range shown in Fig. 3a. The spectral patterns in Fig. 3a remain similar after heat-treatment at 850°C, Only the UV absorption tail is slightly shifted to higher wavelengths, and the intensity of absorption bands slightly increase due to the strong ultraviolet absorption of Ti^{4+} and the scattering caused by the precipitated microcrystal, respectively. But the spectral patterns of V_2O_5-doped samples exhibited different behavior with the increasing temperature. The parent glass doped by V_2O_5 presented a light yellow-green color, and when heated at temperature under 700–750°C, it showed modification of color to claret, corresponding to the intense absorption band in visible region at range of 400–600 nm (see Fig. 3b). The samples, before and after annealing, were amorphous, and beta-quartz s.s proved by XRD, respectively. Comparing between Fig. 3a and Fig. 3b, one would quite naturally conclude that vanadium ions can be considered responsible for the pigmentation, and attribute color change to transformation of structural states of vanadium ions in LAS glasses during heat treatment.



(a)

(b)

FIGURE 3 UV-VIS transmission spectra of the LAS glass heat treated at different temperature for 30 min for (a) undoped glasses; (b) glasses with 0.25-wt% V_2O_5.

Electron Paramagnetic Resonance Spectra

The EPR spectra were used to probe the structural states of vanadium ions in LAS glasses, and the vanadium ions were also used as indicators of structure and dynamic phenomena in crystallization process. No EPR signal was observed in the spectra of undoped glass and glass-ceramics, which indicates that no paramagnetic impurities were present in the starting materials. When various amount of V_2O_5 were added to LAS glass, the EPR spectra of all the investigated samples exhibited resonance signals, as shown in Fig. 4. The EPR spectra of these samples show very similar patterns to results for other glass systems containing vanadium.[23–27] These spectra show a well-resolved hyperfine structure typical for vanadyl ions in C_{4v} symmetry with tetragonally distorted octahedral coordination, and the line feature is typical of the unpaired ($3d^1$) electron of VO^{2+} ions associated with ^{51}V in an axially symmetric crystal field. Comparing the EPR spectra recorded at different V_2O_5 content for glass and glass-ceramics, one observes that the pattern of the spectrum and the line width of spin are independent of increasing V_2O_5 and crystallization process, but all the spectra of glass-ceramics showed a decrease in integrated intensity compared with glass at same composition. Sreekanth[24,25] and Farah[28,29] have studied the

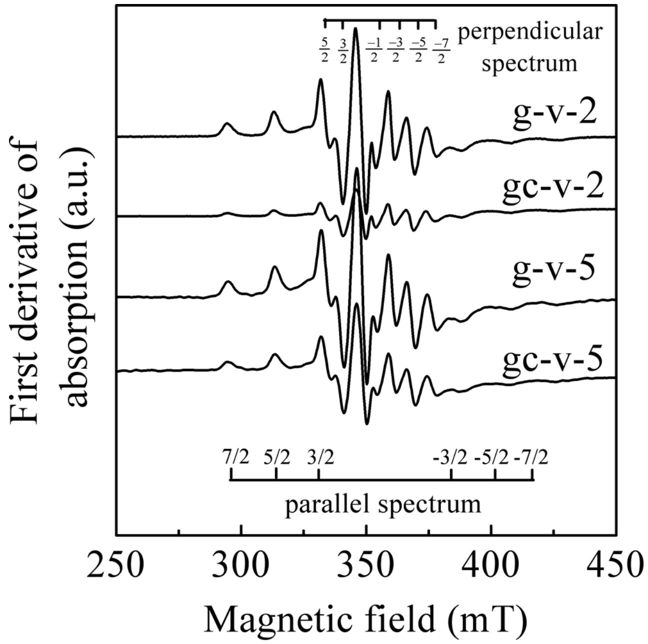


FIGURE 4 **EPR spectra of the LAS glass and glass-ceramics containing V_2O_5. g = glass, gc = glass-ceramics, V-2 = 2-wt% V_2O_5, V-5 = 5-wt% V_2O_5.**

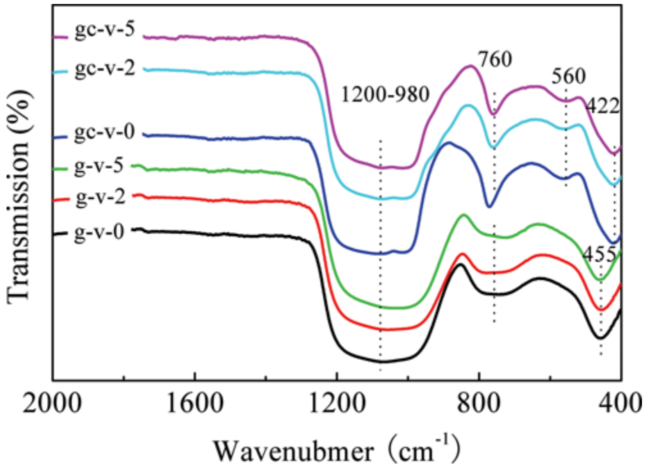


FIGURE 5 **IR spectra of the LAS glass and glass-ceramics doped with different V_2O_5. g = glass, gc = glass-ceramics, V-0 = undoped, V-2 = 2-wt% V_2O_5, V-5 = 5-wt% V_2O_5.**

EPR and optical absorption spectra of V^{4+} ions in alkali calcium borate glasses and calcium silicate glasses extensively, respectively, and two possibilities—four-fold and six-fold symmetry—were found to describe the crystal field of V^{4+} ions in glasses. Given that the EPR spectra are measured at room temperature, it is possible that the second signal attributed to tetrahedral V^{4+} ions could not be separated from that of the octahedral VO^{2+} ions in Fig. 4.

IR Absorption Spectra

The IR spectrum can provide information about molecular vibration or rotation associated with a covalent bond, and usually it is used to survey the variation of glass structure with composition changed. As shown in Fig. 5, IR measurements have been carried out to investigate the structure of the LAS glass and the effect of V_2O_5 on their physical properties. The spectra of glasses extending from 400 to 2000 cm^{-1} are almost identical, exhibiting three main absorption bands. The wide band at high frequency 980–1200 cm^{-1} observed in all samples is characteristic of asymmetric stretching vibrations of the Si-O-Si bonds with three-dimensional network structure. The alumina is preferably located in the tetrahedral network and acts as a network former as silicon in LAS glass, so the asymmetric stretching vibrations of Si-O-Al bonds, ν_{as} (Si-O-Al), is assumed to take part in this broad band. The band located at 760 cm^{-1} is attributed to Si-O-Si symmetric stretching vibrations. The band at 455 cm^{-1} can be assigned to the O-Si-O bending vibrations, which is a characteristic band of the three-dimensional network silicate glasses. These results agree with the spectrum of an amorphous silicate glass structure,[30,31] and the lack of sharp bands mainly results from the high distribution of bond length and the angles between bonds in unordered glasses.

The spectra of glass-ceramics exhibit some features different from those of glasses mentioned above: Some differences in intensity and width at about 760 and 560 cm^{-1} are visible after crystallization. The increasing intensity after crystallization is mainly due to the ordered arrangement of [SiO_4] and much more symmetric Si-O-Si bonds in beta-quartz s.s crystalline phase. The band shift to lower frequency (from 450 cm^{-1} to 420 cm^{-1}) is mainly attributable to the distorted [SiO_4] in beta-quartz s.s. Consequently, symmetry structures in crystals, with low distribution of bond length and the angles between bonds, lead to sharpening and intense absorption bands. However, the IR spectra are not visibly different between undoped samples and glasses containing V_2O_5, and the addition of V_2O_5 does not affect the position and the intensity of the absorption bands. These similar results were also observed in the LAS glass system doped by chromium ions reported by Ei-Diasty,[6] and these results indicate that the vanadium ions act as a network modifier in LAS glass and glass-ceramics.

Raman Spectroscopy

Recently, Raman spectroscopy has been used for purposes beyond the reach of the IR spectroscopy. The Raman spectra of undoped LAS glass in dependence of heat-treat temperature are shown in Fig. 6. The spectra of the initial glasses (Fig. 6, curves a–c) contain weak bands at about 470 and 800 cm^{-1}, which indicate that the structure of starting glass is in perfect disorder, since all bands are weak. Heat-treatment of the glasses at 750–850°C leads to the appearance of weak bands at 1110 cm^{-1}, which could be assigned to asymmetric stretching vibrations of four-fold coordinated titanium (Ti^{4+}-O-Si^{4+}). And also a rather intensive band at about 470 cm^{-1} (Fig. 6, curves d–e), which is characteristic of beta-quartz s.s, manifests crystallization of the main phase. New Raman bands raised at 130, 625 and 800 cm^{-1} are believed to be the result of the formation of zirconia, anatase (Ti$_x$Zr$_{1-x}$O$_2$), and aluminotitanate phase.[4,32,33]

However, the Raman spectra of glass doped by V$_2$O$_5$ present some different characteristic bands as shown in Fig. 7. The behavior of the bands at about 980 and 770 cm^{-1} are of special interest in glass samples with 2-wt% V$_2$O$_5$. The band intensity at 980 cm^{-1} becomes weaker while the relative intensity of band at 770 cm^{-1} becomes stronger with increasing temperature. According to the study of Huaxin Li[34] and Vedeanu,[35] Raman bands at 350, 488, and 697 cm^{-1} and even intense bands at 917~931 cm^{-1} are related with the vibration of those so-called "pyrovanadate" groups. However, the doping rate (2-wt% V$_2$O$_5$) may be not sufficient to form V-O-V connections, and the resonant excitation of V-bonds will also overlap to the background of the host intensity. Thus, the strong bands at 980 cm^{-1} and 770 cm^{-1} are also associated with the vibrations of aluminosilicates groups. But the structure of these bonds is modified by the doping of vanadium ions, which leads to appearance of the considered Raman bands.

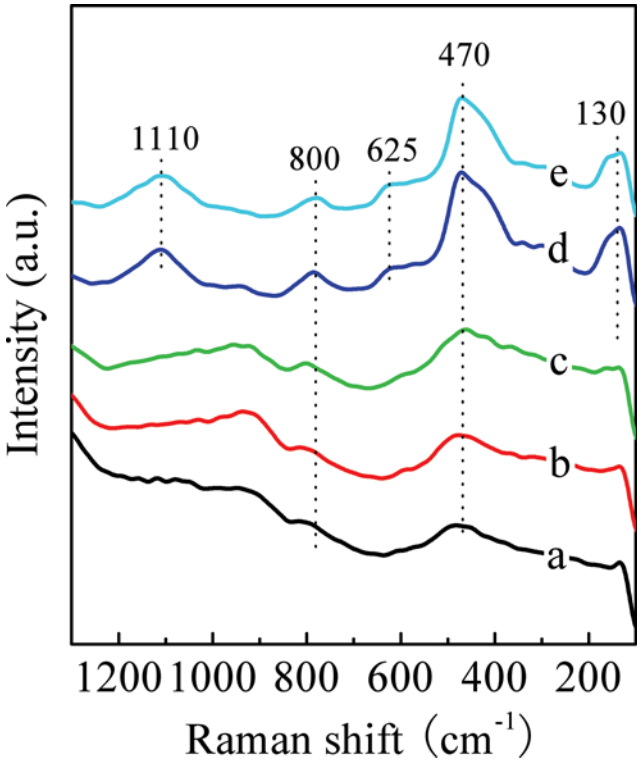


FIGURE 6 Raman spectra of undoped LAS glass heat-treated at different temperature for 30 min (a) initial glass; (b) 700°C; (c) 750°C; (d) 800°C; and (e) 850°C. $\lambda_{exit} = 514.5$ nm.

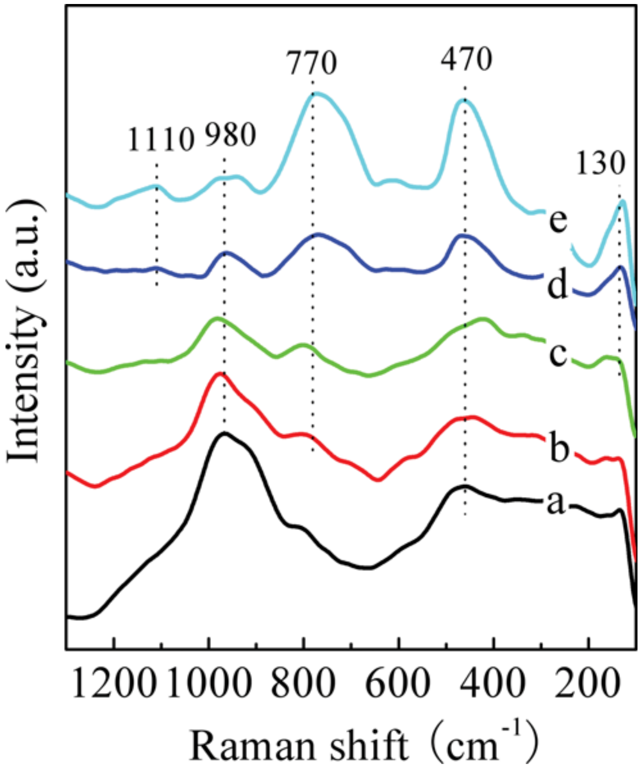


FIGURE 7 Raman spectra of the LAS glass with 2-wt% V$_2$O$_5$ heat-treated at different temperature for 30 min (a) initial glass; (b) 700°C; (c) 750°C; (d) 800°C; and (e) 850°C. $\lambda_{exit} = 514.5$ nm.

DISCUSSION

Vanadium is a transition metal element, and the outer-shell electron is $3d^34s^2$. The V^{5+} ion is ineffective on color in glasses due to no spin-allowed d-d transition, but a paramagnetic ion (such as V^{4+}, V^{3+}) affects strongly the optical absorption when dissolved in glasses in very small amount. According to the studies of Sreekanth Chakradhar,[24,25] the optical band gap energies obtained in Na_2O-K_2O-B_2O_3-V_2O_5 glasses varied form 2.73 to 3.10 eV for both the direct and indirect transitions, which means that the absorption edge in the UV-region was in the range of 400–450 nm. Moreover, two bands characteristic of VO^{2+} ions in tetragonal symmetry have also been observed and assigned to the transitions $^2B_{2g}\rightarrow{}^2B_{1g}$ and $^2B_{2g}\rightarrow{}^2E_g$ in the decreasing order of energy. So, the spectral patterns of the V-doped glass in Fig. 3 can be assigned to characteristic absorption of V^{4+} and/or V^{3+} ions in a distorted coordination situation. In addition, the increasing absorption intensity upon crystallization are also due to scattering absorption of crystallites (>100 nm) with increasing temperature.

In the present work, the vanadium ion in the form of V_2O_5 was used as agent in the melting process to prepare the glass samples. However, during the melting of the glasses at higher temperatures, there may be a conversion state of a part of vanadium ions in V^{5+} to those in V^{4+} or V^{3+}. A detailed analysis of the oxidation-reduction equilibrium of vanadium in the calcium silicates has been given by H. Farah.[29] The redox equilibrium of the vanadium ions with multiple oxidation states can be represented by a mass expression named an "O-type" redox reaction,

$$2V^{5+} + (5-a)O^{2-} \rightarrow 2V^{a+} + \frac{5-a}{2}O_2 \qquad (1)$$

$$V^{a+} + \frac{(2x-1)}{2}O^{2-} + \frac{1}{4}O_2 \rightarrow VO_x^{(a-2x+1)+}, \qquad (2)$$

where a is a valence such as +3 or +4, and x is the number of oxygen atoms associated with the oxidized redox ion in the melt to form an oxocation for one electron change between the valences. So, the V^{5+} ions may take part in network-forming positions with VO_5 trigonal bipyramidal structural units in LAS glass, whereas V^{4+} ions form VO^{2+} complexes, may act as modifiers, and distort the glass network.

However, the structure of vanadium ions and the mechanism of the color change in LAS glass-ceramics have not been clarified yet. Since the EPR spectra show strong dependence on the hyperfine structure of vanadium ions, the spin-Hamiltonian parameters are calculated for further analysis. The EPR spectra expected for V^{4+} ions in glasses can be described using the well-known axial spin Hamiltonian,

$$\begin{aligned} H = {} & g_{\|}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + A_{\|} I_z S_z \\ & + A_{\perp}(I_x S_x + I_y S_y), \end{aligned} \qquad (3)$$

where β is the Bohr magneton; $g_{\|}$ and $g_{\perp}$ are the parallel and perpendicular principal components of the g tensor; $A_{\|}$ and $A_{\perp}$ are the parallel and perpendicular principal components of the hyperfine coupling tensors; B_x, B_y, and B_z are the components of the magnetic field; and S_x, S_y and S_z and I_x, I_y and I_z are the components of the spin operators of the electron and nucleus, respectively.

The solution of the spin-Hamiltonian for the parallel and perpendicular hyperfine lines is

$$B_{\|}(m_I) = B_{\|}(0) - A_{\|}m_I - (63/4 - m_I^2)\frac{A_{\perp}^2}{2B_{\|}(0)} \qquad (4)$$

$$B_{\perp}(m_I) = B_{\perp}(0) - A_{\perp}m_I - (63/4 - m_I^2)\frac{(A_{\|}^2 + A_{\perp}^2)}{4B_{\perp}(0)}, \qquad (5)$$

where m_I is the magnetic quantum number of the vanadium nucleus, which takes the values ±7/2, ±5/2, ±3/2, and ±1/2.

$$B_{\|}(0) = \frac{hv}{g_{\|}\beta} \qquad (6)$$

$$B_{\perp}(0) = \frac{hv}{g_{\perp}\beta}, \qquad (7)$$

where ν is the microwave frequency.

The parameters of this spin Hamiltonian were determined by fitting the observed spectrum to one simulated on computer based on the expressions mentioned above. The g and A values are given in Table 1. The g and A values obtained in the present work are close to the results reported for CaO-SiO_2, Li_2O-P_2O_5, and Al_2O_3-SiO_2 glasses. An octahedral site

TABLE 1 EPR Parameters of Vanadium Ions in LAS Glass and Glass-ceramics Doped by Different V_2O_5

	Glass				Glass-ceramics			
V_2O_5 wt%	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}\,cm^{-1}$	$A_{\perp} \times 10^{-4}\,cm^{-1}$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}\,cm^{-1}$	$A_{\perp} \times 10^{-4}\,cm^{-1}$
2	1.937	1.973	163	58	1.935	1.974	162	59
5	1.937	1.972	162	56	1.937	1.975	162	56

Note. The errors in g and A values are ±0.004 and $3 \times 10^{-4}\,cm^{-1}$, respectively.

with a tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A$. Therefore, it is confirmed that the V^{4+} ions exist as VO^{2+} in octahedral coordination with a tetragonal compression and have C_{4v} symmetry. The vanadyl oxygen is attached axially above the V^{4+} site along the Z-axis (V=O bond), while the sixth oxygen forming the O-VO_4-O unit lies axially bellow the V^{4+} site.

Although V^{3+}/V^{4+} ions pair has been found under oxygen partial pressure, and the V^{4+} ions occupied the other coordination sites in some glasses,[29] the EPR parameters, with nearly equal g and A, have failed to prove whether there is the second kind of configuration of V^{4+} ions state so far. But it is interesting to note that the EPR spectra show a decrease in intensity for the glass-ceramics (see Fig. 4), while the UV-visible and Raman spectra change dramatically with heat treatment in Fig. 3 and Fig. 7, respectively. These results allow us to presume that the second form of vanadyl ion is evident and that the structural state of vanadyl ions changes slightly upon crystallization. As we known, beta-quartz s.s in LAS glass-ceramics is a stuffed derivation of the quartz structure, and Li^+ ions can occupy tetrahedral sites in ordered beta-quartz s.s and occupy six-fold coordinated sites in disordered beta-quartz s.s crystals as the temperature increases.[15,16,18] Since the radius of V^{4+} ions is close to Li^+ (ionic radius of Li^+ is 0.076 nm, while that of V^{4+} is 0.058 nm), V^{4+} ions are expected to move into the structure of beta-quartz s.s crystals and replace Li^+ ions in tetrahedral sites isomorphously. This result can also be regarded as the reason of the lower temperature of the crystallization of LAS glass doped by V_2O_5, and the effects of Li_2O on crystallization in LAS glass.

This result can be proved further by the optical absorption during crystallization. Heat treatment in range of 750–850°C leads to the precipitation of beta-quartz s.s crystals in glassy phase, and the color of glasses changes from light yellow-green to claret, corresponding to the strong absorption at 400–600 nm shown in Fig. 3. According to the ligand field theory, the splitting of energy levels of 3d electrons is sensitive to coordination polyhedron. Hence, the variation of ligand field of V^{4+} ions along with atomic rearrangement can be attributed to the color change during crystallization. Due to high intensity of absorption bands of tetrahedrally coordinated V^{4+} ions, even a small amount of these polyhedrons can produce a pronounced spectrum, the absorption band in the range of 400–600 nm may be due to the absorption of V^{4+} ions in tetrahedral coordination and VO^{2+} ions with increasing degree of tetragonal distorted may be octahedrally coordinated. A similar result has also been discussed for the transparent Ni^{2+}-doped lithium aluminosilicate glass-ceramics.[14] So, the overlapping of the signals for hyperfine structures of V^{4+} in two similar states can be taken as the main reason for nearly equal values of g and A for all the glass samples tested at room temperature.

Though no IR and Raman band related to vanadium was detected visibly in Fig. 5 and Fig. 6, we believed that the weak bands arising from V-bonds were overlapped by those of glasses. However, the effects of vanadium ions on microstructure of the glass-ceramics can be traced from the spectra study. The vibrations of Raman spectra in Fig. 7 especially bear the evidence of the influence of vanadium ions on the structure of host glasses on the level of chemical bonds. So, it is natural to understand the complexity of the structural state of vanadium ions in the lithium aluminosilicate glass-ceramics. Consequently, vanadium ions affect the optical properties and crystallization behavior of the LAS glass and build into the glass network as structural modifier. The V^{4+} ions have multiple preferences for octahedral and tetrahedral coordination, as one can see by analyzing the EPR, UV-visible and Raman spectra. However, it is not clear whether V^{5+}

or V^{3+} exist in the glass, and more detailed research is needed in the future.

CONCLUSIONS

1. The glass samples doped by V_2O_5 show a light yellow-green color, which undergo an evident change to claret during crystallization, and the addition of V_2O_5 also decreases the crystallization temperature of beta-quartz s.s crystal phase.

2. The optical absorption in visible range is the characteristic absorption of V^{4+}, and the variation of absorption region is mainly attributed to the change of vanadium ions' coordination polyhedron during crystallization process.

3. The EPR spectra of V_2O_5-doped LAS glass and glass-ceramics are the characteristic spectra of a hyperfine interaction arising from an unpaired electron with the ^{51}V nucleus. It is found that the V^{4+} ions, formed by redox of V^{5+} ions, exist as the VO^{2+} complex in octahedral coordination with a tetragonal compression with a C_{4v} symmetry in LAS glass.

4. The variations of the optical absorption and Raman spectra reveal that the V^{4+} ions partially replace Li^+ and occupy tetrahedral sites in LAS glass-ceramics after crystallization.

REFERENCES

1. Ferreira da Silva, M. G. The color change of aluminosilicate gel-derived glasses doped with CoO. *Mater. Res. Bull.* **1999**, *34*, 2061–2068.
2. Kang, U. K.; Dymshits, O. S.; Zhilin, A. A.; Chuvaeva, T. I.; Petrovsky, G. T. Structural states of Co(II) in β-eucryptite-based glass-ceramics nucleated with ZrO_2. *J. Non-Cryst. Solids* **1996**, *204*, 151–157.
3. Kang, U. K.; Zhilin, A. A.; Petrovsky, G. T.; Dymshits, O. S.; Chuvaeva, T. I. Structural transformations of nanometer sized crystals in CoO-doped β-eucryptite-based glass-ceramics. *J. Non-Cryst. Solids* **1999**, *258*, 216–222.
4. Bae, S. J.; Kang, U. K.; Dymshits, O. S.; Shashkin, A.; Tsenter, M.; Zhilin, A. A. Raman spectroscopy study of phase transformations in titania-containing lithium aluminosilicate glasses doped with CoO. *J. Non-Cryst. Solids* **2005**, *351*, 2969–2978.
5. Morimoto, S. Formation, absorption and emission spectra of Cr^{4+} ions in Li_2O-SiO_2 system transparent glass-ceramics. *J. Ceram. Soc. Jpn.* **2004**, *112*(9), 486–490.
6. El-Diasty, F.; Abdel Wahab, F. A.; Abdel-Baki, M. Optical band gap studies on lithium aluminum silicate glasses doped with Cr^{3+} ions. *J. Appl. Phys.* **2006**, *100*(093511), 1–7.
7. El-Diasty, F.; Abdel-Baki, M.; Abdel Wahab, F. A.; Darwish, H. Dispersion and thermal properties of lithium aluminum silicate glasses doped with Cr^{3+} ions. *Appl. Opt.* **2006**, *45*(30), 7818–7825.
8. Khonthon, S.; Morimoto, S.; Ohishi, Y. Absorption and emission spectra of Ni-doped glasses and glass-ceramics in connection with its Co-ordination number. *J. Ceram. Soc. Jpn.* **2006**, *114*(9), 791–794.
9. Feng, G.; Zhou, S.; Bao, J.; Wang, X.; Xu, S.; Qiu, J. Transparent Ni^{2+}-doped lithium aluminosilicate glass-ceramics with broadband infrared luminescence. *J. Alloys Compd.* **2008**, *457*(1–2), 506–509.
10. Suzuki, T.; Horibuchi, K.; Ohishi, Y. Structural and optical properties of ZnO-Al_2O_3-SiO_2 system glass-ceramics containing Ni^{2+}-doped nanocrystals. *J. Non-Cryst. Solids* **2005**, *351*, 2304–2309.
11. Dymnikov, A. A.; Dymshits, O. S.; Zhilin, A. A.; Savostjanov, V. A.; Chuvaeva, T. I. The structure of luminescence centers of neodymium in glasses and transparent glass-ceramics of the Li_2O-Al_2O_3-SiO_2 system. *J. Non-Cryst. Solids* **1996**, *196*, 67–72.
12. Kang, U. K.; Zhilin, A. A.; Logvinov, D. P.; Onushchenko, A. A.; Chuvaeva, T. I. Transparent Nd^{3+}-activated glass-ceramics in the Li_2O-Al_2O_3-SiO_2 system: Physicochemical aspects of their preparation and optical characteristics. *Glass Phys. Chem.* **2001**, *27*(4), 344–352.
13. Xia, H.; Zhang, J.; Wang, J.; Nie, Q.; Song, H.. Preparation and optical spectroscopy of Li_2O-Al_2O_3-SiO_2 glasses containing divalent and trivalent europium ions. *Mater. Lett.* **2002**, *53*, 277–281.
14. Fujita, S.; Tanabe, S. Structural evolution of Er3+ ions in Li_2O-Al_2O_3-SiO_2 glass-ceramics. *J. Ceram. Soc. Jpn.* **2008**, *116*(10), 1121–1125.
15. Beall, H.; Pinckney, R. Nanophase glass-ceramics. *J. Am. Ceram. Soc.* **1999**, *82*(1), 5–16.
16. Riello, P.; Canton, P.; Comelato, N.; Polizzi, S.; Verita, M.; Fagherazzi, G.; Hofmeister, H.; Hopfe, S. Nucleation and crystallization behavior of glass-ceramic materials in the Li_2O–Al_2O_3–SiO_2 system of interest for their transparency properties. *J. Non-Cryst. Solids* **2001**, *288*, 127–139.
17. Bengisu, M.; Brow, R. K. Effect of long-term heating and thermal cycling on thermal expansion, phase distribution, and microhardness of lithium aluminosilicate glass-ceramics. *J. Non-Cryst. Solids* **2003**, *331*, 137–144.
18. Arnault, L.; Gerland, M.; Riviere, A. Microstructural study of two LAS-type glass-ceramics and their parent glass. *J. Mater. Sci.* **2000**, *35*, 2331–2345.
19. Bobovich, Y. S.; Zhilin, A. A.; Petrov, V. I.; Tsenter, M. Y.; Chuvaeva, T. I. Evidence in the Raman spectra of a phase-decay process in lithium aluminum silicate glasses containing zirconium dioxide. *Opt. Spectrosc.* **1992**, *72*(6), 758–762.
20. Zhilin, A. A.; Petrov, V. I.; Tsenter, M. Y.; Chuvaeva, T. I. Raman spectroscopy study of the phase decomposition processes of lithium aluminosilicate glasses, containing TiO_2 and ZrO_2. *Opt. Spectrosc.* **1992**, *73*(6), 684–688.
21. Chuvaeva, T. I.; Dymshits, O. S.; Petrov, V. I.; Tsenter, M. Y.; Zhilin, A. A. Low-frequency Raman scattering and small-angle X-ray scattering of glasses inclined to phase decomposition. *J. Non-Cryst. Solids* **1999**, *243*, 244–250.
22. Alekseeva, I.; Dymshits, O.; Ermakov, V.; Zhilin, A.; Petrov, V.; Tsenter, M. Raman spectroscopy quantifying the composition of stuffed β-stuffed derivative phases in lithium aluminosilicate glass-ceramics. *J. Non-Cryst. Solids* **2008**, *354*, 4932–4939.
23. Ardelean, I.; Cozar, O.; Vedeanu, N.; Rusu, D.; Andronache, C. EPR study of V_2O_5-P_2O_5-Li_2O glass system. *J. Mater. Sci.* **2007**, *18*, 963–966.
24. Sreekanth Chakradhar, R. P.; Murali, A. A study of electron paramagnetic resonance and optical absorption spectra of VO^{2+} ions in alkali calcium borate glasses. *J. Lakshmana Rao, Physica B* **2000**, *293*, 108–117.
25. Sreekanth Chakradhar, R. P.; Ramesha, K. P.; Rao, J. L.; Ramakrishna, J. Influence of mixed alkali on the spectral properties of vanadyl ions doped xNa_2O-$(30-x)K_2O$-$60B_2O_3$ glasses: An EPR and optical study. *Mater. Res. Bull.* **2005**, *40*, 1028–1043.
26. Srinivasa Raoa, L.; Srinivasa Reddya, M.; Rami Reddyb, M.; Veeraiah, N. Dielectric dispersion in Li_2O-MoO_3-B_2O_3 glass system doped with V_2O_5. *J. Alloys Compd.* **2008**, *464*, 472–482.
27. Yasoda, B.; Sreekanth Chakradhar, R. P.; Raoa, J. L.; Gopal, N. O. EPR and optical absorption studies of VO^{2+} ions in alkaline earth aluminoborate glasses. *Mater. Chem. Phys.* **2007**, *106*, 33–38.

28. Farah, H. Oxidation-reduction equilibria of vanadium in CaO-SiO_2, CaO-Al_2O_3-SiO_2 and CaO-MgO-SiO_2 melts. *J. Mater. Sci.* **2003**, *38*, 1885–1894.
29. Farah, H. V4+ in quenched calcium silicates: An electron spin resonance spectroscopic investigation. *J. Mater. Sci.* **2003**, *38*, 727–737.
30. Suzdaltsev, E. I.; Borodai, S. P.; Khamitsaev, A. S.; Kharitonov1, D. V. IR spectroscopy study of pre-crystallization and its effect on the phase composition of lithium aluminosilicate glass and glass ceramics. *Refract. Ind. Ceram.* **2004**, *45*(1), 19–24.
31. Nocun, M.; Handke, M. Structural inhomogeneity in glasses from the system Li_2O-Al_2O_3-SiO_2 revealed by IR spectroscopy. *J. Mol. Struct.* **2001**, *596*, 139–143.
32. Furica, K.; Stochb, L.; Dutkiewiczc, J. Raman study of TiO_2 role in SiO_2–Al_2O_3–MgO–TiO_2–ZnO glass crystallization. *Spectrochim. Acta, Part A* **2005**, *61*, 1653–1659.
33. Gabel, F.; Müller, G.; Raether, F.; Kiefer, W.; Pannhorst, W.; Sprengard, R. Quantitative characterisation of nuclei formation by Raman spectroscopy of lithium aluminosilicate glass ceramics doped with titania and zirconia. *Phys. Chem. Glasses* **2002**, *43*, 306–310.
34. Li, H.; Lin, H.; Chen, W.; Luo, L. IR and Raman investigation on the structure of (100-x)[0.33B_2O_3–0.67ZnO]–xV_2O_5 glasses. *J. Non-Cryst. Solids* **2006**, *352*, 3069–3073.
35. Vedeanu, N.; Cozar, O.; Ardelean, I.; Lendl, B.; Magdas, D. A. Raman spectroscopic study of CuO–V_2O_5–P_2O_5–CaO glass system. *Vib. Spectrosc* **2008**, *48*, 259–262.