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STRUCTURE OF LITHIUM PYROSILICATE MELTS ACCORDING TO DATA OF HIGH-TEMPERATURE RAMAN SPECTROSCOPY

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Decomposition of the high-frequency range of Raman spectra for $60Li_2O \cdot 40SiO_2$ melts (Li60) into the Gaussian line shape was performed. The basic structural fragments of melts and their ratio were determined, and the peculiarities of their interaction with the change in temperature were identified.

Keywords: melt structure, silicate melts, Raman spectroscopy.

Introduction

The study of silicate systems is an important task for the optimization of the industrial technologies and geochemical studies. Raman spectroscopy can be carried out directly *in situ* in the melts. Of all the alkali-silicate systems, only sodium silicate has been studied in sufficient detail over the entire range of compositions starting from pure SiO_2 to sodium orthosilicate in a wide temperature range [1, 2], while the melts of $Li_2O–SiO_2$ system were only studied for compositions <50 mol. % Li_2O. Therefore studies of strongly alkaline lithium-silicate melts by means of Raman spectroscopy is a rather critical task. The high-frequency range of the Raman spectra of the melted silicate systems contains information about the present silicon-oxygen tetrahedral units Q^n (silicon-oxygen tetrahedral units with various numbers of bridging oxygen atoms n) and their amounts [3, 4]. Experimental data about the melt structures can be represented in the form of the distribution of structural units Q^n as the function of the composition and temperature.

Research methods

Synthesis of lithium pyrosilicate was carried out from the amorphous SiO_2 (analytical grade) and lithium carbonate Li_2CO_3 (reagent grade). The charge was thoroughly mixed with alcohol in a mortar, then dried and melted in a platinum crucible in a silit furnace at the melt temperature up to 1373 K. To register the Raman spectra the high-temperature experimental apparatus was used, which was based on the DFS-24 spectrometer. For all the spectra obtained, the baseline correction procedure was performed. The spectra were processed using the software package OMNIC Thermo Nicolet. For that, the curve fitting method of Raman spectra as superposition of the lines of Gaussian shape (RS SM) was used. The high-frequency range of the spectrum is the most important in obtaining data about the structure of silicate glasses and melts. The analysis of the patterns of the Raman spectra change as the function of composition, the comparison of the spectra of glasses and the corresponding crystals, the measurement of the band polarization degree, the theoretical calculations of the fluctuations of silicate anions gave the following interpretation of the bands in the high-frequency range of Raman spectra of silicate glasses and melts [3, 4, 6, 7]:

– the band crest in the range of 1050–1100 cm^{-1} is related to the stretching vibrations of the terminal groups of Si–O– in tetrahedral units with one terminal oxygen atom (Q^3);

– the band crests in the range of 950–980 cm^{-1} and 900 cm^{-1} are related to the vibrations of the terminal groups Si–O– and Si–O– in tetrahedral units with two and three non-bridging oxygen atoms (Q^2 and Q^1), respectively;

– the band crest at 850 cm^{-1} is due to stretching vibrations of isolated tetrahedral units of SiO_4^{4-} with all the non-bridging oxygen atoms (Q^0).

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In the low-frequency region (400–700 cm^{-1}) there is the band associated with symmetric stretching and partially bending vibrations of bridges Si–O–Si. Its frequency increases systematically with increasing degree of glass polymerization. In the mid-band frequency region (700–800 cm^{-1}) there is the weak depolarized band, intensity of which decreases with decreasing concentration of silica in the stacks, and it is associated with the deformation vibrations of bridge bonds Si–O–Si in the micro-regions of glasses, the structure of which is close to that of the glassy SiO$_2$.

In fact, this interpretation of Raman spectra of silicate glasses is based on the principles proposed by A.N. Lazarev for the vibrational spectra of silicates [8]. Within this approach it is assumed that the stretching vibrations of silicate anions, characterized by relatively high frequencies, do not interact with the vibrations of the cation sublattice.

To determine the concentration of structural units Q^n we use the intensity of characteristic bands in the high-frequency region of the Raman spectra [9]. To quantify the integrated intensities of the characteristic bands at different temperatures, the high-frequency spectral range of glass and melts is represented as superposition of the lines of Gaussian shape. The project [10] considers various shapes of lines used for simulation of Raman spectra of silicate systems. It is proven that the best of all the options to describe the bands in the spectra of silicate glasses is the superposition of Gaussian shape lines.

The technique of curve fitting for the high-frequency region of the Raman spectra of silicate glasses and melts is described in [9] and [10]. To simulate the strongly alkaline silicate glasses three lines of Gaussian shape are used in [11]. More complex line shapes resulting from vibrations of structural units Q^n are used in [12], which deals with the so-called partial Raman spectra. The authors suggest that each Q^n group has its own partial spectrum, the shape of which does not depend on the concentration of the Q^n-type of a particular kind in a glass sample. In [13], a more complex interpretation of Raman spectra is developed to describe the fine structural features of silicate glasses and melts, the authors consider not only the immediate environment (Q^n-distribution), but also the influence of the second coordination sphere of the central silicon atoms, *i.e.* the influence of the neighboring silicon-oxygen tetrahedral units. For this classification, the following designations are used: Q$^{a/bbb}$, where 'a' stands for the type of the central tetrahedral unit Q, and symbol 'b' is the type of neighboring tetrahedral units Q, connected with it through bridge bonds. The authors suggest that the vibration frequency is not only determined by the second coordination sphere, but also greatly depends on the structures, ring patterns in particular, into which the tetrahedral units are included.

To describe the structure of glasses and melts of Na$_2$O–SiO$_2$ system, the Raman spectra curve fitting technique as superposition of the lines of Gaussian shape is used in [2]. In general, the curve fitting of Raman spectra is a complex and controversial procedure. The basic curve fitting principles are as follows:

– correlation between the characteristic bands in the spectra of silicates in their crystalline, glassy and molten state;

– the minimum number of lines used in the spectrum decomposition procedure;

– the coordinated description of spectra in a wide range of temperatures and compositions within a single structural model;

– regular change in the position and width of the lines in the spectrum with the change of composition and temperature.

Thus, Raman spectra of the melts of sodium–silicate systems have been simulated, and the new interpretation of the high-frequency region has been proposed [2]. The data obtained have allowed to carry out the complete investigation of the sodium-silicate system and to determine the quantitative characteristics of the structural units of melts and glasses.

Results
1. Decomposition of high-frequency Raman spectra region of Li60 melts
Figure 1 shows the Raman spectra of melts of Li60 composition, obtained in the temperature range 1223–1373 K, which were discussed in sufficient detail in [5], so let us briefly highlight the key aspects herein.

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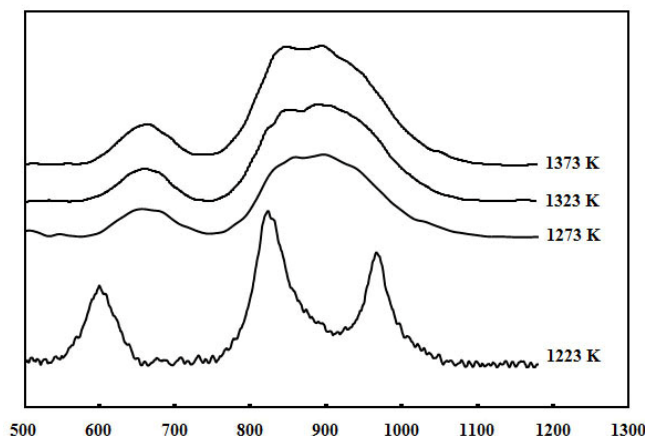**2015, vol. 7, no. 2, pp. 33–38**

Fig. 1. Raman spectra of Li60 melts depending on the temperature [5]

The spectra of melts with this composition have two dominating and the most intense bands with crests around 630 cm^{-1} and 900 cm^{-1}, which relate to vibrations of bonds in groups Si–O–Si and SiO$_4$, respectively. With the melt cooling, narrowing of the bands is observed, and the high-frequency region is represented by two peaks near 820 cm^{-1} and 970 cm^{-1}. It is likely that at the temperature 1223 K, the melt crystallization starts, which is accompanied by the formation of individual clusters of stoichiometric compositions.

2. Decomposition of high-frequency Raman spectra region of Li60 melts

Raman spectra of lithium–silicate melts have been represented as the superposition of lines of Gaussian shape, according to the RS SM. The table shows the positions of bands, designations of the structural units and their interpretation for the lithium pyrosilicate melts.

Interpretation of the characteristic bands in the Raman spectra of lithium pyrosilicate melts

Frequency range, cm^{-1}	Designation of Q^n-units	Band interpretation
825–830	Q^0	Isolated tetrahedral unit with four non-bridging bonds
860–864	Q$^{1'}$	Terminal tetrahedral unit located at the end of the chain structure of finite size
890–898	Q^1	Terminal tetrahedral unit connected with the other similar tetrahedral unit through a bridge bond, *i.e.* a dimer component
929–932	Q$^{2'}$	Tetrahedral unit with two bridge bonds, connected with terminal tetrahedral units Q^1
965–970	Q^2	Tetrahedral unit connected with the similar units Q^2, *i.e.* a chain component
1013–1025	Q$^{3'}$	Tetrahedral unit connected with the chain tetrahedral units Q^2, *i.e.* a branching point of the chain structure

Figure 2 shows the decomposition of the high-frequency region of the spectrum for the Li 60 melts into the superposition of six lines, according to the above interpretation. It is obvious that in the spectrum of the melt obtained at 1223 K, the band around 820 cm^{-1} dominates, that proves the prevailing content of tetrahedral units of Q^0-type, and the less intense band about 980 cm^{-1} corresponds to the presence of tetrahedral units Q^2. Furthermore, other five minor bands corresponding to structural units Q^1, Q$^{2'}$, Q$^{3'}$ and Q^3, are allocated in the spectrum curve fitting. They correspond to vibrations of atoms in the respective tetrahedral units [2]. With a rise in temperature, structural changes take place in the melt, as indicated by increasing intensity of the bands around 900 cm^{-1}, 940 cm^{-1} and 970 cm^{-1}, which corresponds to the growing concentration of the tetrahedral units of Q^1, Q$^{2'}$ and Q^2.
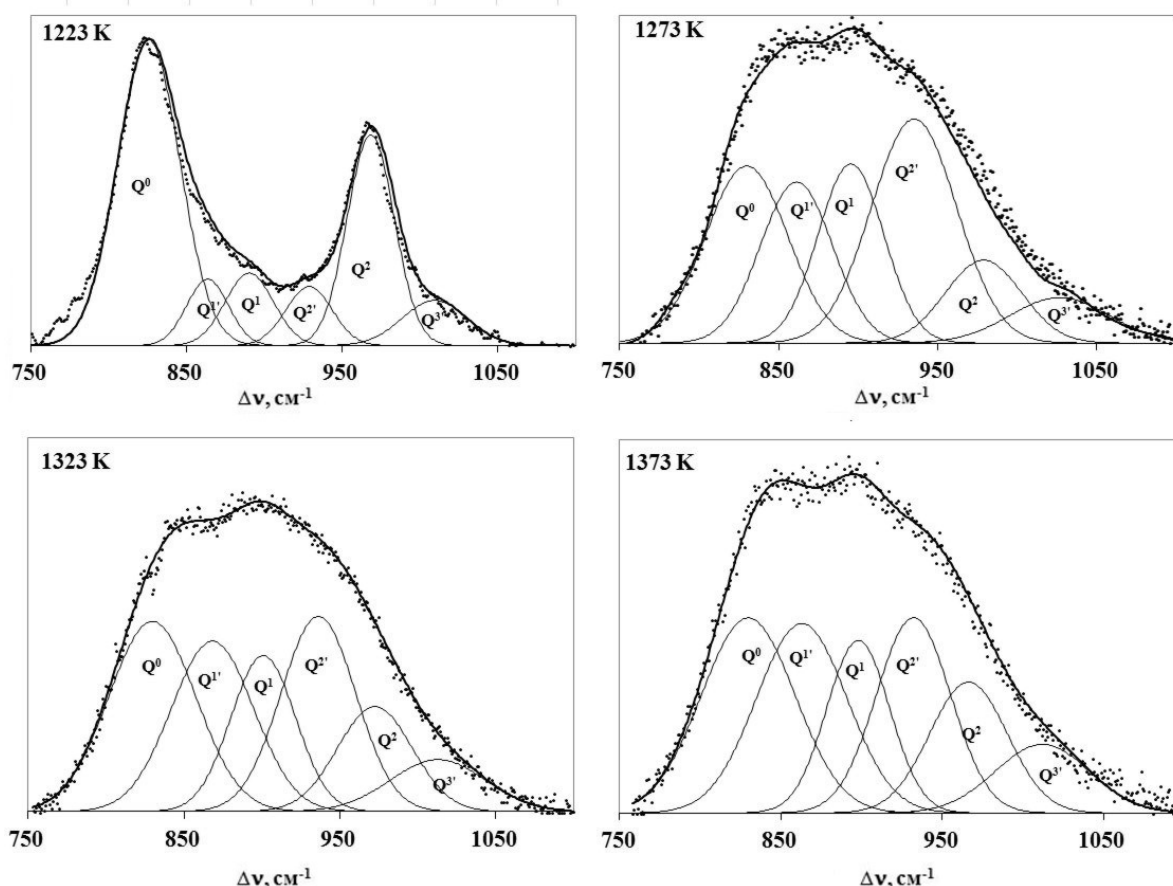
Fig. 2. Curve fitting of high-frequency region of the Raman spectra of Li60 melts

The line intensities obtained from the Raman spectra, corresponding to the vibrations of certain structural units Q^1, Q^2 and Q^3 in the melts of Li60 composition are shown in Figure 3. It is clear that the intensities of the lines corresponding to the vibrations of the tetrahedral units Q^2 and Q^0 remain practically unchanged with the rise in temperature, whereas the intensity of the lines corresponding to vibrations of the tetrahedral units Q^1 and Q^3 decrease. It can be assumed that Q^1 and Q^3 are prevailing in the melt, while the units of Q^3 are of low content. In order to obtain the data on the concentration of structural units in the melts, we suggest the calculation of conversion factors from intensities to concentrations, similar to sodium–silicate system [2].
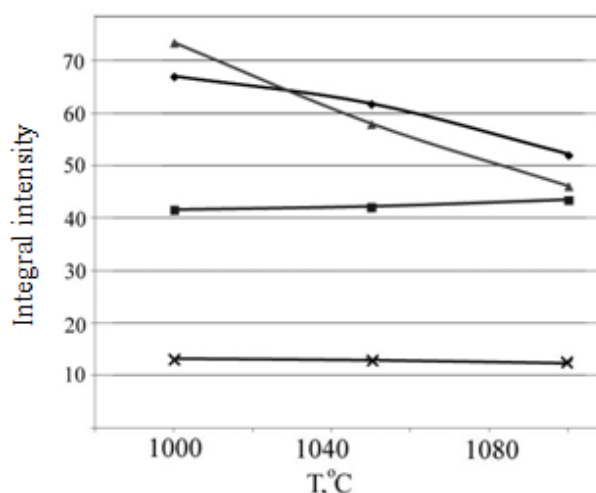

Fig. 3. Change of integral intensities of the bands corresponding to variations in structural units Qn in melts of Li60 composition depending on the temperature (square symbols correspond to structural units Q^2, triangular, cruciform and rhombic ones – to Q^1, Q^3 and Q^0, respectively)

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СТРУКТУРА РАСПЛАВОВ ПИРОСИЛИКАТА ЛИТИЯ ПО ДАННЫМ ВЫСОКОТЕМПЕРАТУРНОЙ СПЕКТРОСКОПИИ КОМБИНАЦИОННОГО РАССЕЯНИЯ

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Проведено разложение высокочастотной области спектров комбинационного рассеяния расплавов состава $60Li_2O \cdot 40SiO_2$ (далее Li60) на линии гауссовской формы. Определены основные структурные фрагменты расплавов и их соотношение, а также выявлены особенности их взаимодействия с изменением температуры.

Ключевые слова: структура расплава, силикатные расплавы, спектроскопия комбинационного рассеяния.

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