STRUCTURE OF B_2O_3 MELT BY RAMAN SPECTROSCOPY

Osipova L.M., Osipov A.A., Bykov V.N.
(Institute of Mineralogy RAS, Ural Branch, Miass, Russia)
armik@ilmeny.ac.ru; fax: (35135) 7-02-86; ph.: (35135) 7-04-08

Key words: *Raman spectroscopy, structure, melt*

Structure of glasses and melts B_2O_3 at temperatures from 20 to 1025^{0}C was investigated by Raman high-temperature spectroscopy. For excitation of Raman spectra the powerful pulse laser and gated photon account system was used. Adjusting on a thermal population of oscillatory levels was carried out for comparison of spectra obtained at different temperatures.

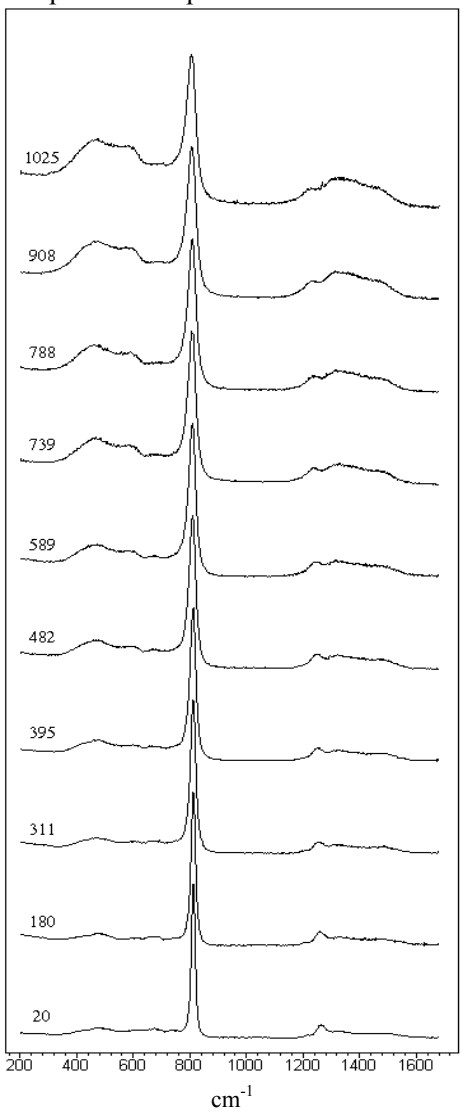

Fig. 1. Raman spectra of vitreous and molten B_2O_3 measured at various temperature.

The obtained Raman spectra of glasses and melts B_2O_3 are shown in a fig. 1. On the basis systematic studies of B_2O_3 [1,2,3,4] is established, that the band with a maximum about 808 cm^{-1} is due to the symmetric breathing vibration of the boroxol rings. According to [5], the bands in the 1200-1600 cm^{-1} rang is assigned by antisymmetric stretching vibrations of base structural units BO_3. The small width of bands ~1215 and ~1260 cm^{-1} in spectra of B_2O_3, and also character of temperature dependence their intensities allows to assume, that the these lines are associated with the vibrations of BO_3 triangles, included in composition of boroxol groups. The band at 1260 cm^{-1} assigned to B-O' stretching in BO_3 triangles of boroxol rings, where O' is not in the ring [2]. At the same time, the wide Raman lines in the frequency range from 1260 to 1600 cm^{-1} are associated with vibrations BO_3-units, which are situated in random network. The bands in the field of low frequencies (300-800 cm^{-1}) are assigned to bending vibrations of planar BO_3 triangles in random network [2].

The increasing of relative intensity of bands in the 1260-1600 cm^{-1} and 300-800 cm^{-1} regions at increasing temperature shows, that at melting glass B_2O_3 transformation of BO_3 triangles in boroxol rings, to BO_3 triangles in a random network is existed.

For quantitative description of this structural reorganization ratios of Raman integrated intensities of bands is used [2]:

$$r_1 = \frac{I_{800}}{I_{300-800}}, \qquad (1) \qquad r_2 = \frac{I_{800}}{I_{1260-1600}}, \qquad (2)$$

where I_{800} is the integrated intensity of a band at 808 cm^{-1}, $I_{300-800}$ is the total integrated intensity of contour in the frequency range from 300 to 820 cm^{-1}, $I_{1260-1600}$ is total integrated intensity of the high-frequency contour.

The temperature dependencies of $r_i(t)$ are presented in a fig. 2. At low temperatures r_i feebly are depends on temperature and the experimental points are well described by the horizontal line. At temperatures is higher then T_g, $r_i(t)$ are satisfactorily described by the curve of the second order. The cross point of these lines corresponds to temperature of a glass transition.

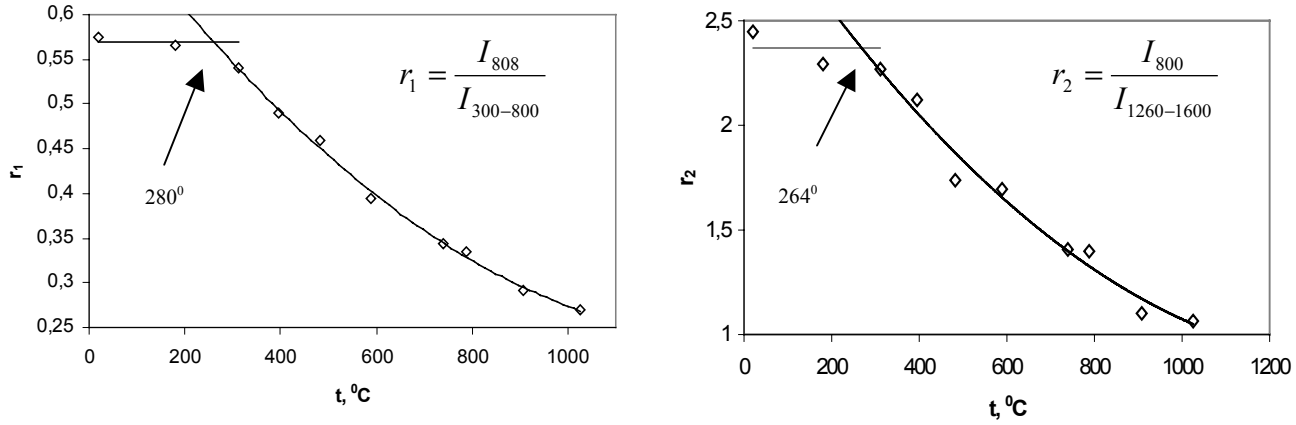

Fig. 2. Temperature dependencies of r_i for vitreous and molten B_2O_3.

For estimation of an enthalpy of formation process of boroxol rings from BO_3 triangles following equation was used[2]:

$$\ln\left[\frac{r_i}{A_i - r_i}\right] = \frac{B_i}{T} + C_i, \qquad (3)$$

where A_i, B_i and C_i - constants, T - temperature. This line features experimental data by the best expedient when Ai is equal to average value r_i in low-temperature region ($T < T_g$). In our case $A_1 = 0,57$, $A_2 = 2,37$. The values ΔH_i were defined by linear least squares. These values are equal ΔH_1 = - 24±1 kJ/mol. (-5,8±0,3 kkal/mol.) and ΔH_2 = - 28±2 kJ/mol. (-6,7 ± 0,5 kkal/mol.) and its also are in good correspondence with magnitude -6,4 ± 0,4 kkal/mol. [2].

Thus, the carried out examinations have shown, that the concentration boroxol groups in structure of melts B_2O_3 is small and BO_3 triangles mainly connected in a random network. The dynamic equilibrium BO_{3k} <=> BO_{3c} is existed in melts B_2O_3, where the inferior index specifies a membership of structural unit to k -boroxol group, c- to a random network. At a temperature drop this equilibrium is shifted to the left, that corresponds to process of integrating of BO_3 units in boroxol rings. ΔH of formation of boroxol rings from BO_3 triangles is equal -24±3 kJ/mol. The process of formation of boroxol groups is favored energetically. The formation of boroxol rings is frozen at temperatures below the glass transition temperature. The structure vitreous B_2O_3 is a random network of connected boroxol groups.

References:

1. *Goubeau F.L., Keller H.* Raman-Spectren und Structur von Boroxol-Verbindungen // Z. Anorg. Allg. Chem., 1953, V. 272, N 5-6, p. 303-312.
2. *Walrafen G.E., Samanta S.R., Krishnan P.N.* Raman investigation of vitreous and molten boric oxide // J. Chem. Phys., 1980, V. 72, N 1, p. 113-120.
3. *Konijnendijk W.L., Stevels J.M.* The structure of borate glasses studied by Raman scattering // J. Non-Crystalline Solids, 1975, N 18, p. 307-331.
4. *Galeener F.L., Lucovsky G., Mikkelsen J.C.* Jr. Vibrational spectra and structure of pure vitreous B_2O_3 // The American Physical Society, Physical Review B, 1980, V. 22, N 8, p. 3983-3990.
5. *Feltz A.* Amorphe und glasartige anorganische festkörper // Moscow, World, 1986, p. 556.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21)'2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/magm-34e.pdf
Published on July 15, 2003