

## High-temperature Raman spectroscopy and thermodynamic modelling of silicate melts, based on the problem-oriented database “Thermo-melt”

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The work is devoted to theoretical and experimental researches of a structure of silicate melts  $M_2O-SiO_2$ , where M - Li, Na, K. The thermodynamic model of silicate melts, founded on spectroscopic data about their real structure was used. As a basis to construction of model the approach elaborated for oxide glasses in work [1] was applied. But as against the given approach the standard Gibbs free energy is expressed through the sum on  $Q^n$ -structural units of a silicate melt. Search of a minimum of free energy of system is carried out by the decision of the system of equations of mass balance of the components and the law of mass action for all reactions proceeding in system.

For the definition of thermodynamic characteristics of these structural units data of silicates were used as initial parameters which have been received for the given systems at the project on creation of the database «Thermo-Melt». At the first stage, the collecting of bibliographic information for anhydrous crystal silicates and their glasses formed in systems O-Si-Me (where Me = Li, Na, K, Rb, Cs) is carried out and files of the literary data are created. The evaluation of the experimental thermodynamic information for the substances formed in considered chemical systems is carried out. Standard values of entropy, enthalpy and standard Gibbs free energy of silicates of alkaline metals are recommended. The new equations for the temperature dependences of the heat capacity of these substances are obtained.

For the testing the model and definition of  $Q^n$ -distribution of structural units experimental quantitative investigation of structure of lithium, sodium and potassium silicate melts were carried out by high-temperature Raman spectroscopy [2]. It is shown, that experimental values of concentration of structural units for these silicate melts and glasses are in a good agreement with the model. It is established that the temperature dependence of  $Q^n$ -distribution in the system  $Li_2O-SiO_2$  differs from the dependence of  $Q^n$ -distribution in sodium and potassium silicate melts.

The work was supported by the Russian Foundation for Basic Research (grants № 07-05-01108, 06-05-64333)

### References

Shakhmatkin B.A. *et al.*, (2001), *Int. Cong. Glass* **1**, 52-60.  
Anfilogov V.N., Bykov V.N., Osipov A.A., (2005), *Silicate melts*, 357.

## Boron isotopes of K-tourmaline from the Kokchetav UHP massif

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Recently, high-K tourmaline (Tur; 2.76 wt%  $K_2O$ ) co-existing with microdiamond was discovered in quartzofeldspathic rocks from Kumdy-kol in the Kokchetav UHP massif, northern Kazakhstan [1]. The sample investigated in our study from the same locality is dominated by quartz, K-feldspar and Tur (~10 vol %), with minor titanite, phengite, chlorite, zircon, biotite, apatite, graphite and sulphide. Mineral assemblages preserved as inclusions in zircon consist of garnet, phengite and coesite. Despite an extensive search, no Tur inclusion was identified in ultrahigh-pressure (UHP) minerals (e.g. zircon, garnet,  $K_2O$ -bearing clinopyroxene). Furthermore, numerous quartz grains, but no coesite or microdiamond was identified as inclusions in Tur in our sample. We therefore interpret K-Tur in our sample to have formed under retrograde  $P$  conditions in the quartz stability field. The chemical compositions of Tur, however, is similar to the Tur for which [1] reported microdiamond inclusions.

Tur in the Kumdy-kol sample is a K-analogue of dravite (0.35 Na pfu; Mg#: ~87) with remarkable contents of tetrahedral B (~3.3 B pfu) and Ca (~0.3 pfu).  $K_2O$  contents are as high as 1.57 wt % (~0.3 K pfu). The Tur displays a very low X-site vacancy (<0.05) and high OH (~3.4 pfu) and F (0.27 pfu) contents. At their rims and along cracks, all Tur grains show a strong decrease in K content to less than 0.05 wt%, accompanied by an increase in Na (~0.5 pfu), in X-site vacancies (0.2 to 0.3 pfu), and a slight increase in Al. All other elements are unzoned.

Tur cores are homogeneous in B isotopes ( $\delta^{11}B = +10.6\%$ ; analysed by SIMS in Heidelberg, Germany). Towards the rims,  $\delta^{11}B$  values decrease to +5.5%. These values are significantly higher than values reported previously for Tur from metasedimentary rocks or any (U)HP rocks (typically -10%). Heavy-B Tur ( $\delta^{11}B > +5\%$ ) has been described only from metapelite-marble contacts [2,3], from partially melted granulites [2], from evaporites, and from hydrous reaction zones around HP metamorphic blocks formed by an influx of external hydrous fluids [4].

Hence, the high modal proportion of heavy-B Tur in the Kokchetav samples is best explained by a post-peak pressure influx of B-rich fluids or melts generated in biogenic-chemical sediments, i.e. carbonates or meta-evaporites.

This work was supported by the Russian Foundation for Basic Research (07-05-00308-a), MK-5077.2006.5, Russian Science Support Foundation and the Belgian Government BOSTCA.

- [1] Shimizu & Ogasawara (2005) *Mitt Öster Min Ges* **150**:141  
[2] Palmer & Slack (1989) *Contrib Min Petrol* **103**: 434-451  
[3] Swihart & Moore (1989)  
[4] Marschall *et al.* (2006) *JPet* **47**: 1915-1942