Setkova T.V.[1], Spivak A.V.[1], Zakharchenko E.S.[1], Borovikova A.Yu.[2], Nesterova V.A.[1,2], Balitsky V.S.[1], Bublikova T.M.[1], Pushcharovsky D.Yu.[2] **Raman spectroscopy of synthetic Ga,Ge-rich tourmaline at high pressure up to 30 Gpa (preliminary data).**

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Abstract. Synthetic tourmaline with 9.4 wt. % Ga_2O_3 and 10.1 wt. % GeO_2 was studied at pressure up to 30 GPa by Raman spectroscopy. There was determined a general dependence of the shift of bands towards higher frequencies with increasing pressure due to decrease in the bond lengths, associated with structural deformations. In the area of 700 cm^{-1} the direction of trend of peak positions changes in the pressure range from 15.12 GPa to 17.64 GPa, the structural transition could be expected in this pressure range.

Keywords: Raman spectroscopy, tourmaline, high pressure, gallium, germanium, synthesis

Introduction. The tourmaline supergroup minerals are characterized by variable composition $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ (X - Na^+, Ca^{2+}, K^+, □ (vacancy); Y (mainly) - Mg^{2+}, Fe^{2+}, Al^{3+}, Li^+ et al.; Z - Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}; T - Si^{4+}, Al^{3+}, B^{3+}; V - $(OH)^-$, O^{2-}; W - $(OH)^-$, F^-, O^{2-} and by the stability in a wide P-T range. At present, it includes over 40 mineral species, as well as numerous synthetic analogues (Bosi, 2018). Tourmaline possesses unique physical properties, such as spontaneous polarization, piezo- and pyroelectricity, infrared radiation and others.

Interest in the study of minerals at high pressure is associated with obtaining new data on the chemical, phase composition and physical properties of deep rocks and minerals. Recently, the studies are stimulated by the progress in the experimental investigations of phases at high-pressure, as well as the development of high-pressure equipment with DAC (Diamond Anvil Cell). Current knowledge of high-pressure powder and single-crystal XRD (up to 60 GPa) is limited by several publications devoted to natural (Werding, 1996; Krosse,1995; Li et al., 2004; Xu et al., 2016; Likhacheva et al., 2019; O'Bannon et al., 2018) and synthetic Mg-Al tourmalines (Berryman et al., 2018). As a result of petrologic studies it was shown that dravite decomposes at 7 GPa and 900°C (Werding, 1996) and at 3-5 GPa and 1000°C (Krosse,1995). Different parameters of this process are dependent on the composition of the sample. The XRD of schorl up to 27.8 GPa did not reveal any phase transition (Xu et al., 2016). Structural changes of uvite were not observed in HP and HT experiments up to 18.4 GPa and 723 K (Li et al., 2004). Maruyamaite (K-tourmaline) (Likhacheva et al., 2019) and synthetic Mg-Al tourmalines (Berryman et al., 2018) are stable at high pressure and phase transitions of these minerals were not detected. However, the recent HP single crystal XRD measurements (O'Bannon et al., 2018) of dravite showed that a phase transition from rhombohedral space group *R3m* to rhombohedral *R3* occurs at pressure 15.4 GPa. The previous results allow concluding that the compressibility and the phase transition of tourmalines have directly depend on their cationic composition. In this light it is interesting to synthesize Ga,Ge-analogues of tourmalines with larger cations in *Y*- and *T*-sites in their structures. These compounds with higher ratio of cationic/anionic radii could be used as structure models of tourmalines at high pressure.

Experimental methods. For high pressure study the Ga,Ge-rich tourmaline crystals with 9.4 wt.% Ga_2O_3 and 10.1 wt.% GeO_2 content were synthesized using a hydrothermal method at temperature 600/650°C and pressure 100 MPa (Vereshchagin et al., 2016; Setkova et al., 2019). Raman-spectroscopy experiments at pressures up to 30 GPa were carried out in a diamond anvil cell (DAC) equipped with 250 mkm culet size anvils. The single-crystal chip of tourmaline 50 mkm in size was loaded and NaCl was used as a pressure medium. The pressure was determined by the calibrated shift of the R_1 fluorescence line of ruby. All experiments were carried out at ambient temperature. Raman spectra of Ga,Ge-rich tourmaline were measured using the apparatus consisting of spectrograph Acton SpectraPro-2500i with detector cooling up to -70°C CCD Pixis2K and the microscope Olympus at IEM RAS. The obtained spectra from three points were averaged and fitting in the Fytik 1.3.1 program.

Results. The most intense peaks (Fig. 1) were identified and trends of their positions as a function of pressure at ambient condition were plotted (Fig. 2). The trends show the general dependence of bands shift towards higher frequencies with pressure increasing. In the region 3400-3600 cm^{-1} the OH^- vibration was also observed, but with increasing pressure its intensity decreased and above 10 GPa was not defined (see Fig. 1). In addition, in the area of 700 cm^{-1} the direction of trend of peak positions changes at pressure from 15.12 GPa to 17.64 GPa. This could indicate a structural transition in this pressure range.

Conclusions. Newly formed Ga,Ge-rich tourmaline crystals were studied by Raman spectroscopy at ambient conditions and at high pressure (up to 30 GPa). Any shifts of the Raman bands positions are associated with the nature of compressibility or/and changes in the structure of tourmaline crystals at increasing pressure. Most bands show the regular shift to the higher frequencies due to lowering of bong lengths till 15.12 – 17.64 GPa. Based on our preliminary experimental data, the phase transition of Ga,Ge-tourmaline could be expected.

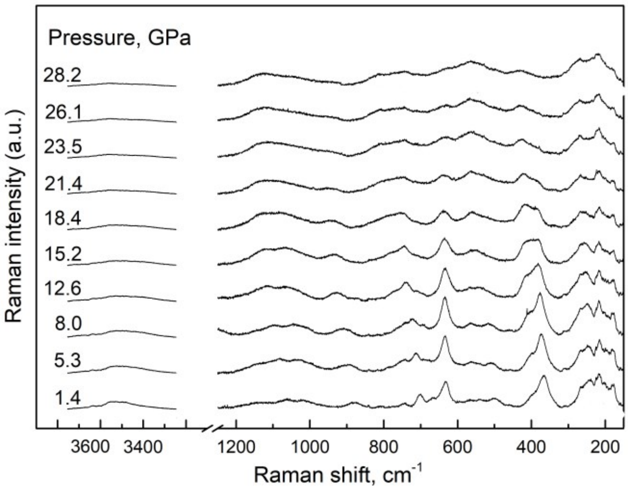

Fig. 1. Raman spectra of Ga,Ge-rich tourmaline at high pressure and ambient temperature.

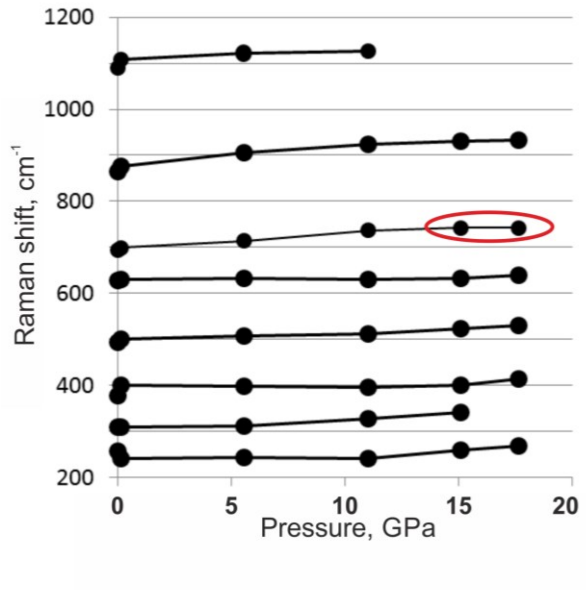

Fig.2 Raman shift of the modes of Ga,Ge rich tourmaline as a function of pressure at ambient temperature

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Zharikov A.V.[1], Lebedev E.B.[2], Rodkin M.V.[3]
Anomalies of rock physical properties due to phase transitions and their possible role in seismotectonic processes

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Abstract. Anomalies of rock elastic properties caused by α-β transition in quartz and their possible effect on the microcracks formation and seismicity are considered. Temperature trends of quartz-containing rocks are characterized by strong inversions in *PT*-conditions of the quartz α-β transition. It is noteworthy that the elastic properties of rocks changed much more significantly than one would expect if based on changes in the properties of quartz individual grains and the mineral content in the rocks. It is assumed that the phase transition can generate a trigger effect, initiating a sharp increase in the velocities of fluid waves, which are associated with seismotectonic processes.

Key words: phase transitions, elastic properties of rocks, seismicity

The importance of phase transitions for understanding the structure and physics of the Earth is well-known [Kalinin et al., 1989; Rodkin et al., 2009; Rodkin & Rundquist, 2017; et al.]. The main seismic boundaries in the mantle are associated with phase transitions. Changes in density due to phase transformations play a crucial role in subduction processes. In addition, phase transformations are accompanied by anomalies of elastic, transport and strength properties of solids [Kalinin et al., 1989; Rodkin & Rundquist, 2017; et al.].

However, the direct study of these phase transformations is strongly difficult because the experiments and precision measurements should be carried out at very high temperatures and pressures. Therefore, for direct experimental study the α-β transition in quartz, which is realized at slightly lower temperatures and pressures, is more suitable. Unfortunately, this effect is not a typical transition of the I-th type, since occurring changes in density and heat content are very small. The relative volume change during the α-β phase transition in quartz is less than 0.6%, so this transformation was even sometimes attributed to transitions of the second type. However, this transformation proved to be the most popular in experimental studies [Kern, 1979; Kalinin et al., 1989; Nikitin et al., 2009; Rodkin et al., 2009]. An additional argument in favor of studying the a-b transition exactly in quartz is that this mineral is the most prevalent in the Earth's crust.

Quartz at T=573°C and atmospheric pressure undergoes a structural phase transition from a low-temperature trigonal α-phase to a high-temperature hexagonal β-phase. With pressure increase, the temperature of the a-β transition also increases (at 106.5 MPa T =595°C, at 939 MPa T=810°C). From here, we can estimate the slope of the Clapeyron-Clausius phase equilibrium curve dT/dp ~ 0.25°C/MPa [Kalinin et al., 1989; Nikitin et al., 2009; Rodkin et al., 2009]. From the comparison of the equilibrium curve of the α-β transition in quartz with the PT-conditions of the earth's crust and mantle, we get that in the earth's crust, α-β transformation can occur in areas with its increased thickness. For example, the occurrence of α-β transformation can be expected in areas of Central Tibet, where the thickness of the earth's crust is abnormally large: up to 70-80 km. However, in the vast majority of the earth's crust, the stability conditions of the low-temperature a-phase are met, and the transition occurs already in the upper mantle. We should expect the occurrence of transformation in the subduction regions and at the depth of the upper mantle, as well.

There is a clear interest to the α-β transformation and in terms of study of related anomalies in the physical properties of the earth's crust and mantle. Changes in elastic properties and the possibility of developing so-called transformational superplasticity are primarily considered as such anomalies. [Greenwood & Johnson, 1965; Kern, 1979; Kalinin et al., 1989]. The possibility of developing transformational superplasticity in a polymorphic (structural) a-β transition in quartz, as applied to the processes in rocks, was discussed in [Kalinin et al., 1989; Schmidt et al., 2003; Rodkin et al., 2009], the last of these monographs presents the results of the most comprehensive research. In combination the experimental data obtained show the development of the whole complex of physical anomalies in the process of α-β transformation, primarily elastic properties, but also deformation and strength. Especially, significant deformations in the area of realization of the α-β transition were observed in quartzite and synthetic quartz under the influence of relatively small external stresses. This work is focused on the anomalies of elastic properties and their possible connection with microcracking and the seismicity.

Experimental studies of elastic and transport properties of quartz-containing rocks at high temperatures and pressures were carried out both in "dry" conditions as well as with water saturation. Experiments have shown significant variability in the obtained temperature trends of compessional wave velocities. At the same time, quartz-containing rocks are characterized by strong inversions in *PT*-area of the α-β transition. It is significant that the physical, in particular, elastic properties of rocks changed much more significantly than one would expect, based on changes in the properties of a single grain of quartz and the mineral content in the rock (Fig. 1). As it was mentioned above, α-β transformation leads to a very small change in density, such changes could only result in a very small changes of elastic properties. It can be assumed that the formation of microcracks on the boundaries of quartz grains cause an abnormally strong drop in elastic characteristics. At the same time, the formation of microcracks on the grain boundaries of quartz, which content in the studied amphibolites was up to 20 % [Kern et al, 2001, Zharikov et al., 1993], could lead to the formation of fluid-conducting clusters in the rock and, as a result, to a sharp, threshold increase in permeability [Zharikov et al., 1993]. This aspect seems to us to be very important.

The assumption about the possibility of intensive crack formation caused by a phase transition agrees with other experimental data. In [Kalinin et al., 1989], the examples that the nature of destruction of solids often changes dramatically during phase transformations are given. In particular, even with relatively small stresses, active cracking can occur, transparent samples lose their transparency, and sometimes the sample seems to crumble into a powder. Naturally, active cracking should be accompanied by a sharp increase in permeability.

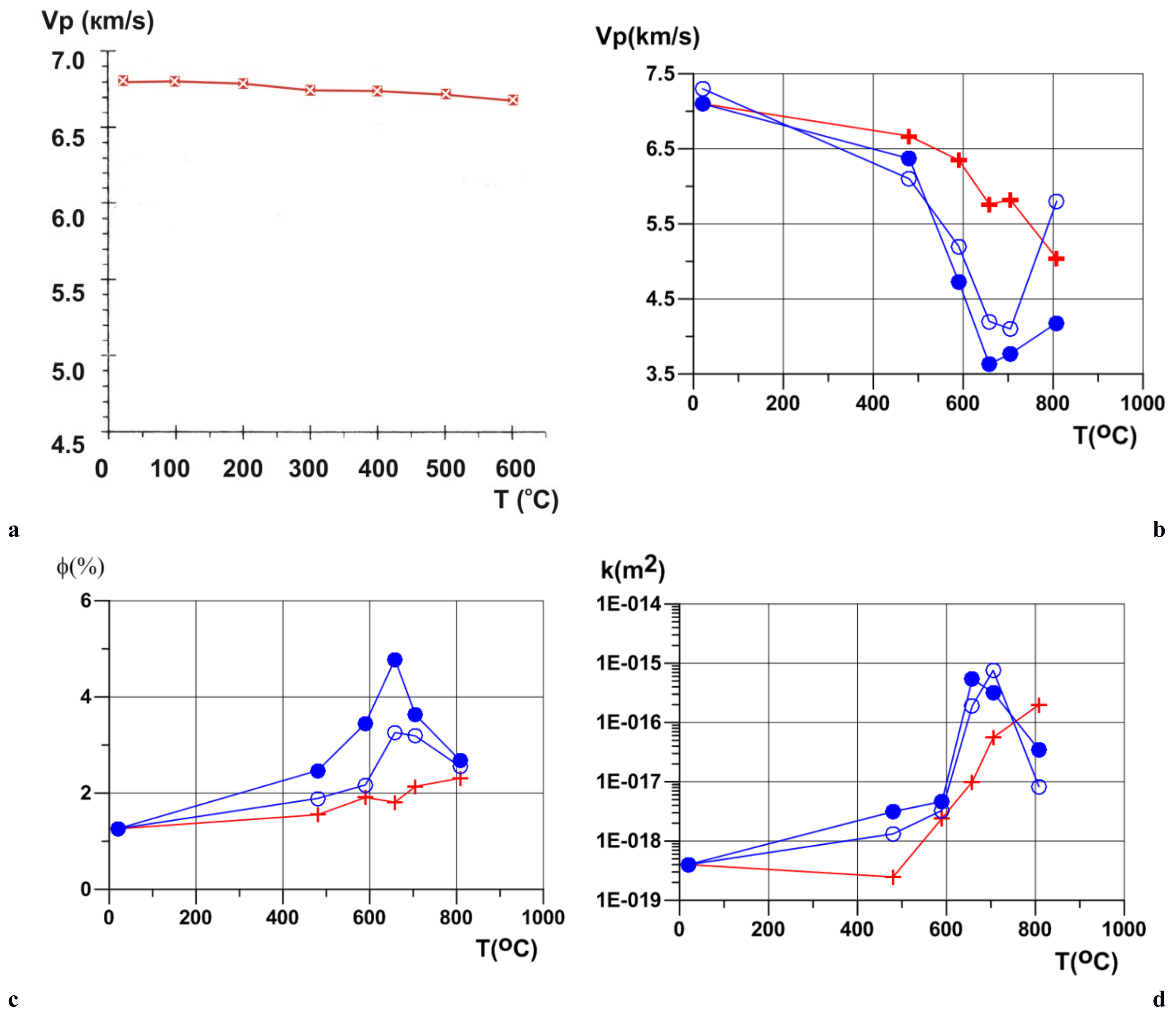

Fig. 1. Dependence of compressional wave velocities (a,b), porosity(c) and permeability (d) in the amphibolite samples on the temperature.

(a) Sample 43276. $P_{conf.}$= 600 MPa, P_{pore}=0, $T_{\alpha\text{-}\beta}$ =715°C,
(b,c,d) Sample Ush. $P_{conf.}$= $P_{pore.}$= 300 MPa, $T_{\alpha\text{-}\beta}$ =650°C, blue marks - experiments in the presence of water, red - in dry conditions.

It should be noted that the effect of a sharp increase in rock permeability under certain PT-conditions, apparently, finds quite strong support in the seismological data. Such anomalies appear to occur systematically during strong earthquakes. In [Rodkin, 2008; Rodkin & Tikhonov, 2016; Rodkin & Rundqvist, 2017], the results of the analysis of the generalized vicinity of a strong earthquake revealed the effect of an abnormal decrease in the depth of foreshocks and aftershocks. An example of such an anomaly is shown in figure 2. The figure shows that the average depth of earthquakes in the close vicinity of a generalized strong earthquake decreases sharply (the ISC world earthquake catalog was used to construct the generalized earthquake vicinity). The nature of growth anomalies in the for- and in- the aftershock areas is visible better in the logarithmic scale along the time axis: the value of the average depth of earthquakes in the forshock and aftershock sequence change with time as log│Δt│, where Δt the time from the moment of the generalized strong earthquake (Fig. 3). Similar anomalies were detected from other data, in particular, based on regional seismicity catalogs. Note that such an anomaly was not detected for the zones of mid-ocean ridges, which can be explained by a different temperature and fluid regime of these areas, in which the main contribution is not water fluid, but fluid-containing melt.

The anomaly is most reasonably explained by the increase in the permeability of the focal area, which leads to a rapid breakthrough of light fluid masses into the upper horizons of the lithosphere.

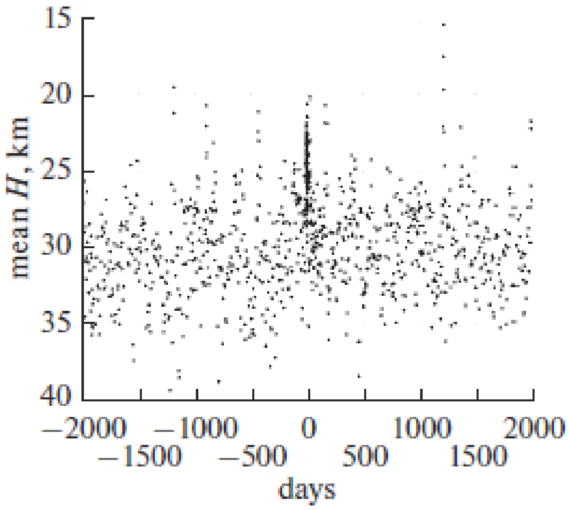

Fig. 2. An example of an anomaly decreasing of the average depth of earthquakes in a generalized vicinity of a strong earthquake. The zero moment of time corresponds to the moment of a generalized strong earthquake.

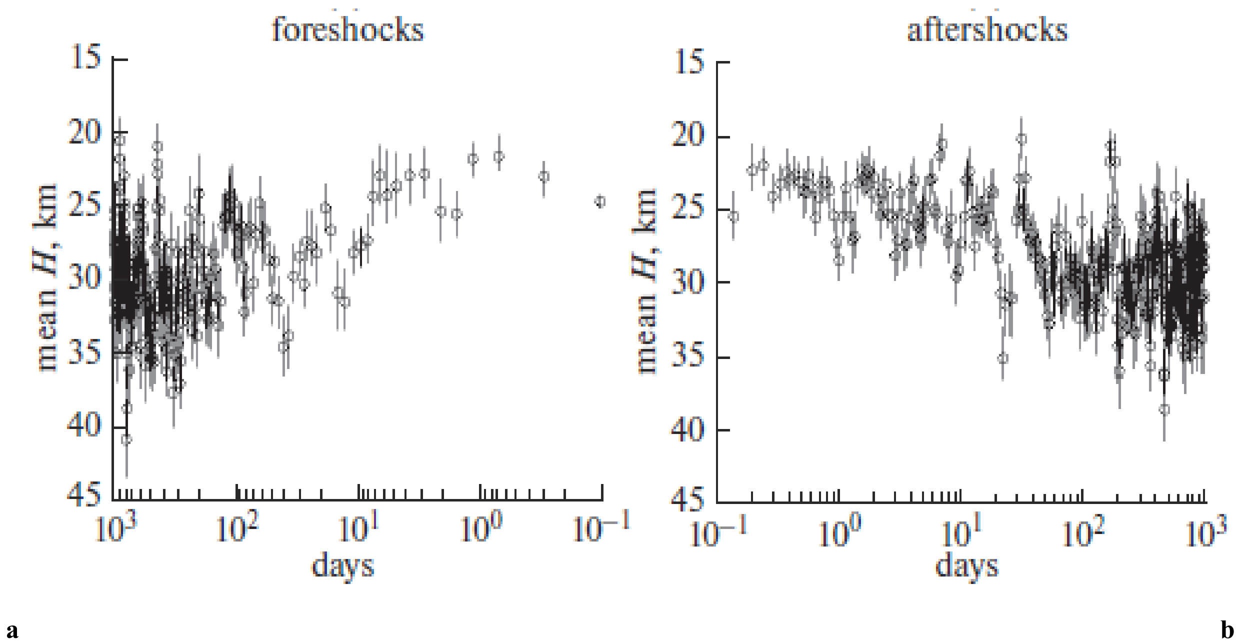

Fig. 3. Trends of the average depth of foreshocks (a) and aftershocks (b) in the vicinity of a generalized strong earthquake.

Taking into account the data on an anomaly of elastic properties in the area of the α-β transition in quartz, it can be assumed that this transition generates a trigger effect, initiating a sharp increase in the velocity of fluid waves, which are associated with seismotectonic processes. Similar processes can also occur in other, less studied, phase transformations.

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