

Physical chemical properties of geomaterials

Spivak A.V.¹, Setkova T.V.¹, Borovikova E.Yu.², Kvas P.S.², Balitsky V.S.¹, Zakharchenko E.S.¹ Raman spectroscopy of synthetic krieselite $\text{Al}_2\text{GeO}_4(\text{OH},\text{F})_2$ at pressure up to 30 GPa UDC 549.731.11; 543.42

¹ IEM RAS (Chernogolovka), ² Lomonosov MSU (Moscow) (spivak@iem.ac.ru)

Abstract. Spontaneous crystals of krieselite (Ge-topaz) were synthesized with using hydrothermal method at temperature 600 °C and pressure 100 MPa. The formula of the synthesized crystals was determined as $\text{Al}_{2.00}(\text{Ge}_{0.87}\text{Si}_{0.09}\text{Al}_{0.04})\text{O}_4(\text{F}_{1.36}\text{OH}_{0.64})$. Raman spectroscopy showed the main differences between spectra of krieselite and topaz at normal conditions. Using *in situ* Raman spectroscopy at high pressures, the dependence of the shift in the position of the main bands of the Raman spectrum on pressure was established. According to the data of Raman spectroscopy, it was revealed that the structure of krieselite does not undergo serious changes up to 30 GPa.

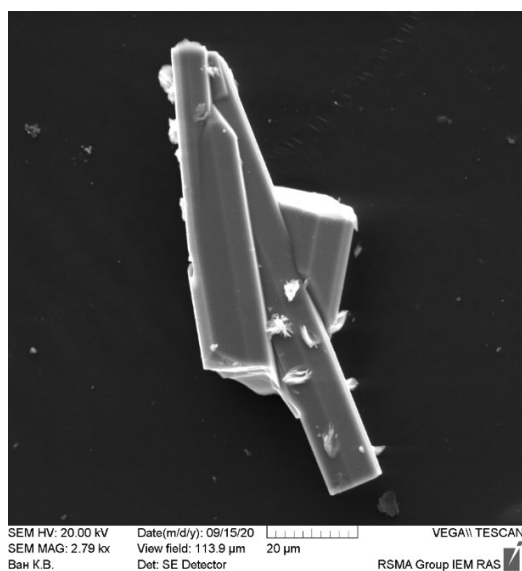
Keywords: krieselite, topaz, germanium, synthesis, Raman spectroscopy, high pressures, structure

Krieselite is the Ge-substituted analog of topaz $[\text{Al}_2\text{GeO}_4(\text{F},\text{OH})_2]$. It occurs as beige to white, hemispherical aggregates and crusts of fibrous crystals up to 50 μm in the Tsumeb mine, Namibia

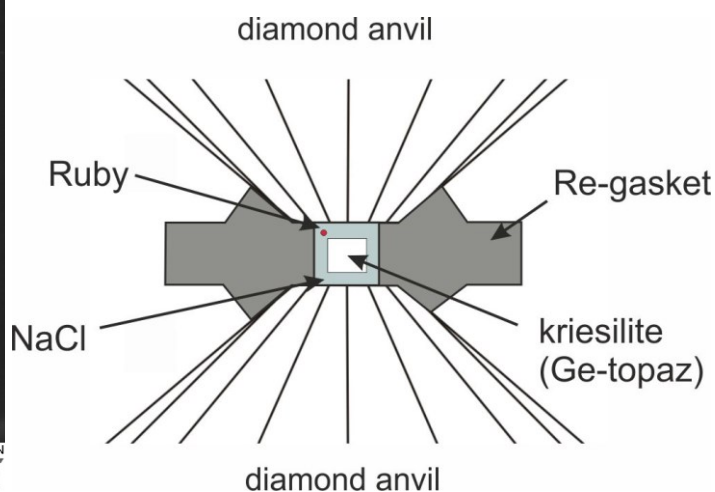
(Schlüter et al., 2010). Previously, the germanium analogue of rhombic aluminosilicate (topaz) was synthesized at high temperature and pressure parameters (temperature 650 °C, pressure 2 GPa) (Wunder, 1997).

Chemical deformations, that can occur in the topaz structure when a larger Ge cation enters, are equivalent to structural changes at high pressure. Changes in the mutual arrangement of the main structural elements of topaz are described as a result of studying the effect of pressure on the structure of topaz (Gatta et al., 2014). The objectives of this work: (1) synthesis of crystals of krieselite of required size for physical research methods; (2) study of the structural features of the obtained crystals by Raman spectroscopy at ambient and high pressures conditions.

Synthesis experiments were carried out by the hydrothermal method in autoclaves at a temperature of 650 °C and a pressure of 100 MPa at the Institute of Experimental Mineralogy of the Russian Academy of Sciences. As a result of the action of acidic fluoride solutions with an excess of GeO_2 on tourmaline of elbaite composition, chryselite was formed in the form of intergrowths and separate colorless prismatic crystals up to 100 μm in size (Fig. 1).



(A)



(B)

Fig. 1. (A) SEM image of a synthetic krieselite crystal; (B) Schematic assembly of a high-pressure cell with diamond anvils for Raman spectroscopy at high pressures.

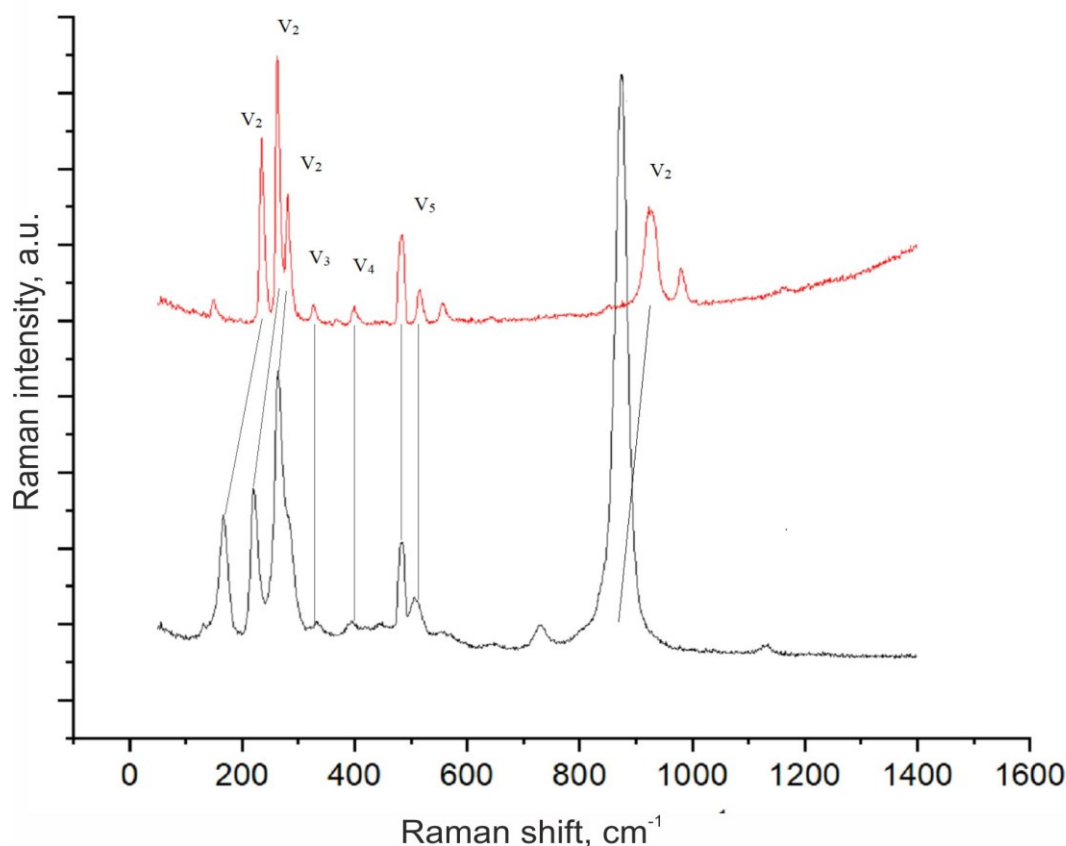


Fig. 2. Raman spectra of synthetic krieselite (black) and topaz (red) at ambient conditions.

The chemical compositions of experimental samples were determined by electron microprobe analysis (EMPA) with using Tescan – Vega II XMU electron microscopy with INCA Energy 450 energy dispersive spectrometer (EDS), equipped with an INCA x-sight semiconductor Si(Li) detector and an INCA Wave 700 wavelength-dispersive spectrometer (WDS) (Oxford Instruments) at IEM RAS. According to the obtained data, the chemical formula of Ge-topaz crystals was determined as $\text{Al}_{2.00}(\text{Ge}_{0.87}\text{Si}_{0.09}\text{Al}_{0.04})\text{O}_4(\text{F}_{1.36}\text{OH}_{0.64})$.

Raman spectra of krieselite at high-pressure were measured using the apparatus consisting of spectrograph Acton SpectraPro-2500i with detector cooling up to $-70\text{ }^{\circ}\text{C}$ CCD Pixis2K and the microscope Olympus with a continuous solid-state monomeric laser with radiation wavelength 532 nm and diode pumping at IEM RAS. The laser beam diameter was 3–5 μm . Raman data were collected by repeated exposures of 540 s (3×180 s). High-pressure Raman-spectroscopy experiments were carried out in a diamond anvil cell (DAC) up to 30 GPa with 1–2 GPa step. NaCl was used as a pressure medium. Figure 1b shows an assemblage of loading DAC with a sample-crystal of krieselite (Ge-topaz)

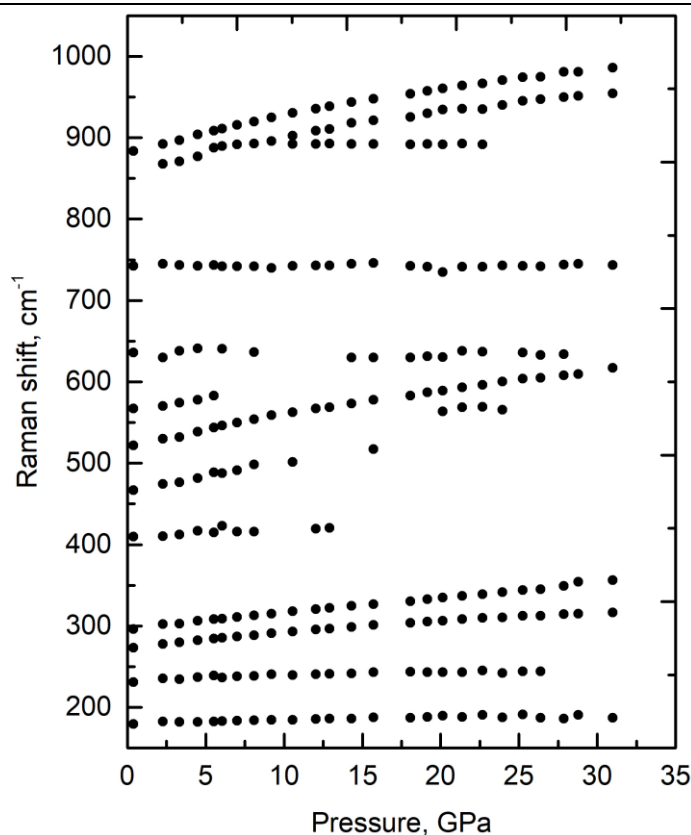
and a ruby. The software Fytik 1.3.1. was used for profile fitting for the Raman band analysis. Figure 2 presents the Raman spectra for krieselite and topaz at ambient conditions.

The main difference between the spectra of krieselite and topaz is associated with the incorporation of germanium into the topaz structure. This is a reason to shift of the bands (Table 1) associated with the vibrations of the $[\text{GeO}_4]$ and $[\text{SiO}_4]$ tetrahedra, as well as with the symmetric bending vibrations of Ge-O and Si-O.

Raman spectroscopy data at pressures up to 30 GPa are shown in figure 3. It is possible to trace the change of the main bands positions of krieselite Raman spectrum with increasing pressure. A gradual change in the Raman spectra is observed at high pressure. But at a pressure 10 GPa, an additional band appears at 890 cm^{-1} . It retains Raman shift position with pressure increase up to 20 GPa. With a further pressure increase, the intensity of this band decreases until it completely disappears. A similar appearance of an additional band as a result of the separation of the main band at 924.6 cm^{-1} at 10.8 GPa was observed in natural topaz (Huang et al., 2010).

Table 1. The position of the main bands (cm^{-1}) of the Raman spectra of synthetic krieselite and topaz

$\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ topaz	239.8	268.1	286.3	332.5	403.5	457.2	852.9	924.6	991.7
$\text{Al}_2\text{GeO}_4(\text{F},\text{OH})_2$ krieselite	182.3	226.4	277.7	300.3	407.5	460.3	742.4	885.4	-

**Fig. 3.** Raman shift of the modes of krieselite as a function of pressure at ambient temperature.

For the first time, spontaneous crystals of krieselite (Ge-topaz) of sufficient size and quality for physical research methods were obtained by the hydrothermal method at a temperature of 600 °C and a pressure of 100 MPa during the recrystallization of elbaite.

Electron microprobe analysis showed that the Ge content in the synthesized crystals is 0.87 a.p.f.u., and the crystal chemical formula can be represented as $\text{Al}_{2.00}(\text{Ge}_{0.87}\text{Si}_{0.09}\text{Al}_{0.04})\text{O}_4(\text{F}_{1.36}\text{OH}_{0.64})$.

Raman spectroscopy at ambient conditions showed the main differences between the spectra of krieselite and topaz.

Using *in situ* Raman spectroscopy at high pressures, the dependence of the shift in the position of the main bands of the Raman spectrum on pressure was established. According to the data of Raman spectroscopy, it was revealed that the structure of krieselite does not undergo serious changes up to 30 GPa. The background and relative shoulder size for the main bands in the spectrum increased insignificantly, which may indicate a weak disordering of the structure.

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