Novel experimental data on hydrothermal growth of phenakite single crystals with Si-Ge substitution

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Silicates are an interesting object for crystallographic and material science research. Representatives of this mineral group are well studied due to the possibility of isomorphic substitution of silicon with germanium in a wide range of germanium concentration. For example, for quartz [1], topaz [2] and tourmaline [3] a large isomorphic capacity has been shown. A special attention of a current research is focused to phenakite, beryllium orthosilicate Be_2SiO_4. For this phase solid solutions with isomorphic germanium were obtained, however, only in a polycrystalline state [4].

We report the results of first experiments on phenakite-like $Be_2[(Si_{1-x}Ge_x)O_4]$ single crystals (up to 1mm) growth and investigation. Experiments were carried out by hydrothermal method. One of experiments was conducted using the technique of temperature-induced zoning. LiF-based solutions are effective for the synthesis of $Be_2[(Si_{1-x}Ge_x)O_4]$ solid solution. As a result of the use of these hydrothermal solutions, uniform single crystals of $Be_2[(Si_{1-x}Ge_x)O_4]$ solid solution (x up to 1) were obtained. Crystal structure of single crystalline $Be_2[(Si_{1-x}Ge_x)O_4]$ samples with x = 0, 0.86 and 1 were refined by direct X-ray diffraction methods. The linear dependance of unit cell parameters, bond lengths and bond angles on germanium concentration was determined. Zoned $Be_2[(Si_{1-x}Ge_x)O_4]$ single crystals (x up to 0.25) were also synthesized using the technique of temperature-induced zoning in experiment. Obtained crystals can be characterized by a striation of wide and thin zones, where thin zones are enriched in germanium compared to surrounding wide zones. Chemical and morphological analysis of the striation showed that (i) the value of germanium effective distribution coefficient is less than 1 and (ii) growth rate decreases from 18 μm/day to 2 μm/day in the direction of hexagonal prism. Raman spectroscopy study of zoned $Be_2[(Si_{1-x}Ge_x)O_4]$ crystals indicated the linear shift of vibration bands in Raman spectra to a lower frequency region with an increase in germanium concentration (x up to 0.25).

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References

[1] V.S. Balitsky et al., Growth and Morphology of High-Germanium Single Crystals, Dokl. Earth Sci., 2017, 477(2): 1437-1440.
[2] A.V. Spivak et al., Raman spectroscopy and high pressure study of synthetic Ga,Ge-rich tourmaline, Spectrochim. Acta A Mol. Biomol. Spectrosc., 2021, 248: 119171.
[3] E.Yu. Borovikova et al., Synchrotron single-crystal XRD, IR- Raman spectroscopy and high pressure study of synthetic krieselite, Spectrochim. Acta A Mol. Biomol. Spectrosc., 2023, 288(5): 122137.
[4] V.S. Kortov et al., Exoelectron Spectroscopy of Traps in Surface Layers of Phenakite and Quartz, Phys. Chem. Miner., 1985, 12: 114-121.