Crystal growth and high pressure Raman spectroscopy study of germanium-rich quartz-like solid solution

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HGQ (high germanium quartz) single crystals with a chemical composition $Si_{1-x}Ge_xO_2$ are prospective piezoelectric material with higher values of piezoelectric constants (for instance, piezoelectric modules d_{11} and e_{11}) in comparison with a pure (non-germanium) α-quartz. Spectroscopy study of $Si_{1-x}Ge_xO_2$ crystals in a wide range of temperatures and composition demonstrated a linear dependence between α→β transition temperature and germanium concentration [1]. However, α-$Si_{1-x}Ge_xO_2$ single crystals were not studied under high pressures. Polymorphic transitions at high pressures were studied *in situ* for the solid solution endmembers SiO_2 and GeO_2 only. For α-SiO_2 and α-GeO_2 polymorphic transition «α-quartz-$P2_1/c$» occurs at 20 GPa and 7 GPa at room temperature, respectively [2]. Described experimental data provide to suggest the correlation between the solid solution composition and the value of pressure of polymorphic transition. In this regard, high pressure study of solid solution with a certain composition is of interest.

Germanium-rich single crystals of $Si_{1-x}Ge_xO_2$ were synthesized in autoclaves by hydrothermal temperature-difference method at temperature 600/650°C and pressure 100 MPa. Boric acid solution was taken as a mineralizer. For the synthesis of $Ge_{1-x}Si_xO_2$, experimental procedure was modified by using evaporative-recycling crystallizer. As the result, uniform single crystals of α-$Si_{1-x}Ge_xO_2$ with x = 0.09, 0.19 and 0.96 were obtained. For determining phase transitions at high pressures, Raman spectroscopy was used. Measurement of Raman spectra at high pressure were carried out in situ using Mao-Bell type diamond anvil cell. The shift of vibration modes to a higher frequencies region with an increase in pressure was shown. Polymorphic transition was determined by a change in a slope of the trend line $\Omega = f(P)$. Experimental data provide to conclude that the pressure value of polymorphic transition mentioned above decreases with increasing germanium concentration in α-$Si_{1-x}Ge_xO_2$ single crystal: 11 GPa for $Si_{0.91}Ge_{0.09}O_2$, 10 GPa for $Si_{0.81}Ge_{0.19}O_2$, 7.5 GPa for $Si_{0.04}Ge_{0.96}O_2$.

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References

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