07.1–7 INFLUENCE OF UNI- AND DIVALENT CATIONS ON GERMANIUM DIOXIDE FORMATION IN HYDROTHERMAL SYSTEMS. Kosova, T.B., Demianets, L.N. Institute of Crystallography, Acad.Sci. USSR, Moscow, USSR

At room temperatures GeO_2 may exist in three polymorphs. Two modifications (tetragonal stable and hexagonal metastable) can be obtained under hydrothermal conditions. The limitation of T-range of GeO_2(hex) crystal growth is determined by kinetics of transition GeO_2 (hex)→ GeO_2(tetr) in the presence of aqueous solutions. Besides, the stability of germanium dioxide substantially depends on cation composition and pH of hydrothermal medium. The use of solvents causes substitution of GeO_2 by germanates. Thermodynamic analysis of GeO_2 stability of both modifications in the presence of uni- and divalent cations at T 25, 200, 300°C has been made. Preliminary thermodynamic properties of germanates, necessary for calculations, were evaluated. One can see (Fig.1) that in the presence of alkaline cations, GeO_2 stability field reduces with the increase of ionic radius of alkaline cations (Li, Na, K). The introduction of divalent cations leads to the further shift of GeO_2 stability limits towards the field of more acid solutions.
The obtained results are confirmed by experimental data. Thus, the crystal growth of GeO_2 (hex) under hydrothermal conditions is possible in weak alkaline and acid solutions on quartz seeds. The stable germanates of alkaline metals of different composition have been obtained in strong alkaline solutions.

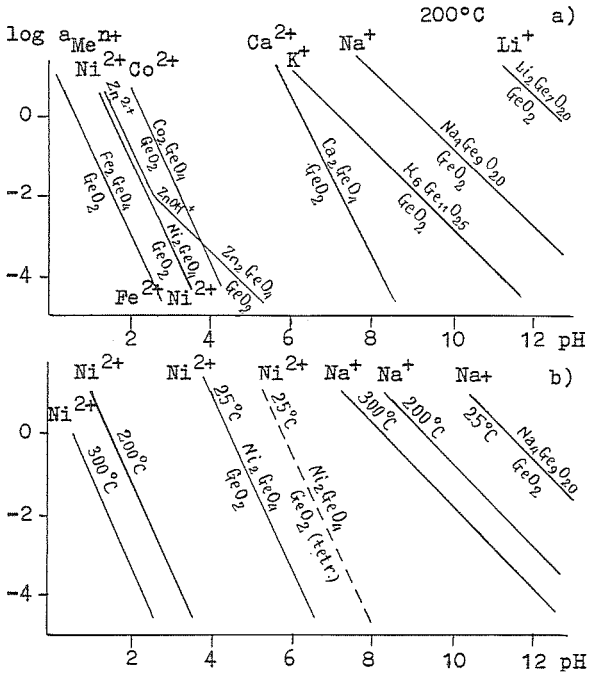

Fig.1 Phase equilibria in the systems GeO_2 – MeO – H_2O and GeO_2 – Me_2O – H_2O at 200°C (a) and 25, 200, 300°C (b).

07.1–8 CRYSTALLIZATION OF SODIUM RARE EARTH SILICATE AND GERMANATE CRYSTALS FROM FLUX. By V.A.Timofeeva and A.B.Bykov, Institute of Crystallography of the USSR Academy of Sciences, Leninsky pr.59, Moscow 117333, USSR.

Crystals of sodium rare earth silicates and germanates were first grown under hydrothermal conditions [1]. Some new crystals together with already known ones 0.5-1 cm in size have been grown from flux. The crystallization fields of $NaYSiO_4$, $NaYSiO_4 \cdot 1/4NaF$ (these crystals have been grown for the first time), $Na_3YSi_3O_9$, $Na_3YSi_4O_{12}$, $NaTRGeO_4$ (TR=Gd, Y, Lu), $Na_3GdGe_4O_{12}$ have been found. The phase equilibria in silicate and germanate flux systems Na_2O – TR_2O_3 – $SiO_2(GeO_2)$ – NaF – V_2O_5 – PbO have both similar and differing features. Therefore, the crystallization field of $NaTRGeO_4$ is the widest in the germanate system while $Na_3TRSi_3O_9$ and $NaTRSiO_4 \cdot 1/4NaF$ have the same particularity in the silicate system. The sodium fluoride does not enter the chemical formula of germanate crystals in contrast to the case of $NaYSiO_4 \cdot 1/4NaF$.

It should be noted that in our experiments the major attention was paid to the growth of $NaTRGeO_4:Nd^{3+}$ crystals since the preliminary spectral and luminescence investigations [2] raised the possibility of stimulated emission in these crystals.
The crystal growth method consists not only in nucleation on a platinum rod and the following growth of crystals by slow cooling of the solution but also in top-seeding growth combined with pulling.
Laser elements in the form of plane parallel plates 2 mm thick were made from the grown crystals measuring up to 1 cm. The results of the spectral and lasing experiments on these specimens allow to suggest that at a suitable geometry of the element continued laser action by pumping of Xe and Kr - lamps can be achieved.

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