ISSN 0869-2904

EXPERIMENT In Mineralogy Petrology Geochemistry Crystallography Geophysics Isotopy GeoSciences

2019 Volume **25** Number **1**

EXPERIMENT in GeoSciences

Mineralogy
Petrology
Geochemistry

Crystallography
Geophysics
Isotopy

Founded in **1991** by

INSTITUTE of

EXPERIMENTAL

MINERALOGY

Russian Academy of Sciences

EXPERIMENT IN GEOSCIENCES is the only journal in English that gives you the latest, most reliable information on advances in experimental mineralogy, petrology, geochemistry, crystallography and geophysics in Russia. The coverage of the journal includes:

- original research and review articles
- abstracts of scientific papers
- proceedings, abstracts and announcements of national and international conferences, symposia and workshop
- information about the leading experimental centers in Russia
- advertisement of new techniques and equipment

Institute of Experimental Mineralogy

Russian Academy of Sciences
142432 Chernogolovka
Academica Osip'yana str, 4,
Moscow region
Russian Federation

http://www.iem.ac.ru

TRANSLATED into ENGLISH by:
the authors

Kovalskaya T.N., Khanin D.A., Varlamov D.A., Kalinin G.M. Allanite synthesis in hydrothermal conditions. Preliminary data.

Institute of Experimental Mineralogy Russian Academy of Sciences tatiana76@iem.ac.ru

Abstract: This work is devoted to the experimental study of the formation of allanite in hydrothermal conditions and isomorphic substitution $Ca^{2+}\leftrightarrow Ce^{3+}$, $Si^{4+}\leftrightarrow Al^{3+}$, $Ca^{2+}\leftrightarrow Y^{3+}$, $Fe^{3+}\leftrightarrow Ce^{3+}$ and $Fe^{3+}\leftrightarrow Y^{3+}$ in it. Conducted 2 series of experiments on the synthesis at a temperature of 500-550 ^{o}C and a pressure of 4 kbar. Various silicate cerium and yttrium phases, including the epidote composition, were obtained in the products.

***Keywords**: epidote, allanite, hydrothermal conditions, experiment, cerium, ittrium, isomorphic substitution, allanite-(Ce), allanite-(Y)*

Minerals of the epidote group are widespread rock-forming and accessory minerals in many types of metamosotic rocks, as well as in a number of igneous and metamorphic rocks (Varlamov et al., 2019). They are a kind of indicators of geochemical processes that occur during the formation and change of a particular rock. The initial interest was caused by the discovery during the field work at the Tykotlov ore occurrence (Polar Urals) of samples of gallium containing allanite (Ce), in intergrowth with Ga epidote (Varlamov et al., 2011). Their joint finding and accretion indicates their simultaneous formation (Kovalskaya et al., 2019), and the unevenness in the redistribution of cerium and gallium on the unusual conditions of their formation. The authors carried out a series of experiments on the synthesis of Ga - epidote in a wide range of compositions at temperatures up to 500 °C and pressures up to 5 kbar. In order to recreate the conditions of formation of the allanite - (Ce) - epidote - (Ga) association and assess the distribution of components, in this work, attempts were made to synthesize allanite under similar conditions. For this purpose, steichometric helium mixtures of allanites of different composition - allanite- (Ce) and allanite- (Y) were prepared. Then the mixture was loaded into platinum ampoules with a diameter of 4-5 mm in the ratio of fluid / sample 1/10. Distilled water was used as a fluid. The experiments were carried out on a high-pressure gas installation with internal heating (UVGD-10000) at a temperature of 500 and 550 ° C and a pressure of 4-5 kbar. The only difference was that before holding at 500 °C and 550 °C and a pressure of 4 kbar, the reaction mixture was kept for 3 hours at a temperature of 1100 ° C and a pressure of 4 kbar. It was necessary to homogenize the mixture. Then, isobaric cooling to 500°C occurred. The duration of the experiments was 10 days.

As a result of the experiments, small intergrowths up to 50 μm, composed of split crystals of cerium-containing epidote, were obtained (Fig. 1).

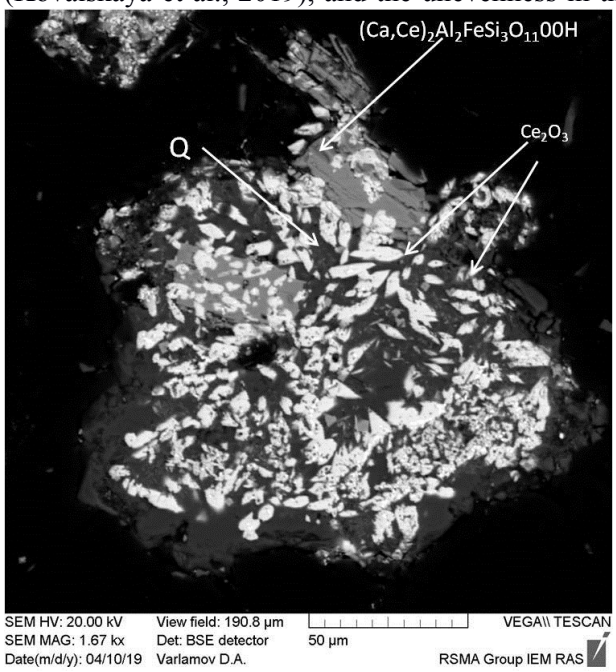

Fig. 1. Crystals of synthesized cerium epidote.

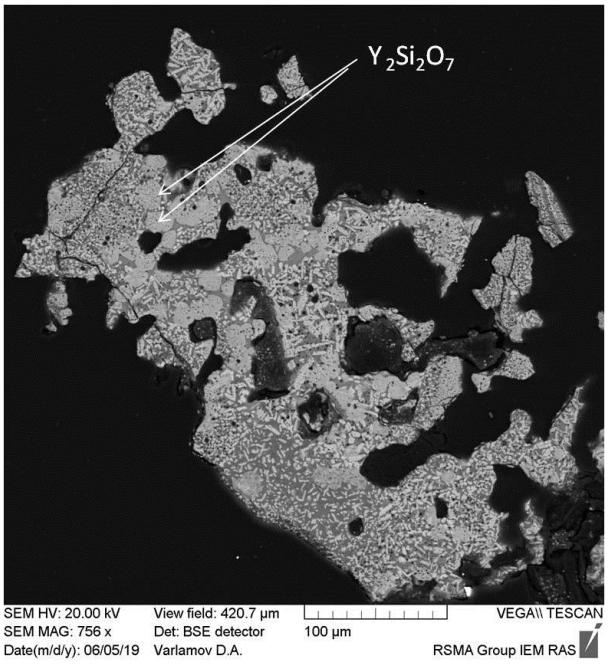

Fig. 2. Crystals of synthetic yttrialite.

These crystals partially grow together with quartz and Ce_2O_3; this experiment was carried out with the complete replacement of $Ca^{2+}\leftrightarrow Ce^{3+}$. The first series of experiments was carried out at a temperature of 550°C and a pressure of 5 kbar. Allanite disintegration similar to the epidote-Ga disintegration described in Kovalskaya et al. (2015) occurred in the products of these experiments. As a result, the formation of a phase with a stoichiometry of the composition corresponding to the formula $Ca_2Ce_2Si_2O_8$ and the phase $Ca_3Ce^{3+}{}_2[SiO_4]_3$,

corresponding in composition to the garnet was observed.

At a temperature of 500°C, the cerium is partially filled with position A, instead of Al. The content of Ce_2O_3 in this case reaches 8.6 wt.%, And Al_2O_3 - 33.2 wt.%. In general, at fairly low temperatures, calcium is almost completely replaced by cerium, as well as partial replacement of aluminum. With an even greater decrease in temperature, only calcium is replaced by cerium, as well as silicon by aluminum to compensate for the charges. At temperatures above 550 °C, a more stable anortite-like cerium phase is formed instead of epidote. In experiments with the replacement of $Ca^{2+} \leftrightarrow Y^{3+}$ at 500 ° C and a pressure of 4 kbar, the most stable phase is yttrialite of composition $Y_2Si_2O_7$ (Fig. 2). The obtained data indicate that, at given P-T parameters, cerium and yttrium silicates are stable, however, such conditions are not sufficient for the formation of allanites as the main phase. In some experiments at a temperature of 500°C, phases similar to allanites by stoichiometry were obtained, but most likely they are the final phases of crystallization. Work on the synthesis and study of allatites, as well as other phases in the system Ca-Ce-Y-Fe-Al-Si-O-H_2O will be continued.

References:

Varlamov D.A., Ermolaeva V.N., Chukanov N.V., Yanchev S., Vigasina M.F., Plechov P.Yu. (2019) New data on the chemical composition and Raman spectra of the minerals of the epidote supergroup. ZRMO, 1, 79-99 (in Russian)

Kovalskaya, TN, Varlamov, D. A., Kotelnikov, A. R., Kalinin, G. M. The possibility of gallium being incorporated into the structure of silicates and aluminosilicates. In Reports of the VIII International Symposium "Mineral Diversity - Research and Conservation" (2015), National Museum of the Land and People of Sofia, pp. 142–145. (in Russian)

Kovalskaya T.N., Varlamov D.A., Kotelnikov A.R., Chukanov N.V., Kalinin G.M. (2019) Hydrothermal synthesis of gallium epidote - an analogue of the phase Ca2Al2Ga (Si3O12) (OH) from Tykotlovsk gold-sulphide manifestation. Geochemistry, 10, in print. (in Russian)

Varlamov D., Soboleva A., Mayorova T., Kotelnikov A., Kovalskaya T. (2011) Abstr. of vi int. symposium "Mineral diversity - research and preservation", Sofia, Bulgaria, Earth and Man National Museum, 22

Nesterova V.A.[1,2], Setkova T.V.[2], Pushcharovsky D.Yu.[1], Balitsky V.S.[2], Borovikova E.Y.[1], Nekrasov A.N.[2], Bublikova T.M.[2], Kvas P.S.[1,2] Hydrothermal synthesis of gallium-, germanium bearing tourmaline's analogue.UDC 549.612

[1]Department of Geology, Lomonosov MSU, Moscow, [2]IEM RAS, Chernogolovka (v_nest.243@mail.ru)

Abstract. (Ga, Ge)-bearing tourmaline was synthesized in hydrothermal condition at temperature 600-650 °C and pressure of 100 MPa in solutions of boric acid on elbaite seed. The newly formed layer of tourmaline reaches a thickness of 50-100 microns in a direction of the third order axis. The content of Ga_2O_3 and GeO_2 is about 20 and 2 wt. % respectively. EMPA – analysis detected uniform gallium and germanium spreading. Raman spectroscopy confirmed the identity of the overgrown layer to the mineralogical group of tourmaline.

Keywords: *tourmaline, crystal growth, hydrothermal synthesis, gallium, germanium, aluminosilicate, borosilicate, Raman spectroscopy.*

Introduction. It is known that tourmaline is widely used in radio engineering because of its pyro and piezoelectric properties, as well as in in the jewelry industry due to great variety of its color. Since today, it was not possible to obtain synthetic crystals of tourmaline of sufficient size. Mainly natural samples of tourmaline are used for industrial purposes. Therefore, researches related to tourmaline's growth are very important nowadays. At the end of 2018 it was established (O'bannon et al., 2018) that the space group of tourmaline is R3m in crystals, subjected to pressure of 15.4 GPa, may be replaced by R3, first of all, due to distortion of silica oxide T_6O_{18} rings. By the example of a large group of minerals and synthetic crystals it was shown that changes in their structures under the influence of high pressures can be simulated chemically by introducing larger cations into their structure. In this case, ion radii ratio of the cation/anion will increase, and corresponding chemical deformations in structure can be considered similar to the high-pressure one. It is known that gallium and germanium in chemical properties are similar to aluminum and silicon respectively, but the ions size of Ga^{3+} and Ge^{4+} is more ($r Ge^{4+}/r Si^{4+}$=2.04; $r Ga^{3+}/r Al^{3+}$=1.17). In this regard, synthesis of tourmaline crystals in which gallium and germanium will isomorphically replace aluminum and silicon is of considerable interest. In addition to comparing structural characteristics of such crystals with the structural changes of tourmaline under high pressure, it can be assumed such crystals will have more pronounced pyro-and piezoelectric properties. Previously similar effect was already established by the example of Ge-rich quartz crystals (Balitsky et al., 2017).

Experimental methods. Crystal growth of Ga- and Ge-bearing tourmaline was performed in thermogradient hydrothermal conditions at a temperature of 600-650 °C and a pressure of 100 MPa in autoclaves made of Cr-Ni alloy. The previously developed method of tourmaline growth on seed was taken as a basis (Setkova et al., 2009; Setkova et al. 2011; Vereshchagin et al. 2016). Mixture of synthetic quartz and corundum fragments