HYDROTHERMAL RECONSTRUCTION OF CRYSTAL STRUCTURE OF PEGMATITIC ALLANITE

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INTRODUCTION

Allanite-(Ce) is a mineral of allanite subgroup belonging to epidote group with general formula $A_2M_3[Si_2O_7|SiO_4]O(OH)$ (Armbruster et al. 2006). It is characterized by a complex composition and large amount of different cations with large ionic radii such as REE, but also with variable content of radioactive elements such as Th and U. Another important characteristic of allanite-(Ce) is more or less pronounced metamict state. Numerous articles have been published on the subject of metamictization (Ewing 1987; 1994 Graham and Thornber, 1974).

Epidote group minerals are stable over a wide range of temperatures and pressures. They are typical metamorphic minerals, but also very common in igneous rocks and hydrothermal veins. They also occur in sediments as detrital heavy minerals (Franz & Liebscher 2004).

Very common method of restoring crystal structure is by heat treatment in different conditions, but always in dry atmosphere (Berman 1955). Heating of allanite-(Ce) yields a sudden collapse of crystal structure after initial recrystallization and decomposition to new phases (Bonazzi & Menchetti 1994). Besides, oxidation of some elements occurs (Fe^{2+} Fe^{3+}, Ce^{3+} Ce^{4+}) which aids formation of new phases (Bonazzi & Menchetti 1994).

Janeczek and Ebby (1993) are the only ones so far who have reported successful hydrothermal treatment and restored crystal structure of metamict gadolinite.

The goal of this work is to restore the crystal structure of allanite through recrystallization in hydrothermal conditions at low temperatures with preservation of OH^- in the crystal structure.

SAMPLE CHARACTERIZATION AND EXPERIMENTAL METHODS

Nine samples of allanite – (Ce) originating from different localities were analysed. Eight samples are black, four of which exhibit waxy and four of them glassy luster. One sample is olive – green in color, exhibiting waxy luster.

All samples were separated from visible impurities using a stereomicroscope. Samples used for analyses were either crushed to powder (for X-ray powder diffraction analyses) or in the form of small polished chips (for EDS and WDS analyses).

All samples used for X-ray powder diffraction were annealed in air for 24h at 650°C and 1000°C.

Two samples have been hydrothermally treated in a microwave digestor Microwave Anton Paar 3000 with rotor 16HF - 100. Samples, along with distilled water, were put in a cuvete

and heated for 20 min in the temperature interval 200-260°C.

Three samples were treated in autoclave Perkin – Elmer. The samples and distilled water were put in a teflon container (5 ml of water for 0.2 g of sample). The container was closed in the autoclave and the system was heated in several occasions: the sample 1202 was heated for 2 and 5 hours at 150°C; the samples 1204 and 1205 were heated for 2 and 24 hours at 150°C.

Powder samples were examined by X-ray powder diffraction using PHILLIPS PW 3040/60 X'Pert PRO diffractometer with Cu$K\alpha$ radiation upon 45kV and 40 mA. Step size was 0.02° with a counting time of 2 s per step. Diffraction patterns were analyzed by X'Pert High Score Plus programme (Panalytical 2004).

Samples for electron microprobe analyses were small polished chips. Only natural unheated samples were analysed and examined for homogeneity.

EDS analyses were performed by SEM+EDS Oxfords instruments Vega TS5136 MM, Tescan and WDS analyses by CAMECA SX100 microprobe. ED spectra were examined using Oxford instruments programme INCA 200.

The analyses of crystallite size and strain of the sample 1202 was performed using X'Pert High Score Plus programme and CeO_2 as a standard.

RESULTS

X-ray pattern of all unheated samples show high background as well as small and wide diffraction peaks which indicate that samples are metamict but not completely amorphous (fig. 1). With annealing samples at 650°C in air during 24 hours they recrystallize (fig. 1) what is evidenced by appearance of new diffraction peaks all of which belong to allanite-(Ce). These diffraction peaks are sharper and with higher intensities compared to those of unheated samples. The crystal structure of the samples annealed at 1000°C, in air, collapses and a variety of new phases occur, like hematite, cerianite, feldspar, uraninite, thorite and britholite-like phase (fig. 1). Appearances of uraninite and thorite have not been recorder in literature yet, probably due to a small content of U and Th in mixture of many different phases.

X-ray patterns of hydrothermally heated samples exhibit evidence of recrystallization, also as samples annealed at 650°C.

Samples hydrothermally heated in autoclave during the period of 5 hours exhibit higher rate of recrystallization than those heated during 2 hours at the same temperature (fig. 2). This is evident through appearance of diffraction peaks with higher intensities and more narrow diffraction peaks. There is no indication of new phases in either case. Samples heated during 24 hours did not show much improvement in recrystallization at the same temperature.

Samples hydrothermally treated in the microwave digestor also exhibit recovery of the structure without appearance of new phases (fig. 2), similarly as samples treated in autoclave.

Changes in crystallite size and strain in the crystal structure of hydrothermally treated samples occur already at low temperatures and pressures and in short period of time (table 1). In comparison with the recovery of structure of annealed samples, recrystallization through hydrothermal treatment is relatively faster and at substantially lower temperatures.

Table 1. Crystallite size and structure strain of one of the samples

Sample	Crystallite size (Å)	Strain (%)
1202	74.6	0.590
1202_ak_1	94.1	0.479
1202_ak_2	167.1	0.489

EDS and WDS analyses have showed heterogenous composition of the samples but in most cases the composition with following elements was detected: Si, Al, Fe, Ca, Mg, REE (La, Ce) and O. Ratios of REE/Ca are from 0.08 to 0.82 and of Ce/La from 1.6 to 2.1. All results point to allanite-(Ce). Numerous other cations with various radii and charges such as Ti, Na, K, Ba, Y, Nd, Pr were detected in the structure along with radioactive nuclides Th and U. Representative WDS analysis of sample 1201 (in wt. % oxides): 30.481 SiO_2, 15.703 Al_2O_3, 5.19 FeO, 12.00 Fe_2O_3, 9.562 CaO, 0.800 MgO, 0.468 MnO, 0.414 TiO_2, 12.056 Ce_2O_3, 5.961 La_2O_3, 0.207 Y_2O_3, 3.597 Nd_2O_3, 0.486 Sm_2O_3, 1.195 Pr_2O_3, 0.219 Gd_2O_3 and 0.74 ThO_2 yields the formula:

$$(Ca_{0.98}Mn_{0.02})_{\sum 1.00}(Ce_{0.42}La_{0.21}Nd_{0.12}Pr_{0.04}Sm_{0.02}Y_{0.10}Gd_{0.01}Th_{0.02}Mn_{0.02})_{\sum 0.87}(Al_{0.70}Fe^{3+}_{0.1}{}_6Mg_{0.11}Ti_{0.03})_{\sum 1.00}Al(Fe^{2+}_{0.30}Fe^{3+}_{0.70})_{\sum 1.00}[SiO_4|Si_2O_7](O_{0.90}F_{0.10})(OH)$$

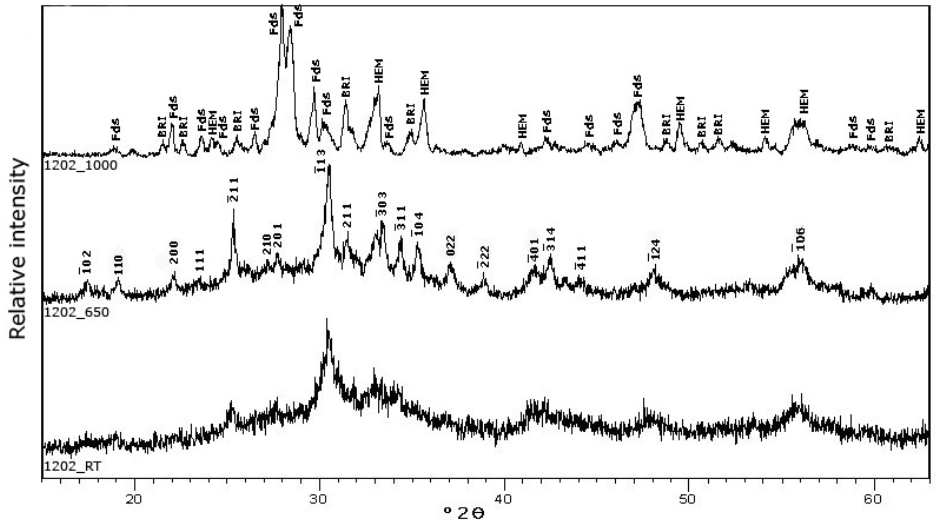

Figure 1- Comparison of unheated and samples annealed at 650 and 1000°C
(Fds-feldspar; HEM-hematite; BRI- britholite-like phase)

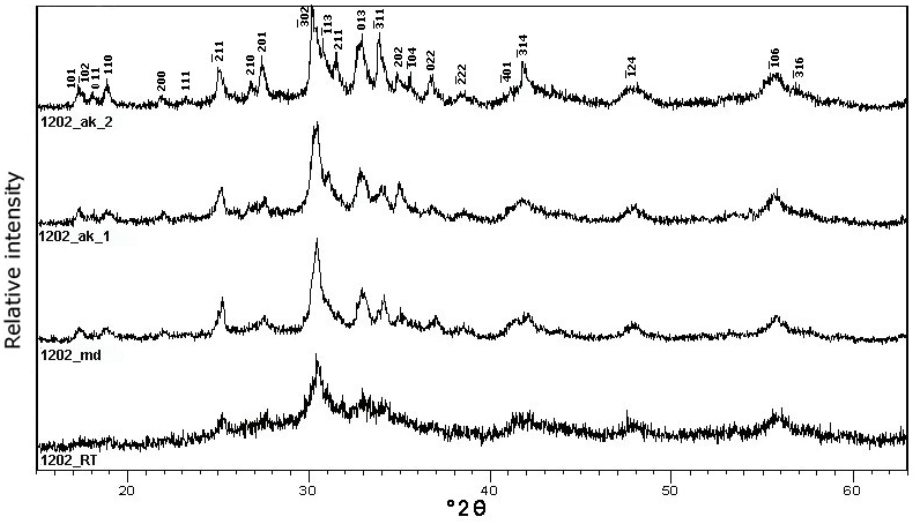

Figure 2 - Comparison of unheated (1202) and samples treated in autoclave for 2 (1202_ak_1) and 5 (1202_ak_2) hours and microwave digestor (1202_md_1)

DISCUSSION

Due to the important content of structural water, the recovery of crystal structure of allanite is impossible to accomplish by annealing in the air at temperatures higher than 850° C (Berman 1955). Such a heating results in formation of new phases (Bonazzi & Menchetti 1994). Parallel to confirmation of previously observed phases uranium and thorium oxides are also observed during experiments in this work.

Janeczek & Ebby (1993) suceeded in restoring crystal structure of gadolinite, by hydrothermal treatment. This is now successfully applied in the case of allanite. With increasing the time of hydrothermal treatment at the same temperature (150°C) from 2 to 5 hours, the rate of recrystallization was higher and without traces of new phases (fig. 2). Samples hydrothermally treated for 24 hours did not show much improvement in restoring crystal structure in comparison with those treated at shorter intervals nor the rate of recrystallization was higher than between samples heated for 2 and 5 hours.

Strain and crystallite size analyses support the statement that recrystallization of sample treated for 5 hours is higher than for sample treated for 2 hours. Slight increase in strain in the case of longer hydrothermal treatment is possibly due to partial oxidation or because oxydation potential was not controlled. This process could also affect the expected recrystallization during 24 hours treatment.

It is important to point out that the crystal structure already recovers at relatively low temperatures and pressures. By analyzing X-ray patterns of hydrothermally heated samples for 2, 5 and 24 hours it is important to notice that temperature has more significant effect on the recrystallization than the time does.

EDS and WDS analyses showed that chemical composition of all samples

is consistent with the composition of allanite-(Ce) and none new-formed phased were observed.

Radioactive decay of Th and U is believed to be main reason for metamictization. But as the cause of metamictization it is important to take into consideration complex composition of samples and different ionic radii of elements present in structure. It is probable that they make the crystal structure unstable and susceptible to metamictization.

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