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THE SWELLING OF Ge-TAENIOLITE SERIES MICAS WITH WATER

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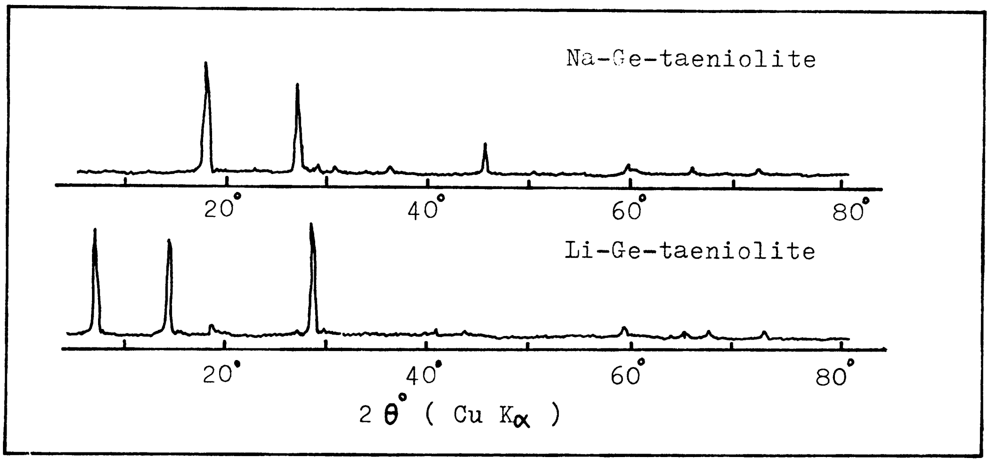
Germanium substituted analogues of Na-taeniolite and Li-taeniolite, i.e. , Na-Ge-taeniolite $NaMg_2Li(Ge_4O_{10})F_2$ and Li-Ge-taeniolite $LiMg_2Li(Ge_4O_{10})F_2$ were found to be expanded by water . However , the hydration tendencies of these Ge-taeniolites were found to be somewhat weaker than those of the corresponding silicon substituted analogues .

Although detailed investigations on the swelling of Na-taeniolite $NaMg_2Li(Si_4O_{10})F_2$ 1) and Li-taeniolite $LiMg_2Li(Si_4O_{10})F_2$ 2) were reported by the authors previously , studies on the corresponding germanium substituted analogues of them , i.e. , Na-Ge-taeniolite $NaMg_2Li(Ge_4O_{10})F_2$ and Li-Ge-taeniolite $LiMg_2Li(Ge_4O_{10})F_2$, have been lacking . Recently we could substantially synthesize both these germanium taeniolites , and investigated the water uptake and dehydration processes of them extensively , using high temperature X-ray diffraction , TG and DTA methods . Crystallochemical similarity between these silicates and germanates was observed as was expected . The hydration tendencies of these two series micas were also compared .

Mixtures of 1 mol-NaF , 1 mol-LiF , 2 mol-MgO , and 4 mol-GeO_2 , which were special grade reagents , were melted in a sealed platinum crucible at 1250 °C for 5 hrs , and then crystallized into Na-Ge-taeniolite at the cooling rate of 3 °C/min. . Li-Ge-taeniolite was also synthesized by the same method from the corresponding mixtures , which consisted of 2 mol-LiF , 2 mol-MgO and 4 mol-GeO_2 . The crystal aggregates of Na-Ge-taeniolite thus obtained were powdered , and purified by the sedimentation in distilled water . On the other hand the crystal aggregates of Li-Ge-taeniolite , which were immersed into distilled water , were bloated into a stable suspension ,and then purified by centrifugation . The samples thus purified were dried at 130 °C and then studied by the X-ray diffraction method . The X-ray diffraction patterns for Na-Ge-taeniolite and Li-Ge-taeniolite are shown in Fig.1 . The formation of both Ge-taeniolites was also ascertained by chemical analysis.

Fig. 2 shows the changes of X-ray diffraction patterns in the (001) reflection region of Na-Ge-taeniolite caused by the water uptake into the interlayer sites , when the samples are wetted by distilled water . The hydrated state A in Fig. 2 seems to be a so-called one-layer hydrated type , because the clearance space , i.e. , the difference between the interlayer distance d (001) of anhydrous Na-Ge-taeniolite (9.97 Å) and that of the hydrated one (12.68 Å) , is 2.71 Å , which is nearly equal to the OH-O distance (2.76 Å) in ice crystal 3) .

Fig. 1 X-ray diffraction patterns of Na-Ge-taeniolite and Li-Ge-taeniolite . Li-Ge-taeniolite is already hydrated absorbing water vapour in air .



The crystalline state of Na-Ge-taeniolite corresponding to maximum swelling is one-layer type , and a higher hydrated type is never obtained , whereas that of Na-taeniolite is two-layer type . The interlayer distance of one-layer hydrated Na-Ge-taeniolite is distinctly larger than that (12.26 Å) of one-layer hydrated Na-taeniolite , a fact to which the difference between ionic radius of Si^{4+} (0.40 Å) and that of Ge^{4+} (0.50 Å) may be responsible . This one-layer hydrated type of Na-Ge-taeniolite is unstable , and is easily dehydrated at room temperature and humidity .

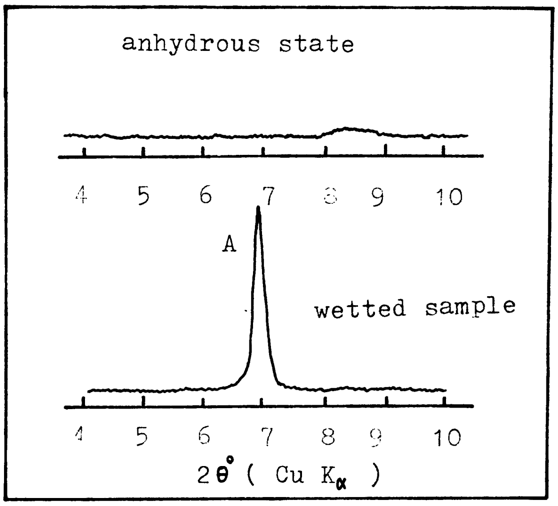
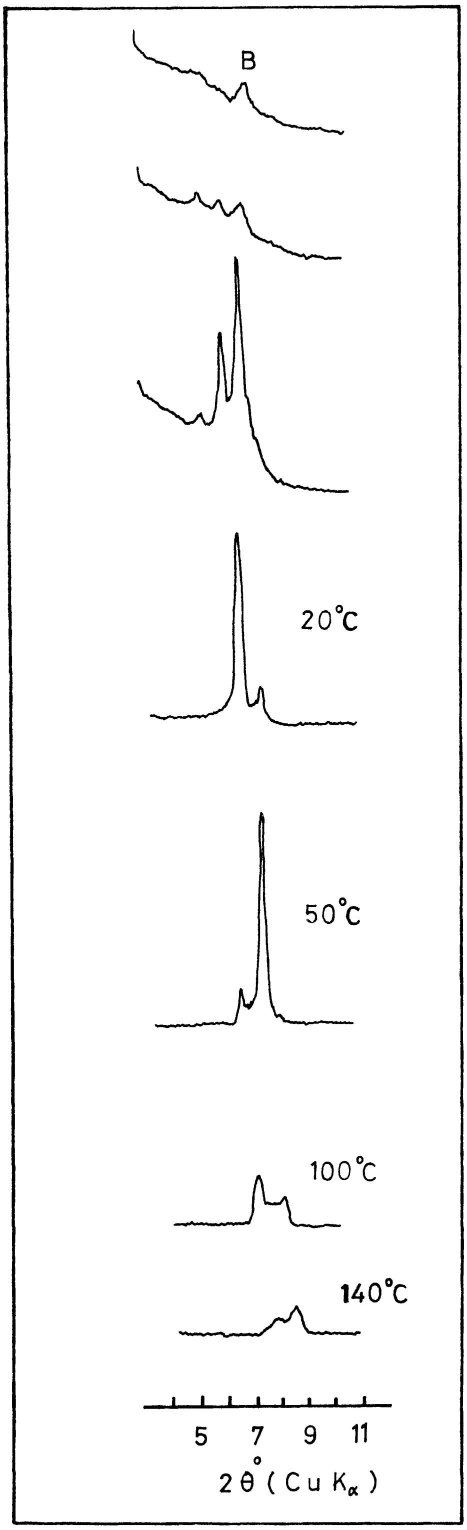


Fig.2 Changes of X-ray diffraction patterns in the (001) reflection region of Na-Ge-taeniolite caused by water uptake .

Fig. 3 shows the changes of X-ray diffraction patterns in the (001) reflection region of Li-Ge-taeniolite caused by the decrease of water content . Li-Ge-taeniolite gel showed no diffraction peak except a weak one at 14.2 Å (B in Fig. 3) , whereas Li-taeniolite gel shows a weak one at 15.2 Å . It seems that the band scattering at the low diffraction angle in Fig.3 is caused by random water uptake into the interlayer sites of Li-Ge-taeniolite . It is obvious from this diffraction pattern that nearly free swelling occurs in Li-Ge-taeniolite - water system as in Li-taeniolite - water system . The interlayer distances of (001) for predominant crystalline swelling states of Li-Ge-taeniolite , are 10.6 Å (monohydrate state) , 12.5 Å (one-layer type) , 14.2 Å (trihydrate state) , and 15.5 Å (two-layer type) , while those of the corresponding states of Li-taeniolite are 10.4 Å , 12.2 Å , 13.9 Å , and 15.2 Å respectively . As shown before for Na-Ge-taeniolite and Na-taeniolite ,

Fig. 3 Changes of X-ray diffraction patterns in (001) reflection region caused by decreasing water content of Li-Ge-taeniolite .

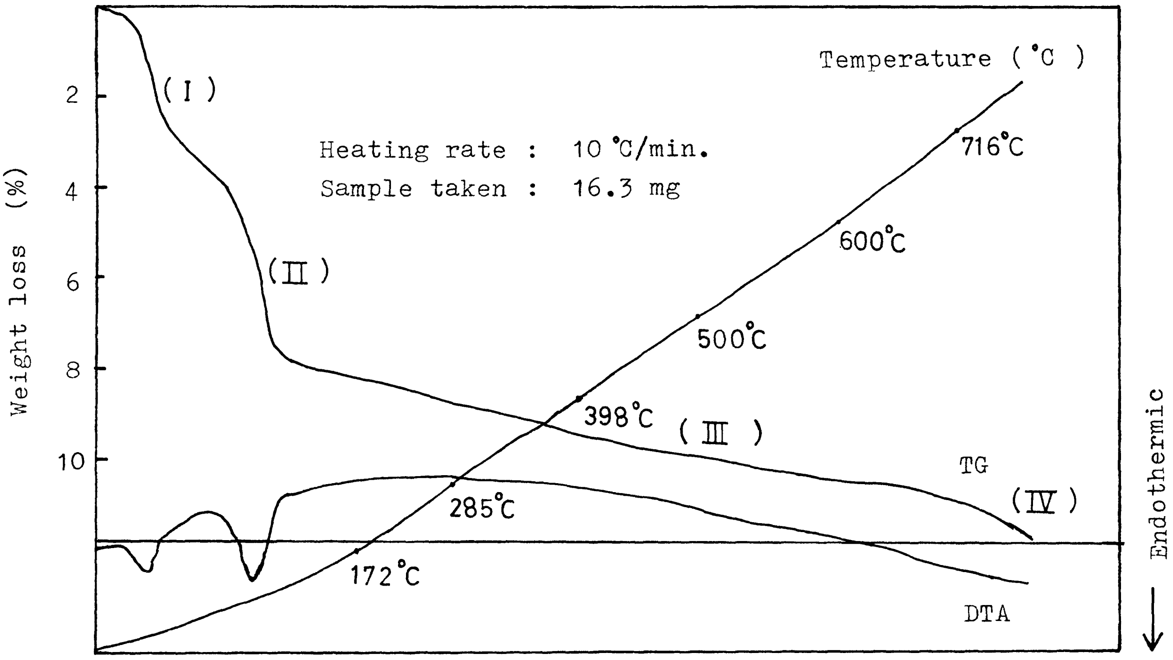


the interlayer distances of hydrated Li-Ge-taeniolites are also slightly longer than those of corresponding hydrated Li-taeniolites .
The dehydration processes of hydrated Li-Ge-taeniolites are almost the same as those of hydrated Li-taeniolites , but the formers are dehydrated at slightly lower temperature than the latter .
This increased dehydration tendency of hydrated Li-Ge-taeniolites is also demonstrated by the DTA endothermic peak temperature ; i.e. , the peak temperature is 123 °C for one-layer hydrated Li-Ge-taeniolite , which is lower than 136 °C for the same hydrated state of Li-taeniolite .

These slightly easier dehydration or weaker hydration tendencies of Ge-taeniolites in comparison with those of corresponding taeniolites may be explained by the difference between the configurational stability in the interlamellar region of Ge-taeniolites and that of taeniolites .
The sodium ion and lithium ion can not establish contacts with surface oxygens of silicate or germanate layers as effectively as the potassium ion does , because of their small ionic radii .
Thus there will be a close approach between interlayer Li^+ or Na^+ ion and Si^{4+} or Ge^{4+} ion , so that the repulsion between these cations will be considerable . But the degree of this repulsion will be substantially smaller for Ge-taeniolites than for taeniolites , because Ge^{4+} ion is larger than Si^{4+} ion , i.e. ,interionic distances between Ge^{4+} and Li^+ or Na^+ ion in Ge-taeniolites are longer than those between Si^{4+} and Li^+ or Na^+ ion in taeniolites .
So it will be reasonable to expect that the hydration of Ge-taeniolites will occur more mildly than that of taeniolites . It also seems that these effects , in combination with large hydration energies of interlayer Li^+ and Na^+ ions , are the predominant reasons why Ge-taeniolites can swell with water .

The TG curve for hydrated Li-Ge-taeniolite (14.2 Å phase) was recorded by a thermobalance . It is obvious from Fig. 4 that the TG curve consists of four stages , the last one (Ⅳ) being due to the thermal decomposition of the sample . Thus the dehydration occurs in three stages .

Fig. 4 TG and DTA curves of trihydrated Li-Ge-taeniolite



The first stage (I) in the TG curve is due to the dehydration process from 14.2 Å phase to 12.5 Å phase , in accordance with the high temperature X-ray diffraction studies . The second stage (II) can also be ascribed to the dehydration process from 12.5 Å phase to 10.6 Å phase . The third stage (III) on the weight loss curve is then attributed to the dehydration process from 10.6 Å phase to anhydrous Li-Ge-taeniolite . The total weight loss attains 10.6 % , which is nearly the same value as 9.80 % of the calculated value of 14.2 Å phase (trihydrate state) , chemical composition of which can be reasonably expressed as $LiMg_2Li(Ge_4O_{10})F_2\cdot3H_2O$. The weight losses of the second stage and the third one are 3.5 % and 3.0 %, respectively . From these results 12.5 Å phase and 10.6 Å phase can be expressed as $LiMg_2Li(Ge_4O_{10})F_2\cdot2H_2O$ and $LiMg_2Li(Ge_4O_{10})F_2\cdot1H_2O$, respectively , because the theoretical value based on the chemical composition shown above is calculated to be 3.27 % for each stage . The weight loss of hydrated Li-Ge-taeniolite is fairly small in comparison with hydrated Li-taeniolite , because of its larger molecular weight .

Thus the similarity and the differences between Ge-taeniolites and taeniolites are demonstrated . From the swelling characteristics , crystal structures and chemical compositions , hydrated Li-Ge-taeniolite and Na-Ge-taeniolite might be reasonably called as Ge-fluor-hectorite .

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