

Studies on the Stability of the Radioactive Minerals at High Temperature

By

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Abstract

Monazite lattice is found to be stable up to the temperature higher than those at which zircon, gadolinite and allanite lattices are broken down.

Introduction

The radioactive minerals are apt to be transformed into metamict state.

The term "metamict state" is somewhat ambiguous. The writers give to the term a definition as follows: the metamict state is that which shows itself only in radioactive minerals, and in which state the original crystallinity is reduced to some extent and in the extreme case to glassy state.

It is interesting, however, that monazite in the metamict state has not been found, notwithstanding its high content of *Th*. The writers¹⁾ studied, in 1954, on allanites with Norelco X-ray diffractometer and obtained diffraction patterns of the minerals which were in the various stages of the metamict state, from almost completely in a crystalline state to completely in a glassy state. From the patterns it was found that the allanite lattice was transformed into metamict state, being accompanied with lattice expansion.

In view of the experimental result, the writers thought that the metamictization might be no more than the phenomenon of expansion followed by melting. Of course, the expansion and melting were not understood in the sense that each of them extends over all portions of the substance uniformly and simultaneously, but in the sense that, subdividing the substance into small statistical portions, in the earlier stage of the metamictization the expanded portions prevail and in the later stage the melted portions. The expansion was conceived to be due to the atoms which, knocked by the alpha-particles, left their normal positions and occupied their places interstitially; and the melting to be due to the heat generated at the time when the alpha-particles, at the end of their travels, or the recoil atoms came into collisions with atoms.

The writers²⁾ examined, in the same year, the effects of the heat-treatment

on allanites which were in the metamict state, but not in its extremity, at the temperature of several hundred degrees and in the vacuum, expecting that the effects might be revealed in the lattice contraction and the increase of crystallinity. The results were just as expected. The same results were obtained with gadolinite.

According to the writers' view of the metamictization, why monazite is not transformed into metamict state may be due to its high melting temperature, and if so, the lattice expansion must take place in monazite too. The writers also examined the spacings of monazites which differed in localities, and found slight differences in the spacings among them. The effect of the heat-treatment on the specimens was revealed in the lattice contraction only, the specimen greater in spacings showing more remarkable contraction. The lattice contraction in this case was, of course, very slight compared with those of allanite and gadolinite. The writers reported in the previous paper that the effect of the metamictization on monazite was revealed in the lattice expansion only.

Recently, the writers measured, although only in a qualitative way, the temperatures at which crystal lattices were broken down on some radioactive minerals. The results are all favourable to the writers' view of the metamictization.

Experimental

Specimens submitted to the experiments were allanite from Anak-ub, Korea, gadolinite from Arendal, Norway, monazite from Nogizawa-mura, Japan and zircon from Burma. These specimens were those in the least metamict state among the respective ones in the writers' hand. Zircon from Mineyama-chô, Japan was also submitted to the experiment. The specimen was more, however by a little, metamictized than that from Burma. The degree of the metamictization was examined by the X-ray diffraction patterns. In the X-ray diffractometry, Geiger counter X-ray diffractometer of North American Philips Co. was used, radiating $Cu-K\alpha$ with Ni -filter, throughout.

Each of the crystals of allanite, gadolinite, monazite and zircon from Japan which amounts to about 0.5 g in weight was kept in a crucible without cover, made of Al_2O_3 (98.5%) together with the seger cones. The crucibles were put into the furnace and they were heated on the outside by the oxyacetylene flame, with care so that the flame might not touch the specimens. The temperature in the crucibles were thus measured by the seger cones as well as by means of the optical pyrometry. The specimens were heated up to ca 1800°C and taken out of the furnace and quenched in the air.

In this experiment, allanite melted completely and soaked into the crucible. So did gadolinite too, but the bottom of the crucible in which gadolinite had been put was bitterly eroded. Zircon presented an appearance of slight melting with

several pinholes on the surface, while monazite showed only a slight change in colour. The zircon and monazite heated to ca 1800°C were crushed into powders and submitted to the X-ray diffractometry. In Fig. 3 are shown the diffraction patterns of the heated and the unheated zircon for comparison and in Table 3 the spacings calculated from the peaks of the diffraction patterns. In Fig. 5 are shown the diffraction patterns of the heated and the unheated monazite and in Table 4 the spacings calculated from the peaks of the diffraction patterns. Spacings were calibrated by the method of the least squares using silicon diffraction patterns. From the tables, therefore, are excluded the spacings of the peaks of the diffraction patterns whose values of 2θ are less than 25.65°. Considerations to the results will be given together with those obtained in the subsequent experiments.

The crystals of allanite, gadolinite, monazite and zircon were crushed into powders and formed into cones out of the powders as large as the seger cone. Zircon submitted to this experiment was that from Burma. Each of the cones was stood in the crucible without cover, made of the same material as in the preceding experiment together with the seger cones and the crucibles were heated in the same manner said above. The measurements of the temperatures at which cones of the specimens curve were also carried out in the same way. As soon as the cone of the specimen curved, the crucible was taken out of the furnace and quenched in the air. The cones were crushed into powders and submitted to the X-ray diffractometry. The spacings were calculated from the peaks of the diffraction patterns. They were calibrated in the same method.

Allanite

The cone of allanite from Anak-ub, Korea has been found to curve at the temperature of ca 1400°C. In Fig. 1 is shown the diffraction pattern of the cone curved, and are also shown the diffraction pattern of the unheated specimen and that of the heated at ca 800°C for two hours in the vacuum for comparison.

In Table 1 are shown the spacings whose values of 2θ are in a range from 25.65° to 35.5°. The indices of the spacings are calculated with lattice constants determined by UEDA.³⁾

Table 1. Spacings of allanite from Anak-ub, Korea

<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (800°C)	<i>d</i> (1400°C)
201	3.239 Å	3.240 Å	3.258 Å
			3.193
			3.135
			3.037
			2.947
$\begin{pmatrix} 11\bar{3} \\ 302 \end{pmatrix}$	2.916	2.909	

Table 1. (cont.)

<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (800°C)	<i>d</i> (1400°C)
020	2.872	2.870	2.870 2.840
211	2.816	2.819	
(013 300)	2.709	2.704	2.709 (2.669 2.662)
31 $\bar{1}$	2.619	2.617	
202	2.554	2.554	2.518

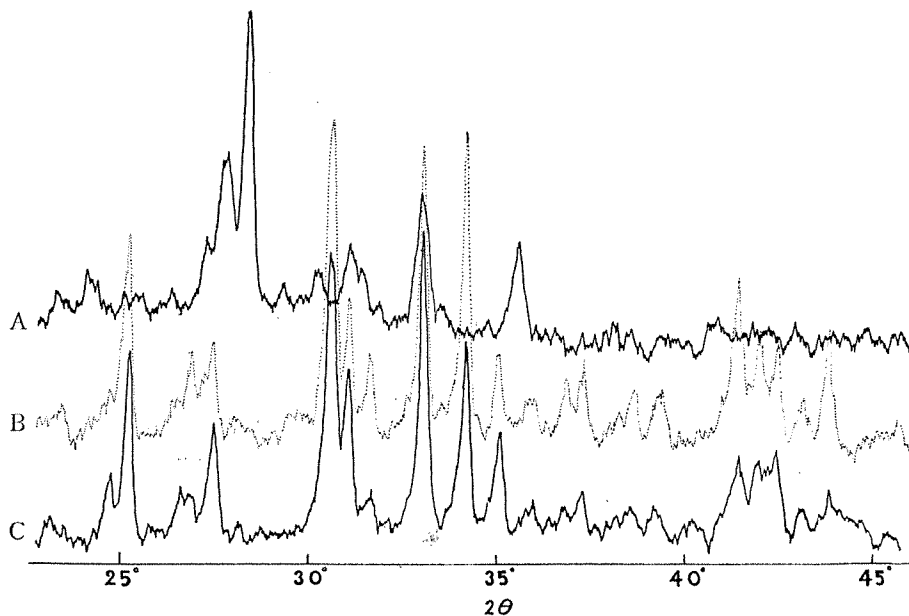


Fig. 1. Diffraction patterns of allanite from Anak-ub, Korea. *Cu-Kα* (with *Ni*-filter), 35*kV*, 15*mA*. Scan speed 1° per minute, scaler 4, time constant 8, chart speed ½ inch per minute, slits 1°-0.006"-1°. A. Heated to ca 1400°C. B. Heated at ca 800°C for two hours in the vacuum. C. Unheated.

From this result allanite lattice has proved to break down at the temperature below 1400°C.

Gadolinite

The cone of gadolinite from Arendal, Norway has been found to curve at the temperature of ca 1500°C. In Fig. 2 is shown the diffraction pattern of

the cone curved, and are also shown the diffraction pattern of the unheated specimen and that of the heated at ca 800°C for two hours in the vacuum for comparison.

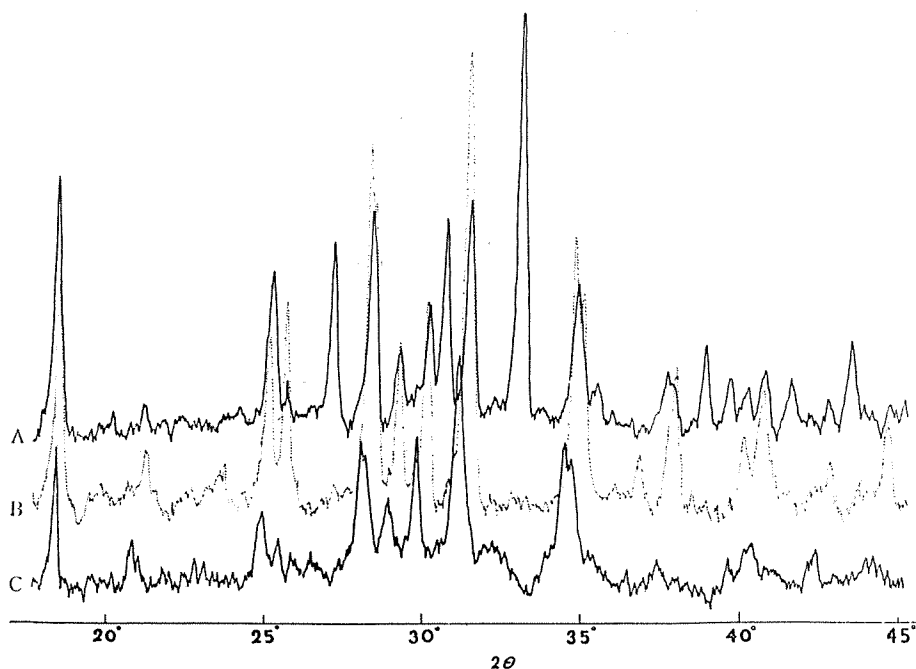


Fig. 2. Diffraction patterns of gadolinite from Arendal, Norway. *Cu-K α* (with *Ni-filter*), 35*kV*, 15*mA*. Scan speed 1° per minute, scaler 4, time constant 8, chart speed ½ inch per minute, slits 1°-0.006"-1°. A. Heated to ca 1500°C. B. Heated at ca 800°C for two hours in the vacuum. C. Unheated.

In Table 2 are shown the spacings whose values of 2θ are in a range from 25.65° to 45°. The indices of the spacings are calculated with lattice constants determined by ITO and MORI.⁴⁾

Table 2. Spacings of gadolinite from Arendal, Norway

<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (800° C)	<i>d</i> (1500° C)
			3.262 Å
112	3.171 Å	3.139 Å	
112	3.153	3.125	3.129
013	3.082	3.041	3.037
120	2.984	2.952	2.947
			2.897

Table 2 (cont.)

<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (800° C)	<i>d</i> (1500° C)
($\begin{smallmatrix} 12\bar{1} \\ 121 \end{smallmatrix}$)	2.864	2.834	2.826
			2.694
($\begin{smallmatrix} 11\bar{3} \\ 113 \end{smallmatrix}$)	2.597	2.568	2.561
($\begin{smallmatrix} 12\bar{2} \\ 122 \end{smallmatrix}$)	2.580	2.554	
			2.519
031	2.464	2.436	
($\begin{smallmatrix} 200 \\ 014 \end{smallmatrix}$)	2.400	2.366	2.378
			2.307
			2.267
032	2.270	2.243	2.236
130	2.240	2.212	2.205
			2.163
($\begin{smallmatrix} 11\bar{4} \\ 114 \end{smallmatrix}$)	2.128	2.108	2.110
			2.074
($\begin{smallmatrix} 13\bar{2} \\ 132 \end{smallmatrix}$)		2.024	2.024

From this result gadolinite lattice has proved to be persistent even at the temperature of ca 1500°C, although with other phase.

To the spacings of the phase here produced can be given indices as follows, assuming that the phase is isometric. Doing so, $a=9.23 \text{ \AA}$ is obtained.

<i>d</i>	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	<i>hkl</i>
3.262 Å	0.056	0.056	220
2.897	0.071	0.070	310
2.694	0.082	0.084	222
2.307	0.112	0.112	400
2.267	0.116	0.119	($\begin{smallmatrix} 410 \\ 322 \end{smallmatrix}$)
2.074	0.138	0.140	420
1.921	0.161	0.167	422
1.718	0.201	0.202	($\begin{smallmatrix} 520 \\ 432 \end{smallmatrix}$)
1.616	0.227	0.223	440

Zircon

The cone of zircon from Burma has been found that it does not curve even at the temperature of ca 1950°C. In Fig. 3 are shown the diffraction patterns of the cone heated to that temperature and the unheated specimen for comparison.

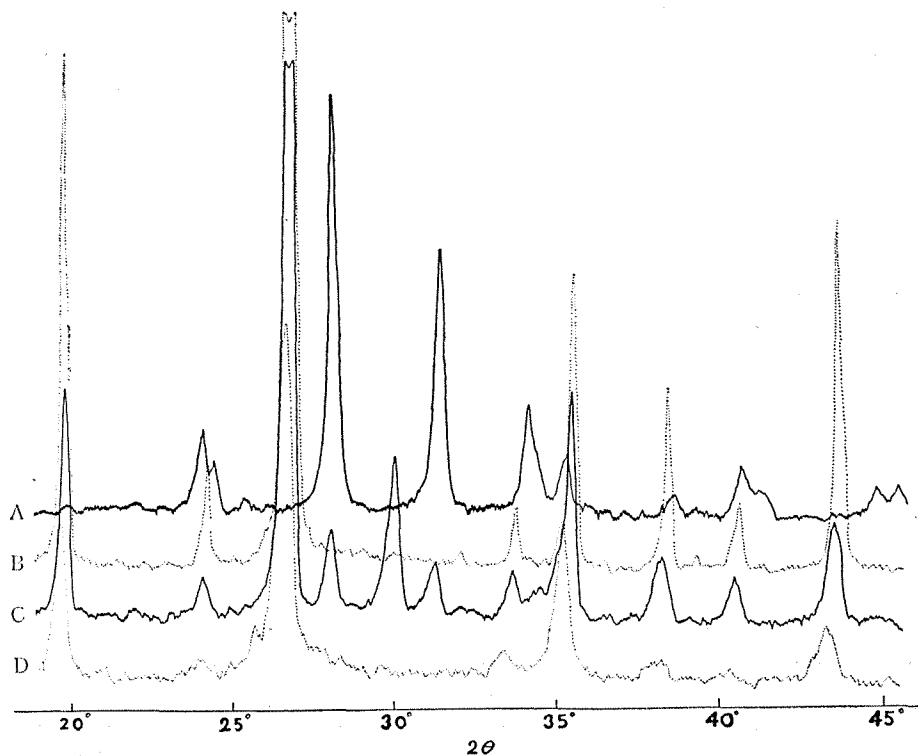


Fig. 3. Diffraction patterns of zircon from Mineyama-chō, Japan and Burma. *Cu-Kα* (with *Ni*-filter), 35*kV*, 15*mA*. Scan speed 1° per minute, scaler 4, time constant 8, chart speed ½ inch per minute, slits 1°-0.006"-1°. A. Heated to ca 1950°C (from Burma). B. Unheated (from Burma). C. Heated to ca 1800°C (from Mineyama-chō, Japan). D. Unheated (from Mineyama-chō, Japan).

In Table 3 are shown the spacings whose values of 2θ are in a range from 25.65° to 46°.

Table 3. Spacings of zircon from Mineyama-chō, Japan and Burma

From Mineyama-chō, Japan			From Burma			Baddeleyite	
<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (1800°C)	<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (1950°C)	<i>hkl</i>	<i>d</i>
200	3.334 Å	3.319 Å	200	3.306 Å		11 $\bar{1}$	3.18 KX
		3.171			3.171 Å		
		2.968				111	2.85
		2.855			2.843		

Table 3. (cont).

From Mineyama-chô, Japan			From Burma			Baddeleyite	
<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (1800°C)	<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (1950°C)	<i>hkl</i>	<i>d</i>
211	2.680	2.655	211	2.649	2.624	020	2.63
					2.545	(200 102)	2.55
112	2.543	2.524	112	2.519			
220	2.342	2.342	220	2.335		(012 120)	2.34
					2.330		
202	2.233	2.221	202	2.217		211̄	2.23
					2.215	121̄	2.20
					2.184		
301	2.086	2.073	301	2.063		112	2.01
					2.020	202̄	2.00
					1.992		

In Table 3 are inserted the spacings of baddeleyite which are introduced from the cards of the X-ray diffraction data (A. S. T. M.). Comparing the spacings of the products of heating to ca 1800°C and ca 1950°C with those of unheated zircon and of baddeleyite, it is seen that at the temperature of ca 1800°C zircon coexists with baddeleyite and probably one more phase and that at the temperature of ca 1950°C zircon lattice is completely broken down. The indices of the spacings of zircon are calculated with lattice constants determined by VEGARD³⁾ and those of baddeleyite with lattice constants determined by RUFF

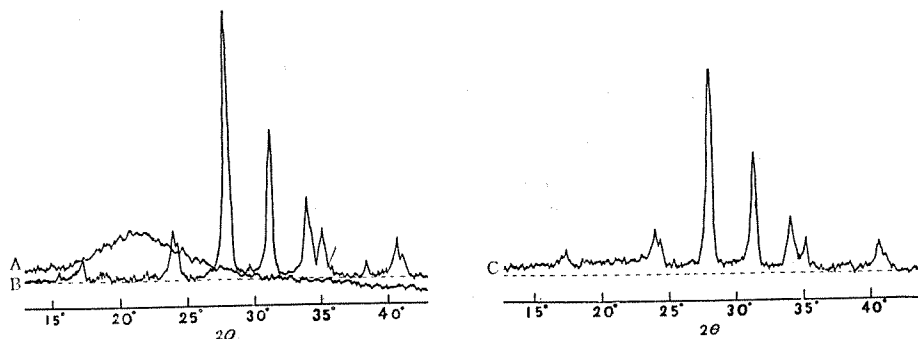


Fig. 4. Diffraction patterns of (A) commercial silica glass, (B) commercial baddeleyite, (C) mixture of the above two components (Mol. ratio, 1 : 1). *Cu-Kα* (with *Ni*-filter), 35*kV*, 10*mA*. Scan speed 2° per minute, scaler 8, time constant 4, chart speed 1/2 inch per minute, slits 1°-0.006"-1°.

and EBERT⁶⁾.

Free silica is presumable to be present in the product which is yielded by heating zircon to 1950°C, notwithstanding no suggestion of its being in the diffraction pattern. With regard to this point, following patterns shown in Fig. 4 are very instructive.

Monazite

The cone of monazite from Nogizawa-mura, Japan has also been found that it does not curve at the temperature of ca 1950°C. In Fig. 5 are shown the diffraction patterns of the cone heated to that temperature and the unheated specimen for comparison.

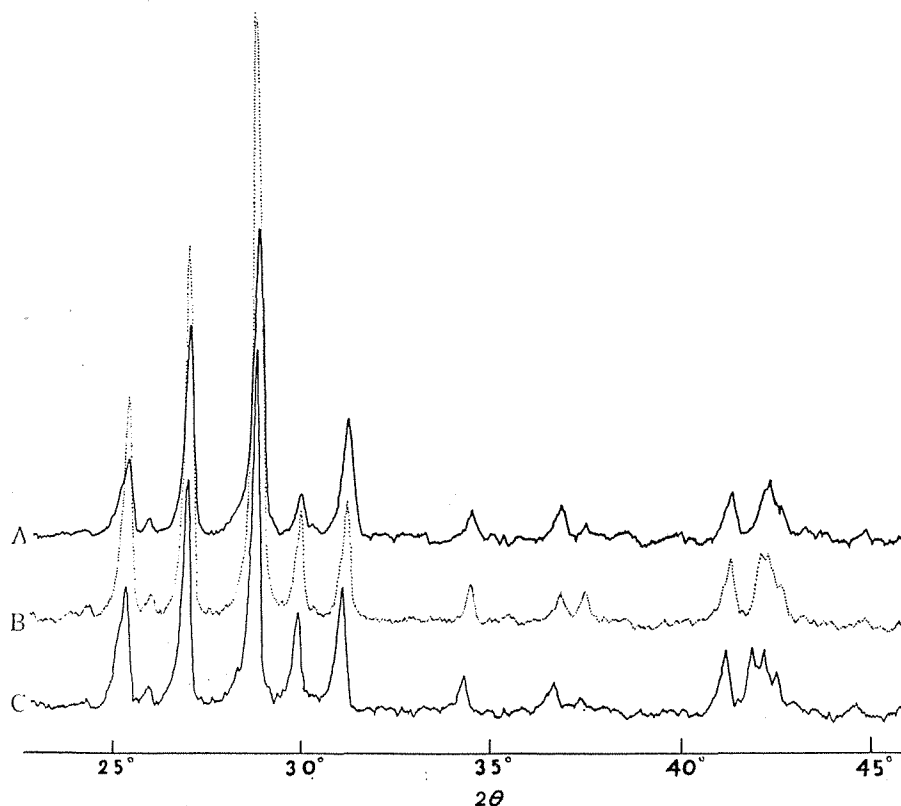


Fig. 5. Diffraction patterns of monazite from Nogizawa-mura, Japan. *Cu-K α* (with *Ni*-filter), 35kV, 15mA. Scan speed 1° per minute, scaler 8, time constant 8, chart speed ½ inch per minute, slits 1°-0.006"-1°. A. Heated to ca 1950°C. B. Heated to ca 1800°C. C. Unheated.

In Table 4 are shown the spacings whose values of 2θ are in a range from 25.65° to 45° calculated from the diffraction patterns. The indices of the spacings

are calculated with lattice constants determined by UEDA⁷⁾.

Table 4. Spacings of monazite from Nogizawa-mura, Japan

<i>hkl</i>	<i>d</i> (unheated)	<i>d</i> (1800°C)	<i>d</i> (1950°C)
200	3.294 Å	3.282 Å	3.282 Å
120	3.092	3.082	3.082
012	2.870	2.860	2.855
(112 112)	2.604	2.595	2.595
	2.447	2.433	2.433
220	2.400	2.394	2.392
(113 031)	2.186	2.181	2.181
212	2.151	2.140	
	2.138	2.131	2.131
310	2.122	2.116	2.117
311	1.962	1.957	1.957
(230 222)	1.895	1.889	1.891
032	1.873	1.866	1.866
320	1.860	1.853	1.854
	1.765	1.755	1.756
040	1.748	1.744	1.744
(123 312)	1.740	1.733	1.733
(140 041)	1.690	1.686	1.687

From this result it is seen that monazite lattice is evidently persistent even at the temperature of ca 1950°C.

Discussion

Many authors have hitherto observed the effect of the heat-treatment at high temperature on zircon, however, no one has ever observed on allanite, gadolinite and monazite so far as literatures are concerned. STACKELBERG⁸⁾ and his coworkers observed that slightly metamictized zircons (sp. gr., 4.32 and 4.17) heated at 1450°C for 6 hours gave better diffraction patterns and increased in specific gravities. These authors⁹⁾ later observed that bitterly metamictized zircons (sp. gr., 3.972 and 3.945) heated at 1450°C for 6 hours recovered their own lattices and also increased in specific gravities. Similar experiments were carried out by KOSTYLEVA¹⁰⁾¹¹⁾ and PABST¹²⁾. In the present investigation, the cone of zircon has not curved at the temperature of ca 1950°C, nevertheless the product of heating to ca 1800°C has proved to consist of zircon and other phases and that to ca 1950°C has proved no presence of zircon. Zircon lattice is, therefore,

likely to be broken down at the temperature in the neighbourhood of 1800°C. According to the literature,* the melting point of zircon is $2430^{\circ}\pm 20^{\circ}\text{C}$. The temperature, however, must probably be the eutectic point of baddeleyite (melting point $2690^{\circ}\pm 20^{\circ}\text{C}$) with SiO_2 in the molecular ratio of 1 : 1.

The cone of allanite has curved at the temperature of ca 1400°C and the product of heating to that temperature has proved absence of allanite. The cone of gadolinite has curved at the temperature of ca 1500°C and the product of heating to that temperature has proved to consist of gadolinite and other phase. Accordingly, allanite lattice must be broken down at the temperature lower than 1400°C, and gadolinite lattice is likely to be broken down at the temperature in the neighbourhood of 1500°C.

The cone of monazite has not curved even at the temperature of ca 1950°C and the product of heating to that temperature has proved to be monazite. Unfortunately, the writers could not carry on the experiment at a higher temperature, none the less, it is found that monazite lattice is stable at the temperature higher than those at which zircon, gadolinite and allanite lattices are broken down. The writers conceive that why monazite is not transformed into metamict state is due to the fact that it is stable up to higher temperature.

SLATER¹³⁾ has summarized the theoretical consideration with respect to the radiation damage of the lattice. According to him, the kinetic energy of the alpha-particle at the time when it is projected is ca 6×10^6 ev. During the time that the particle has high energy, it displaces atoms, knocking on them, and produces interstitial atoms and vacant sites. The energy of the alpha-particle at the end of the travel is dropped to ca 4×10^4 ev. and that of the recoil atom is ca 10^5 ev. These energies are dissipated in the collision with atoms. The kinetic energy passed on to the atoms is so great as to correspond to an exceedingly high temperature, of the order of several hundred thousand degrees. HURLEY and FAIRBAIRN¹⁴⁾ have stated, in this connection, that even if the energy is shared by one ev. to the neighbouring atoms the energy of each atom still corresponds to more than the boiling point even for a refractory material.

At the present time, the energy of the alpha-particle, at the end of the travel, and that of the recoil atom are usually presumed to be exceedingly great. Accordingly, the fact that certain radioactive minerals are not transformed into metamict state is apt to be considered to be due to the easiness of their recrystallization. It may be true in the case of the secondary minerals, such as autunite, however, may be inapplicable to the case of the primary minerals, such as monazite. If the reason why monazite is not transformed into metamict state is the easiness of its recrystallization, lattice expansion would not take place in that mineral. The writers are convinced that the energies said above are corresponding to the temperature in the neighbourhood of the

* Handbook of Physical Constants, Geol. Soc. Am., Special Papers, No. 36 (1954).

melting point of monazite at most.

Just as the writers finished writing the present paper, they received the Mineralogical Abstract, Vol. 12, No. 10. According to the Abstract, KARKHANAVALA and SHANKAR¹⁵⁾ have recently found a partly metamictized monazite. The discovery is indeed favourable to the writers' view of the metamictization.

Acknowledgment

The writers wish to express their sincere thanks to Dr. T. ITO, Professor of Tokyo University and Kyoto University for his kindness in granting them the use of the Norelco X-ray diffractometer. The writers are also indebted to Messrs. S. TODA and N. TODA of Toda Laboratory of the Refractory Materials who afforded facilities for their experiments.

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