An X-ray Study of the Reaction of Calcium Oxide and Calcium Chloride in the Decomposition of Monazite

K. N. Kartha

This paper outlines a review of the structure of monazite, methods f its decomposition and results of an X-ray study of monazite before nd after treatment with a mixture of calcium oxide and calcium loride, in connection with the separation of phosphate from monazite.

THE uses of rare earth oxides, thorium oxide, and phosphates, essential components of monazite in the refractory field are already well established.[1–7] It was considered worthwhile to find out n easy method to decompose monazite. Chemical nvestigations proved that if monazite was heated with mixture of calcium oxide and calcium chloride, and the heated mass is leached with dilute acids, phoshates could be separated. A paper was earlier ublished by the author[8, 9] about these findings. To upport the efficiency of separation of phosphate, in he above method, an X-ray study of the monazite efore and after treatment with a mixture of calcium xide and calcium chloride was taken up.

Structure of monazite

Monazite is primarily an anhydrous phosphate of are earths, such as cerium, lanthanum and didyminum with small and varying amounts of thorium oxide usually ranging from 3 to 9 per cent.[10] It is believed o be commonly an accessory constituent of gneissoid ocks and is found widely distributed in India, Australia, Japan, U.S.A. and Brazil.

Typical analyses of the Indian monazite done in he American Institute of Mining and by Sydney J. Johnstone[11, 12] give the general idea of the components of monazite (Table I). It was originally beieved that thorium existed as thorium phosphate in monazite, like the other rare earth phosphates. But it was disproved and a plausible explanation of the structure of monazite was given by A. W. Wylie.[13] According to him, thoria which is usually present, is held during crystallisation of the phosphate from its parent magma because of its favourable ionic size. To compensate for the increased cationic charge of the thorium ion, the resulting lattice must possess an mperfect structure in which some of the sets of equivaent cationic positions are only partially occupied. Thus, it may not be unreasonable to suppose that some of the impurities like silica, lime, urania, etc. occupy position in the lattice of the mineral.[14] This view accommodates the analysis of monazite as given by Tateo Ueda[15] viz., Ce_2O_3 55·41% ; P_2O_5 26·69 ; ThO_2 11·73 ; SiO_2 2·73 ; CaO 1·11 ; Fe_2O_3 1·49 ; Al_2O_3 0·09 ; and H_2O 0·15 per cent.

Karkhanavala, Tateo Ueda et al reported that X-ray study of natural monazite[16, 17, 18] showed that monazite remained in the metamict shape and the petrological studies confirmed this result. The cell parameters according to them are a_o 6·66A°, b_o 6·98A°, C_o 6·32A° and B 76° 38.
The space group is P_2/n (C_25h).

TABLE I

Analysis of monazite

Constituents	Analysis of Sydney Johnstone[12]	Analysis of Tateo Ueda[15]	Analysis of American Inst. of Mining[11]	Author's analysis[8]
ThO_2%	10·22	11·73	8·1	8·31
Ce_2O_3%	31·90		30·6	62·19
La_2O_3%	28·00		15·7	
Nd_2O_3%			10·5	
Pr_2O_3%			2·9	
Y_2O_3%	0·46		1·0	
Sm_2O_3%				
Al_2O_3%	0·17	0·09		
Fe_2O_3%	1·5	1·49		2·02
CaO%	0·20	1·11		
SiO_2%	0·90	2·73	2·4	
P_2O_5%	26·82	26·69	26·2	26·98
Loss on ignition%	0·46	0·15		

Methods of decomposition of monazite

The usual method of chemical analysis of monazite is by dissolving it in hot conc. sulphuric acid, followed by separating the thorium sulphate and the rare earth sulphates in ice cold water from the insolubles. Thorium is then separated from the solution by precipitating with potassium iodate, and phosphorus by ammonium molybdate. Thorium can also be separated as double sulphate or double carbonate. The commercial process of decomposing monazite is by alkali treatment.[19] Very fine monazite powder is treated with sodium hydroxide and digested at high temperature. The trisodium-phosphate formed, is separated and the thorium and rare earths are dissolved in conc. hydrochloric acid. Thorium oxide is preferentially precipitated and separated by adding ammonium carbonate taking advantage of the solubility of the rare earth carbonates. Some improvement in the method has been recently suggested by the Soviet Atomic Energy Establishment.[20] By this, monazite is crushed and treated in a hot ball mill with 75% sodium hydroxide for 4 hours and the insolubles in the batch are subjected to a second treatment with more sodium hydroxide in the heated ball mill.

A reference to the literature shows that breaking up of phosphorus bearing materials has been carried out in America by heating them with some fluxes.[21]

Mr. K. N. Kartha, Junior Research Fellow, National Metallurgical aboratory, Jamshedpur.

Natural phosphate rocks, such as Florida-land-pebbles, are similar to apatite and monazite.[14] There are a number of patents taken in America in which it is claimed that heating phosphate rock with different compositions of silica alone or with silica and alkaline earth compound brings about reactions by which phosphate is rendered citrate soluble. Tromel[22] proposes by adding CaO and SiO_2 to phosphate rock calcining at about 1,450°C to produce a compound $9\,CaO.\ P_2O_5\text{–}3\,SiO_2$ or $16\,CaO.\ P_2O_5.SiO_2$. Rothe[23] has tried the same experiment with alkali oxide, with salts like potassium sulphate, alkali chloride, silica, calcium or magnesium carbonate at 900°C in the presence of steam. Wiborgh[24] proposed heating intimate mixtures of finely ground phosphate rock and an alkali metal hydroxide or carbonate, to bright redness in a suitable furnace, until a sintered or semi-fused mass is obtained. Waggman and Easterwood Henry[25] have reported that while the same general principles are followed in all of these processes, the mode of procedure and proportions of the several ingredients used are varied by the different inventors. There also appears to be a wide difference of opinion regarding the chemical reaction involved. Investigation to separate phosphate from monazite, was taken up and the following method was found feasible.[8, 9]

Powdered monazite was mixed with an equal quantity of quicklime and half the quantity of calcium chloride. The mixture was heated to 800°C, cooled and leached with dilute sulphuric acid. The phosphate alone came into solution which was filtered, separated, and converted into super phosphates. It was also found that by a first treatment with dilute hydrochloric acid, the phosphate could be separated, and by a second treatment with conc. hydrochloric acid the residues could be dissolved, from which, thorium oxide could be separated. The efficiency of the process in separating phosphate and rare earths was studied by X-ray analysis.

EXPERIMENTAL PROCEDURE

Experiment I

Natural monazite was physically purified by passing through an isodynamic separator. It was powdered to −200 mesh. A very fine capillary glass fibre was uniformly coated with a thin layer of Canada balsam and the monazite powder was smeared over it. The fibre was rolled between two glass plates to make it uniformly coated with monazite powder. A Debye-Scherrer photograph of this sample was taken using filtered CrK_α radiation generated by a Raymax rotating anode type machine at 30 kV and 40 ma and a 6 cm Unicam 525 camera. The sample was exposed for a period of 9 hours and the film was developed for 5 minutes. The diameter of the various diffraction rings was measured and the intensity of the lines was visually judged. The d-values were calculated for comparison with the standard index card No. 4-0612 published by the A.S.T.M. and also with the results published by other workers[16] (Table II) (Fig. 1).

Experiment II

With a view to compare the effects of heating monazite *(i)* without any addition, *(ii)* with calcium oxide and *(iii)* with a mixture of calcium oxide and calcium chloride, the following samples were prepared:

(i) Monazite sand powdered to −200 mesh (2·5 gm) *(ii)* Monazite sand powdered to −200 mesh (1·25 gm) was mixed thoroughly in an agate mortar with 1·25 gm of calcium oxide. *(iii)* 1 gm of powdered monazite (−200 mesh) was mixed with 1 gm of calcium oxide and then one ml. of fifty per cent solution of calcium chloride. The materials were thoroughly mixed and dried.

The three samples were heated in a "globar" electric furnace to a temperature of 770°–800°C, and soaked at that temperature for two hours. These were later on cooled and powder diffraction X-ray pictures of samples I and II were taken. Sample No. III contained unreacted calcium chloride. So the sample was

TABLE II

d-values from the X-ray photo of natural monazite

Line	Exptl. data		Standard card No. 4-0612		Extracts from values got by other workers[16]		Remarks
	d-value	Intensity	d-value	Inty.	d-value	Inty.	
1	3·482	W			3·50	M	
2	3·462	V.W.	—	—	—	—	Within experimental error, the values got agree with the Standard Card and data published by other workers.
3	3·272	S	3·31	70			
4	3·080	S	3·09	100			
5	2·958	W	2·99	20			
6	2·856	S	2·88	70			
7	2·614	V.W.	2·61	20			
8	2·444	V.W.	2·45	30			
9	2·182	S	2·19	40			
10	2·128	S	2·14	60			
11	1·963	S	1·97	50			
12	1·865	S	1·88	60			
13	1·738	S	1·75	60			
14	1·690	S	1·70	40			
15	1·613	W	1·61	10			
16	1·540	W	1·54	40			
17	1·469	W	—		1·47	M	
18	1·339	S	—		1·34	M.S.	
19	1·282	S	—		1·28	M.S.	
20	1·236	S	—		1·23	M.S.	
21	1·191	S	—		1·20	W	
22	1·171	S	—		1·17	V.W.	
	I		II		III		

I. Chromium radiation
II. Copper radiation
III. Do
W.=Weak
V.W.=Very Weak
S.=Strong
M.=Moderate
M. S.=Moderately strong.

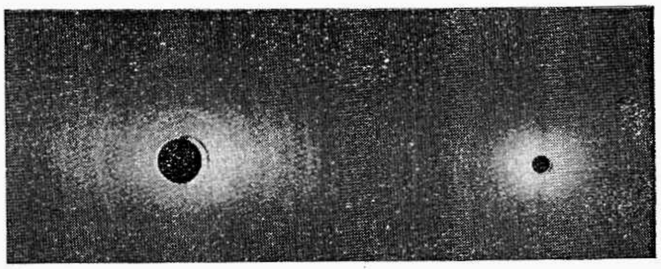

Fig. 1.

X-ray picture of natural monazite.

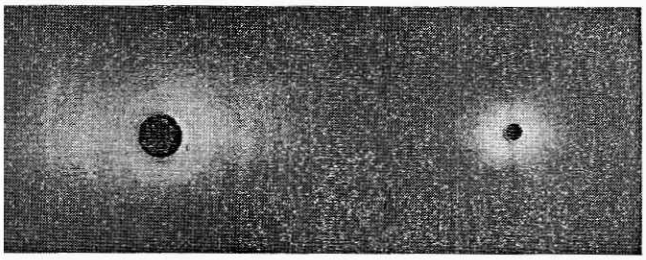

Fig. 2.
X-ray picture of heated monazite

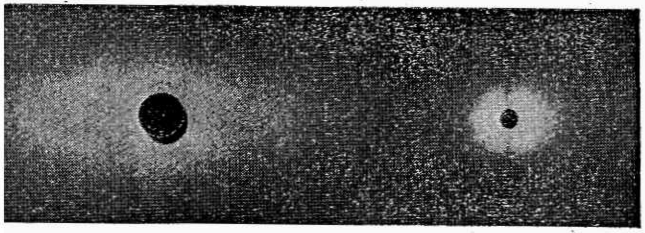

Fig. 3.
X-ray picture of monazite and calcium oxide heated.

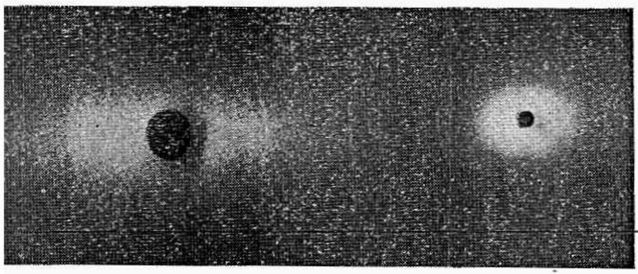

Fig. 4.
X-ray picture of a mixture of monazite, calcium oxide and calcium chloride heated.

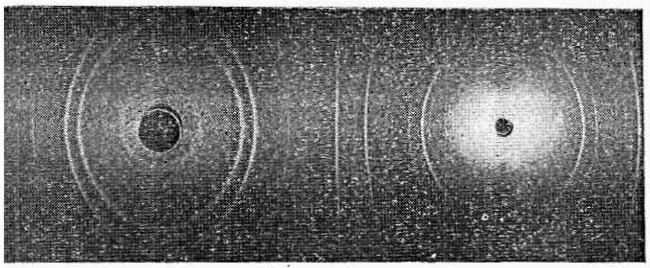

Fig. 5.
X-ray picture of residues after separation of the phosphates.

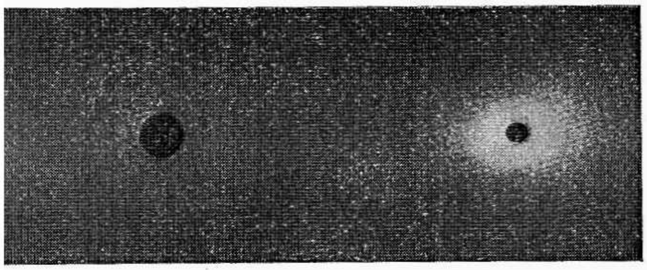

Fig. 6.
X-ray picture of phosphates separated from monazite.

powdered well again, and put in water, and boiled. The solution was filtered and washed with hot water till the residue became free of chloride, which was tested with a silver-nitrate solution. The powder was dried and X-ray photograph was taken (Figs. 2, 3, 4). The d-values of all the samples were calculated and tabulated in Table IV.

Experiment III

The sintered product obtained after heating sample III was washed and the residue was then leached with dilute ten per cent hydrochloric acid and boiled for five minutes in the same way as described in a previously published paper[9]. The solution was cooled and filtered and the residue was washed free of chlorides and dried. Figure 5 shows the X-ray photo of this powder. To the filtrate from the above, ammonium chloride solution was added and the phosphate was precipitated by adding ammonium hydroxide. The precipitate was washed free of chlorides, dried and immediately filled in a capillary tube and sealed and its X-ray photo was taken (Fig. 6). The d-values of the above two photos are tabulated in Table V.

Results and discussion

Table II and Fig. 1 show that almost all the lines and d-values calculated therefrom, agree with those of the standard card. D-value of the lines which could not be compared with standard card, were compared with those already published[16] by Karkhanavala and others. Table III gives a comparison of the d-values of natural monazite and heated monazite. The results show that there is apparently no change in the d-values of the heated monazite excepting that some more lines could be clearly seen, the d-values of which also agree with those reported by Karkhanavala.[16] Thus it is seen that the monazite does not undergo any decomposition by heating up to 800°C (cf Figs. 1 and 2). A slight elongation of the lattice is reported by T. Ueda[26] to result when monazite is heated about 1960°C. The d-value of all the samples investigated have been compared with those of heated monazite rather than natural monazite as all samples have been heated under identical conditions. Table IV gives a comparison of the values obtained by heating monazite with calcium oxide alone and with a mixture of calcium oxide and calcium chloride. No change was observed to result due to heating with calcium oxide alone. The additional lines found may be due to conversion of CaO to calcium hydroxide (by absorption of moisture during the preparation of sample for the X-ray examination) d-values of which tallied with those furnished in the standard. When absorption of moisture was minimised by enclosing the powder in a sealed glass capillary, CaO lines were obtained in the photograph. But lines 2, 5, and 8 in Column II of Table IV relating to Fig. 3 show that these do not appear to arise from either monazite or calcium hydroxide. Line 2 may indicate the presence of calcium phosphosilicate, 5 and 8 of cerium phosphate and perhaps confirm the earlier suggestions[8,9] that calcium oxide alone could only decompose 2·41% of phosphate, leaving the remaining monazite unaffected. The d-values obtained from the photograph (Fig. 4) definitely show that monazite reacts when heated with a mixture of calcium oxide and calcium chloride. In Column III of Table IV relating to Fig. 4, lines of the mixture of the oxide of thorium and cerium, the various oxides of rare earth elements and calcium phosphate can be seen. Lines with

TABLE III

Comparison of the d-values of natural monazite and heated monazite

Line no.	Natural monazite		heated monazite		from ref. 16		Remarks
	d-values	Intensity	d-values	Intensity	d-values	Intensity	
1	3·482	W	3·479	W	3·50	M	
2	3·462	V.W.	3·382	W	3·33	70	Standard Card 4-0612
3	3·273	S	3·283	S	3·28	S	
4	3·080	S	3·071	S	3·09	V.S.	Almost all the d-values of the heated monazite agree with those of natural monazite and data published by other workers.
5	2·958	W	2·979	W	2·97	W	
6	2·856	S	2·843	S	2·86	V.S.	
7	2·614	V.W.	2·594	W	2·60	M	
8	2·444	V.W.	2·419	W	2·40	V.W.	
9	2·182	S	2·191	S	2·19	M	
10	2·128	S	2·130	S	2·14	S	
11	1·963	S	1·961	S	1·97	S	
12	1·865	S	1·900	W	1·90	M	In the heated monazite lines 2,7,12,14, 15,21 and 22are new.
13	1·738	S	1·867	S	1·87	S	
14	1·690	S	1·798	V.W.	1·81	V.W.	
15	1·613	W	1·757	S	1·75	S	
16	1·540	W	1·736	S	1·72	M	
17	1·469	S	1·690	S	1·71	W	
18	1·339	S	1·603	W	1·61	M	
19	1·282	S	1·537	S	1·54	M	
20	1·236	S	1·466	S	1·47	M	
21	1·191	S	1·370	V.W.	1·37	M	
22	1·171	S	1·341		1·34	M.S.	
23			1·330	S	1·33	M.S.	
24			1·279	S	1·28	M.S.	
25			1·233	S	1·23	M.S.	
26			1·191	W	1·186	V.W.	
27			1·17	S	1·17	V.W.	

W.= Weak
V.W.= Very Weak
S.= Strong
V.S.= Very Strong
M.= Moderate
M.S.= Moderately Strong.

the d-values 3·479 (weak), 2·843 (strong), 1·680 (strong), 1·603 (weak), 1·233 (strong), and 1·17 (strong) found in Fig. 2 and Table II are seen without much change in Fig. 4 and Table IV also. This can be interpreted as showing the presence of some unreacted monazite and is in agreement with the results got by wet analysis as has been already published[9]. In the first treatment of the flux, only 26·11 out of the original 26·9 per cent of phosphate present in monazite can be separated. In other words, the efficiency of separation in the first leaching is 97%. The second treatment practically eliminates the remaining three per cent. A decomposition of some of the rare earth oxide also appears possible from an examination of the lines with d-values 3·04, 2·30, 3·15, 2·75, 1·95, etc., experiments about which are in progress. Table V shows the d-value of the residue got after separation of phosphate, and that of the phosphate fraction. The monazite residue after separating the phosphate contains a mixture of the oxides of thorium and rare earth along with a little undecomposed monazite and the d-values obtained from its photo compare with the standard card values. The lines in Fig. 6 are only a few and they appear to be due to calcium phosphate. As the attempt was only to separate the phosphate from monazite by this method, and also to avoid the presence of excess of acid and calcium chloride found in the filtrate, calcium phosphate was precipitated from filtrate. The precepitate was ignited and its X-ray picture was taken.

From the results obtained, the following inferences are drawn :

(i) Monazite when heated alone up to 800°C does not undergo any change.

(ii) Not many changes take place when monazite is heated either with calcium oxide or calcium chloride.

(iii) Decomposition takes place when monazite is heated with a mixture of calcium oxide and calcium chloride.

Comparison of the d-value of heated Mzt, Mzt+CaO, Mzt+CaO+CaCl$_2$

Line No.	I		II					III					IV
	Heated Mzt		Mzt+CaO		Standard Card No.		Inference	Mzt+CaO+CaCl$_2$		Standard Card No.		Inference	Remarks
	d-value	Inty.	d-value	Inty.	d-value	Inty.		d-value	Inty.	d-value	Inty.		
1	3·479	W	4·483	S	4–0733 / 4·9	74	Ca(OH)$_2$	3·477	W	2–1380 / 3·48	50	Rare earth	In column II lines 1,7,11,13,15,17, and 18 represent unreacted Ca (OH)$_2$ and lines 3,4,6,9,10,12,14, 16 and 19 unreacted monazite.
2	3·382	W	3·332	V.W.	5–0646 / 3·8	60	Ca(PO$_{11}$)$_2$ (SiO$_4$)$_2$	3·153	S	2–1295 / 3·16	70	(CeTh)O$_2$	
3	3·283	S	3·289	W	—	—	Mzt	2·026	W	4–0632 / 3·04	100	CePO$_4$	
4	3·071	S	3·089	S	—	—	Mzt	2·846	W	2–1380 / 2·84	90	Rare earth	
5	2·979	W	3·026	W	4–0632 / 3·04	100	CePO$_4$	2·752	S	2–1295 / 2·75	40	(CeTh)O$_2$	
6	2·843	S	2·863	S	—	—	Mzt	2·624	W	4–0733 / 2·62	100	Ca(OH)$_2$	
7	2·594	W	2·616	V.S.	4–0733 / 2·628	100	Ca(OH)$_2$	2·344	V.W.	4–0632 / 2·37	20	CePO$_4$	In column III lines 1,4,8,11,17, and 19 show rare earths, lines 2,5, 10,12,13,15,16 combination of cerium and thorium oxides (cerium gets separated from the other rare earths) and line 18 unreacted monazite.
8	2·419	W	2·236	W	4–0632 / 2·21	Trace	CePO$_4$	2·308	V.W.	2–1380 / 2·30	20	Rare earth	
9	2·191	S	2·126	W	—	—	Mzt	2·139	V.W.	3–0718 / 2·15	100	Ca$_3$(PO$_4$)$_2$	
10	2·130	S	1·961	V.W.	—	—	Mzt	1·946	S	2–1295 / 1·95	100	(Ce Th)O$_2$	
11	1·961	S	1·923	S	4–0733 / 1·923	42	Ca(OH)$_2$	1·835	W	2–1380 / 1·82	70	Rare earths	
12	1·900	W	1·862	W	—	—	Mzt	1·660	S	2–1295 / 1·66	100	(CeTh)O$_2$	
13	1·867	S	1·798	S	4–0733 / 1·796	36	Ca(OH)$_2$	1·590	V.W.	2–1295 / 1·59	50	(CeTh)O$_2$	
14	1·798	V.W.	1·746	W	—	—	Mzt	1·793	V.W.	3–0713 / 1·80	20	(Ca$_3$(PO$_4$)$_2$	
15	1·757	S	1·692	S	4–0773 / 1·687	21	Ca(OH)$_2$	1·377	V.W.	2–1295 / 1·38	40	(CeTh)O$_2$	
16	1·736	S	1·604	W	—	—	Mzt	1·265	S	2–1295 / 1·27	80	(CeTh)O$_2$	
17	1·690	S	1·446	W	4–0733 / 1·449	13	Ca(OH)$_2$	1·247	V.W.	2–1380 / 1·26	60	Rare earths	
18	1·603	W	1·312	W	4–0833 / 1·314	8	Ca(OH)$_2$	1·233	S	—	—	Mzt	
19	1·537	S	1·233	S	(Table III)	—	Mzt	1·181	S	2–1380 / 1·17	70	Rare earths	

W. Weak
S. Strong
V.S. Very Strong

TABLE V

d-values of monazite residues and phosphate fraction of monazite

	I						II						III
Line No.	Rare earth residues d-values	Inty.	Standard Card No.	Standard d-value	Inty.	Inference	Phosphate fraction d-value	Inty.	Standard Card No.	Standard d-value	Inty.	Inference	Remarks
1	3·49	W	2–1380	3·48	50	Rare earths	3·434	S	3–0713	3·41	30	$Ca_3(PO_4)_2$	In column I lines 1, 3, 6, 11 and 14 are found to have different intensity. This can be due to the difference of chromium radiation and copper radiation or as the standard compared in Samarskite (containing almost all rare earths.)
2	3·17	S	2–1380	3·16	70	,,	2·83	S	3–0713	2·85	100	,,	
3	2·75	S	2–1380	2·74	20	,,	3·1	S	3–0713	3·17	70	,,	
4	2·13	W	2–1380	2·15	50	,,							
5	1·95	V.S.	2–1295	1·95	100	$(CeTh)O_2$							
6	1·82	W	2–1380	1·82	70	Rare earth							
7	1·66	V.S.	2–1295	1·66	100	$(CeTh)O_2$							
8	1·59	S	2–1295	1·59	50	,,							
9	1·42	W	2–1380	1·42	90	Rare earth							
10	1·38	S	2–1380	1·37	60	,,							
11	1·35	W	2–1380	1·35	60	,,							
12	1·26	S	2–1380	1·26	60	,,							
13	1·23	S	2–1380	1·22	70	,,							
14	1·17	W	2–1380	1·17	70	,,							

W. = Weak S. = Strong V.S. = Very Strong

The part played by calcium chloride in this reaction can be explained as follows :

(*i*) Calcium chloride might have reacted with the monazite in a way similar to the following reaction :

$2\ CePO_4 + 3CaCl_2 \quad \dots \quad Ca_3\ (PO_4)_2 + 2\ CeCl_3$

$2\ CeCl_3 + 3\ CaO \quad \dots \quad 3\ CaCl_2 + Ce_2O_3$

where Ce represents the rare earths in the monazite.

(*ii*) Calcium chloride which fuses at a temperature of 740°C enclaves the mixture of monazite and calcium oxide, or partly dissolves the calcium oxide in it, so that at high temperature the reaction between monazite and calcium oxide may be made easier. In this case the reaction may be similar to :

$2\ CePO_4 + 3\ CaO \quad \dots \quad Ca_3(PO_4)_2 + Ce_2O_3$ where Ce represents the rare earth in the monazite.

The second argument is more feasible as it is noted from literature[27] that calcium chloride acts as a vehicle for calcium oxide to react with other substances.

Conclusions

X-ray study of monazite heated by itself, with calcium oxide and calcium chloride singly as well as in combination confirmed the earlier finding from chemical investigations (published earlier) that heating with calcium oxide alone decomposes the monazite very little whereas heating with a mixture of calcium oxide and calcium chloride decomposes the monazite which can be leached by acid and separated as calcium phosphate, rare earth oxides and other compounds. X-ray analysis also shows that the rare-earths are also likely to get decomposed which may facilitate the separation of the individual rare earths by the same technique and this fact is under examination.

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