

STUDIES ON TRAVANCORE MONAZITE

VI. Investigation on the Solid-Solid Reaction between Monazite and Sodium Carbonate by Differential Thermal Analysis and by X-Ray Diffraction*

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Optimum conditions for the removal of phosphatic content in monazite sand by sintering with sodium carbonate are described in the previous papers in the series.† Results of investigation by D.T.A. and X-ray diffraction of the solid-solid reaction between monazite sand and sodium carbonate are now given. The D.T.A. curve shows that it is a slow exothermic reaction. X-ray diffraction patterns, besides confirming the constituents in the sintered product identified chemically, show the presence of a new phase.

NUMEROUS references are available in literature regarding the apparatus, technique and applications of differential thermal analysis.¹⁻⁶ Many types of thermal changes of simple and complex materials have been studied by this technique. Much data have been compiled that the procedure is now almost a routine one in the analysis of various inorganic compounds, minerals and ores.

EXPERIMENTAL

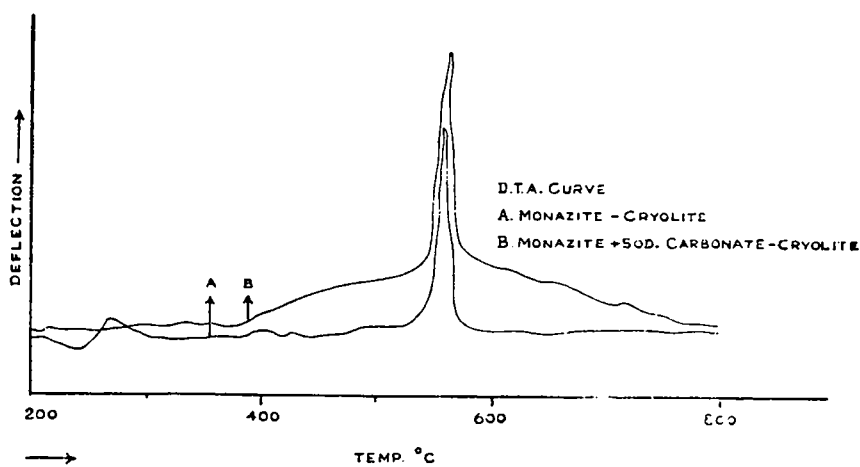
It was felt that this technique could profitably be employed in understanding some features of the thermal decomposition of monazite by sintering with sodium carbonate at 750° C.

The sample holder was a cylindrical silver block, 2 cm. in height and 1.5 cm. in diameter. There were three holes drilled on the block, each

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† Part V of the series is published in the *Bulletin of the Central Research Institute*, University of Travancore, 1957, 5 (1), 21,

2 cm. diameter and 8 mm. deep, one hole for the thermo-couple to note the temperature of the block, the second hole for the reference material and the third for the sample. The block was clamped vertically inside the tubular furnace mounted vertically. The furnace was heated electrically with a rise in temperature of 10° C. per minute. The reference material used was cryolite. The thermo-couples were of chromel-alumel. The differential thermo-couple was connected, after magnification of the current, to an automatic recording device, the thermal curve being continuously plotted as the heating of the material progressed. The experiment was first carried out with one of the holes packed with pure powdered monazite sand, and the other hole with cryolite, the reference material. The thermal curve was then recorded with an intimate mixture of monazite sand and sodium carbonate in one of the holes and with cryolite in the other. A and B represent the curves thus obtained.



D.T.A. Curve—Sintering Monazite Sand with Sodium Carbonate.

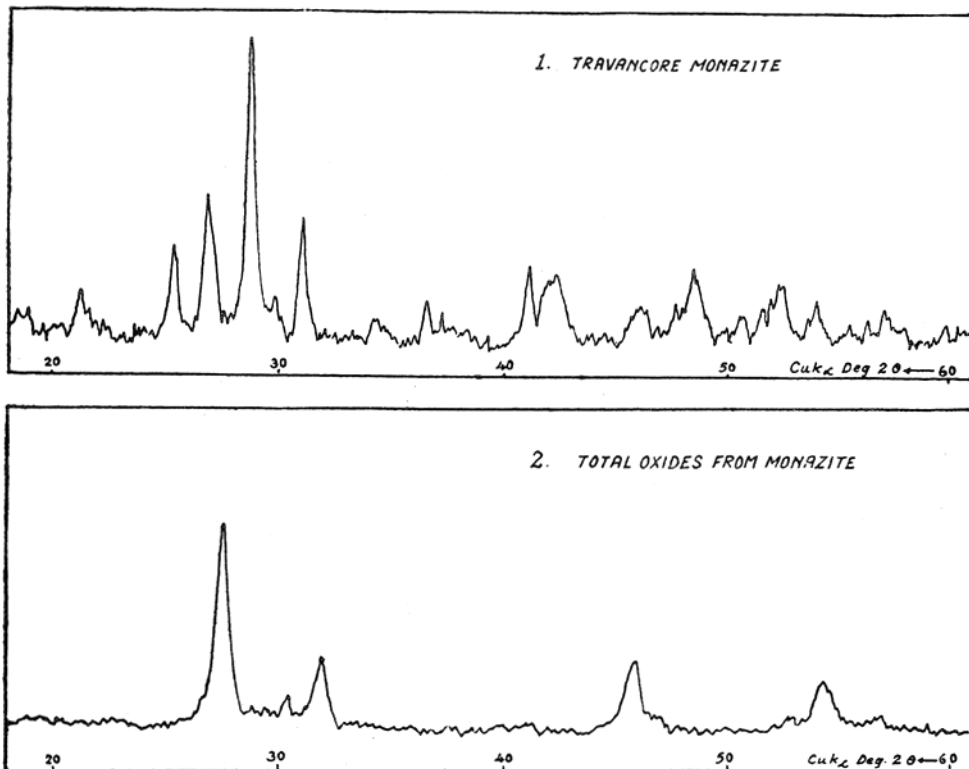
X-ray diffraction patterns.—With a view to gain some insight into the nature of the products formed during sintering of the sand with sodium carbonate, X-ray patterns of the reaction products at various stages were recorded and examined. For purposes of comparison and identification, diffraction patterns of monazite, total oxides from monazite by oxalate ignition, synthetic mixture of sodium carbonate and sodium phosphate and a fused sample of monazite with sodium carbonate were also recorded.

The instrument used was Phillip's wide range diffractometer, an automatically recording Geiger counter instrument, with $\text{CuK}\alpha$ radiation, filtered through nickel and operated at 40 K.V.P. and 15 mA. The scanning speed

used in all these recordings were 2° , 2θ /minute. The results are given in Figs. 1-10.

Figure 1.—This is the diffraction pattern of Travancore monazite, used in these studies. The slide was made with powdered sand and put in the instrument. The peaks are in general agreement with those given in ASTM X-ray card file.

Figure 2.—This is the pattern obtained from the total basic oxide in monazite sand. A little sand was digested with twice its weight of sulphuric acid, cooled and extracted with water. The rare-earths and thorium were



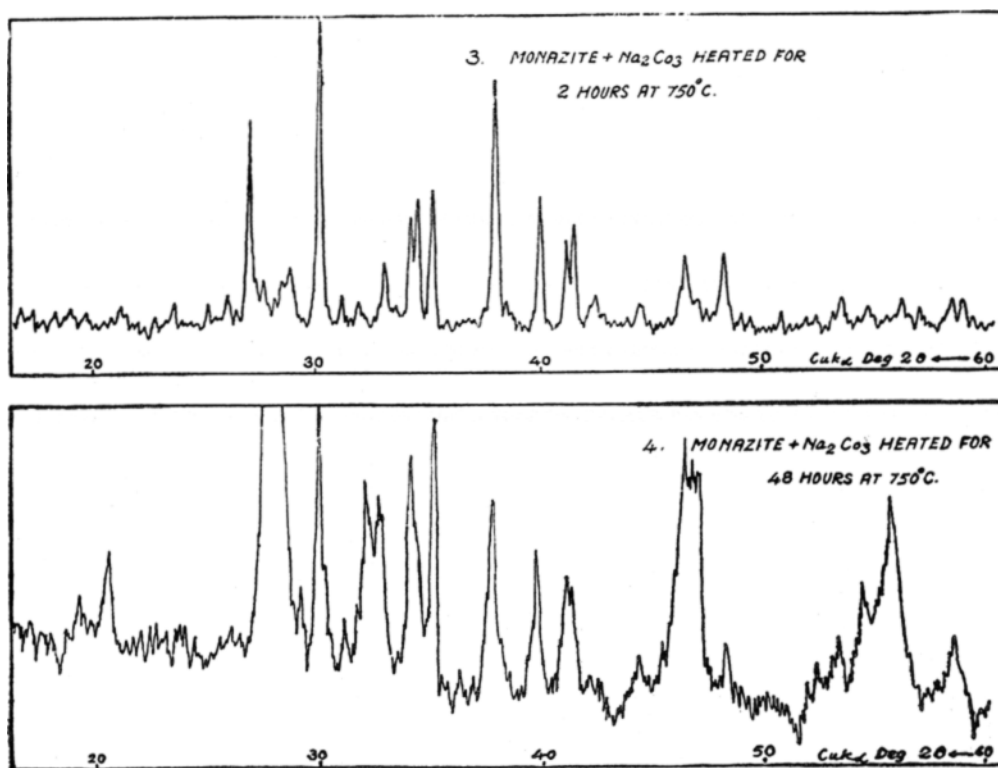
FIGS. 1-2

X-Ray Diffraction Patterns of Travancore Monazite and of Total Oxides from Monazite.

precipitated with oxalic acid. The oxalate precipitate was filtered, washed and ignited at 850°C . The slide was prepared from the oxides thus obtained. The graph shows a fluorite phase which is poorly crystallised but which has a large spacing, indicating maximum solid solution. $a_0 = \text{N } 5.60$. Why this phasing is larger than that of sodium carbonate fused oxides (Fig. 5) is difficult to explain.

Figure 3.—This is the pattern obtained from the product of sintering at 750°C . for 2 hours of monazite sand and anhydrous sodium carbonate in the ratio 1:2 by weight. From the graph, traces of monazite may still be seen but a new phase, sodium phosphate and sodium carbonate can be detected. In the water extract dried at 160°C . (Fig. 9), $\text{Na}_3\text{PO}_4\cdot\text{H}_2\text{O}$ is found and thus P_2O_5 availability (chemically) is correlated with formation of Na_3PO_4 at the leaching stage. "Ceria" has not crystallised appreciably at this stage as it does in Figs. 4 and 5. The new phase is characterized by the appearance of at least 2 diffraction maxima at 3.29 \AA and 2.61 \AA . It is apparently unstable in water or sodium carbonate solution dissociating to PO_4^{3--} ions.

Figure 4.—The sintering of monazite and sodium carbonate at 750°C . was carried out for 48 hours. The slide was prepared from this product and examined. The pattern obtained shows excess of sodium carbonate and



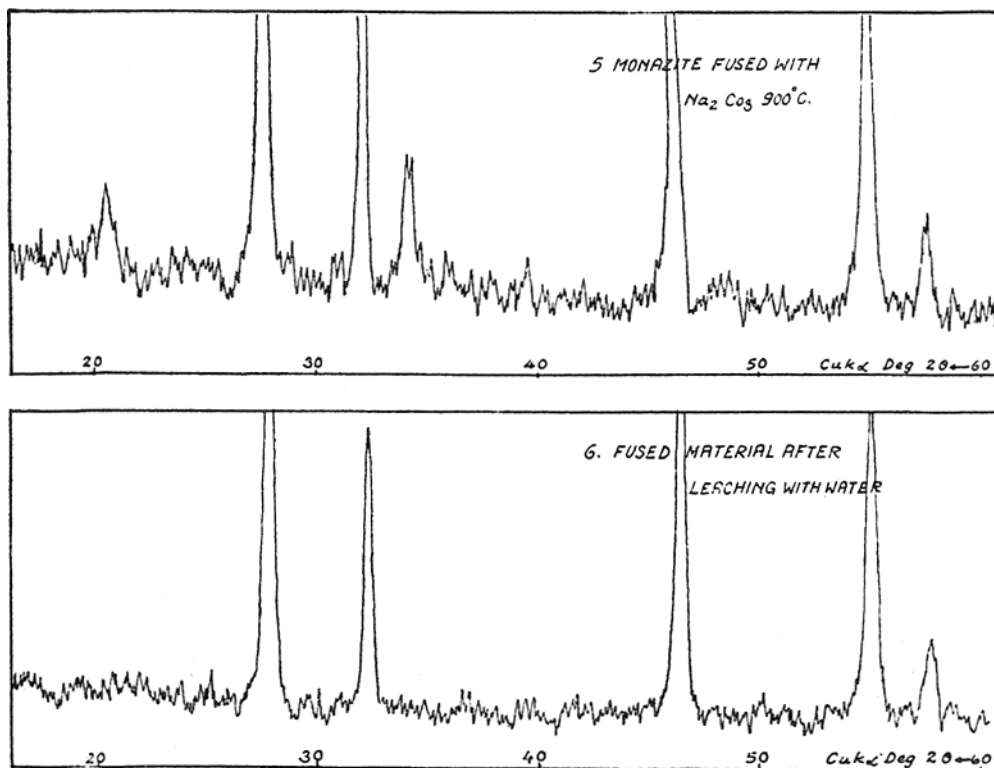
Figs. 3-4

X-Ray Diffraction Patterns of Monazite and Sodium Carbonate Heated for Different periods of time.

fairly crystallised 'CeO₂' phase. The peaks are very broad, representing either fine particle size or a mixture of several phases each with a different amount of R₂O₃ in solid solution. There is a noticeable increase in the average lattice parameter, but not as much as in Fig. 5, suggesting that at this stage not all the R₂O₃ has been absorbed in the CeO₂ lattice.

Figure 5.—For a comparative study, total oxides from monazite obtained by fusion with sodium carbonate were examined. The pattern consists almost entirely a single oxide phase with the fluorite structure representing 'CeO₂' with some larger ions (probably trivalent) in solid solution. Lattice spacings are considerably expanded amounting to approximately $a_0 = 5.54$ as compared to $a_0 = 5.411$ for pure CeO₂.

Figure 6.—The sand after fusion with the sodium carbonate was leached with water and the residue thus obtained was examined. The pattern shows only 'CeO₂' solid solution phase.

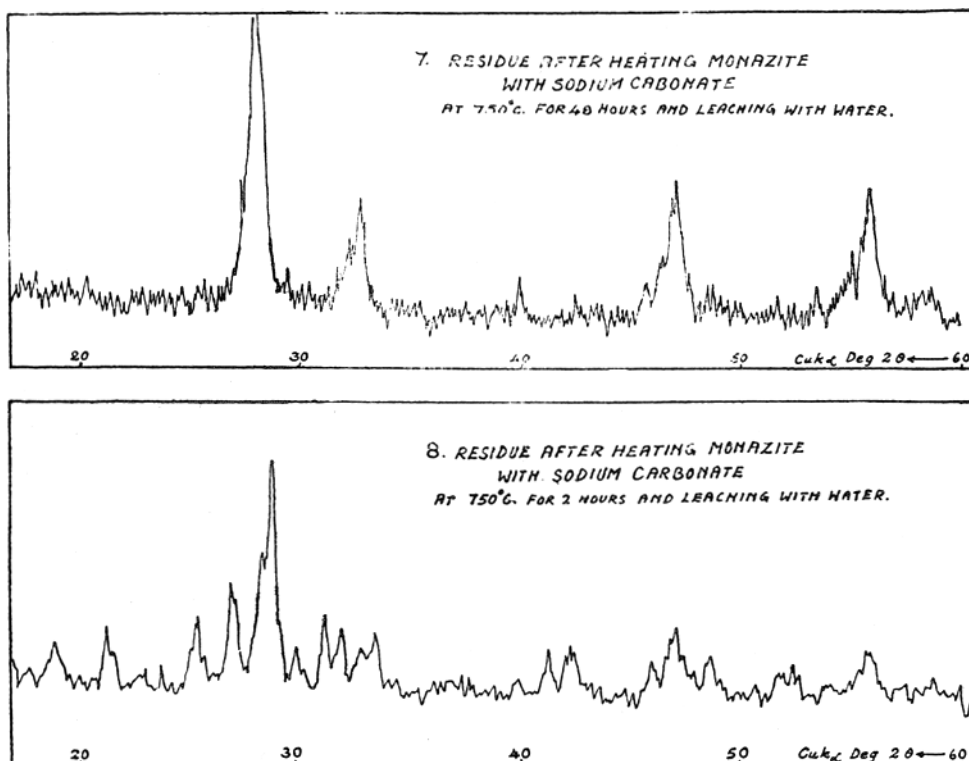


FIGS. 5-6

X-ray Diffraction Patterns of the Fusion Products of Monazite with Sodium Carbonate,

Figure 7.—This is the pattern of the residue after leaching with water of the product obtained by sintering at 750°C . for 48 hours. It shows clearly mixture of various 'CeO₂' solid solution phases with unit cells ranging upwards from pure CeO₂, but smaller than those in Fig. 6.

Figure 8.—This is the pattern of the residue after leaching with water of the product obtained by sintering at 750°C . for two hours. Unreacted monazite and very poorly crystallised 'CeO₂' can be detected clearly from the figure. It is interesting to note that this 'CeO₂' has the spacings of nearly pure CeO₂, with none of the other rare-earths as yet admitted into solid solution.

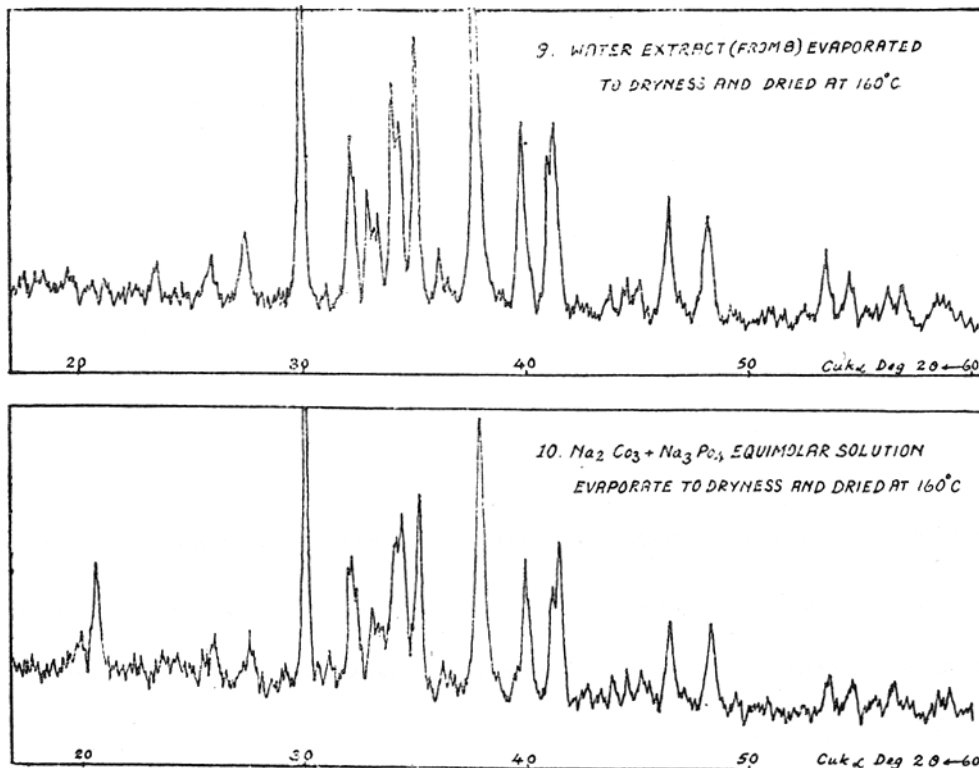


FIGS. 7-8

X-Ray Diffraction Patterns of the Leached Products of Sintering Monazite with Sodium Carbonate.

Figure 9.—The water extract from Fig. 8 was evaporated to dryness and dried at 160°C . for 6 hours. The slide was prepared from this material and examined. The pattern shows the presence of Na₂CO₃ and Na₃PO₄ · H₂O,

Figure 10.—For comparison of the results in Fig. 9, a solution of sodium carbonate and sodium phosphate in equimolar ratio was prepared, evaporated to dryness and dried at 160° C. for 6 hours. The product thus obtained was thus examined as before. From the peaks, presence of Na_2CO_3 , $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ can be detected.



FIGS. 9-10

X-Ray Diffraction Patterns of the Water Extract from (8) and of a Synthetic Mixture of Sodium Carbonate and Sodium Phosphate.

DISCUSSION

From the nature of the curves obtained in the differential thermal analysis it may be presumed that the decomposition is a slow exothermic reaction starting at about 400° C. and completing at 760° C. The characteristic cryolite peaks are seen in both the figures near 560° C. It is also seen that the heat of reaction of the change is very small. No distinctive peaks are obtained thereby indicating the absence of any specific temperature at which the decomposition takes place. It may be possible that the decomposition

temperature of each rare-earth phosphate and carbonate may be different but close by, so that when a complex material as monazite is studied, it will be difficult to interpret the results. The two simultaneous reactions that take place during sintering, viz., conversion of rare-earth phosphate to the carbonate and thermal decomposition of the carbonate to the oxide may affect the net thermal effect observed.

The X-ray diffraction patterns of the various decomposition products of monazite are in good agreement with the data collected chemically and the conclusion arrived therefrom. It has not been possible to record the diffraction pattern *in situ* at the reaction temperature of 750° C. so that the presence or otherwise of any rare-earth carbonate as an intermediate product may be established. The product obtained by sintering (Fig. 3) gives a pattern with characteristic peaks for sodium carbonate, sodium phosphate and the 'fluorite' peaks of cerium earth oxide together with a new phase characterised by two diffraction maxima at 3.29 Å and 2.61 Å. It has not been possible to identify this new phase chemically. The difference in carrying out the sintering for 48 hours instead of two hours, is not very markable except that the 'CeO₂' phase has crystallised better (Fig. 4). Excess monzite also is absent. The products obtained after decomposition of monazite sand by several methods, and removal of all soluble matter, have been examined. The difference is mainly in the extent to which 'CeO₂' has crystallised and to the amount of R₂O₃ that has gone in solid solution. The water extract of the sintered product has been evaporated, dried at 160° C. and examined. The pattern thus obtained can be compared with that of synthetic mixture of sodium carbonate and sodium phosphate (Figs. 9 and 10). The close similarity of the peaks in the two patterns prove beyond doubt the identity of the products formed during the reaction.

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