SOLID PHASE REACTIONS WITH TUNELLITE MINERAL

Hüseyin GÜLENSOY and T. TEBERDAR

İstanbul University, Faculty of Chemistry

SUMMARY. — The solid phase reactions between tunellite mineral ($SrO \cdot 3B_2O_3 \cdot 4H_2O$) and Na_2CO_3 have been investigated.

The yield of the solid phase reactions which take place between both the original mineral and the dehydratized form and Na_2CO_3 have been studied for a series of temperatures. The yield is approximately 25-27 percent.

These solid phase reactions were investigated also with DTA and X-ray analyses.

It is observed once more that tunellite mineral has been transformed into veatchite, after 500°C temperature.

The product at the end does not consist only of $Na_2B_4O_7$, but some other intermediate and end products of sodium boron compounds have been formed.

INTRODUCTION AND HISTORY

Until recently it has been thought that the substances could only react in their liquid forms. Some experiments, however, were made to prove the opposite of this assumption. For example, in 1900, it has been shown that, brass will be formed as a result of grinding the mixture of copper and zinc powder and heating them at the same time. Furthermore it is shown that calcium oxide and silicate acid anhydrite will be transformed into calcium silicate state, not necessarily in the presence of liquid medium.

The reactions between the powder mixtures of solid substances have been investigated since 1912, particularly by A. Hedvall, G. Tammann and W. Jander. Thus it is understood that almost all metals and inorganic salts will enter solid phase reactions well below the melting point of each substance.

It is known that the atom ions or molecules in a crystal lattice are arranged in a definite pattern in the space, and heat vibrations occur at temperatures below the melting point. As a result of the rise in temperature, the vibrations increase and the atom ions, leaving their places, cause diffusion. Thus, the reaction between the faces of these atom ions and other substances with which they are in contact, takes place as a result of the mobility possessed by these ions at a certain temperature. For the continuation of such a reaction between two components at least the mobility of one of the components and its diffusion is necessary. As'a result, a concentration equilibrium is formed between two solid phases.

When the pulverized mixtures of different materials are heated, changes in the interior state and the accompanying rate of reaction will occur at a given and relatively low temperature intervals, due to the fact that all the reactions showing exponential growth are exothermic. Heat evolved during this reaction causes an increase of temperature of the substance. As a result, the rate of the reaction is relatively higher and an increase of temperature is recorded. Thus the autocatalysis of the solid phase reaction is accelerated.

While studies are carried out on extracting borax from colemanite ore which occurs widespread in Turkey, it has been established that on heating the original or dehydrated form of colemanite with Na_2CO_3 + $NaHCO_3$ mixture, it will be converted into $Na_2B_4O_7$ at a yield of 60 percent.

Similar solid phase reactions of the ulexite and inyoite minerals are also studied. It has also been shown that the ulexite and inyoite minerals in their original or dehydrated forms will react with Na_2CO_3 in solid phase.

Although the 60 percent yield, indicated above, would seem satisfactory for the colemanite mineral, the same thing cannot be stated for tunellite mineral. Tunellite occurrences of Turkey are very limited, and economic production of borax from this mineral is at present considered impossible.

APPARATUS AND METHODS

1. Solid phase reactions

From the powder mixture of tunellite and soda, prepared stoichiometrically even, 5.0000 gram portion is taken at each time and this mixture is heated at 100-150-250-350-450-550-650 and 750°C respectively in a platinum crucible. The heating period of each portion is three hours exactly. The mixture heated in this way is filtrated following its extraction with 100 ml of 90°C water. The $Na_2B_4O_7$ value is obtained by multiplying the B_2O_3 content of the filtrate, determined volumetrically, with an appropriate factor.

Original tunellite mineral is not soluble in water. If the solid phase reaction between the tunellite mineral and the Na_2CO_3 had not taken place in the sample mixture heated at a suitable temperature indicated above, the $B_4O_7^{-2}$ anion would not be present in the dissolution obtained as a result of the extraction.

2. Differential thermal analysis

The apparatus used for DTA studies consists of a horizontal cylindric-shaped oven and a pyrometer combined of Pt/Pt-Rh thermocouples and a galvanometer with microampere sensitivity (or a recorder).

In the microcalorimetric analysis carried out with DTA, one end of the thermoelement is placed in the tunellite specimen, while the other end is placed in the mixture of [original tunellite + Na_2CO_3].

It is to be emphasized that the substances in which the ends of the thermoelement is placed should have an equivalent content of tunellite. The thermal results obtained during the removal of the crystal water from the specimens will destroy each other and the true thermal aspect of the reactions between solid phases will be observed.

The rate of increase of temperature in the DTA studies is selected to be 300°C/h. Graphics are obtained with a recorder automatically. The sensitivity of the apparatus is adjusted to be 0.1 mV.

In a second study, the solid phase reactions between dehydrated tunellite mineral and Na_2CO_3, under the same conditions, are investigated.

3. X-ray analysis

The stoichiometric mixture of the original and dehydrated form of tunellite mineral and Na_2CO_3 was heated at a given temperature and then cooled for 24 hours; following this, the mass obtained was pulverized and investigated with x-ray methods.

Powder diffraction method was employed in this study. The diagrams are obtained automatically with a recorder.

CONCLUSION AND DISCUSSIONS

From stoiciometric mixture of original tunellite mineral and soda, prepared according to the formula given below, 5 gr portion is taken at each time and heated in a platinum crucible at 100-150-200-250-. . . . . .750°C, respectively, and each specimen was extracted with 100 ml of 90°C water $2(SrO\text{-}3B_2O_3\text{-}\ 4H_2O)+3Na_2CO_3 \longrightarrow 2SrCO_3+3Na_2B_4O_7+CO_2+8H_2O$.

The $B_4O_7^{-2}$ determination of the liquid extraction was done by volumetric methods. Figure 1 shows the values obtained.

The graph was drawn between the temperature - B_2O_3 percent. The value of B_2O_3 % in the ordinate can be multiplied with 1.66 factor and the $Na_2B_4O_7$ value of the solution will be obtained.

Close investigation of the graph showed that the maximum limit of the reaction is 700-750°C and this is the temperature at which the last 1 mole of water in the tunellite mineral is removed.

Thus the change of structure of the tunellite mineral causes the crystal structure of this mineral to become more active.

The graph will also show that the tunellite mineral possesses a certain activity at the temperature at which the first 3 moles of water are removed from the structure.

Another similar work on the reaction between dehydrated tunellite mineral and Na_2CO_3 was done under the same conditions. The graph obtained as a result of these studies is shown in Figure 2.

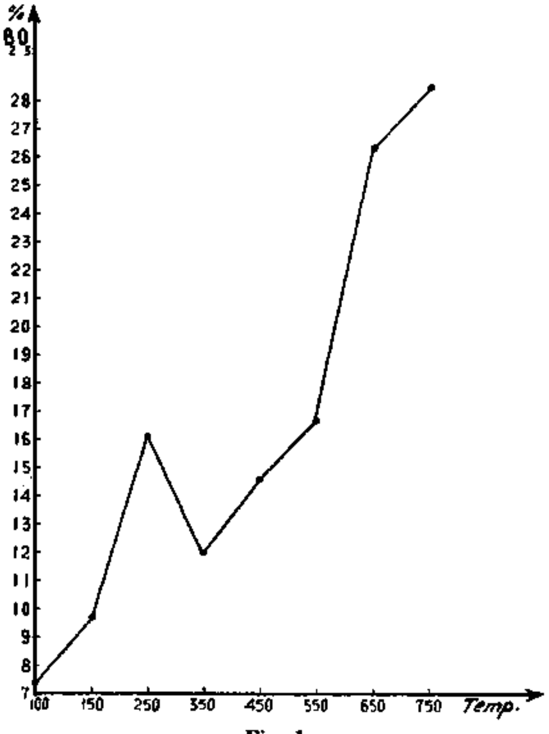


Fig. 1

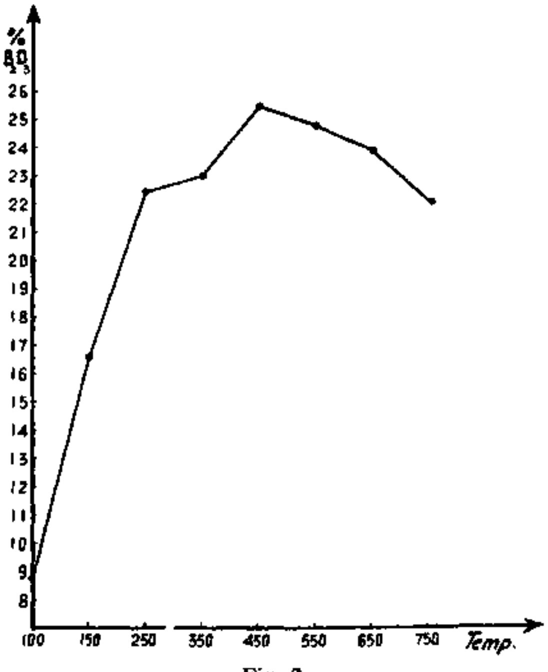


Fig. 2

The original and dehydrated forms of tunellite mineral were heated with Na_2CO_3, the mass not being subject to mixing. The yield of these studies was approximately 25-27 %.

The conclusions to be drawn from Figure 2 are indicated below: The reaction between dehydrated tunellite and Na_2CO_3 takes place at a lower temperature compared to original tunellite. The reason is that the dehydrated tunellite was activated as a result of the dehydration process before reacting with Na_2CO_3.

It is also believed that the mechanical mixing of the mixtures entering reaction at the temperature where the reaction between tunellite mineral and Na_2CO_3 takes place, will increase the yield. Thus the contact-surface of the particles will be increased.

Also the change of CO_2 concentration in the atmosphere of the medium in which the reaction takes place will enable us to obtain various yields. Indeed it is clearly understood that it is necessary to remove the CO_2 formed in order to prevent the partial reversion of the reaction to the left, assuming that the reaction of $2(SrO \cdot 3B_2O_3 \cdot 4H_2O) + 3Na_2CO_3 \text{———} 2SrCO_3 + 3Na_2B_4O_7 + 8H_2O + CO_2$ is reversible.

Similarly the increase of soda content of the mixture will result in a higher yield of borax.

DTA studies were also made along with the solid phase reactions. The diagram of the differential thermal analysis using (original tunellite + Na_2CO_3) - (original tunellite) is shown in Figure 3.

The 50-90°C peak observed in the diagram, indicates that the first mole of water is removed from the structure. In the range between 90°C and 650°C some exothermic peaks are produced and these show the progress of reaction which takes place between the Na_2CO_3 and dehydrate tunellite.

Following this, the results obtained from the solid phase reactions between the original tunellite and Na_2CO_3 mixture at various temperatures are studied with X-ray methods.

Before the study of the graph resulted from solid phase reactions, close investigation of the graph in Figure 4, which characterizes original tunellite specimen, is necessary.

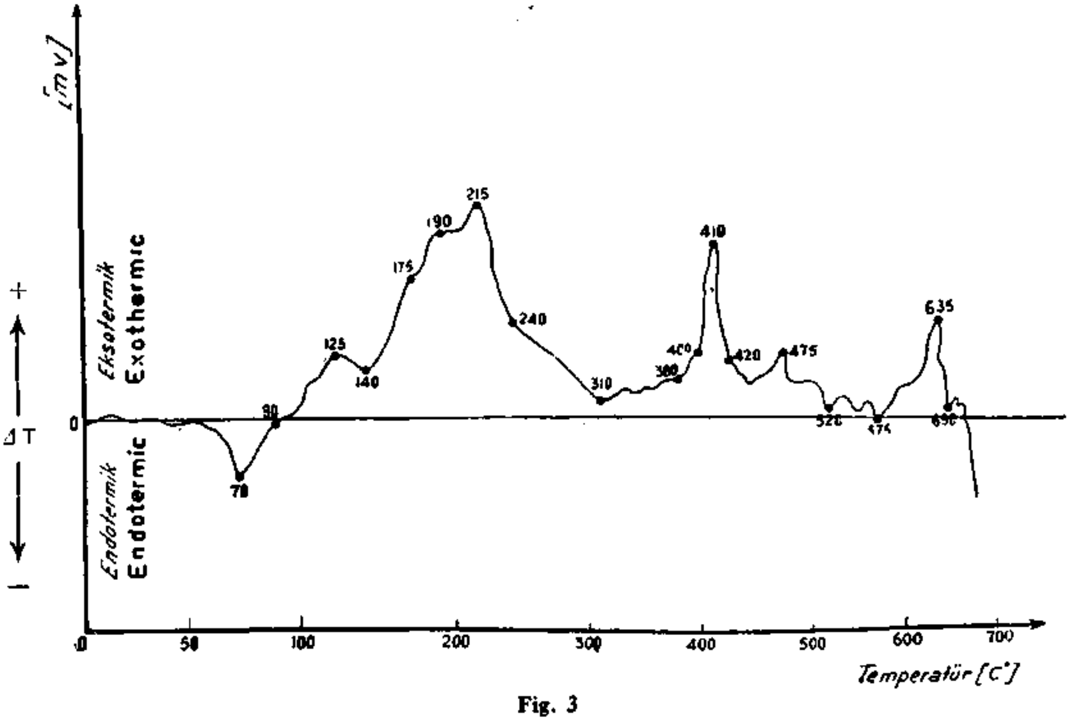


Fig. 3

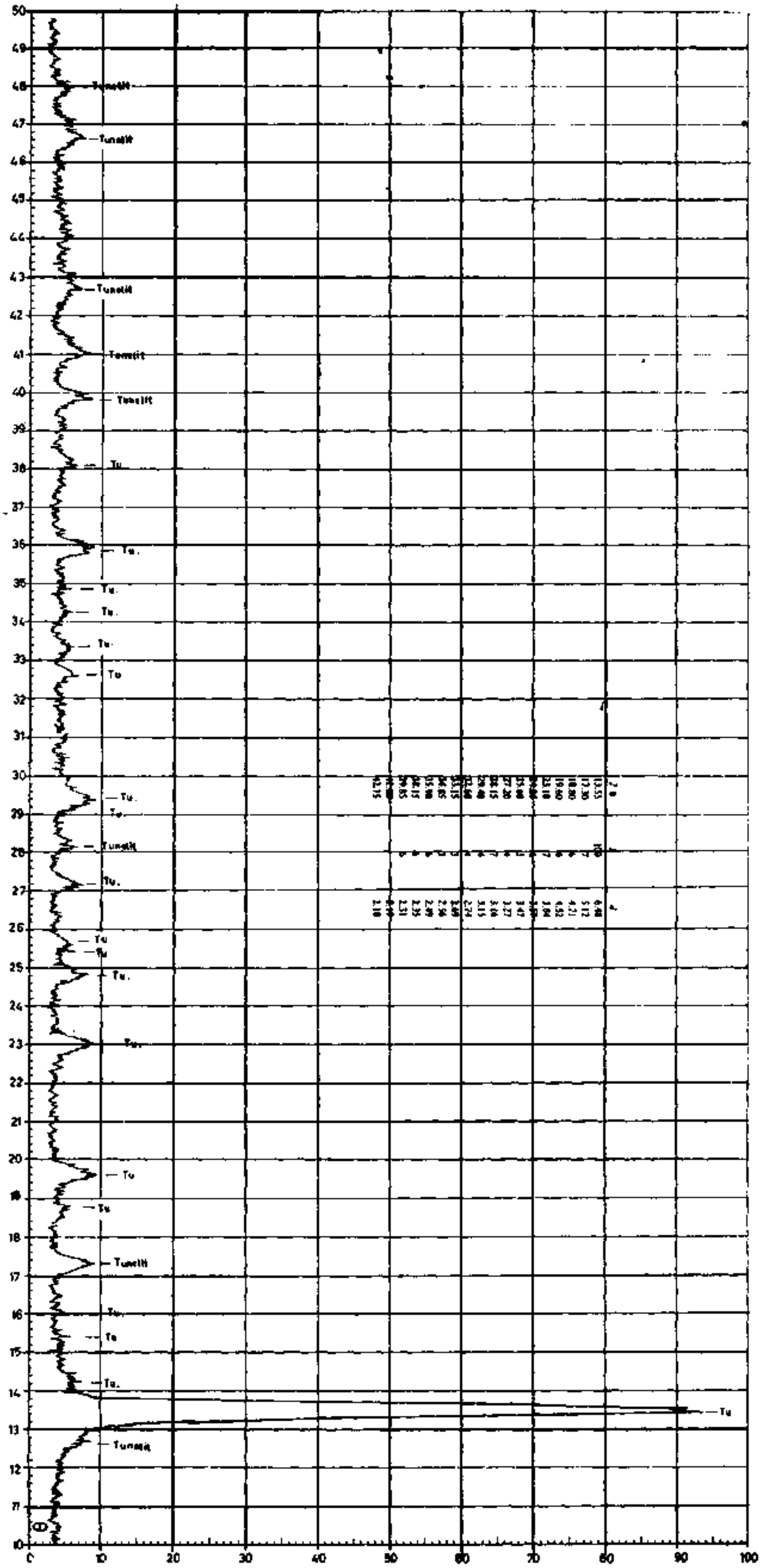
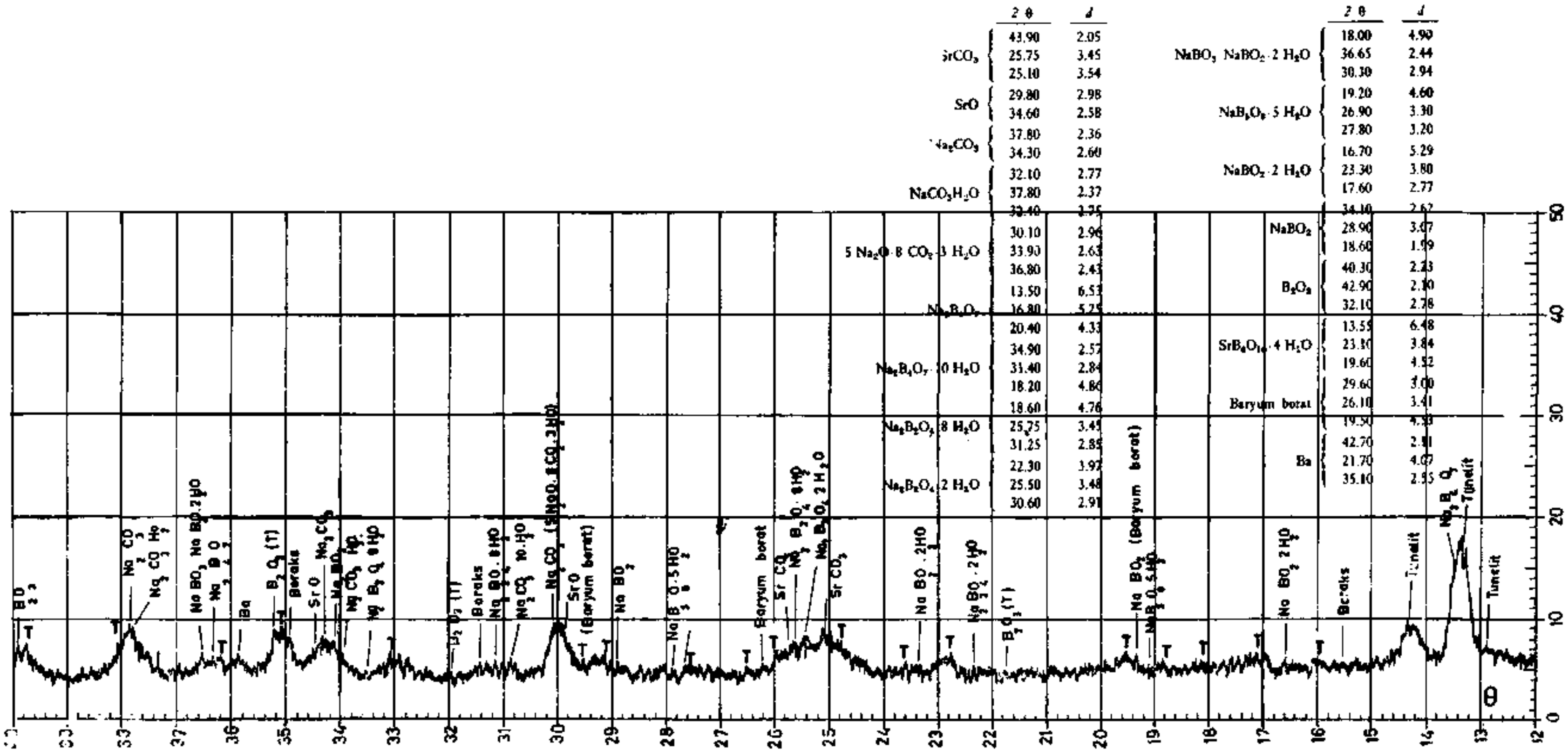


Fig. 4 - Powder diffraction X-ray diagram of original tunellite mineral at ordinary temperatures.



	2 θ	d
SrCO$_3$	43.90	2.05
	25.75	3.45
	25.10	3.54
SrO	29.80	2.98
	34.60	2.58
Na$_2$CO$_3$	37.80	2.36
	34.30	2.60
NaCO$_3$H$_2$O	32.10	2.77
	37.80	2.37
	32.40	3.75
5 Na$_2$O · 8 CO$_2$ · 3 H$_2$O	30.10	2.96
	33.90	2.63
	36.80	2.43
Na$_2$B$_4$O$_7$	13.50	6.53
	16.80	5.25
	20.40	4.33
Na$_2$B$_4$O$_7$ · 10 H$_2$O	34.90	2.57
	31.40	2.84
	18.20	4.86
Na$_2$B$_2$O$_5$ · 8 H$_2$O	18.60	4.76
	25.75	3.45
	31.25	2.85
Na$_2$B$_2$O$_4$ · 2 H$_2$O	22.30	3.97
	25.50	3.48
	30.60	2.91

	2 θ	d
NaBO$_3$ NaBO$_2$ · 2 H$_2$O	18.00	4.90
	36.65	2.44
	30.30	2.94
NaB$_5$O$_8$ · 5 H$_2$O	19.20	4.60
	26.90	3.30
	27.80	3.20
NaBO$_2$ · 2 H$_2$O	16.70	5.29
	23.30	3.80
	17.60	2.77
NaBO$_2$	34.10	2.62
	28.90	3.07
	18.60	1.99
B$_2$O$_3$	40.30	2.23
	42.90	2.10
	32.10	2.78
SrB$_6$O$_{10}$ · 4 H$_2$O	13.55	6.48
	23.10	3.84
	19.60	4.52
Baryum borat	29.60	3.00
	26.10	3.41
	19.50	4.33
Ba	42.70	2.11
	21.70	4.07
	35.10	2.55

Fig. 5 - X-ray diagram of the intermediate products formed at 100°C as a result of the solid reaction between tunellite and Na$_2$Co$_3$ mixture.

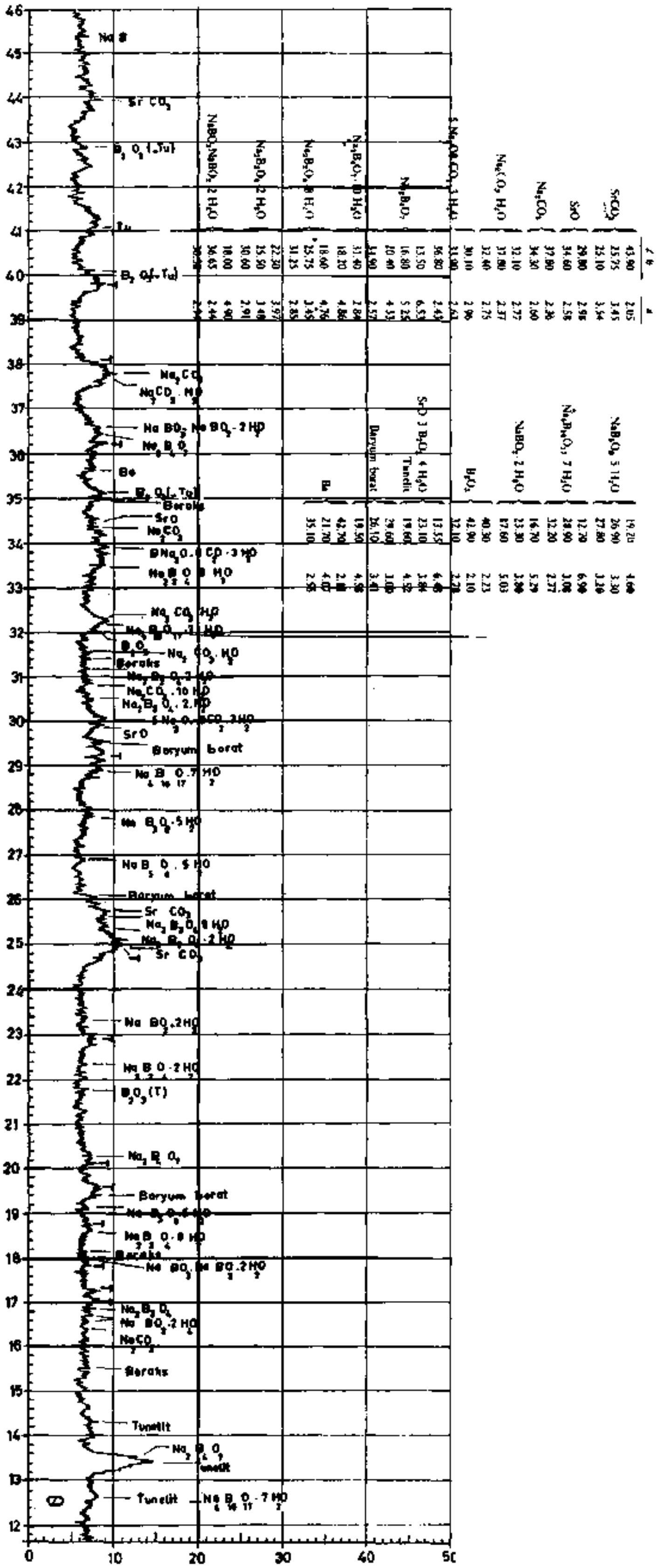


Fig. 6 - X-ray diagram of the intermediate products formed at 150°C as a result of the solid reaction between tunellite and Na_2CO_3 mixture.

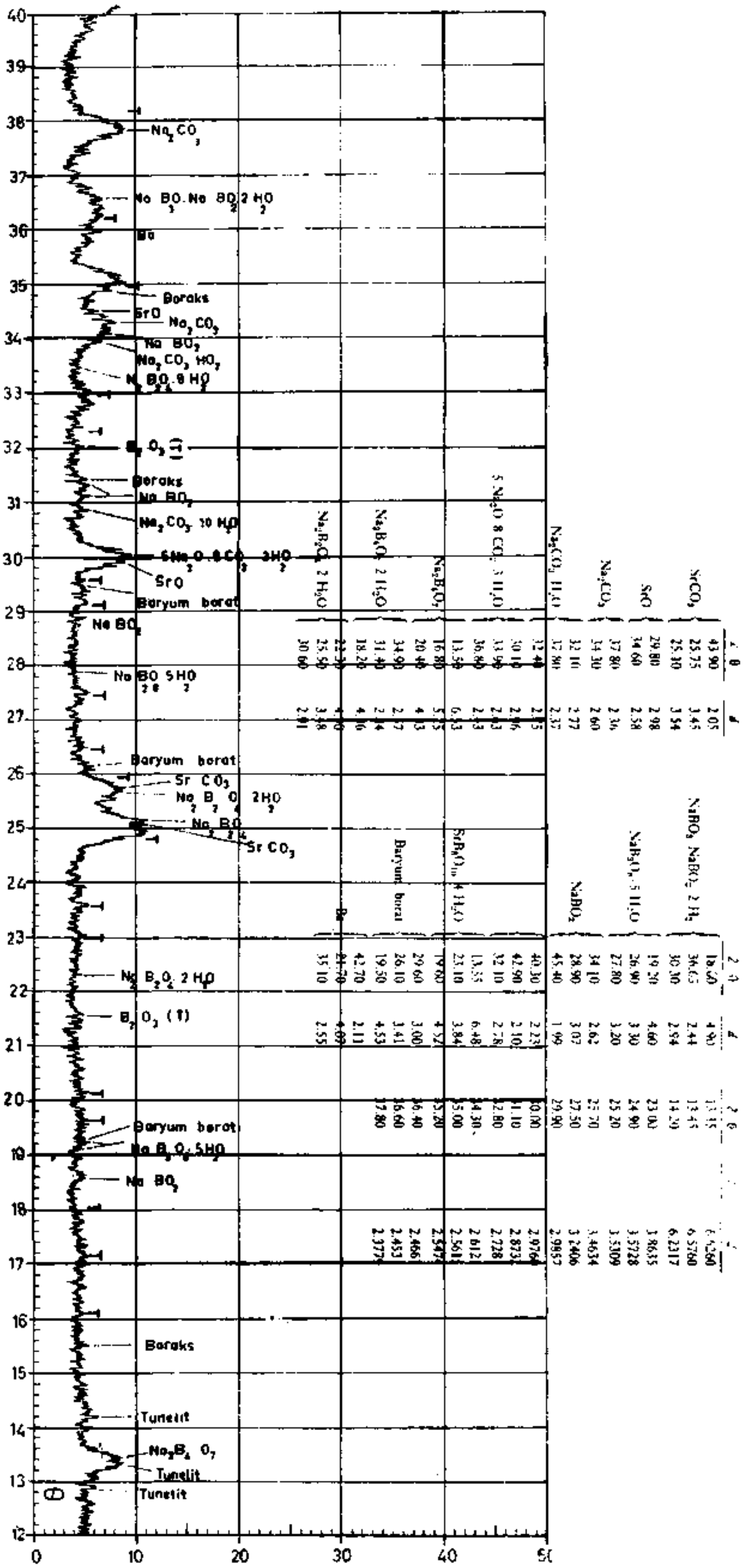
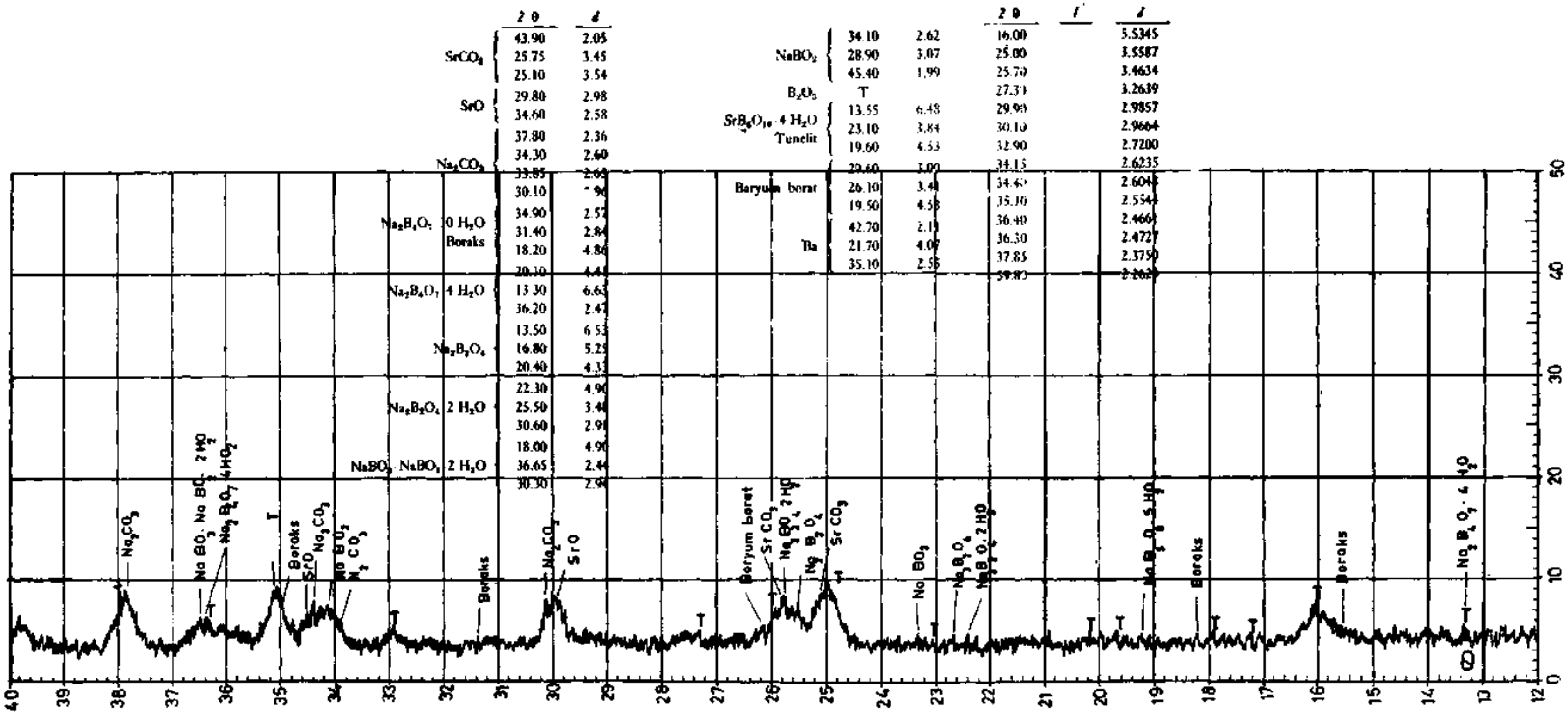


Fig. 7 - X-ray diagram of the intermediate products formed at 200°C as a result of the solid reaction between tunellite and Na_2CO_3.

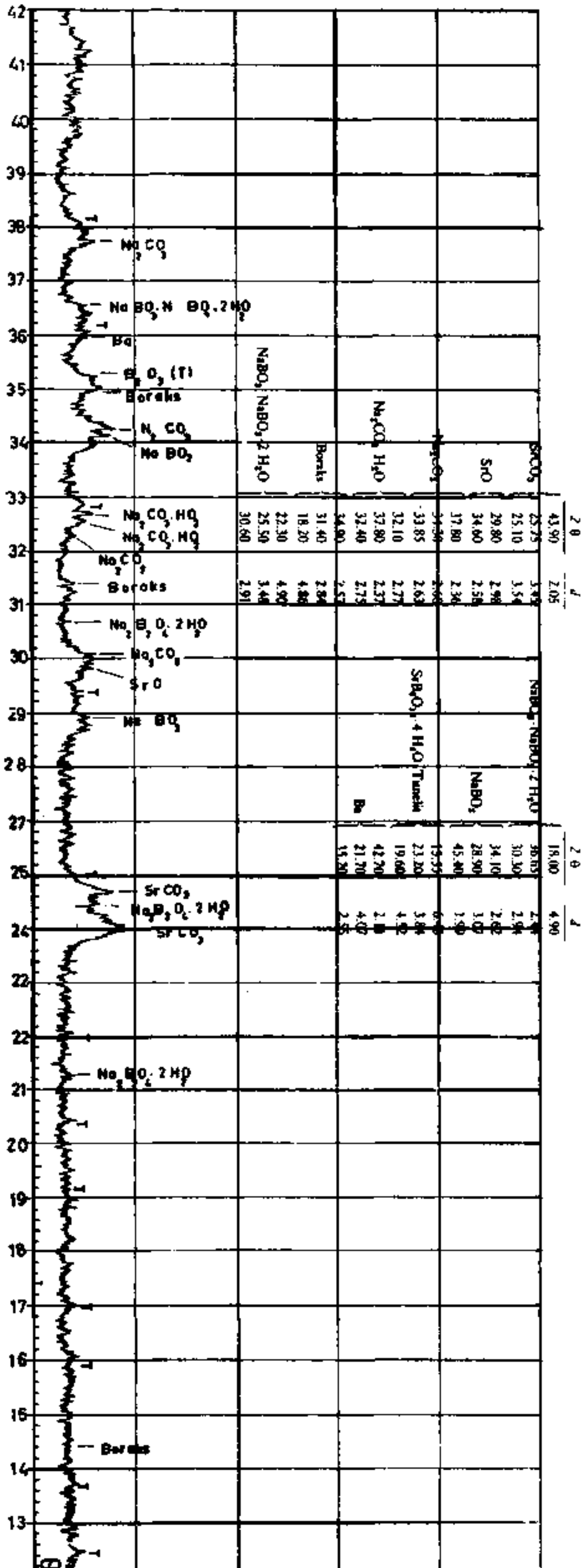


	2 θ	d
$SrCO_3$	43.90	2.05
	25.75	3.45
	25.10	3.54
SrO	29.80	2.98
	34.60	2.58
Na_2CO_3	37.80	2.36
	34.30	2.60
	33.85	2.65
	30.10	2.96
$Na_2B_4O_7 \cdot 10\ H_2O$ Boraks	34.90	2.57
	31.40	2.84
	18.20	4.86
	20.10	4.41
$Na_2B_4O_7 \cdot 4\ H_2O$	13.30	6.63
	36.20	2.47
$Na_2B_2O_4$	13.50	6.53
	16.80	5.25
	20.40	4.33
$Na_2B_2O_4 \cdot 2\ H_2O$	22.30	4.90
	25.50	3.48
	30.60	2.91
$NaBO_3 \cdot NaBO_2 \cdot 2\ H_2O$	18.00	4.90
	36.65	2.44
	30.30	2.94

$NaBO_2$	34.10	2.62
	28.90	3.07
	45.40	1.99
B_2O_3	T	
$SrB_6O_{10} \cdot 4\ H_2O$ Tunelit	13.55	6.48
	23.10	3.84
	19.60	4.53
Baryum borat	29.60	3.00
	26.10	3.41
	19.50	4.58
Ba	42.70	2.11
	21.70	4.07
	35.10	2.56

2 θ	I	d
16.00		5.5345
25.00		3.5587
25.70		3.4634
27.31		3.2639
29.90		2.9857
30.10		2.9664
32.90		2.7200
34.15		2.6235
34.40		2.6048
35.10		2.5544
36.40		2.4661
36.30		2.4727
37.85		2.3750
39.85		2.262

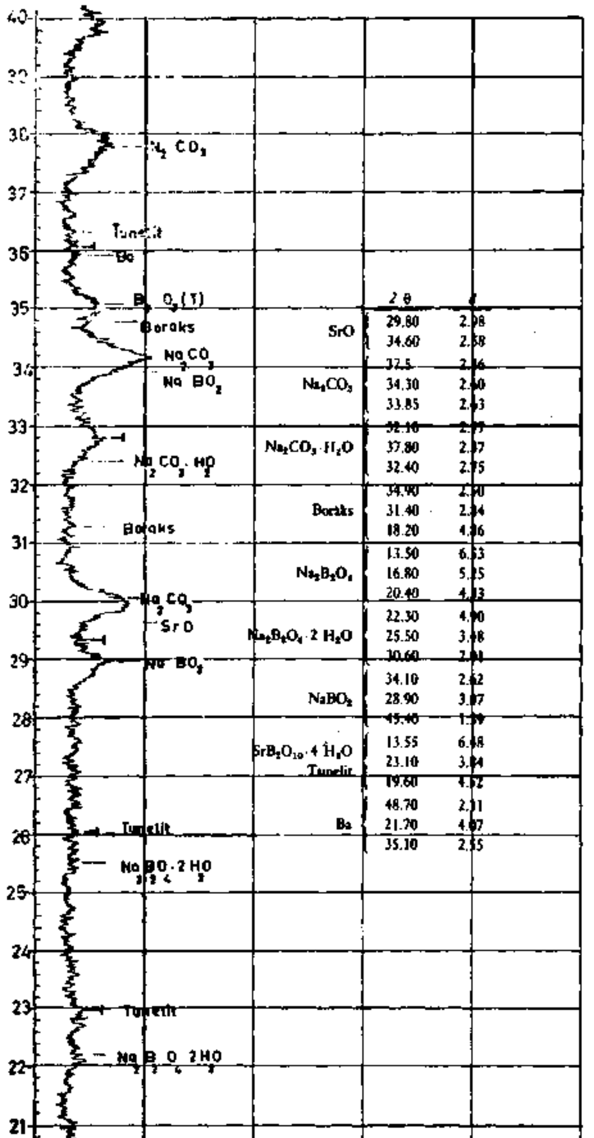
Fig. 8 - X-ray diagram of the intermediate products formed at 275°C as a result of the solid reaction between tunellite and Na_2CO_3.



	2θ	d
$SrCO_3$	43.90	2.05
	25.75	3.45
	25.10	3.54
SrO	29.80	2.98
	34.60	2.58
	37.80	2.36
Na_2CO_3	34.30	2.60
	33.85	2.63
$Na_2CO_3 \cdot H_2O$	32.10	2.77
	37.80	2.37
	32.40	2.75
	34.90	2.57
Boraks	31.40	2.84
	18.20	4.86
$NaBO_2 \cdot NaBO_2 \cdot 2H_2O$	22.30	4.90
	25.50	3.48
	30.60	2.91

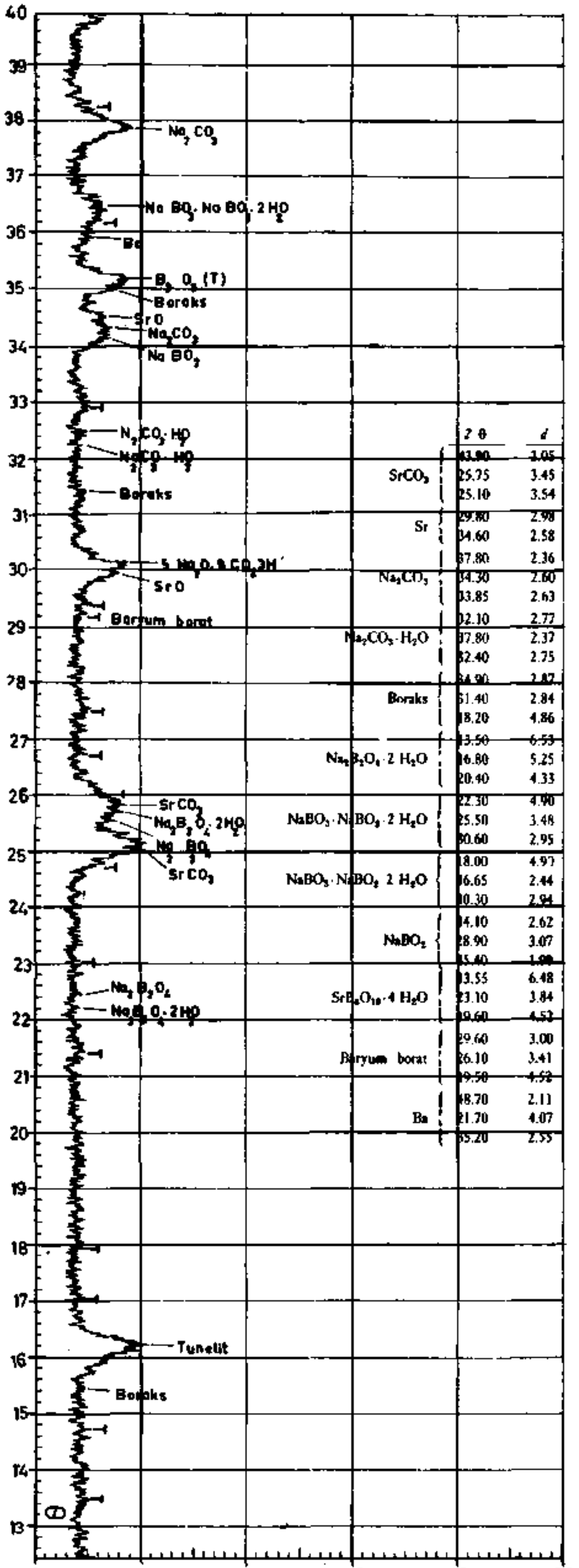
	2θ	d
$NaBO_2 \cdot NaBO_2 \cdot 2H_2O$	18.00	4.90
	36.65	2.4[illegible]
	30.30	2.94
$NaBO_2$	34.10	2.62
	28.90	3.07
	45.40	1.99
$SrB_6O_{10} \cdot 4H_2O$ Tunelit	15.55	6.[illegible]
	23.20	3.84
	19.60	4.52
Ba	42.70	2.[illegible]
	21.70	4.07
	35.20	2.55

Fig. 9 - X-ray diagram of the intermediate products formed at 375°C as a result of the solid reaction between tunellite and Na_2CO_3.



	2 θ	d
SrO	29.80	2.98
	34.60	2.58
Na_2CO_3	37.5	2.36
	34.30	2.60
	33.85	2.63
$Na_2CO_3 \cdot H_2O$	32.10	2.77
	37.80	2.37
	32.40	2.75
Boraks	34.90	2.50
	31.40	2.84
	18.20	4.86
$Na_2B_2O_4$	13.50	6.53
	16.80	5.25
	20.40	4.33
$Na_2B_4O_7 \cdot 2H_2O$	22.30	4.00
	25.50	3.48
	30.60	2.91
$NaBO_2$	34.10	2.62
	28.90	3.07
	45.40	1.99
$SrB_6O_{10} \cdot 4H_2O$ Tunelit	13.55	6.48
	23.10	3.84
	19.60	4.52
Ba	48.70	2.11
	21.70	4.07
	35.10	2.55

Fig. 10 - X-ray diagram of the intermediate products formed at 500°C as a result of the solid reaction between tunellite and Na_2CO_3.



	2 θ	d
	43.90	3.05
$SrCO_3$	25.75	3.45
	25.10	3.54
	29.80	2.98
Sr	34.60	2.58
	37.80	2.36
Na_2CO_3	34.30	2.60
	33.85	2.63
	32.10	2.77
$Na_2CO_3 \cdot H_2O$	37.80	2.37
	32.40	2.75
	34.90	2.87
Boraks	31.40	2.84
	18.20	4.86
	13.50	6.53
$Na_2B_2O_4 \cdot 2\ H_2O$	16.80	5.25
	20.40	4.33
	22.30	4.90
$NaBO_3 \cdot NaBO_2 \cdot 2\ H_2O$	25.50	3.48
	30.60	2.95
	18.00	4.97
$NaBO_3 \cdot NaBO_2\ 2\ H_2O$	36.65	2.44
	30.30	2.94
	34.10	2.62
$NaBO_2$	28.90	3.07
	45.40	1.99
	13.55	6.48
$SrB_6O_{10} \cdot 4\ H_2O$	23.10	3.84
	19.60	4.53
	29.60	3.00
Baryum borat	26.10	3.41
	19.50	4.52
	48.70	2.11
Ba	21.70	4.07
	35.20	2.55

Fig. 11 - X-ray diagram of the intermediate products formed at 600°C as a result of the solid reaction between tunellite and Na_2CO_3.

X-ray diagram of the tunellite + Na_2CO_3 mixture heated at 100°C and then cooled is given in Figure 5. In this figure the peaks of the new intermediate products formed as a result of the solid phase reactions can also be observed.

The X-ray diagram of the solid phase reaction at 150°C is given in Figure 6.

The names of the intermediate-products formed at certain temperatures, during the solid phase reactions are shown both on the peaks to which they belong and at the upper corner of the graph.

The X-ray diagram of the solid phase reaction at 200°C is shown in Figure 7.

A close investigation of the Figures 6 and 7 will show that there are no significant differences between the two figures. In Figure 7, however, the $SrCO_3$, $Na_2B_4O_7$, NaBO2, NaB_5O_8-$5H_2O$ peaks are more strikingly observed.

The X-ray diagram of the solid phase reactions at 275°C is given in Figure 8. Figure 8 is somewhat different from Figure 7. The change of structure of the tunellite mineral from this temperature on, causes the differences observed in Figure 8. In Figure 8 it is also observed that the characteristic peaks observed previously change their positions.

In Figure 9, where the X-ray diagram of the solid phase reactions at 375°C is given, it is observed that most of the intermediate products are no longer present. For example, the $NaB_5O_8 \cdot 5H_2O$ and $NaBO_2 \cdot 2H_2O$ compounds disappear, leaving their place to $NaBO_2$ anhydrite, and through the decomposition of the tunellite crystal lattice, tunellite is converted into veatchite.

The diagram resulting from solid phase reactions at 500°C is given in Figure 10.

In this diagram it is observed that while the characteristic peaks of the tunellite mineral disappear, the characteristic peaks of the veatchite are produced.

The intermediate products formed as a result of the solid phase reactions, at this temperature are given below:

$Na_2B_4O_7$-$2H_2O$, $Na_2B_4O_7$, $NaBO_2$, $Na_2B_2O_4$, B_2O_3, $SrCO_3$ and SrO.

The diagram of the solid phase reaction at 600°C is given in Figure 11. In this diagram it is apparent that the characteristic peaks of $SrCO_3$ disappeared completely. The intermediate products of this reaction at this temperature are, $Na_2B_4O_7$, $NaBO_2$, $Na_2B_2O_4 \cdot 2H_2O$, B_2O_3 and SrO.

The X-ray studies show that at the end of the solid phase reaction between tunellite mineral and Na_2CO_3 not only borax, as indicated in the stoichiometric equation, but also some other borate compounds are formed.

Translated by: F. E. DİKMEN

Manuscript received January 77, 1972

BIBLIOGRAPHY

ALPAR, S.R. & GÜLENSOY, H. (1961) : *Rev. Fac. Sci. Istanbul,* vol. *27.* 153-65.

BOWDER, YOFFE (1958) : *Fast reactions in solids, London.*

GUICHARD, M. (1925) : *Bull. Soc. Chim. 37.* 212, 62.

———(1925) : *Bull. Soc. Chim. 37.* 251, 61.

HAUFFE, K. (1955) : Reaktionen in U. anfesten Stoffen. *Springer.* Berlin.

HEDVALL. Reactions with activated solids. Goteburg.

TUGTEPE, M. & SANIGÖK, Ü. (1962) : *Rev. Fac. Sci. Istanbul,* vol. *28.* 98-113.

———&———(1962) : *Rev. Fac. Sci. Istanbul* vol. *28.* 114-136.