

THERMAL DECOMPOSITION OF AXINITE

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Abstract

The thermal decomposition of axinite was studied by means of thermal, FTIR and X-ray methods. Dehydroxylation takes place in a rather narrow temperature range, the maximum of the corresponding peak being at ca. 900°C. The decomposition products are anorthite, rankinite and probably also small amounts of other, partly amorphous phases.

Keywords: axinite, dehydroxylation, structure rebuilding, thermal decomposition

Introduction

Axinite is a borosilicate of very complex structure and variable chemical composition [1, 2]. In its crystal lattice there exist peculiar $B_2Si_8O_{30}$ groups, in which two boron tetrahedra share three corners each, linking together four Si_2O_7 groups (Fig. 1). These $B_2Si_8O_{30}$ groups are nearly planar and form distinct tetrahedral layers, alternating with sheets of edge-sharing octahedra. The latter are composed of finite chains of six octahedra of the type Fe-Al-Al-Al-Al-Fe, cross-linked by distorted CaO_6 and $CaO_5(OH)$ polyhedra. OH groups are coordinated by Ca and Al ions as well as other ions substituting for them (e.g. Fe, Mn).

It appears that no detailed report has appeared in the literature on the study of the thermal decomposition of axinite.

Experimental

The sample examined comes from a pegmatite in the 'Grabina' granite open-pit near Strzegom, Lower Silesia (Poland). Axinite occupied the central part of a miarolitic pegmatite, filled with calcite. Numerous, fine axinite crystals were intergrown with calcite or overgrown on smoky quartz, feldspar and epidote. The mineral in question is transparent, brownish in colour, with a vivid lustre. It represents a rather common (Fe, Mn)-variety of this mineral, with low Mg, Zn and Ti content (Table 1). The $Fe^{3+}:Fe^{2+}$ ratio was established on the basis of Möss-

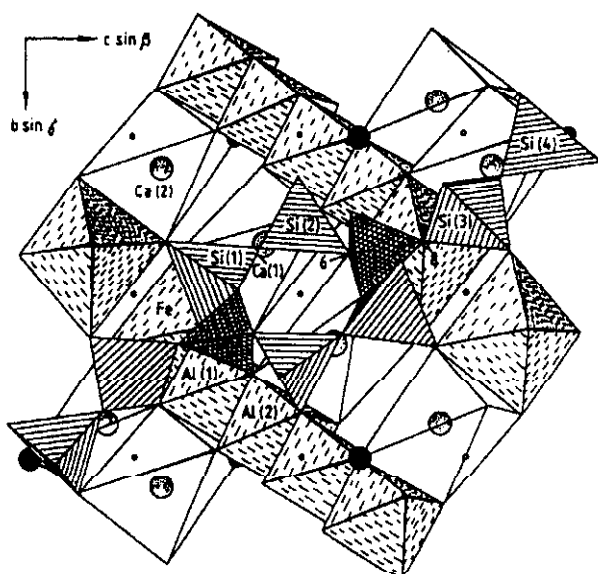


Fig. 1 Fragment of the axinite structure projected down the a-axis. Full circles are (OH) ions in the upper layer, smaller full circles (only partly visible) denote (OH) ions in the lower anion layer. Two $[BO_4]$ tetrahedra are triangle-shaded. Modified after [1]

Table 1 Chemical composition of axinite from Strzegom

| Component | Mass/% | Element | Amount of ion |
|--------------------------------|--------|------------------|---------------|
| SiO ₂ | 41.80 | Si | 7.894 |
| Al ₂ O ₃ | 20.81 | Al | 4.638 |
| TiO ₂ | 0.06 | Ti | 0.008 |
| B ₂ O ₃ | 5.15 | B | 1.679 |
| Fe ₂ O ₃ | 1.13 | Fe ³⁺ | 0.161 |
| FeO | 6.26 | Fe ²⁺ | 0.989 |
| CaO | 19.34 | Ca | 3.913 |
| MgO | 0.40 | Mg | 0.113 |
| MnO | 3.58 | Mn | 0.573 |
| ZnO | 0.03 | Zn | 0.004 |
| Na ₂ O | 0.04 | Na | 0.015 |
| K ₂ O | 0.06 | K | 0.014 |
| H ₂ O(+) | 1.40 | OH | 1.764 |
| | | O | 30.236 |
| Total: | 100.06 | | |

bauer investigations [3]. The formula, neglecting the elements occurring in quantities smaller than 0.1 wt%, is:



Changes occurring in the structure of axinite during heating were studied by means of X-ray and FTIR methods. The DTA, TG and DTG curves were first recorded in order to choose appropriate temperatures for taking samples for further X-ray and IR studies. In the following runs, heating was stopped at the established temperatures and the sample was investigated after cooling to room temperature.

TG, DTG and DTA curves were recorded simultaneously by means of a computer-controlled derivatograph C (MOM, Hungary).

100 mg samples of axinite were heated in Pt crucibles, in air, at a heating rate of $10^{\circ}\text{C min}^{-1}$.

DTA curves of axinite were recorded by using a Perkin-Elmer DTA-7 analyser, nitrogen atmosphere and a heating rate of $2.5^{\circ}\text{C min}^{-1}$.

X-ray powder patterns were obtained by means of a DRON-3 (former USSR) diffractometer, using Ni-filtered CuK_{α} radiation.

Fourier-transform infrared spectra were recorded by using a BIORAD FTIR spectrometer. Samples were prepared as KBr discs in a proportion of 1 mg sample to 300 mg KBr.

Results

The DTA curve of axinite exhibits one endothermic effect within the temperature range $860\text{--}920^{\circ}\text{C}$ (Fig. 2). It has a distinct inflection at about 900°C clearly visible when low heating rate is applied (Fig. 3, see DDTA curve). The endothermic effect is accompanied by a 0.72 wt% loss in the TG curve due to the release of water molecules, formed as a result of dehydroxylation of the mineral. The theoretical mass loss resulting from the H_2O^+ the content (1.4 wt%) is to a considerable degree compensated by the oxidation of Fe^{2+} .

The dehydroxylation of other axinite samples (from Switzerland and France) occurs in a similar temperature range and the respective endothermic peaks also display a weak but visible asymmetry.

On the basis of the DTA curve of axinite from Strzegom three samples were chosen for further investigations, obtained by heating to the following temperatures: 864°C (i.e. the beginning of the DTA dehydroxylation effect), 897°C (i.e. the inflection point on the DTA curve), and 930°C (i.e. the end of dehydroxylation).

The X-ray diffraction pattern of the non-heated sample is typical of axinite (Table 2, Fig. 4), no additional reflections being recorded. It testifies the purity of the material studied. The same remark refers to the IR spectrum (Figs 5, 6) [4]. The position of the absorption band at ca. 3385 cm^{-1} , due to hydroxyl groups, in-

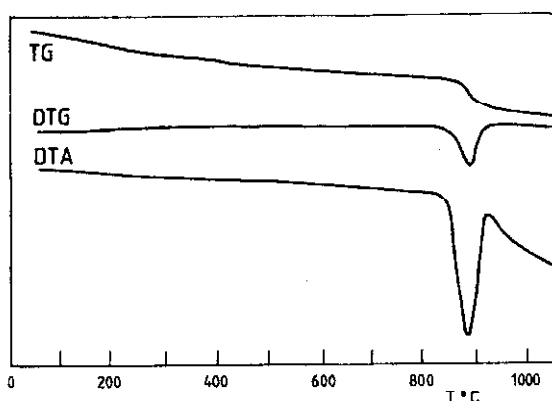


Fig. 2 Simultaneous TG, DTG and DTA curves of axinite from Strzegom. Heating rate: $10^{\circ}\text{C min}^{-1}$

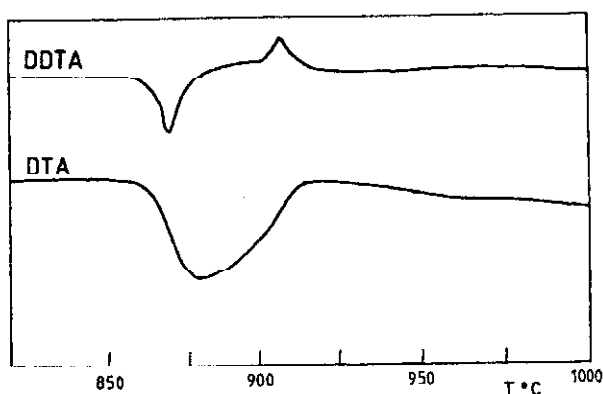


Fig. 3 DTA and DDTA curves of axinite from Strzegom. Heating rate: $2.5^{\circ}\text{C min}^{-1}$

indicates that they are only slightly involved in H-bonds whose length is ca. 2.83 \AA [5]. The band is slightly asymmetric, showing a shoulder on the lower frequency side. After deconvolution (Fig. 7) two components (a more intensive band at 3386 and a smaller one at 3355 cm^{-1}) appeared. A slight asymmetry of this band was recorded also in the IR spectra of other axinite samples (from Switzerland and France). It indicates that the OH...O bond length in the axinite crystal lattice is somehow diversified, which can result also in the above mentioned inflection on the DTA curve.

The X-ray pattern, recorded after heating the sample up to 864°C , does not indicate distinct phase transformations. The axinite structure has essentially been preserved, however, some changes in the intensity ratio of reflections and a few reflections not recorded previously are observed. The latter have not been unequivocally identified. More distinct changes appear in the IR spectrum in the

Table 2 X-ray data for axinite from Strzegom and its decomposition products

| Axinite | | T_{room} | | 864°C | | 897°C | | 930°C | | Anorthite | | Rankinite | |
|------------------|-----|-------------------|-----|------------------|-----|------------------|-----|------------------|-----|------------------|-----|------------------|-----|
| JCPDS 27-76 | | T_{room} | | 864°C | | 897°C | | 930°C | | JCPDS 20-20 | | JCPDS 23-124 | |
| d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I |
| 6.289 | 70 | 6.34 | 15 | 6.35 | 44 | 6.36 | 18 | 6.36 | 2 | 6.410 | 4 | 6.536 | 8 |
| 4.525 | 30 | 4.55 | 9 | 4.57 | 17 | 4.71 | 5 | 4.68 | 3 | 4.695 | 12 | 4.484 | 30 |
| 3.984 | 20 | 3.95 | 5 | 4.00 | 13 | 4.03 | 31 | 4.04 | 33 | 4.032 | 45 | 3.992 | 11 |
| 3.676 | 60 | 3.65 | 7 | 3.68 | 17 | 3.77 | 13 | 3.77 | 21 | 3.788 | 25 | 3.788 | 50 |
| 3.460 | 80 | 3.46 | 32 | 3.48 | 88 | 3.50 | 37 | 3.64 | 16 | 3.623 | 30 | 3.509 | 4 |
| 3.279 | 60 | 3.25 | 7 | 3.30 | 16 | 3.36 | 19 | 3.47 | 8 | 3.460 | 12 | 3.367 | 25 |

Table 2 Continued

| Axinite JCPDS 27-76 | | T_{room} | | 864°C | | 897°C | | 930°C | | Anorthite JCPDS 20-20 | | Rankinite JCPDS 23-124 | |
|------------------------|-----|-------------------|-----|------------------|-----|------------------|-----|------------------|-----|--------------------------|-----|---------------------------|-----|
| d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I |
| 3.165 | 90 | 3.16 | 86 | 3.16 | 94 | | | 3.25 | 39 | 3.257 | 50 | | |
| 3.077 | 40 | 3.08 | 7 | 3.09 | 29 | 3.06 | 5 | 3.14 | 24 | 3.205 | 60 | 3.205 | 60 |
| 3.021 | 50 | | | 3.04 | 6 | | | | | 3.195 | 100 | | |
| 2.994 | 60 | 3.01 | 22 | 2.992 | 60 | 3.005 | 17 | 3.02 | 19 | 3.185 | 90 | 3.017 | 100 |
| 2.967 | 50 | 2.966 | 5 | | | | | 2.950 | 7 | | | 2.907 | 60 |
| | | | | | | 2.902 | 29 | 2.900 | 13 | | | | |
| 2.874 | 30 | 2.892 | 12 | 2.899 | 40 | 2.837 | 50 | 2.842 | 7 | 2.825 | 20 | | |
| 2.809 | 100 | 2.805 | 100 | 2.824 | 100 | | | | | | | | |
| 2.793 | 40 | | | 2.777 | 27 | | | | | | | | |
| 2.667 | 40 | | | 2.554 | 19 | 2.713 | 10 | 2.711 | 3 | | | 2.717 | 80 |
| 2.646 | 40 | | | | | 2.649 | 7 | 2.656 | 11 | 2.653 | 12 | | |

Table 2 Continued

| Axinite JCPDS 27-76 | | T_{room} | | 864°C | | 897°C | | 930°C | | Anorthite JCPDS 20-20 | | Rankinite JCPDS 23-124 | |
|------------------------|-----|-------------------|-----|------------------|-----|------------------|-----|------------------|-----|--------------------------|-----|---------------------------|-----|
| d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I | d_{hkl} | I |
| 2.564 | 60 | 2.559 | 21 | 2.561 | 57 | 2.563 | 6 | 2.574 | 6 | 2.558 | 6 | | |
| 2.475 | 20 | 2.477 | 6 | 2.476 | 7 | 2.519 | 8 | 2.519 | 18 | 2.525 | 20 | | |
| 2.421 | 50 | 2.429 | 5 | 2.437 | 19 | 2.440 | 4 | | | 2.439 | 6 | | |
| 2.398 | 10 | | | 2.394 | 40 | | | | | | | | |
| 2.364 | 50 | 2.362 | 7 | | | 2.379 | 6 | | | 2.387 | 4 | | |
| 2.275 | 30 | | | 2.277 | 11 | | | | | | | | |
| 2.252 | 30 | 2.253 | 5 | | | | | | | | | | |
| 2.191 | 60 | 2.191 | 8 | | | | | | | | | | |
| 2.165 | 70 | 2.159 | 22 | 2.182 | 64 | | | | | | | 2.169 | 20 |
| | | | | | | 2.182 | 32 | | | | | | |
| 2.062 | 50 | 2.059 | 9 | 2.066 | 23 | 2.136 | 8 | 2.139 | 11 | 2.141 | 15 | | |
| 2.041 | 50 | 2.034 | 23 | | | 2.103 | 9 | | | 2.096 | 10 | | |
| 1.996 | 30 | 1.997 | 36 | 2.003 | 53 | 2.032 | 28 | 2.040 | 6 | | | | |

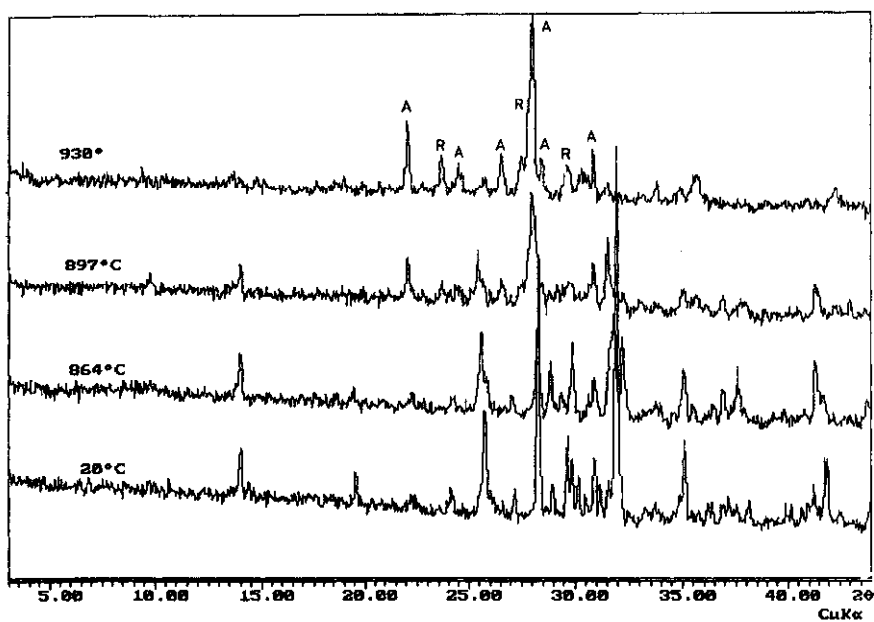


Fig. 4 X-ray powder pattern of axinite from Strzegom and its decomposition products.
A – anorthite, R – rankinite

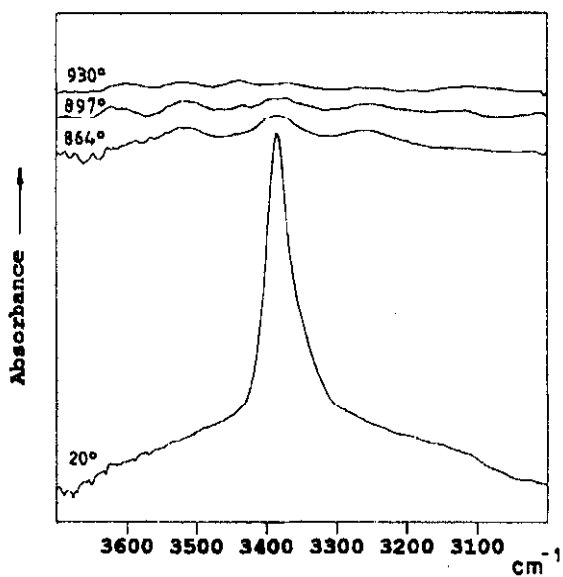


Fig. 5 FTIR spectra of axinite from Strzegom and its decomposition products in the spectral region of 3700–3000 cm⁻¹

fundamental region of Si–O and B–O vibrations (Fig. 6). The fine structure of the axinite spectrum in the most part disappears indicating considerable disordering of its structure.

Heating of the sample up to 897 °C results in the destruction of the axinite structure. The only detected crystalline phase are anorthite, $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ and rankinite, $\text{Ca}_3[\text{Si}_2\text{O}_7]$, accompanied probably by amorphous phases. Two broad absorption bands in the 900–1100 cm^{-1} region of the IR spectrum are certainly due to the already mentioned disordering of the silicates.

It should be emphasized that Si_2O_7 groups occur in the crystal structure of axinite, which can facilitate the formation of rankinite, which is just a disilicate.

Further heating of the sample, up to 930°C, results most probably in a structural ordering of silicates and certainly also in a partial recrystallization of amor-

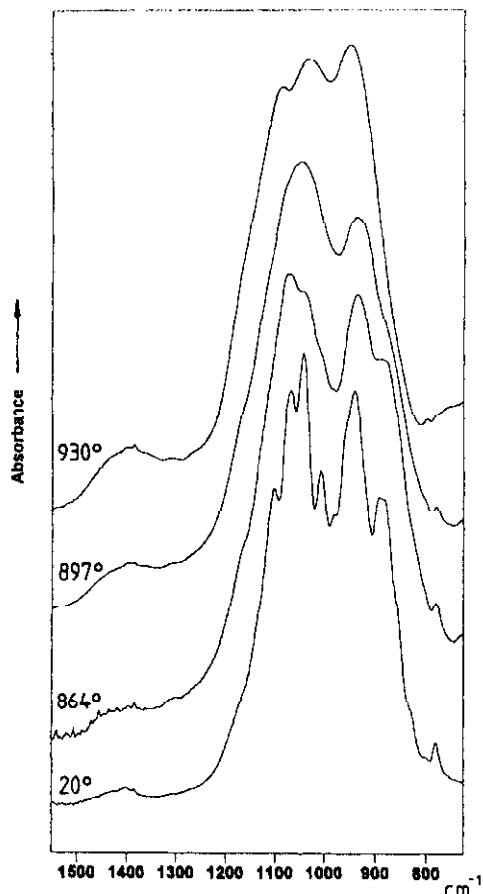


Fig. 6 FTIR spectra of axinite from Strzegom and its decomposition products in the spectral region 1500–800 cm^{-1}

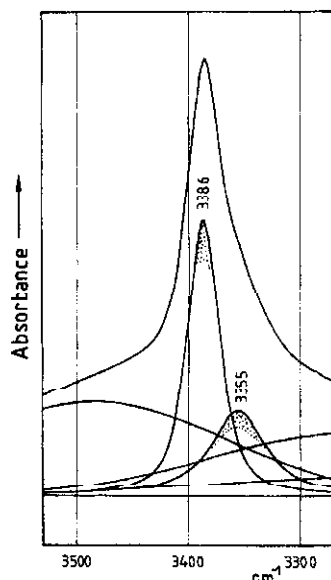


Fig. 7 A fragment of IR spectrum of axinite from Strzegom and deconvolution products of the absorption band ca. 3385 cm^{-1}

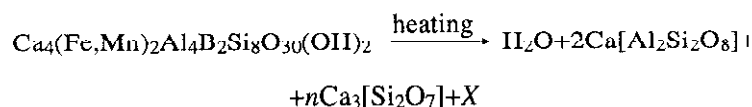
phous phases. This could explain the distinct domination of anorthite over rankinite in the final product of our experiment, which is supported by the X-ray pattern (Fig. 4). Also the IR spectrum (Fig. 5) becomes similar to that of anorthite [4], its fine structure being well visible.

Mössbauer investigations of the products obtained by the heating of axinite up to 930°C (J. Kraczka, pers. commun.) have shown that Fe occurs exclusively in the trivalent state. The presence of a small amount of hematite could be identified, the remaining part of Fe^{3+} being hosted by non-magnetic phases. However, due to the low content of these phases and superposition of their X-ray reflections on the diffraction pattern of anorthite and rankinite, their unequivocal identification was not possible.

Conclusions

On the basis of the above mentioned data some conclusions were drawn concerning the mechanism of the thermal decomposition of axinite.

It seems reasonable to assume that the thermal decomposition of axinite can be described by the following equation:



where: $0 < n < 2/3$, and X corresponds to the sum of further products, probably at least partly amorphous. The quantity of anorthite, being the main product of decomposition of axinite, must be limited by its Al content. The quantity of rankinite results probably from the binding of the remaining part of Ca by silica. Based on these assumptions we should expect the presence of significant amounts of other components (Fe_2O_3 , MnO , B_2O_3 , SiO_2) in the decomposition products of axinite heated up to 930°C . They are most probably partly amorphous. However, the presence of small amounts of crystalline phases is not excluded, the more so as in the X-ray diffraction pattern of the sample heated up to 897 and 930°C some weak reflections appeared, which do not belong to anorthite or rankinite. On the basis of Mössbauer spectroscopic studies only a small amount of hematite could be unequivocally established.

As has already been emphasized, Si_2O_7 groups occurring in the crystal structure of axinite might facilitate the formation of rankinite, which is just a disilicate. This reaction has, therefore, some topotactic features [6].

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