The basic crystallographic data of AgTh$_2$(PO$_4$)$_3$ single crystals have been determined for the first time by means of X-ray diffraction methods. The crystals are monoclinic, space group is Cc with four formula units per unit cell. The dimensions of the unit cell are: $a = 17.385$ Å, $b = 6.815$ Å, $c = 8.148$ Å, $\beta = 101.10^\circ$.

Using the Sawyer and Tower method it has been proved that the crystals possess ferroelectric properties. Performing the measurements at room temperature the values of spontaneous polarization and coercive field in the direction normal to (100) face have been determined.

**INTRODUCTION**

The results of recent experimental investigations have shown an interesting fact that some phosphates without the hydrogen bond, as NaTh$_2$(PO$_4$)$_3$ and NaU$_2$(PO$_4$)$_3$, also possess ferroelectric properties [1, 2]. The crystals are monoclinic, with space group Cc and four formula units per unit cell. These results have incited us to continue with investigation of the properties of other isomorphous and isostructural substances. Now our attention has been oriented to AgTh$_2$(PO$_4$)$_3$. The preparation of this compound and its interplanar spacings were published in 1964 [3].

The present paper deals with preparation and morphological analysis of AgTh$_2$(PO$_4$)$_3$ crystals, determination of unit cell dimensions and ferroelectric hysteresis loop trace results.

**EXPERIMENTAL**

In our work we modified a little the original procedure for preparation of AgTh$_2$(PO$_4$)$_3$. The crystals were prepared by heating a mixture of stoichiometric proportions of ThO$_2$, AgNO$_3$ and HPO$_3$. An excess of HPO$_3$ would unfavourably act on crystallization. The mixture was heated at 1200 °C for 24 hours in air. After that the system was cooled to room temperature in 24 hours. AgTh$_2$(PO$_4$)$_3$ crystals were separated by dissolving the soluble substances first in boiling water and then in HNO$_3$ (1 : 1).

Morphological analysis of obtained crystals was done by means of an optical goniometer. The procedure for determination of unit cell parameters depended on the shape of valuable crystals and it was chosen as follows. At first approximate values of $a$, $b$ and $c$ were obtained using the oscillation X-ray diffraction photographs. Then by means of a counter diffractometer and using plate-shaped crystals with well-formed (100) and (110) faces, very accurate values of $a \sin \beta$ and $b$ were determined from $h00$ and $kh0$ reflections at high Bragg angles. Using rotation of a very thin needle-like crystal around its [001] axis in a precise Debye-Scherrer camera all
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possible reflections $hk0$ at highest Bragg angles were recorded. In this case $a \sin \beta$ and $b$ were deduced even more accurately. It was not possible to measure the angle $\beta$ using optical goniometer because of very bad crystal faces with index $l$. $\beta$ was determined using the Weissenberg method by rotation of a crystal around $b$ axis. $\beta$ and $c$ were calculated together using powder pattern reflections with known indices at small Bragg angles recorded by means of diffractometer. In this case we used several groups of three reflections (one of them was always the line 600 as angular standard) taking into account the previously determined values of $a \sin \beta$ and $b$. The values of $c$ and $\beta$ deduced in this way were more accurate than the values obtained from oscillation and Weissenberg photographs, respectively. The whole procedure was undertaken because of great difficulties and uncertainties in determination of indices of powder pattern reflections for Bragg angles above $40° (2\theta)$. In all cases CuKα radiation was used and the diffraction patterns were recorded at room temperature $(25 \pm 1)°C$.

Using the same procedure the unit cell parameters of NaTh$_2$(PO$_4$)$_3$ were also determined in order to make a comparison between unit cell sizes of the two compounds. Unit cell parameters of NaTh$_2$(PO$_4$)$_3$ were published earlier but not with such accuracy [4].

Ferroelectric properties were investigated using the same method as in earlier work [1, 2]. The samples were of similar size as previously, as well as the way of preparing the electrodes. This time the samples selected for electrical measurements were annealed at $800 °C$ for 140 hours, and then slowly cooled to room temperature at a rate of $10 °C/hour$. The annealing at higher temperatures cannot be recommended. After a prolonged heating at $1050 °C$ crystals start to decompose. White patches of ThO$_2$ appear on the crystal surface (Fig. 1a,b,c,d Appendix IV., p. 1062i.).

### RESULTS

The results of morphological investigation of a number of crystals are summarized in Fig. 2. The crystals appear most frequently as small platelets with dominant(100) or (110) forms, or they are elongated along $c$ axis having needle-like shape. Other crystal forms seldom appear and they are not well developed. The crystal shape depends in a great deal on the way of preparation. Crystals grown in a Pt crucible were nearly all needles, but platelets appear when using a Pt dish.

The unit cell parameters of AgTh$_2$(PO$_4$)$_3$ and NaTh$_2$(PO$_4$)$_3$ are listed in Table 1.

<table>
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<th>$a$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\beta$ ['']</th>
<th>$a \sin \beta$ [Å]</th>
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<tr>
<td>AgTh$_2$(PO$_4$)$_3$</td>
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<td>8.148</td>
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<td>17.060</td>
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<tr>
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<td>6.813</td>
<td>8.150</td>
<td>101.10</td>
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