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X-ray, Dielectric, and Optical Study of Ferroelectric Lead Metatantalate and Related Compounds

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Single crystals of ferroelectric lead metatantalate, $PbTa_2O_6$, have been grown using $Pb_2V_2O_7$ as a flux. An X-ray and optical study shows that $PbTa_2O_6$ has orthorhombic symmetry with

$$a_0 = 17\cdot68,\ c_0 = 7\cdot754\ \text{Å},\ b_0/a_0 = 1\cdot002$$

at room temperature. The ferroelectric axis is perpendicular to the [001] direction. Dielectric constant and birefringence along the three directions have been measured as a function of temperature through the Curie point at 265 °C. The crystals remain orthorhombic in the paraelectric region.

A dielectric and X-ray study of the solid solution systems $Pb(Ta,Nb)_2O_6$, $(Pb,Ba)Nb_2O_6$, and $(Pb,Sr)Ta_2O_6$ shows the existence of a phase boundary in the first two systems, separating different ferroelectric modifications. Besides the ferroelectric modification, $PbTa_2O_6$ has a non-ferroelectric, rhombohedral form.

1. Introduction

Investigations following the discovery of ferroelectricity in barium titanate, $BaTiO_3$, have revealed ferroelectric properties in a number of double oxides. These include lead metatantalate, $PbTa_2O_6$, and lead metaniobate, $PbNb_2O_6$, which are ferroelectric with Curie temperatures at 260 °C. (Smolenskii & Agranovskaya, 1954) and 570 °C. (Goodman, 1953), respectively. $PbNb_2O_6$ belongs to the orthorhombic system with

$$a_0 = 17\cdot65,\ b_0 = 17\cdot91,\ c_0 = 7\cdot736\ \text{Å}$$

at room temperature. The large unit cell made it difficult to understand the structural implications of the occurrence of ferroelectricity in this crystal. Recently Francombe & Lewis (1958) have carried out dielectric, optical, and X-ray studies on single crystals of $PbNb_2O_6$. These authors have drawn attention to the close structural resemblance between the paraelectric phase of $PbNb_2O_6$ and some tetragonal tungsten bronzes. These structures bear a similarity to the perovskite structure in possessing BO_6 octahedra surrounding an A ion. Looking at the structure of $PbNb_2O_6$ in this manner, it may be possible to understand the ferroelectric behavior of this crystal.

Compared with the rather detailed studies made on $PbNb_2O_6$, relatively little information is available on the related compound, $PbTa_2O_6$, since the latter has been studied only in the polycrystalline form. The purpose of the present investigation is to carry out X-ray, dielectric, and optical studies on single crystals of $PbTa_2O_6$. This study has been extended to the solid solution system $PbTa_2O_6$–$PbNb_2O_6$, in order to elucidate any structural distinction between these two ferroelectric compounds.

2. Polymorphism and crystal growth

Studies on the polymorphism of $PbNb_2O_6$ had revealed the existence of a non-ferroelectric modification in addition to the ferroelectric form. In the case of $PbTa_2O_6$, only the ferroelectric modification had been reported (Smolenskii & Agranovskaya, 1954; Francombe & Lewis, 1958). However, an X-ray examination of samples prepared at different temperatures indicated the existence of other modifications. The detailed results of the study of the polymorphism of this compound will be discussed elsewhere in a paper on the phase relationships in the system $PbO–Ta_2O_5$ (Subbarao, 1959). Only the pertinent information is presented here.

Depending upon the temperature of formation, $PbTa_2O_6$ exists in two forms, rhombohedral and orthorhombic. The rhombohedral phase is stable only below about 1150 °C. and is not ferroelectric. The transformation from the rhombohedral to the orthorhombic phase is slow. Once formed, the orthorhombic form could not be transformed into the rhombohedral modification by heat treatments.

Crystals of the rhombohedral phase cannot be made by melting the compound. Because of the high melting point (>1500 °C.) of $PbTa_2O_6$ and the volatility of PbO at these temperatures, single crystals of orthorhombic $PbTa_2O_6$ could not be grown from the melt. Crystals of the two forms were finally grown from a $Pb_2V_2O_7$ flux, as was suggested by Cook (1958*b*).

2·1. *Rhombohedral* $PbTa_2O_6$

A mixture of PbO, Ta_2O_5,* and V_2O_5 in the molar ratio 3:1:1 (corresponding to $PbTa_2O_6:Pb_2V_2O_7$ ratio of 1:1) was used. A typical batch consisted of 20·1 g. PbO, 13·3 g. Ta_2O_5, and 5·46 g. V_2O_5. The platinum crucible, containing the mixture, was embedded in alumina powder. It was heated in a globar furnace to 1100 °C. and was held at that temperature for 4 hr. The furnace was then cooled at the rate of 40 °C./hr. No measurable weight loss was observed after this heat treatment. The resulting mass was placed in hot dilute nitric acid for several hours to dissolve the flux and the crystals were then washed in running water. Hexagonal-shaped crystals that were approximately 0·5 mm.^{2} in area and 0·4 mm. in thickness were obtained. These crystals are clear and are optically uniaxial. The powder pattern of the crushed crystals agrees with that of $PbTa_2O_6$ powder prepared at 900 °C. On the basis of the oscillation and Weissenberg study, these crystals were found to possess rhombohedral symmetry. The single crystal data, together with the powder pattern, give the following rhombohedral parameters at room temperature: $a_R = 7{\cdot}147$ Å and $\alpha_R = 94° \, 47'$. The corresponding hexagonal spacings are $a_H = 10{\cdot}52$ and $c_H = 11{\cdot}30$ Å. The lines of the powder pattern of the rhombohedral $PbTa_2O_6$ with $2\theta < 60°$ are indexed in Table 1 and the intensities are expressed as the peak heights on the diffractometer chart. The measured density of about 6·6 g.cm.$^{-3}$ suggests 2 molecules per unit cell. The lattice parameters of rhombohedral $PbTa_2O_6$ given above are quite close to those of rhombohedral $PbNb_2O_6$, i.e., $a_R = 7{\cdot}168$ Å and $\alpha_R = 93° \, 52'$ (Cook, 1958*a*) and $a_R = 7{\cdot}184$ Å and $\alpha_R = 93° \, 55'$ (Roth, 1959).

Table 1. *X-ray diffraction powder data for rhombohedral* $PbTa_2O_6$

($a_R = 7{\cdot}147$ Å, $\alpha_R = 94° \, 47'$, Cu $K\alpha$ radiation)

hkl	d_o (Å)	d_c (Å)	*I*
110	4·79	4·801	2
$11\bar{1}$	4·217	4·225	2
111	3·762	3·766	7
120	3·061	3·062	93
$11\bar{2}$	3·034	3·037	100
$22\bar{1}$	2·364	2·364	3
$\bar{1}3\bar{1}$	2·232	2·233	3
$13\bar{1}$	2·157	2·157	28
$03\bar{2}$	2·056	2·055	3
222	1·885	1·883	10
$23\bar{2}$	1·760	1·762	35
$03\bar{3}$	1·755	1·753	34
330	1·603	1·601	26
$14\bar{2}$	1·591	1·593	3

2·2. *Growth of ferroelectric* $PbTa_2O_6$ *crystals*

The same mixture as was used for growing the rhombohedral $PbTa_2O_6$ crystals was utilized for the growth of ferroelectric crystals. It was heated at the rate of 250 °C./hr. to 1400 °C., soaked at that temperature for 18 hr., and then cooled to room temperature at the rate of 40 °C./hr. The flux was dissolved in the same manner as was described in the previous section. These crystals were generally of the order of 10 microns. In order to obtain larger crystals the following procedure was adopted. These small crystals were mixed with sufficient PbO and V_2O_5 to give an equimolar mixture of $PbTa_2O_6$ and $Pb_2V_2O_7$ and the mixture was subjected to the same heat treatment as outlined above. This resulted in some crystals that were $1 \times 1 \times 4$ mm. in size. They were generally parallelepipeds. The weight loss was 1–2% due to the heat treatments. Spectrographic analysis shows the vanadium content of these crystals to be $<0{\cdot}1\%$. The powder pattern of the crushed crystals is identical to that of ferroelectric $PbTa_2O_6$. The morphology of crystals smaller than approximately 40 microns is characterized by the existence of {100} faces and smaller (110) faces, but (101) and (011) faces never appear. Crystals as large as 100 microns frequently exhibit only {100} faces. These crystals are generally elongated along the [001] axis.

3. Ferroelectric $PbTa_2O_6$

3·1. *Room-temperature study*

Observation of the conoscopic interference figures with the polarizing microscope show that the $PbTa_2O_6$ crystals are biaxial. The orientation of the acute and the obtuse bisectrix cannot be determined on the basis of these observations alone, because the brushes, or the points of emergence of the optic axes, lie outside the field of vision in every case. The color symmetry in the conoscopic interference figure obtained with

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* The Ta_2O_5, containing less than 0·02% Nb, was supplied by the Kennametal Company.

white light points definitely to orthorhombic symmetry. The largest refractive index (n_γ) is along the crystallographic [001] direction.

Thin (001) sections often appear twinned. The twin boundary is oriented approximately along (110) but always appears curved and irregularly shaped. The twinning rule is a rotation by 90° around the [001] direction, so that the [100] and [010] axes of two adjacent twins are interchanged. This follows from the fact that in thin sections both twins exhibit the same interference color, but any retardation plate shows that the slow ray of one twin is perpendicular to the fast ray of the other, and vice versa.

The birefringence of several selected crystals was measured at room temperature by means of a Berek compensator. With this method, the largest error involved in the determination of the birefringence is due to the measurement of the thickness of the crystal. This error may amount to 10–15%. For the measurement of crystals in the directions perpendicular to [001], care was taken to select untwinned specimens. The results reported below represent an average of over 20 different crystals of each orientation:

$$n_\beta - n_\alpha = 0{\cdot}016$$
$$n_\gamma - n_\beta = 0{\cdot}043$$
$$n_\gamma - n_\alpha = 0{\cdot}059$$

The optic sign is therefore positive.

An X-ray study of twinned single crystals of ferroelectric $PbTa_2O_6$ showed that a and b are nearly equal, the ratio b/a being of the order of the Cu $K\alpha_1$ and $K\alpha_2$ splitting, i.e., about 1·002. The room temperature lattice parameters of the orthorhombic $PbTa_2O_6$ are:

$$a_0 = 17{\cdot}68,\ b_0 = 17{\cdot}72,\ c_0 = 7{\cdot}754\ \text{Å}\,.$$

The a and c values were obtained from an X-ray powder pattern, in which several reflections with $2\theta < 60°$ were indexed. The b/a ratio was used to obtain the b value. The measured density of these crystals is about 7·9 g.cm.$^{-3}$ giving 16 molecules per unit cell. All the (hkl) reflections with $l = 2n+1$ were very weak in the case of $PbTa_2O_6$ as was noted for $PbNb_2O_6$.

Due to the extremely small magnitude of the orthorhombic distortion, the powder patterns of ferroelectric $PbTa_2O_6$ can be indexed quite well on the basis of a tetragonal cell. The spacings for a tetragonal cell of $PbTa_2O_6$ ($a_0 = 12{\cdot}49$, and $c_0 = 3{\cdot}875$ Å) taken by Francombe & Lewis (1958) correspond to the true (110) and (002) spacings.

A comparison of the lattice parameters of $PbTa_2O_6$ with those of $PbNb_2O_6$, i.e.,

$$a_0 = 17{\cdot}65,\ b_0 = 17{\cdot}91,\ c_0 = 7{\cdot}736\ \text{Å}$$

(Francombe & Lewis, 1958) shows that while the a and the c parameters are essentially the same, the b/a ratio of 1·002 for $PbTa_2O_6$ is much smaller than the value of 1·016 for $PbNb_2O_6$. This may be related to the larger birefringence values reported for $PbNb_2O_6$ (Francombe & Lewis, 1958) compared with those for $PbTa_2O_6$.

The dielectric constant was measured on a number of selected crystals parallel and perpendicular to the [001] axis. These measurements were carried out on a General Radio capacitance bridge type 716-C with a measuring field of about 10 V.cm.$^{-1}$ at a frequency of 10 kilocycles per second. The accuracy of the dielectric constant is estimated to be $\pm$15–20%. The major source of error is the measurement of the dimensions of the small and somewhat irregular crystals. The dielectric constant along the [001] axis is about 150. Perpendicular to this axis, approximate values of either 300 or 700 are usually obtained. The latter values are dependent upon the twin configuration of the crystals.

Hysteresis loops were observed for these crystals perpendicular to the c-axis. The loops did not completely saturate at field strengths of the order of 25 kV. cm.$^{-1}$ at 60 cycles per second. An approximate value of $8\text{–}10 \times 10^{-6}$ coul cm.$^{-2}$ was estimated for the spontaneous polarization at room temperature. This is about 3 times the value reported for polycrystalline $PbTa_2O_6$ (Smolenskii, 1956). Only a linear relationship exists between polarization and applied electric field in $PbTa_2O_6$ crystals along the [001] direction up to a field strength of about 15 kV. cm.$^{-1}$.

3·2. *Phase transition*

The volume change at the Curie point is small as shown by the small magnitude of the anomaly in the linear thermal expansion of polycrystalline $PbTa_2O_6$ at the transition (Fig. 1). The thermal expansion of a cylindrical sample about 3 cm. long and 0·4 cm. in diameter was measured by using a fused quartz tube dilatometer with an optical lever magnification of about 500. The coefficient of linear thermal expansion is about 4×10^{-6} per °C. below and 8×10^{-6} per °C. above the phase change.

The birefringence of $PbTa_2O_6$ crystals was measured

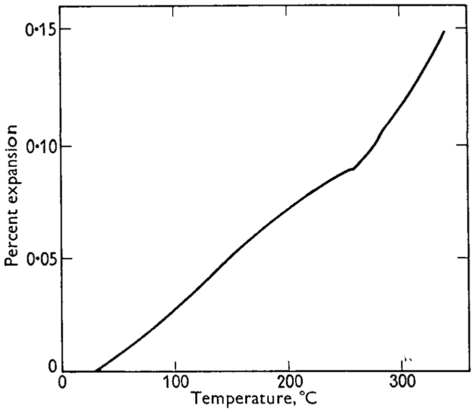

Fig. 1. Linear thermal expansion of polycrystalline $PbTa_2O_6$.

from room temperature to 365 °C. by means of a Berek compensator and a Leitz heating microscope stage which allows very close control of the temperature. In this case, the relative accuracy is that of the Berek compensator, about 2%. The results are shown in Fig. 2.

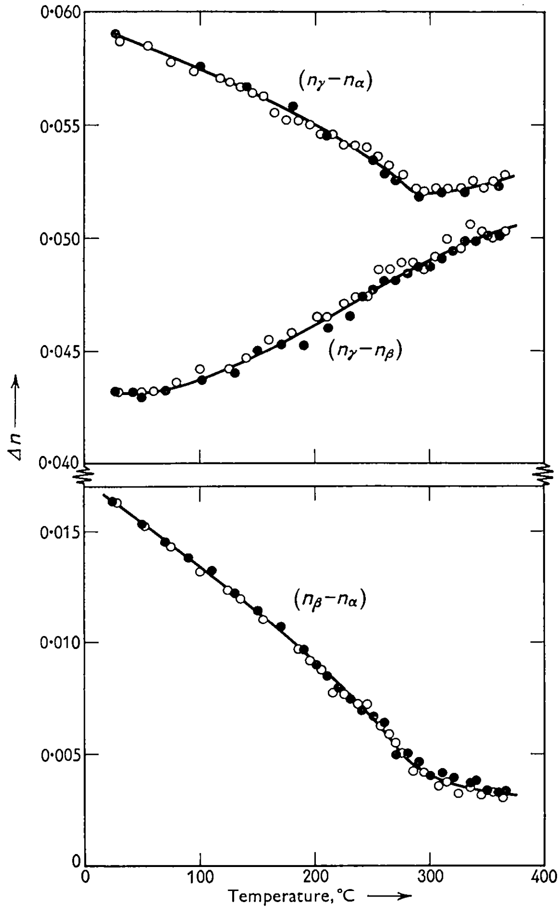

Fig. 2. Birefringence of $PbTa_2O_6$ as a function of temperature. Heating cycles; open and full circles refer to different crystals.

It is typical of these $PbTa_2O_6$ crystals that the ferroelectric transition at approximately 265 °C. cannot be detected by visual observation of crystals on the microscope stage. Above the phase change, the deviation from tetragonal symmetry is even smaller than below, $n_\beta-n_\alpha$ being of the order of 0·003 at 360 °C., but the crystals are still biaxial. The (110) twin boundaries do not disappear and the twins maintain the same relative orientation, with respect to each other, as below the transition. The temperature dependence of birefringence of the $PbTa_2O_6$ crystals suggests a second order phase change in $PbTa_2O_6$.

The variation of the dielectric constant of $PbTa_2O_6$ crystals with temperature was measured parallel and perpendicular to the c-axis from room temperature to 300 °C. (Fig. 3). The dielectric constant along the c-axis is the smallest of the three values and does not show any anomalous behavior. This is in agreement with the fact that $PbTa_2O_6$ is not ferroelectric along the c-axis. On the other hand, the dielectric constant values in the two directions perpendicular to the c-axis increase with increasing temperature, one direction giving a higher peak value than the other at the Curie point (Fig. 3). The smaller peak may be due to the twin configuration of the crystals. The fact that the dielectric constant values along the two directions perpendicular to the c-axis are not equal shows that orthorhombic symmetry is maintained above the Curie point.

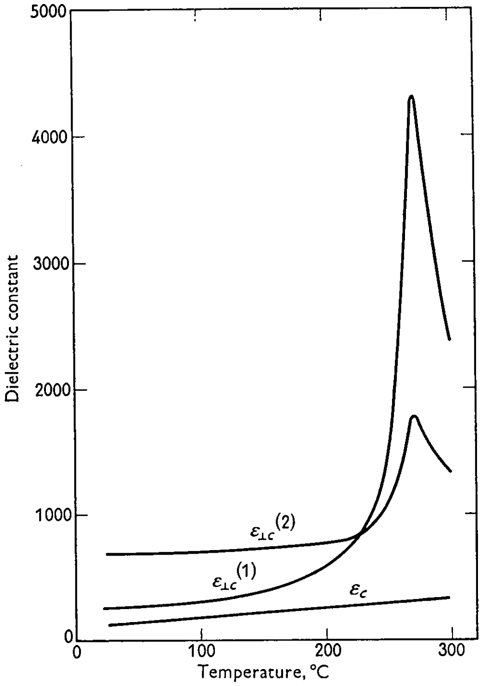

Fig. 3. Temperature dependence of dielectric constant of $PbTa_2O_6$ single crystals.

The dielectric constant in the direction showing the highest peak at the Curie point obeys the Curie-Weiss law in the paraelectric region:

$$\varepsilon \simeq C/(T-T_0)\,, \tag{1}$$

where ε is the dielectric constant at temperature T, T_0 is the Curie-Weiss temperature, and C is the Curie constant. Values of $T_0=237$ °C. and $C=1{\cdot}5\times10^5$ °C. were obtained for $PbTa_2O_6$. This value of the Curie constant is the same order of magnitude as that for $BaTiO_3$ and $PbNb_2O_6$ (Goodman, 1953). The reciprocal dielectric constant shows a linear dependence upon temperature immediately below the Curie point. The slope of this linear portion is about a third of the reciprocal of the Curie constant.

4. Solid solution study

In order to carry out a structural study of solid solutions in the system $PbTa_2O_6$–$PbNb_2O_6$, various compositions were prepared from the constituent oxides. Appropriate firing temperatures in the range 1300–1450 °C. were selected to obtain the ferroelectric phase. The lattice parameters of solid solutions in this system obtained from Norelco diffractometer tracings are shown in Fig. 4. The spacings for pure $PbNb_2O_6$ from this study (a_0 = 17·64, b_0 = 17·94, and c_0 = 7·740 Å) are in good agreement with the literature values (Roth, 1957; Francombe & Lewis, 1958). The *a* and the *c* spacings change linearly with composition in this system, but the *b* spacing shows a discontinuity between 45 and 50% $PbNb_2O_6$. This sudden decrease in the *b* parameter is clearly evident in the following pairs of reflections: (280) and (820), (600) and (060), and (510) and (150). The *b* parameter is not shown in Fig. 4 for compositions containing 0 to 45% $PbNb_2O_6$, since *b* is too close to *a* in these compositions to be distinguished in X-ray powder patterns. Such a discontinuity in the lattice parameter must be due to a change in the structure.

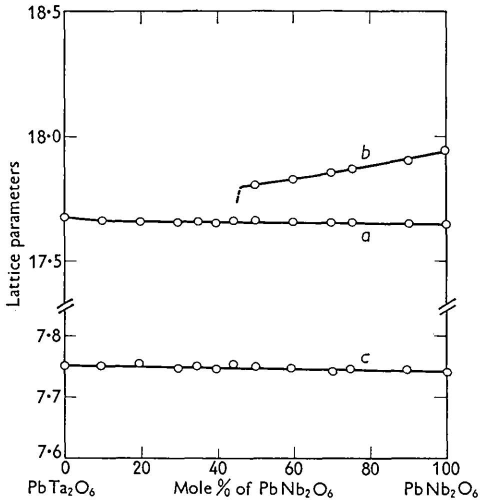

Fig. 4. Lattice parameters in the system $PbTa_2O_6$–$PbNb_2O_6$.

The existence of a phase boundary between ferroelectrics of two different structures may be confirmed by an investigation of their dielectric properties. With this in view, the temperature dependence of the dielectric constant of a number of compositions in this system were measured on ceramic discs. The transition temperatures detected by these measurements are shown in Fig. 5. The curve showing the variation of the Curie temperature with composition displays an anomaly at about the same composition where an abrupt decrease in the *b* parameter was noted, thus confirming the existence of two distinct ferroelectric phases. Careful examination of the temperature dependence of the dielectric constant of specimens close to the phase boundary did not reveal any additional anomalies suggesting that this boundary is essentially perpendicular to the composition axis. This phase line is similar to the one observed between the tetragonal and rhombohedral perovskite phases in the system $Pb(Ti, Zr)O_3$ (Shirane & Suzuki, 1952).

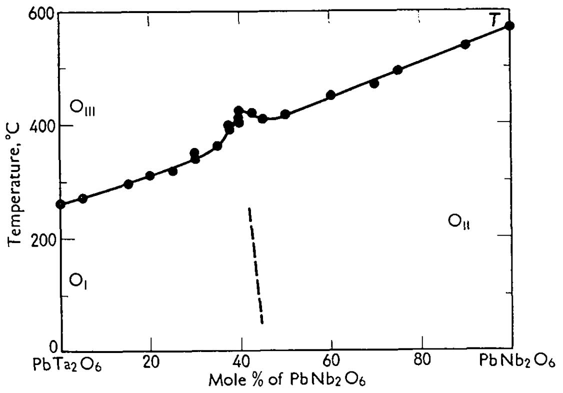

Fig. 5. Transition temperatures in the system $PbTa_2O_6$–$PbNb_2O_6$.

Because of the discovery of two ferroelectric phases in the $Pb(Ta, Nb)_2O_6$ system, solid solutions in the systems $PbNb_2O_6$–$BaNb_2O_6$ and $PbTa_2O_6$–$SrTa_2O_6$ were studied. A minimum in the Curie temperatures was observed at about 35% $BaNb_2O_6$ in the $(Pb, Ba)Nb_2O_6$ system. A phase boundary exists at this composition separating the $PbNb_2O_6$ type solid solutions from the $(Pb_{1-x}, Ba_x)Nb_2O_6$ type (with $0{\cdot}60 > x > 0{\cdot}35$) ferroelectrics, as substantiated by Francombe's (1959) recent results. A single crystal study showed that the *c* parameter of

$$(Pb_{0{\cdot}5}, Ba_{0{\cdot}5})Nb_2O_6$$

is approximately one half of that observed in $PbTa_2O_6$ and $PbNb_2O_6$. A dielectric study of the $(Pb,Ba)Nb_2O_6$ system was made by Goodman (1957) and Isupov &

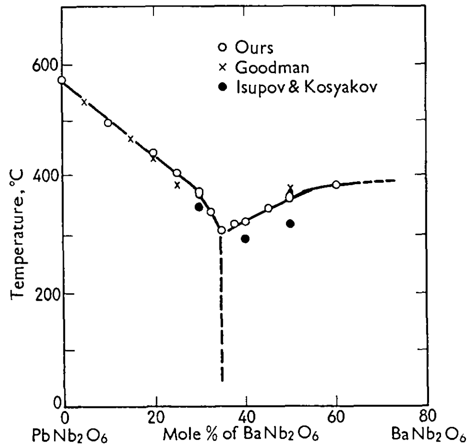

Fig. 6. Transition temperatures in the system $PbNb_2O_6$–$BaNb_2O_6$.

Kosyakov (1958) also, and their results are included in Fig. 6.

In the (Pb, Sr)Ta_2O_6 system, the Curie point decreases essentially linearly with Sr content. For 50% $SrTa_2O_6$, the maximum Sr addition studied, the Curie temperature is at −100 °C.

5. Discussion

The results of the present study of ferroelectric $PbTa_2O_6$ may be compared with the properties of ferroelectric $PbNb_2O_6$. Both these compounds possess orthorhombic symmetry, comparable lattice parameters, and a ferroelectric axis perpendicular to [001]. However, there seems to be some important differences between these two compounds. In the pseudo-cubic ferroelectric crystals of the perovskite or pyrochlore type, the spontaneous polarization can appear along any one of the three original cube edges. On the other hand, Francombe & Lewis (1958) have cited $PbNb_2O_6$ as an example of a 'two-dimensional' ferroelectric, since spontaneous polarization can occur in two directions, identified with the [100] and [010] axes of the orthorhombic unit cell. However, $PbTa_2O_6$ appears to represent a 'unidirectional' ferroelectric, in spite of the smaller orthorhombic distortion of $PbTa_2O_6(b/a=1{\cdot}002)$ compared to that of $PbNb_2O_6(b/a=1{\cdot}016)$. This is supported by the following considerations. The maximum polarization measured on some crystals was more than twice that on other crystals, when a field of about 25 kV. cm.$^{-1}$ was applied perpendicular to the c-axis. The dielectric constants in the two directions perpendicular to the c-axis (and the temperature variation of these values) were essentially unchanged upon repeated heating through the Curie temperature. Furthermore, the optical observation of the (110) twin boundaries as the crystal was heated through the phase transition did not reveal any movement of these boundaries. These observations suggest that the (110) twin boundaries in $PbTa_2O_6$ crystals cannot be moved either by an applied field of the order of 25 kV. cm.$^{-1}$ or by heating them through the Curie temperature; this implies that the [100] and [010] axes cannot be interchanged by these treatments.

In the paraelectric state, $PbNb_2O_6$ is reported to be tetragonal, and $PbTa_2O_6$ is orthorhombic. Francombe & Lewis have drawn attention to the close structural resemblance between the paraelectric $PbNb_2O_6$ and some tetragonal tungsten bronzes. These structures are related to the ABO_3 perovskite structure in possessing rings of BO_6 octahedra surrounding the A ions. The similarity of the lattice parameters and the X-ray diffraction line intensities of $PbTa_2O_6$ and $PbNb_2O_6$ suggests that the structure of both these compounds is derived from the same basic structure.

A comment on the Curie temperature of $PbTa_2O_6$ seems to be in order. The Curie point (265 °C.) observed in the present study may be compared with the values in the literature. Smolenskii & Agranovskaya (1954) gave a value of 260 °C., and Isupov (1957) gave 240 °C. However, Francombe & Lewis obtained a value of 150 °C. Furthermore, the Curie temperatures of solid solutions in the system Pb(Ta, Nb)$_2$O$_6$ reported by Francombe & Lewis are lower than those obtained in the present study, the difference increasing with larger Ta content. As already mentioned, the niobium content of our crystals is <0·02% and vanadium content <0·1%. Polycrystalline samples of $PbTa_2O_6$ prepared from three different sources of Ta_2O_5 gave essentially the same Curie point. After the work reported here was completed, a paper by Coates & Kay (1958) came to the authors' attention. Coates & Kay did not observe ferroelectric behavior in $PbTa_2O_6$ but suggested a possible antiferroelectric transition at about 70 °C. These results are not in agreement with the results presented here.

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