



Ferroelectric phase transition temperatures of self-flux-grown RbTiOPO₄ crystals

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Abstract

A series of RTP crystals have been grown by the top-seeded solution growth method from self-fluxes containing different [Rb]/[P] atomic ratios (1.25–2) and solute concentrations (0.55–1.1 g-RTP/g-flux) covering a large portion of the RTP crystallization field in the Rb₂O–P₂O₅–TiO₂ ternary system. The Curie points of as-grown crystals have been determined using the standard dielectric (capacitance) technique, and they show a spread from 770 to 800 °C. This indicates a clear correlation between the crystal stoichiometry and the flux chemical composition in similarity with KTP crystals. The major difference from the KTP case is that each growth sector (solidified simultaneously) in nominally pure RTP crystals exhibits its specific Curie temperature. Chemical analysis and intentional doping experiments show that trace impurities may have a very limited influence on this effect. The abrupt changes of the Curie temperatures along simultaneously grown surfaces are discussed in terms of the diverse incorporation mechanisms of the stoichiometric components or native defects into specific crystallographic faces during growth.

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1. Introduction

Rubidium titanyl phosphate, RbTiOPO₄ (RTP), belongs to the isomorphic MTiOXO₄ family (KTP-family) of ferroelectric nonlinear optical and electro-optic crystals, where M = {K, Rb, Cs or Tl} and X = {P or As (for M = Cs only)} [1]. It is a particularly useful material for such electro-optic applications as high-frequency Q-switching and light modulation [2], due to its large electro-optic coefficients, high damage threshold and the absence of piezoelectric ringing. Low ionic conductivity RTP crystals are required for low leakage current operation of the devices. It has been shown that the one-dimensional ionic conductivity of KTP-family crystals is associated with site-to-site hopping of the monovalent cations along Z-directed channels in the tetragonal crystal framework [3]. Obviously, a vacancy-assisted

conductivity mechanism is involved. It is thus important, in the case of RTP, to monitor the concentration of Rb vacancies, or the degree of Rb stoichiometry, which may and usually does depend on the crystal growth conditions. Some basic ideas about such dependence for growing RTP crystals from self-fluxes can be based on the knowledge accumulated with similarly grown KTP crystals.

We have shown earlier [4] that the specific values of the ferroelectric transition (Curie) temperatures can be a good measure of the degree of potassium stoichiometry in KTP crystals grown from self-fluxes, namely potassium phosphates with differing [K]/[P] molar ratios. The larger is this ratio, or the richer (in potassium) is the flux, the higher is the potassium content in the crystal, which is manifested in its higher Curie temperature value. Accordingly, a KTP crystal growing out from a particular self-flux, say K₆P₄O₁₃, exhibits an ever increasing Curie temperature due to the gradual enrichment of the flux (and the crystal) in potassium. The change in the crystal chemical composition, e.g.

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stoichiometry, in course of growth inevitably results in gradual variation of some physical properties [5,6]. For example, appreciable gradients in the refractive indices from the seed to peripheral areas have been observed in large KTP crystals [6].

Similar effects may exist in RTP crystals, but they have not been examined until now. The dependence of the chemical composition of RTP crystals on the self-flux used and its variation in course of single crystal growth is of paramount importance for device applications. In the present work, we have grown a series of RTP crystals from self-fluxes with different [Rb]/[P] atomic ratios and with variable initial RTP relative concentration in the flux. The corresponding Curie temperatures have been measured and the results discussed in terms of the compositional variation of RTP crystals as a function of the self-flux chemical composition. A peculiar dependence of the Curie temperature on the growth morphology of RTP crystals has been revealed and studied as well.

2. Experimental

A series of RTP crystals have been grown by the top-seeded solution growth (TSSG) method with and without pulling from self-fluxes containing different rubidium to phosphorus atomic ratios, $R = [\text{Rb}]/[\text{P}]$ (with R varying from 1.25 to 2) and various solute concentrations (0.55–1.1 g-RTP/g-flux) covering a large portion of the RTP crystallization field in the $\text{Rb}_2\text{O}-\text{P}_2\text{O}_5-\text{TiO}_2$ ternary system. Solutions of RTP in self-fluxes were prepared by reacting the Aldrich 3N purity TiO_2 , Rb_2CO_3 and Merck (Suprapur) $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ in appropriate proportions. The main self-flux, or solvent, used for the RTP crystal growth is Rb6 ($\text{Rb}_6\text{P}_4\text{O}_{13}$, $R = 1.5$). Other self-fluxes, such as Rb4 ($\text{Rb}_4\text{P}_2\text{O}_7$, $R = 2$) or Rb10 ($\text{Rb}_{10}\text{P}_8\text{O}_{25}$, $R = 1.25$), were also used for the purposes of the current investigation.

The charges were loaded into 200–1000 ml Pt crucibles and subjected to 24 h soaking through homogenization aided by a Pt stirrer prior to crystal growth. The crucibles were mounted in a custom-made resistance furnace with a long hot zone allowing to obtain a quite uniform temperature distribution with a gradient not exceeding 2 °C in the solution. The pulling/rotation mechanisms and the online temperature and weight control were realized using the “Ariel-1” crystal growth system developed by Raicol Crystals Ltd. The seed rotation rates varied from 70 to 20 rpm at different stages of growth. Variable pulling rates, from 0.02 to 1 mm/day were employed. Fine adjustment of the seeding temperature was achieved by repeated seeding with the seed-solution contact control using a thermoelectric circuit. The general temperature range for growth of RTP crystals from different self-fluxes was 980–880 °C,

while the temperature lowering rates changed from 0.5 to 3 °C/day. As a result, RTP crystals of $50 \times 60 \times 50 \text{ mm}^3$ dimensions along the X , Y and Z axis and weighing up to 450 g could be routinely obtained.

Z-cut plane parallel crystal samples with thicknesses varying from 0.5 to 1.5 mm were used for determination of the Curie temperatures by a standard dielectric technique, namely recording the capacitance anomaly at the ferroelectric transition temperature. The samples were linked into an a.c. impedance bridge circuit based on a Hewlett-Packard Model 4276A LCZ meter operating at a 20 kHz frequency. Pt electrodes were applied to both sides of a sample that was placed in a shallow gradient resistance furnace and ramped rapidly to the expected phase transition range, where a heating rate of 0.5–1.0 °C/min was employed. Two Pt/Pt–13%Rh thermocouples were attached to both sides of the sample, and the accuracy of the Curie temperature determination was better than 0.5 °C.

3. Results and discussion

Most of the samples used for determination of the Curie temperatures, T_c , were based on relatively small RTP crystals grown from four selective rubidium phosphate self-fluxes (with R varying from 1.25 to 2) with different initial concentrations of the solute (RTP). Crystals grown under variable initial parameters were expected to exhibit variable T_c values accordingly, in similarity with KTP [4]. Supplementary samples were fabricated from large RTP crystals. By definition, the first and last to crystallize portions of the crystal had solidified from fluxes with lower and higher Rb concentrations in the liquid respectively. The latter should be richer in the stoichiometric Rb component and have a higher T_c value. A direct proof of this assumption is given in Fig. 1, where the Curie temperatures of the top and bottom parts of a 300 g RTP crystal pulled on a [1 0 0]-oriented seed are given. The specific separation between the T_c values (782 and 787 °C hereby) depends not on the crystals weight, but rather on the relative solute content in the solution. However, before engaging in the study of the Curie temperature dependencies on the flux chemical composition, we will address a peculiar effect revealed in course of taking the capacitance versus temperature characteristics, $C = C(T)$, of some RTP samples.

Fig. 2 shows two representative $C = C(T)$ dependences of many such curves obtained, which are composed of two peaks featuring two Curie temperatures. A closer examination of the samples exhibiting two peaks has revealed that they have been cut from crystal areas comprising two different growth sectors, and that the Pt electrodes cover areas containing both sectors. In general, RTP crystals like other KTP-family crystals contain fourteen growth sectors displayed through four

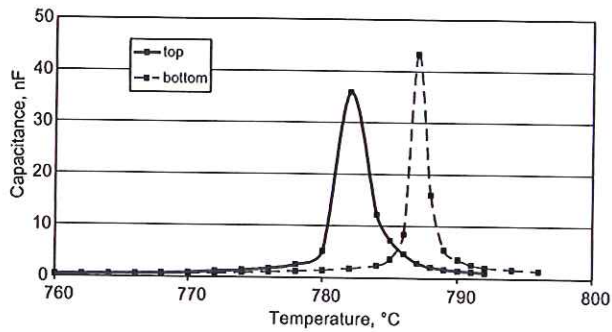


Fig. 1. Capacitance versus temperature curves of the top and bottom parts of a 400 g RTP crystal grown by the TSSG method with pulling on an X -oriented seed (100 growth sector).

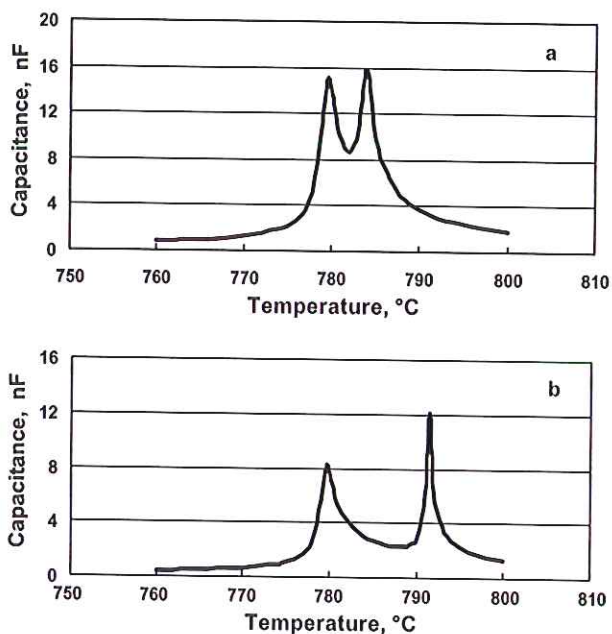


Fig. 2. Capacitance versus temperature curves from crystal areas around the boundaries of (201)/(011) growth sectors (a) and (201)/(100) growth sectors (b).

types of well developed facets: $2 \times \{100\}$, $4 \times \{110\}$, $4 \times \{011\}$ and $4 \times \{201\}$, in its typical morphological habit [7]. The number of growth sectors and the volume and geometry of each particular sector depend on the growth direction and type (submerged, TSSG, with or without pulling). Fig. 3 shows schematically the structure of main growth sectors in two RTP crystals grown by the TSSG method from fluxes, one with pulling on an X -oriented seed and the other without pulling and grown on a Z -oriented seed. Samples for T_c measurements are machined from Z -cut slices shown in the figure for both cases. Apparently, Pt electrodes can cover either a single growth sector or two sectors. We reiterate that double-peaked $C = C(T)$ characteristics are obtained in the latter case.

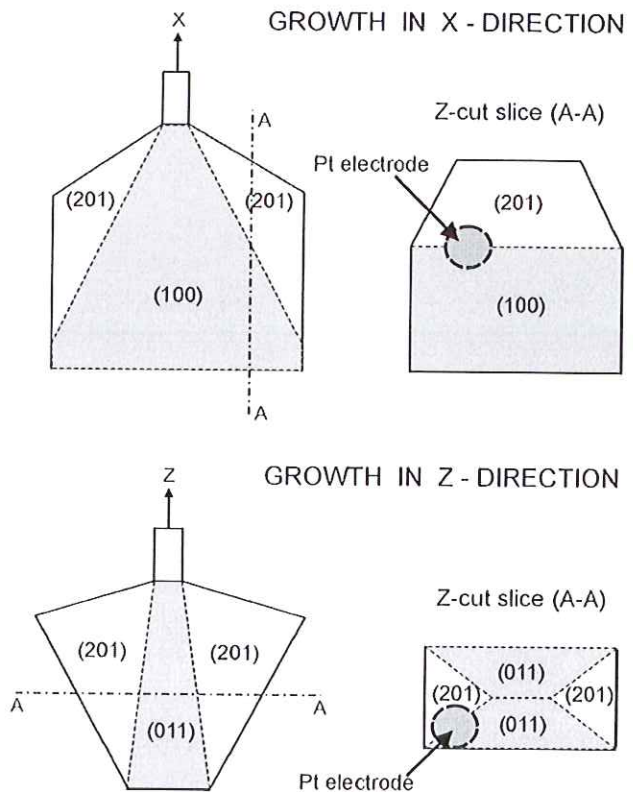


Fig. 3. Schematic representation of growth sectors developed in RTP crystals grown on X and Z -oriented seeds. Z -cut slices may contain two growth sectors, which can be partially included in the area below the Pt electrode.

The results described above imply that the variation of the Curie temperature, or of the chemical composition of RTP crystals, as a function of the flux chemical composition must be studied for each growth sector separately. Preferentially, care should be taken in covering a single growth sector with the electrode for the dielectric measurements. Yet, double-peak $C = C(T)$ characteristics can be used if the assignment of each peak to a specific growth sector is sufficiently clear. In Fig. 4, the results for three growth sectors, of the $\{100\}$, $\{011\}$ and $\{201\}$ types, are presented separately. For each sector the Curie temperature as a function of RTP concentration (in weight units) is given for self-fluxes with different R values. The nearly linear dependencies obtained are in full similarity with the KTP case [4]: (a) the lower is the RTP concentration, in any self-flux, the higher is the T_c of the crystal and (b) for any given RTP concentration, the T_c is higher for self-fluxes with higher values of R . The combined result is that a higher Curie temperature corresponds to a higher overall concentration of the Rb-ions in the solution and, therefore, to higher rubidium content in the crystal. Naturally, in the course of RTP crystal growth the solution becomes gradually enriched in rubidium. The important practical consequence of this behavior is that a rubidium con-

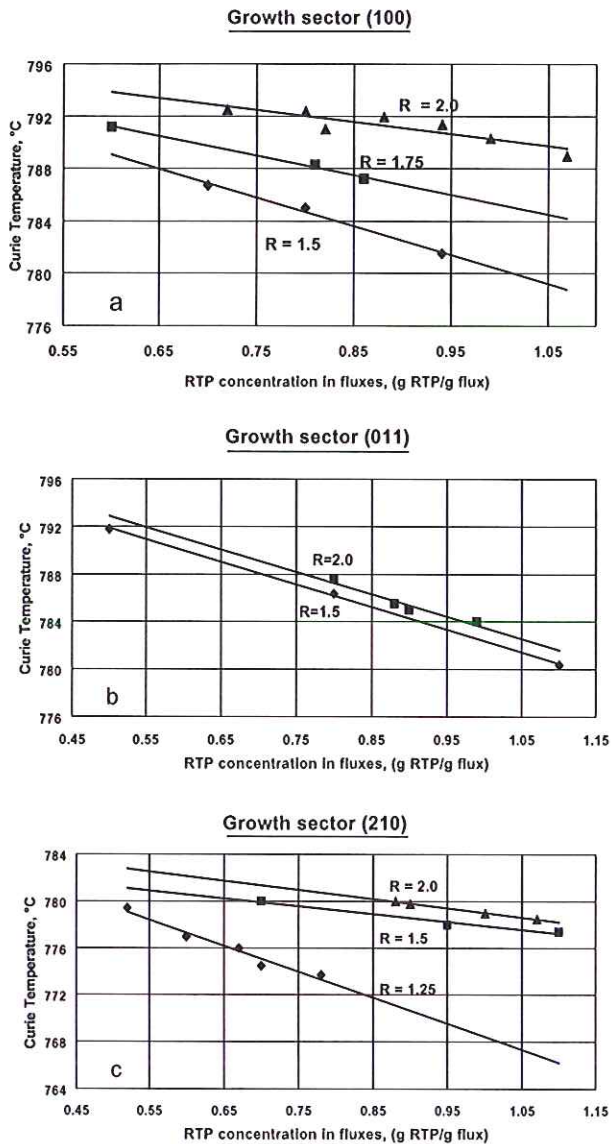


Fig. 4. Curie temperatures as a function of RTP concentration in the solution for various self-fluxes, measured separately for three growth sectors: (a) {100}, (b) {011} and (c) {210}.

centration gradient builds up in the as-grown crystal. This gradient is not averaged out during the cool-down stage, since the diffusion coefficient of Rb-ions is presumably very small. In fact, the K-ion diffusion in KTP at growth temperatures is quite small [8], and it should be even smaller in the case of substantially larger Rb-ions.

The observed span of T_c values, from 770 to 800 °C, is much narrower than the corresponding range of Curie temperatures in KTP (880–980 °C). In addition, the slopes of the linear dependencies are shallower in the case of RTP. We presume, therefore, that the overall extent of change of Rb-stoichiometry in RTP crystals is essentially smaller than the corresponding variation of K-stoichiometry in KTP crystals.

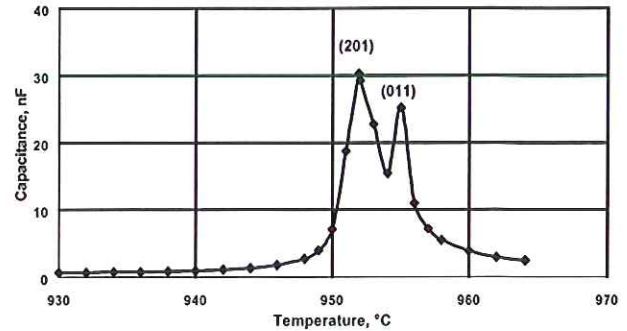


Fig. 5. Capacitance versus temperature curve over the (201)/(011) growth sector boundary of a Pb-doped (700 ppm) KTP crystal.

The main distinctive feature of RTP crystals is that they exhibit abrupt “jumps” in the Curie temperature over boundaries between any pair of simultaneously solidifying growth sectors of different types, as can be deduced from Fig. 4. A sign of a double peak in the $C(T)$ curve has been reported for the isomorphous CTA (CsTiOAsO_4) crystal [9], but has never been observed in nominally pure KTP crystals. Only deliberately doped KTP may show a double peak in the $C(T)$ characteristic with an electrode spreading over two adjacent growth sectors. An example is given in Fig. 5, where a 700 ppm Pb-doped KTP crystal is shown to produce a 3 °C difference in the T_c values over a (011)/(201) growth sector boundary. Similar results have been obtained with Al-doping of KTP, and they can be explained in terms of different distribution coefficients of the dopants at different growth faces along the crystal/melt interfaces.

In view of the doping effect in KTP, we have looked into the purity of the RTP crystals grown in this study. The main bulk of residual metal impurities in the RTP crystals may originate from the 3N Rb_2CO_3 used in synthesis of the starting materials for crystal growth. In Table 1, we list the major metal impurities in the Rb_2CO_3 powder (given by the manufacturer) and in the grown RTP crystal, the latter evaluated by means of glow discharge mass spectroscopy. Apparently, only Cs, K and Si are present in the carbonate. Silicon is present at a level of several tens of ppm in both the starting material and the RTP crystal. It is difficult to assess the distribution coefficient of this element, since silicates present in the growth system may be an additional silicon source. Anyway, Si at the same level of several ppm is usually found in our KTP crystals without causing the appearance of double Curie temperature peaks. The large Cs ions are not easily accommodated in the RTP lattice and the analytical results prove it. On the contrary, potassium readily enters the RTP lattice, and is the only impurity that can be suspected of affecting the structural properties of the RTP crystal.

In order to check the possible influence of the impurity we have grown an RTP crystal with a delib-

Table 1
Concentrations of metal impurities in Rb_2CO_3 starting material and in as-grown RTP crystals

Material	Cs	K	Na	Li	Al	Ba	Ca	Cr	Cu	Fe	Mg	Ni	Mn	Pb	Si
Rb_2CO_3 (ppmw)	375	440	14	24	2	10	3	1	<1	5	4	<1	<1	4	85
RTP ^a (ppmw)	5	325	1.3	0.05	2	0.8	1.2	<1	0.35	2.5	0.35	0.1	0.02	0.44	80

^a Northern Analytical Laboratory Inc., Merrimack, NH, USA.

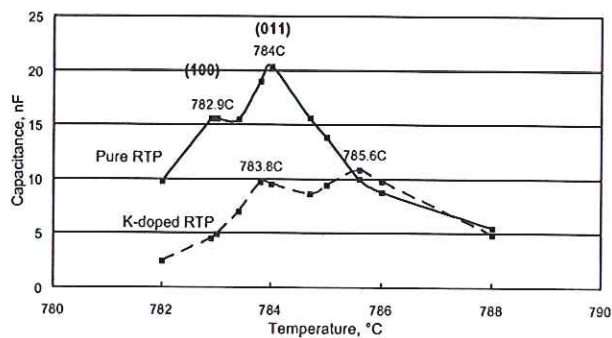


Fig. 6. Curie temperature shift in K-doped (2300 ppm) RTP crystal.

erate potassium doping. Chemical analysis has shown that the sample prepared for Curie temperature measurements contains 2300 ppm of K-ions. Its $C = C(T)$ characteristic is shown in Fig. 6 together with a similar sample fabricated of an undoped RTP crystal (electrodes covering the (100)/(011) growth sector boundary have been applied to both samples in a similar fashion). Obviously, the potassium doping introduces some disorder into the RTP crystal lattice causing a shift (increase) in the Curie temperature. A very slight increase in the peak separation can be explained by the existence two distinct Rb sites in the noncentrosymmetric room-temperature RTP phase, Rb(1) and Rb(2), that have an oxygen coordination of VIII and IX respectively, and the selective occupation of these sites by the K and Rb-ions [10].

The existence of double peaks in the $C(T)$ curves of nominally pure RTP crystals, with a separation of over 10 °C between the Curie temperatures on a single sample, cannot be explained by the presence of trace impurities. We recall also that the growth temperatures are 100–200 °C higher than the T_c s in our experiments, and the crystals solidify in the pseudosymmetric mmm phase [11] where the R(1) and R(2) sites are symmetrically identical [12]. However, the likely diverse formation mechanisms of native defects within the various growth facets at high temperatures may cause a variation in the statistical distribution of the Rb-ions between the Rb(1) and Rb(2) sites during cooling through the ferroelectric phase transition. The defects may be associated not only with the rubidium and associated oxygen vacancies, but also with other stoichiometric components, namely titanium and phosphorus ions. Initial attempts to identify any deviation from the stoichiometric

composition of these components using the electron-microprobe technique did not contribute positive results. More promising experiments involving single crystal X-ray diffraction, electron paramagnetic resonance and electron–nuclear double resonance are currently being planned.

4. Conclusions

RTP crystals grown from self-fluxes may undergo the ferroelectric phase transition in a relatively wide temperature range, from 770 to 800 °C, depending on the flux chemical composition in terms of the [Rb]/[P] atomic ratio. The actual Curie temperature values are defined by the rubidium stoichiometry in the crystal. They can serve as a good relative measure of the compositional variation in large RTP crystals (from the seed area to the periphery), which is always associated with a gradual variation in the physical properties, such as the refractive indices. These results are very similar to the effect of potassium stoichiometry in KTP crystals. The main distinction is that, unlike KTP, nominally pure RTP crystals exhibit different Curie temperatures for different growth sectors, even when solidified at the same time. Preliminary measurements show that this effect is almost not associated with the trace impurities present in the crystal, but rather with the native defects to be identified in the future.

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