A new flux for the fast growth of potassium titanyl phosphate (KTP) single crystals

S. SUMA, N. SANTHA, M. T. SEBASTIAN
Regional Research Laboratory, Trivandrum 695019, India
E-mail: mts@csrrltd.ren.nic.in

Single crystals of the non-linear optical material KTiOPO₄ (KTP) have been grown using a new KBa₃(PO₃)₅·2K₂O flux, which produced faster growth than existing fluxes. Crystals of size 6 mm × 4 mm × 2 mm were grown from the flux in a day. Perhaps relatively large crystals may be grown commercially in a short time. © 1998 Chapman & Hall

1. Introduction
Potassium titanyl phosphate (KTiOPO₄ or KTP) has several unique properties such as large non-linear optical (NLO) coefficients, wide acceptance angles, phase matching properties and high optical damage threshold, making this material attractive for frequency doubling and parametric devices [1–4]. It has a high conversion efficiency for second harmonic generation. Its large electro-optic coefficients and low dielectric constant make it very useful for various electro-optic applications such as Q switches and modulators [3]. The figure of merit of a KTP electro-optic waveguide modulator is reported to be twice that of any other inorganic material. This indicates that KTP is a promising material for integrated optic applications [5]. The crystals are transparent over a wide wavelength range, chemically and thermally stable and non-hygroscopic.

2. Crystal Growth
KTP crystals cannot be grown by conventional melt techniques, because they decompose on melting at 1172°C [6]. But they can be grown by hydrothermal and flux methods at temperatures far below the melting point [6–11]. In 1981 the Airtron Company started to grow KTP commercially using the hydrothermal method developed by du Pont [8]. The hydrothermal method requires very sophisticated pressure equipment and has the additional disadvantage of OH⁻ incorporation into the crystal lattice, which deteriorates the NLO properties. The crystal growth by this method is very small, about 1 mm per day. The alternative method for growing KTP is the high temperature solution or flux method [6, 9–11]. K₆P₂O₁₃ is conventionally used as a commercial flux; it may also be modified by WO₃. One of the problems when growing KTP from K₆P₂O₁₃ flux is the formation of inclusions due to constitutional supercooling [12]. An important rheological parameter in this respect is the high viscosity of K₆P₂O₁₃ flux. The high viscosity of the flux leads to glass formation during fast cooling. Hence a very slow cooling (cooling rate 4–20°C per day) is needed to grow this crystal [13]. The WO₃-containing phosphate fluxes have lower viscosity but unfortunately a considerable amount of tungsten inbuild takes place and the crystals are coloured [14]. We report the use of a new flux which overcomes many of the problems encountered in the growth of KTP crystals by the K₆P₂O₁₃ flux.

3. KTP crystal growth in the new KBa₃(PO₃)₅·2K₂O flux
We have found a new flux or molten solution to grow transparent KTP crystals. The following equation gives a general description of the growth process:

\[ KH_2PO_4 + TiO_2 \rightarrow KTiOPO_4 + H_2O \] (1)

\[ 5KH_2PO_4 + 2BaCO_3 \rightarrow KBa_3(PO_3)_5 \cdot 2K_2O + 2CO_2 + 5H_2O \] (2)

where KBa₃(PO₃)₅·2K₂O is the flux.

The flux containing KTP powder melts and crystals are formed on cooling. The solubility has been determined by introducing excess crystals (solute) in the solvent (KBa₃(PO₃)₅·2K₂O) at different controlled temperatures. After dissolution has proceeded for 6 h the undissolved material is separated from the saturated solution and weighed. The loss in weight due to dissolution at different temperatures has been calculated and plotted against temperature [15]. At higher temperatures KTP is more soluble in KBa₃(PO₃)₅·2K₂O molten solvent than in K₆P₂O₁₃ [6]; at lower temperatures KTP is less soluble in KBa₃(PO₃)₅·2K₂O molten solvent than in K₆P₂O₁₃. This behaviour favours crystal growth (Fig. 1). Thermal analysis (DTA) showed that the flux melts at 795°C.

For a typical growth run, KH₃PO₄ and TiO₂ were weighed in stoichiometric proportions as per Equation 1 and mixed well in an agate mortar. The mixture was then calcined at 800°C for 4 h. The calcined material (KTP) was then powdered well. KH₃PO₄ and BaCO₃ were weighed in stoichiometric proportions as per Equation 2 and mixed well. The mixture was then kept at 650°C for 4 h and again powdered well after cooling to room temperature to get the flux.
Figure 1 Comparison of the solubility of KTP in two fluxes: (a) KBa$_2$(PO$_4$)$_3$·2K$_2$O, (b) K$_8$P$_2$O$_{13}$ [6].

Figure 3 X-ray powder diffraction pattern of KTP grown in (a) K$_8$P$_2$O$_{13}$ and (b) KBa$_2$(PO$_4$)$_3$·2K$_2$O (Si internal standard used for (a)).

Temperature range 1130–1050 °C. The growth period was about a day, including the heating up and homogenization time.

Several experiments using different solute/solvent ratios have shown that about 25 wt % of the flux gives good crystals. The as-grown crystals of KTP were removed by dissolving the flux in dilute HNO$_3$. The dimensions of the KTP crystals obtained were up to 6 mm × 4 mm × 2 mm when the cooling rate was 120 °C. The crystals were transparent, Fig. 2a shows a scanning electron microscopy (SEM) photograph and Fig. 2b an optical photograph of a rapidly grown crystal. The microcracks appearing on the crystals are due to the fast cooling. The morphology of the as-grown crystals is in agreement with morphologies reported by Bolt and Bennema [16]. The crystals show NLO properties. The powder X-ray diffraction patterns of KTP grown in K$_8$P$_2$O$_{13}$ and KBa$_2$(PO$_4$)$_3$·2K$_2$O fluxes are comparable (Fig. 3). Chemical analysis (ICP) of the as-grown crystals shows 0.128% of Ba incorporation from the flux into the KTP crystals.

The KTP crystals grown in this new flux are free of OH$^-$ incorporation, as shown by the IR spectrum recorded in the range 400–4000 cm$^{-1}$ (Fig. 4). Incorporation of OH$^-$ deteriorates the NLO properties and has been reported [14] both for hydrothermally grown and K$_8$P$_2$O$_{13}$ flux grown crystals. The as-grown crystals were chemically etched in a 1:1 mixture of 40% HF and 97% H$_2$SO$_4$ [17] and observed under a scanning electron microscope. The concentration of etch pits shows strong local variations (Fig. 5). Dislocation densities vary from zero to 5000 per square millimetre (40% HF–97% H$_2$SO$_4$ in 1:1 mixture has not been used earlier for estimating dislocation densities in KTP). Etch pits with hollow cores are

Different fractions (wt %) of the flux were then thoroughly mixed with the KTP powder. The KTP–flux mixture was taken in an open 70 ml platinum crucible and heated to 1130 °C and soaked at this temperature for 2 h to achieve homogenization. Alternatively one can weigh and mix the chemicals for the KTP and flux simultaneously. In this case considerable frothing may take place during the heating-up period. The melt (KTP and flux) was then cooled at a rate of 120 °C per day. The KTP crystallized during cooling in the temp-

Figure 2 A rapidly grown KTP crystal: (a) SEM photograph, (b) optical photograph.