Effect of Phosphorus Sources on Synthesis of $KTiOPO_4$ Thin Films by Sol−Gel Method

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Single-phase KTP thin films were synthesized from metal−organic compounds by the sol−gel method. Various phosphorus compounds were examined for the preparation of a KTP precursor. Phosphorus compounds with hydroxy groups were reacted with Ti alkoxides producing Ti−O−P bonds, which prevented the evaporation of phosphorus compounds during heat treatment. When $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$ was used, a monomeric KTP precursor was obtained. In contrast, precursors with a complicated structure were formed from P_4O_{10}, $(\mathrm{EtO})\mathrm{P(OH)}_2$, and $(\mathrm{MeO})\mathrm{P(OH)}_2$. Since the monomeric KTP precursor was more favorable for synthesis of crystalline KTP thin films at low temperatures, it was used to crystallize KTP thin films at 600 °C on glass substrates.

I. Introduction

Potassium titanyl phosphate ($KTiOPO_4$ or KTP) has remarkable nonlinear optical coefficients, wide acceptance angles, thermally stable phase-matching properties, and high optical damage threshold. Therefore, KTP has been used for the generation of second harmonic waves from 1064 nm of a Nd:YAG laser.[1−3]

KTP single crystals have been synthesized since 1976.[4] Because incongruent melting of the KTP crystal occurs at about 1160 °C, single crystals of KTP have been grown by hydrothermal method or flux method.[4−6] However, both methods have problems with the inclusion of the hydroxy group or the flux.

The sol−gel method has the advantages of synthesizing high-purity materials at low processing temperature, feasible composition control, good homogeneity, and versatile shaping. Since the control of intermolecular reactions is one of the key processing factors in the sol−gel method, the choice of starting materials is extremely important for synthesis of crystalline KTP thin films. Barbé et al. reported the synthesis of KTP films with a second phase on $LaGaO_3$ substrates using a mixture of $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$ and $(^n\mathrm{BuO})\mathrm{P(O)(OH)}_2$.[7] Hirano et al. reported the synthesis of single-phase KTP films on $NdAlO_3$ substrates using $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$.[8] The number of OH groups in the starting phosphorus compound affects the structure of the precursor, which leads to a different crystallization temperature of KTP. The lower crystallization temperature is required to avoid the formation of a second phase by the reaction between KTP and substrates. Schmutz et al. reported the formation of titanium phosphates and KTP using phosphorus compounds from P_4O_{10} and alcohols.[9] However, the relation between the starting phosphorus compounds and the crystallization behavior of KTP, especially in thin films on substrates, was not investigated in detail.

This paper describes the effect of the phosphorus compounds on the synthesis of KTP films using metal alkoxides. Various pentavalent and trivalent phosphorus compounds with and without hydroxy groups were investigated. Pentavalent and trivalent phosphorus compounds containing OH groups were found to give single-phase crystalline KTP, with the monohydroxy phosphorus compound being superior to dihydroxy compounds for the low-temperature crystallization of KTP films on substrates.

II. Experimental Procedure

Triethyl phosphate ($\mathrm{OP(OEt)}_3$, Kojundo Chemicals), phosphorus pentoxide (P_4O_{10}, Kishida Chemicals), di-*n*-butyl phosphate ($(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$, Tokyo Kasei Chemicals), ethyl phosphonate ($(\mathrm{EtO})\mathrm{P(OH)}_2$, Aldrich Chemical Co., Inc.), methyl phosphonate ($(\mathrm{MeO})\mathrm{P(OH)}_2$, Aldrich Chemical Co., Inc.), and trimethyl phosphonate (($\mathrm{P(OMe)}_3$, Kojundo Chemicals) were selected as starting phosphorus compounds. Phosphorus pentoxide (P_4O_{10}) was reacted with absolute ethanol to produce a mixture of diethyl phosphate ($(\mathrm{OEt})_2\mathrm{P(O)(OH)}$) and ethyl phosphate ($(\mathrm{OEt})\mathrm{P(O)(OH)}_2$), which were used as starting phosphorus compounds. Titanium ethoxide ($\mathrm{Ti(OEt)}_4$, Kojundo Chemicals) and potassium ethoxide (KOEt, Kojundo Chemicals) were used as starting materials of Ti and K, respectively. Ethanol was used as a solvent for solutions prepared from $\mathrm{OP(OEt)}_3$, P_4O_{10}, $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$, and $(\mathrm{EtO})\mathrm{P(OH)}_2$, while methanol was used for the precursor solutions prepared from $(\mathrm{MeO})\mathrm{P(OH)}_2$ and $\mathrm{P(OMe)}_3$. Ethanol and methanol were dried over magnesium alkoxide and distilled before use.

As shown in Figure 1, the phosphorus compound and titanium ethoxide were dissolved in dried alcohol and refluxed

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(1) Bierlein, J. D.; Vanherzeele, H. *J. Opt. Soc. Am. B* **1989**, *6*, 622.

(2) Driscoll, T. A.; Hoffman, H. J.; Stone, R. E.; Perkins, P. E. *J. Opt. Soc. Am. B* **1986**, *3*, 683.

(3) Hagerman, M. E.; Poeppelmeier, K. R. *Chem. Mater.* **1995**, *7*, 602.

(4) Zumsteg, F. C.; Bierlein, J. D.; Gier, T. E. *J. Appl. Phys.* **1976**, *47*, 4980.

(5) Jacco, J. C.; Loiacono, G. M.; Jaso, M.; Mizell, G.; Greenberg, B. *J. Cryst. Growth* **1984**, *70*, 484.

(6) Laudise, R. A.; Cava, R. J.; Caporaso, A. J. *J. Cryst. Growth* **1986**, *74*, 275.

(7) Barbé, C. J.; Harmer, M. A.; Scherer, G. W. *J. Am. Ceram. Soc.* **1995**, *78*, 2033.

(8) Hirano, S.; Yogo, T.; Kikuta, K.; Noda, K.; Ichida, M.; Nakamura, A. *J. Am. Ceram. Soc.* **1995**, *78*, 2956.

(9) Schmutz, C.; Basset, E.; Barboux, P.; Maquet, J. *J. Mater. Chem.* **1993**, *3*, 393.

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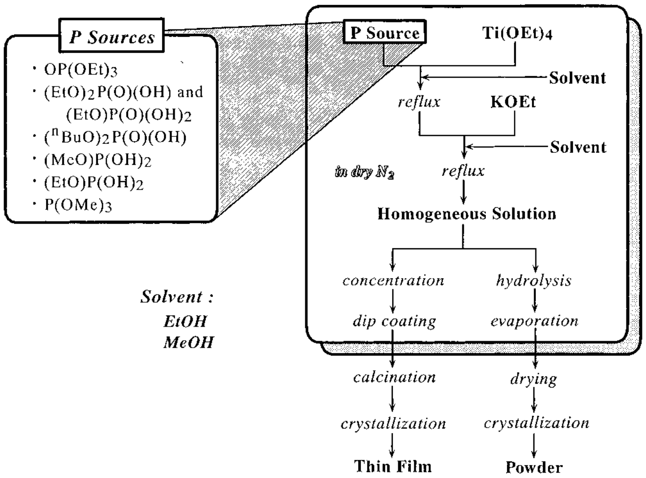

Figure 1. Experimental procedure for preparation of KTP powders and thin films.

for 17 h. Potassium ethoxide was then added to the solution, which was refluxed for 20 h (P:Ti:K = 1:1:1 mole ratio).

The precursor solutions were hydrolyzed with excess water, and the solvents were then evaporated from the solutions to obtain precursor powders. KTP thin films were prepared by the dip-coating method. Glass (Corning 7059) and sapphire C plates were used as substrates and were dipped into the precursor solution concentrated to 0.35 mol/L by removal of solvent under vacuum. The substrate was withdrawn at a fixed speed of 1.5 mm/s and dried under nitrogen. The precursor film was then calcined under a steam of H_2O/O_2 vapor at 350 °C. The oxygen gas bubbled through water at 45 °C (P_{H_2O}, 72 mmHg) was introduced to the furnace. The calcined film was crystallized under O_2 at 5 °C/min at 600 °C for 2 h. Alternatively, the precursor film was heated at 10 °C/min up to 650 °C in H_2O/O_2 vapor and then kept at 650 °C for 2 h under O_2. The coating−crystallization process was repeated to increase the film thickness. The film thickness was measured using a scanning electron microscope (SEM).

FT-IR spectra were measured by liquid film and Nujol methods. Solution ^{31}P NMR spectra of the precursors were recorded at 101.26 MHz in methanol or ethanol, using H_3PO_4 as a standard. The molecular weight of the KTP precursor was measured cryoscopically using benzene as a solvent.[10] The burn-out behavior was analyzed by thermogravimetry. The crystal structures of the powders and thin films were characterized by X-ray diffraction analysis (XRD) using Cu Kα radiation with a monochromator.

III. Results and Discussion

(1) Reaction of P_4O_{10} and EtOH. Phosphorus pentoxide was reacted with absolute ethanol yielding diethyl phosphate and ethyl phosphate as follows:[11]

$$P_4O_{10} + 6EtOH \rightarrow 2(EtO)_2P(O)(OH) + 2(EtO)P(O)(OH)_2$$

Phosphate compounds constitute several configurations of apex-shared PO_4 tetrahedron including Q^0 (PO_4), Q^1 ($O_3P{-}O{-}PO_3$), and Q^2 ($O_3P{-}O{-}PO_2{-}O{-}PO_3$). The Q^1 and Q^2 types contain P−O−P bonds, which are not present in the Q^0 type. Since no P−O−P bonds exist in crystalline KTP, the Q^0 structure compounds are considered to be appropriate KTP precursors.

Therefore, the reaction conditions of phosphorus pentoxide and ethanol were adjusted to produce only the Q^0 type phosphorus compounds, $(EtO)_2P(O)(OH)$ and $(EtO)P(O)(OH)_2$. The molar ratio of ethanol to phosphorus pentoxide was 30. The different types of phosphorus compounds and their relative amounts were analyzed by ^{31}P NMR spectra, since Q^0, Q^1, and Q^2 type structures appear at around 0, −11, and −22 ppm, respectively.[12] As shown in Table 1, when P_4O_{10} is stirred in ethanol at room temperature, Q^1 and Q^2 type compounds remain even after the reaction for 72 h. On the other hand, 2 h of refluxing produces a large amount of Q^0 type compounds, and after refluxing for 24 h, no Q^1 or Q^2 types are detected. Thus, this refluxing method was applied to synthesize the starting phosphorus compounds used in the preparation of the KTP precursor solution.

Table 1. Effect of Stirring or Refluxing Time on Relative Amount of Condensed Structures of PO_4 Tetrahedra

time (h)	Q^0 (%)	Q^1 (%)	Q^2 (%)
	Stirring		
0.5	26.0 (2.2)[a]	49.6	24.4
2	35.0 (3.5)	46.8	18.2
6	29.4 (1.7)	55.5	15.1
72	56.5 (7.8)	42.9	0.6
	Refluxing		
0	26.0 (2.2)	49.6	24.4
2	79.0 (8.9)	21.0	0.0
24	100.0 (6.1)	0.0	0.0

[a] H_3PO_4.

(2) Synthesis of Precursor Solution. Homogeneous KTP precursor solutions were prepared by the reaction of the phosphorus compounds with $Ti(OEt)_4$ and KOEt. When $Ti(OEt)_4$ was refluxed in solution with a phosphorus compound containing hydroxy groups, such as $(EtO)_2P^V(O)(OH){-}(EtO)P^V(O)(OH)_2$, $(EtO)P^{III}(OH)_2$, or $(MeO)P^{III}(OH)_2$, white insoluble solids precipitated out. However, the addition of KOEt to the reaction and refluxing resulted in a homogeneous precursor solution. On the other hand, when $OP^V(OEt)_3$, $(^nBuO)_2P^V(O)(OH)$, or $P^{III}(OMe)_3$ was selected as a phosphorus source, no precipitation occurred after the reaction of the phosphorus compound with $Ti(OEt)_4$, and homogeneous KTP precursor solution was obtained.

Inhomogeneous KTP precursor solutions were occasionally obtained when $(EtO)_2P^V(O)(OH){-}(EtO)P^V(O)(OH)_2$ was used as a starting material. This can be attributed to the reaction of phosphoric acid with KOEt, yielding potassium dihydrogen phosphate (KH_2PO_4), which is insoluble in EtOH. The presence of free H_3PO_4 is thought to be the result of the random cleavage of the P−O bond in P_4O_{10} by alcohol during the initial synthesis step of the Q^0 species (see Table 1).[11] Therefore, a phosphorus source that contains no phosphoric acid is preferred for the preparation of the coating solution.

(3) Structure of KTP Precursors. The KTP precursors formed from $(^nBuO)_2P(O)(OH)$, $(EtO)P(OH)_2$, and $(MeO)P(OH)_2$ are found to yield a single-phase KTP above 500−550 °C as described in section 4. Figure 2 shows ^{31}P NMR spectra of starting $(^nBuO)_2P(O)(OH)$, the Ti−P alkoxide, and the KTP precursor. The spectrum of the starting $(^nBuO)_2P(O)(OH)$ is comprised of a typical single signal of pentavalent phosphorus at 0.0 ppm (Figure 2a).[12] The Ti−P alkoxide is a mixture of

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(10) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice Hall: Englewood Cliffs: NJ, 1970; p 283.

(11) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley-Interscience: New York, 1973; Vol. 6, p 222.

(12) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Wazer, J. R. *^{31}P Nuclear Magnetic Resonance*; John Wiley & Sons: New York, 1967; p 319.

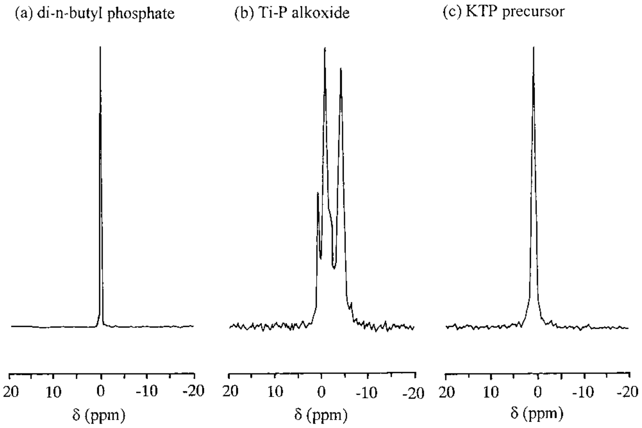

Figure 2. ^{31}P NMR spectra of (a) di-*n*-butyl phosphate, (b) Ti−P alkoxide, and (c) KTP precursor prepared using di-*n*-butyl phosphate.

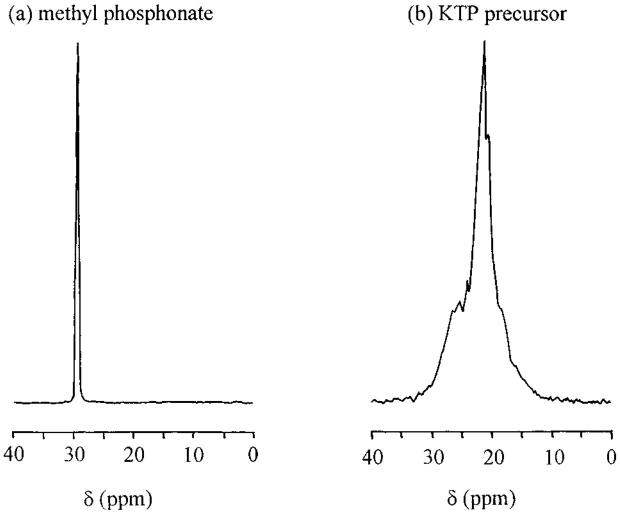

Figure 3. ^{31}P NMR spectra of (a) methyl phosphonate and (b) KTP precursor prepared from methyl phosphonate.

at least three species in equilibrium as shown in Figure 2b. However, the single signal at 1.0 ppm in Figure 2c indicates that the KTP precursor contains one kind of phosphorus(V). The molecular weight of the KTP precursor in benzene solution was found by cryoscopy to be 460 ± 30 g/mol. The proposed molecular structure of $[(^n\mathrm{BuO})_2\mathrm{P(O)}{-}\mathrm{O}{-}\mathrm{Ti(OEt)_4}]\mathrm{K}$ from IR, ^{1}H NMR, and ^{31}P NMR spectra has a molecular weight of 476.5 g/mol.[8] Therefore, the KTP precursor synthesized from $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$ is monomeric.

The IR spectrum of the product from the reaction of $\mathrm{(MeO)P(OH)_2}$ and $\mathrm{Ti(OEt)_4}$ showed no indication of hydroxy group. This indicates the formation of Ti−O−P bonds in Ti−P alkoxide through the elimination of alcohol as shown below:

$$\mathrm{(MeO)P(OH)_2} + \mathrm{Ti(OEt)_4} \rightarrow \mathrm{(MeO)P(O{-}Ti(OEt)_3)_2} + 2\mathrm{EtOH}$$

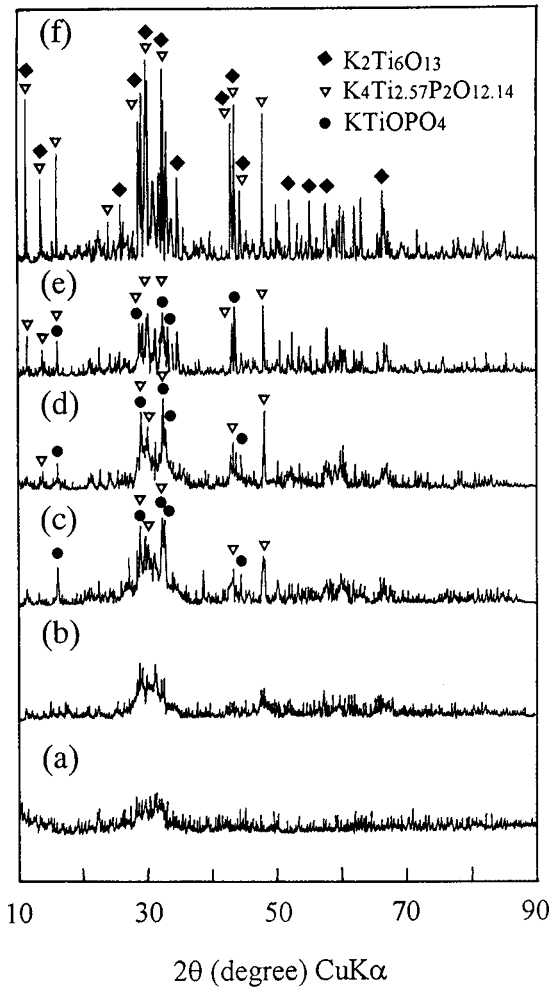

Figure 4. XRD profiles of KTP powders prepared from triethyl phosphate heat-treated at temperatures from 500 to 900 °C for 1 h: (a) as-prepared, (b) 500, (c) 600, (d) 700, (e) 800, and (f) 900 °C.

Figure 3 shows ^{31}P NMR spectra of $\mathrm{(MeO)P(OH)_2}$ and the KTP precursor. Since the Ti−P alkoxide was insoluble in methanol, its NMR spectrum was not taken. $\mathrm{(MeO)P(OH)_2}$ shows a signal at 29.2 ppm, which supports the existence of the trivalent phosphorus atom.[12] The spectra of the KTP precursor shown in Figure 3b are composed of several signals at around 23 ppm, suggesting the presence of several P(III) species. This implies that, in contrast to the case of $(^n\mathrm{BuO})_2\mathrm{P(O)(OH)}$ shown in Figure 2c, the difunctional $\mathrm{(RO)P(OH)_2}$ does produce a mixture of several KTP precursors with complicated structure. Although the KTP precursors were soluble in alcohol, they are insoluble in benzene, chloroform, and dimethyl sulfoxide. The low solubility of the precursors suggests their complicated structures.

(4) Crystallization of KTP Powders. All precursor solutions synthesized in section 2 were hydrolyzed with excess water, dried, and then heat-treated at various temperatures, followed by the analysis by XRD.

Figures 4 and 5 show the XRD profiles of KTP powders prepared from $\mathrm{OP^V(OEt)_3}$ and $\mathrm{P^{III}(OMe)_3}$, respectively. Both XRD profiles show the formation of $\mathrm{K_4Ti_{2.57}P_2O_{12.14}}$ and $\mathrm{K_2Ti_6O_{13}}$,[13] which increase in amount with increasing heat treatment temperatures. No single-phase KTP was formed from these precursors, suggesting the partial evaporation of phosphorus during heating when the starting phosphorus compound has no hydroxy groups.

Figures 6 and 7 show the XRD profiles of KTP prepared from $[\mathrm{(EtO)_2P^V(O)(OH)}{-}\mathrm{(EtO)P^V(O)(OH)_2}]$ ($\mathrm{P_4O_{10}}$−EtOH system) and $\mathrm{(MeO)P^{III}(OH)_2}$, crystallized at 550 and 500 °C, respectively. Single-phase KTP was obtained from the both precursors, which contained OH groups. As with the $\mathrm{(MeO)P(OH)_2}$ precursor, the KTP precursor prepared from $\mathrm{(EtO)P^{III}(OH)_2}$ began to crys-

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[13] The data files of 40-0403 and 40-0310 from the Joint Committee of Powder Diffraction Standards.

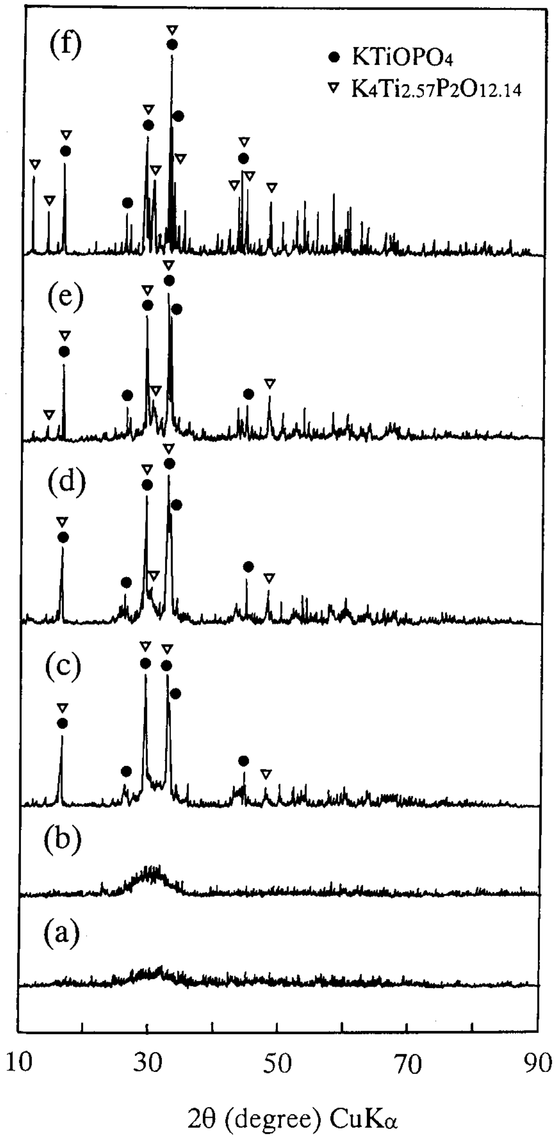

Figure 5. XRD profiles of KTP powders prepared from trimethyl phosphonate heat-treated at various temperatures between 450 and 900 °C for 1 h: (a) as-prepared, (b) 450, (c) 500, (d) 600, (e) 700, and (f) 900 °C.

tallize at 500 °C, giving a single-phase KTP. The formation of single-phase KTP above 550 °C from $(^{n}BuO)_2P^{V}(O)(OH)$ reactant has been shown in our previous work.[8] These results imply that the precursors containing hydroxy group(s) form single-phase crystalline KTP without loss of phosphorus, regardless of the valency of the phosphorus.

The powder prepared from the $(^{n}BuO)_2P^{V}(O)(OH)$-derived KTP precursor at 550 °C was white. However, the KTP precursor powders from $(EtO)_2P^{V}(O)(OH)$–$(EtO)P^{V}(O)(OH)_2$, $(EtO)P^{III}(OH)_2$, and $(MeO)P^{III}(OH)_2$ were dark gray after heat treatment at 550 °C, remaining gray until 650 °C, and finally turning white at 700 °C. The colored powder showed a small weight loss depending upon the amount of residual carbon by thermogravimetry. Residual carbon was detected in the gray precursor powders even after heat treatment at 650 °C. Compared to the precursors prepared from the monohydroxy $(^{n}BuO)_2P(O)(OH)$, those derived from the dihydroxy phosphorus compounds are considered to have a more complicated structure. The burn-out of organics in the precursors does not proceed at low temperatures, as well in which dihydroxy structures are included as in the monomeric KTP precursor derived from $(^{n}BuO)_2P(O)(OH)$. This phenomenon can be understood as the higher content of residual carbon in the KTP powders from the dihydroxy compounds at 550 °C.

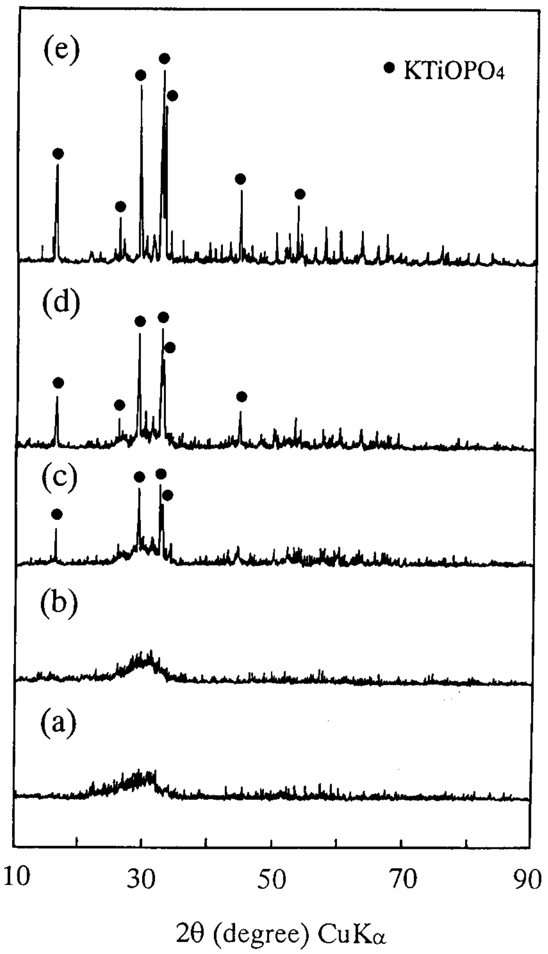

Figure 6. XRD profiles of KTP powders prepared from phosphorus pentoxide heat-treated at temperatures from 500 to 700 °C for 1 h: (a) as-prepared, (b) 500, (c) 550, (d) 600, and (e) 700 °C.

(5) Preparation of KTP Thin Films. KTP films were prepared from the KTP precursor solutions derived from $(^{n}BuO)_2P(O)(OH)$ and $(MeO)P(OH)_2$. No hydrolysis was performed in order to investigate the effects of number of hydroxy group bonded to phosphorus.

(a) KTP Thin Films Prepared from $(^{n}BuO)_2P(O)(OH)$. The precursor films were calcined at 350 °C in H_2O/O_2 flow and crystallized at 600 °C under O_2 (Figure 8a). The H_2O/O_2 vapor treatment was found to enhance the quality of the crystalline films of desired phases.[14–18] Crack-free and highly transparent KTP thin films of 2 μm thickness were prepared by this treatment. In addition, KTP films were crystallized at 550 °C on sapphire C substrates.

(b) KTP Thin Films Prepared from $(MeO)P(OH)_2$. The precursor films were calcined at 350 °C in flow of H_2O/O_2 mixture vapor. However, upon raising the temperature to 600 °C under O_2 (Figure 8a), KTP crystalliza-

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(14) Hirano, S.; Kato, K. *Adv. Ceram. Mater.* **1988**, *3*, 503.

(15) Hirano, S.; Kato, K. *J. Non-Cryst. Solids* **1988**, *100*, 538.

(16) Hirano, S.; Yogo, T.; Kikuta, K.; Morishita, T.; Ito, Y. *J. Am. Ceram. Soc.* **1992**, *75*, 1701.

(17) Hirano, S.; Yogo, T.; Kikuta, K.; Araki, Y.; Saito, M.; Ogasahara, S. *J. Am. Ceram. Soc.* **1992**, *75*, 2785.

(18) Yogo, T.; Kikuta, K.; Niwa, K.; Ichida, M.; Nakamura, A.; Hirano, S. *Proc. SPIE (Sol–Gel Opt. III)* **1994**, *2288*, 484.

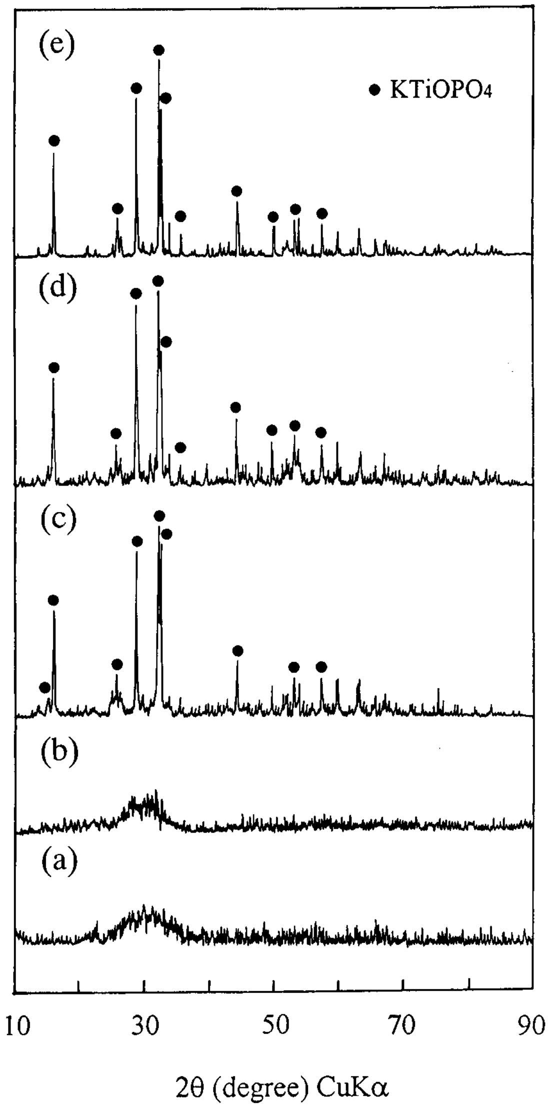

Figure 7. XRD profiles of KTP powders prepared from methyl phosphonate heat-treated at various temperatures between 450 and 700 °C for 1 h: (a) as-prepared, (b) 450, (c) 500, (d) 550, and (e) 700 °C.

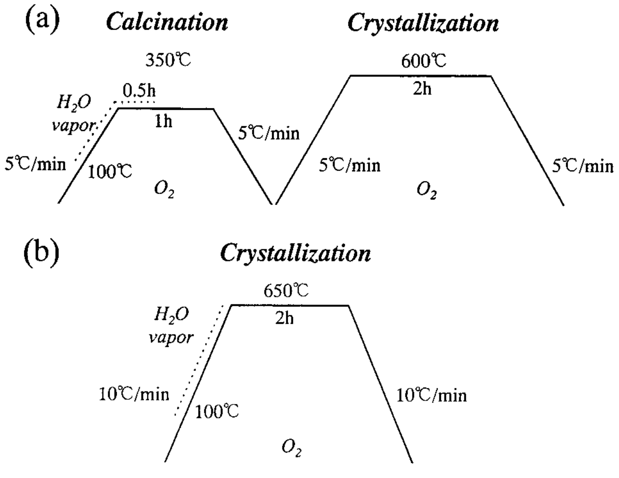

Figure 8. Heating schedules for preparation of KTP thin films. (a) Calcination at 350 °C under H_2O/O_2 followed by crystallization at 600 °C under O_2. (b) Heat treatment up to 650 °C under H_2O/O_2 followed by crystallization at 600 °C under O_2.

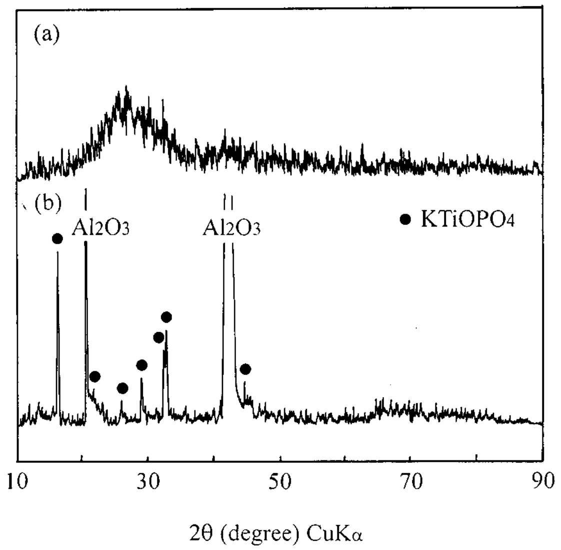

Figure 9. XRD profiles of KTP films from the precursor using methyl phosphonate crystallized at 650 °C for 2 h: (a) KTP film on a glass substrate and (b) KTP film on a sapphire C substrate.

tion did not occur. The precursor films were heated to 650 °C under H_2O/O_2 vapor, and then heated for an additional 2 h at 650 °C under O_2 (Figure 8b). No crystalline KTP was formed on the glass substrates as shown in Figure 9a, while crystalline KTP thin films of 2 μm thickness were prepared on sapphire C substrates at 650 °C as shown in Figure 9b. The crystallized KTP films are polycrystalline and include no second phase.

As discussed previously, the KTP precursor prepared from $(MeO)P(OH)_2$ would have a complex structure and might be polymeric. Rearrangement of atoms and elimination of organic components in the polymerized precursors are more difficult than those in the monomeric precursor from $(^nBuO)_2P(O)(OH)$. The crystallization temperature of KTP films on substrates increases with increasing the complication in precursor structure. A study on the precise mechanism of crystallization on sapphire C is now in progress.

IV. Conclusions

The proper selection of phosphorus compounds was found to be one of the key processing factors for the synthesis of single-phase KTP films by the sol–gel process. The precursors prepared from phosphorus compounds with hydroxy groups were found to give a single-phase KTP powder after heat treatment above 500 °C. A phosphorus compound with two hydroxy groups, either $(EtO)P^{III}(OH)_2$, $(MeO)P^{III}(OH)_2$, or a mixture of $(EtO)_2P^V(O)(OH)$ and $(EtO)P^V(O)(OH)_2$, was reacted with Ti alkoxide yielding a KTP precursor with a complicated structure. A mixture of $(EtO)_2P^V(O)(OH)$ and $(EtO)P^V(O)(OH)_2$ prepared from P_4O_{10} included a small amount of H_3PO_4 as a byproduct of the reaction. H_3PO_4 reacted with KOEt to generate an insoluble product (KH_2PO_4) in ethanol, resulting in the formation of an inhomogeneous mixture. $(^nBuO)_2P(O)(OH)$ has one hydroxy group and gave a monomeric KTP precursor, from which a single KTP phase crystallized at 600 °C on a glass substrate, suggesting that a phosphorus precursor compound with one hydroxy group is more favorable than those with two hydroxy groups for the synthesis of crystalline KTP thin films at lower temperatures.

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