High-Temperature Decomposition of $KTiOPO_4$

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It has been shown that potassium titanyl phosphate, $KTiOPO_4$, decomposes at elevated temperatures with the evolution of gaseous phosphorus and potassium oxides and formation of solid titanium dioxide. Microscopic investigation and kinetic analysis reveal that the decomposition develops on the surface of KTP microcrystals. A fit of the kinetic curves in the deceleratory period to the Ginstling-Brounshtein equation has shown that the high-temperature decomposition of KTP is limited by diffusion at the reaction interface. The apparent activation energy of the decomposition was determined to be equal to 2.3 ± 0.2 eV.

Introduction

The nonlinear optical properties of potassium titanyl phosphate, $KTiOPO_4$ or KTP, were first reported in 1976.[1] Since that time its physical properties have been extensively studied and presently KTP is considered one of the most promising nonlinear optics materials because of its efficiency at doubling Nd:YAG laser light. Its practical value as an optical and electrooptical material results from its large temperature window, extremely low onset power threshold, high-power conversion efficiency, wide-wavelength range of phase-matching capabilities, large nonlinear optical coefficients and high threshold to laser-induced damage. Attention has been focused on $KTiOPO_4$ for sum and difference frequency mixing, optical parametric oscillation and electrooptic switching, where it is competitive with Ti-doped $LiNbO_3$ waveguides. It should be possible to use monocrystalline KTP films deposited on substrates as an alternative to hydrothermally grown optical grade KTP crystals[2] or high-temperature flux-grown crystals. Thin-film deposition techniques such as laser ablation, magnetron sputtering, or chemical vapor deposition offer more efficient methods compared to high-pressure, hydrothermal techniques.

Current research on the growth of KTP thin films is remarkably unexplored.[3,4] The deposition of polycrystalline KTP, its compatibility, and orientation on substrates and optical properties are not well understood. The most universal deposition techniques, such as magnetron sputtering or laser ablation of metal oxides rely on the use of dense, low porosity, ceramic targets prepared at high-temperature. It is known that KTP melts incongruently at 1172 °C in air and at 1158 °C in an argon atmosphere according to the decomposition reaction:[5]

$$KTiOPO_4(s) \rightarrow TiO_2(s, rutile) + KPO_3(l) \qquad (1)$$

Little is known about the behavior of KTP below its melting point. However, interesting observations have been reported:[6] "a seed crystal was determined to require the controlled dissolution of the original seed surfaces prior to initiation of supersaturation and consequent growth. It is assumed that this necessity has as its basis a surface degradation phenomenon that occurs during the brief interval the seed crystal is exposed to the air inside the heated furnace cavity to its immersion in solution." The reasons for this deterioration, which must reflect some form of thermal instability of KTP below its melting point, remain unresolved. Others[7] have shown that at temperatures near 900 °C the following defect formation reaction occurs:

$$KTiOPO_4 \rightarrow K_{1-x}TiOPO_{4(1-x/8)} + (x/2)K_2O \qquad (2)$$

The concentration of potassium vacancies, x, in KTP crystals was found to be 0.01–0.1 at. %. It is quite evident that any crystal growth procedure, including all types of flux techniques, is a steady-state process, and, thus, defects which accumulate during growth remain at low temperatures and reflect the thermodynamic equilibrium associated with the growth conditions. It is not known whether this process of vacancy formation can be stopped spontaneously at some specific concentration of defects or how it affects the stability of the KTP crystalline network. Consequently, it is difficult to say anything regarding the nature of KTP crystals after extended heat treatment.

In many attempts to obtain dense KTP ceramic targets suitable for magnetron sputtering, specific changes in the crystallinity of the sintered KTP targets and the presence of a second phase were observed. Our observations and the reported defect chemistry of KTP[7] prompted the careful investigation of the high-temperature behavior of KTP. In this paper we demonstrate that KTP decomposes completely in the solid-state with time at elevated temperatures. The solid product of the decomposition is titanium dioxide while phosphorus and potassium go into the gas phase. This process develops on the surface of the KTP microcrystals and provides a natural explanation for the "degradation" of seed crystals.[6] The defect formation described in eq 2 can be considered to occur in

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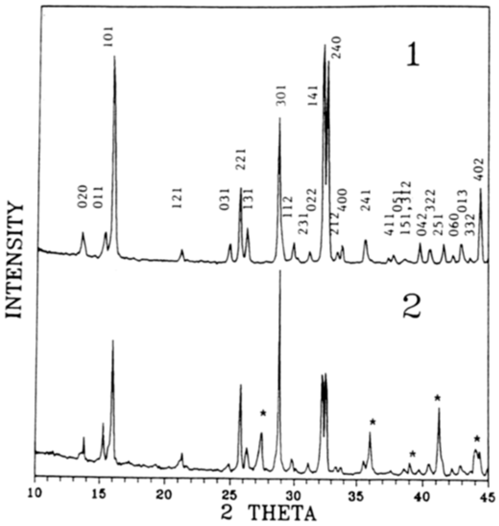

Figure 1. (1) X-ray pattern of the sintered $KTiOPO_4$ powder. (2) X-ray pattern of $KTiOPO_4$ powder after heat treatment at 1050 °C in a nitrogen atmosphere. Asterisks mark peaks belonging to TiO_2 (rutile).

the initial stage of the decomposition process and may correspond to the nucleation period. The practical consequences of decomposition at high temperature are discussed.

Experimental Section

Polycrystalline KTP was synthesized according to reaction 3 using reagent grade titanium dioxide (anatase) and monobasic potassium phosphate. Appropriate amounts of starting reagants

$$TiO_2(s) + KH_2PO_4(s) \rightarrow KTiOPO_4(s) + H_2O(g) \qquad (3)$$

were ground and thoroughly mixed. A platinum crucible containing the reactive mixture was placed into a muffle furnace and the temperature was ramped slowly to 250 °C. The sample was then removed from the furnace and ground. The temperature was then raised to 600 °C and the specimen was calcined for 1 day. After additional grinding, the temperature was increased to 850 °C and the sample was sintered for 3 days with two intermediate grindings to prepare pure-phase $KTiOPO_4$. To obtain well-shaped microcrystals and no traces of starting reagents and to prevent unintended contamination, the platinum crucible was covered with a flat alumina lid and fired, in the final stage, at 950–1050 °C. After this heat treatment, the formation of a glasslike residue was observed on the inner surface of the alumina lid.

It is important to stress that during the final firing stage (at 950–1050 °C) pure-phase KTP powder was used. Consequently, the formation of a glasslike compound on the inner surface of the covering alumina plate substantiates that the pressure of saturated vapors in equilibrium with the KTP crystals in air was appreciable and that these vapors reacted with the ceramic cover. EDAX (Hitachi S-U) analysis provided the following chemical composition of the glasslike phase: K:Al:P = 3.59:2.00:3.14. The crystalline form of the compound $K_3Al_2(PO_4)_3$ is described in JSPDS-ICDD library and the ratio of constituent cations which had been found by EDAX corresponds to this compound with a slight excess of phosphorus and potassium. Owing to the evolution of the constituents from KTP at elevated temperature, the optimum firing temperature was determined to be not higher than 850 °C, a platinum lid was used to protect the sintering material from possible contamination, to decelerate the evaporation process, and to prevent the consumption of the vapors (that is the decrease of their pressure) and reaction with the ceramic container.

The X-ray pattern of the sintered powder is presented in Figure 1.1. All peaks correspond to $KTiOPO_4$ (JCPDS card 35-802) as reported by Tordjman et al.[8] The micrograph of the KTP powder is shown in Figure 2. The microcrystals are of irregular form with distinctly shaped facets. The chemical composition of several of the largest crystals was determined by EDAX, within the limits of the method's uncertainties, to be K:Ti:P = 1:1:1. This cation ratio matches that of pure-phase $KTiOPO_4$.

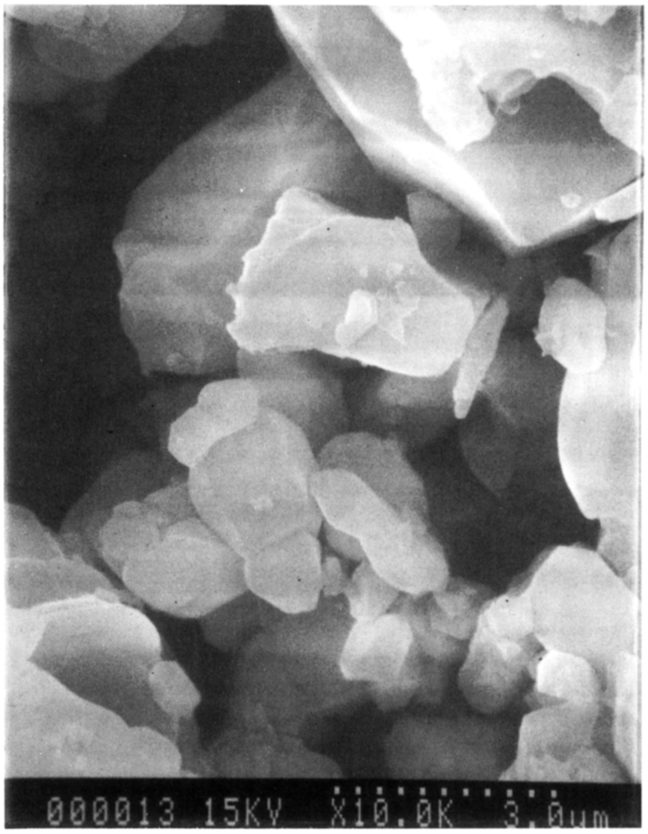

Figure 2. SEM micrograph of the sintered KTP powder.

Table I. Microchemical Analysis of KTP Powder after Heat Treatment at 1050 °C in a Nitrogen Atmosphere

no.	P, at %	K, at %	Ti, at %	magnification
1	24.16	24.84	51.00	800
2	32.31	31.39	36.30	13 000
3	2.03	1.30	96.67	10 000
4	28.36	32.25	39.39	11 000
5	0.56	0.44	99.00	25 000

Microchemical analyses of polycrystalline KTP powder after an isothermal thermogravimetric run at 1050 °C in a nitrogen atmosphere for 1000 min are presented in Table I. The first line of the table illustrates the average surface composition of a rather large aggregate of smaller crystals while the next four lines show the composition of separate microcrystals in this intergrowth. The chemical composition averaged through several dozen microcrystals consistently revealed a larger titanium content and smaller potassium and phosphorus contents compared to the expected theoretical ratio. Among the many constituent microcrystals, some contain cation ratios close to the KTP chemical formula (lines 2 and 4, Table I) and some grains contain virtually only titanium cations (lines 3 and 5, Table I). This fact reflects that these grains consist of a specific, almost pure, titanium oxide. The X-ray analysis of the powder after TG runs revealed the presence of extra peaks in previously phase-pure compound (Figure 1.2). These impurity peaks were found to correspond to titanium dioxide (rutile).

Results and Discussion

The TGA data coupled with chemical analysis support the supposition that $KTiOPO_4$ vaporizes in the solid state

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[8] Tordjman, I.; Masse, R.; Guitel, J. C. *Z. Kristallogr.* **1974**, *139*, 103.

at an appreciable rate at elevated temperatures and decomposes according to the net reaction

$$KTiOPO_4(s) \rightarrow (1-\alpha)KTiOPO_4(s) + \alpha TiO_2(s) + (\alpha/2)(P_2O_5 + K_2O)(g) \quad (4)$$

where α represents the extent of decomposition. Strictly speaking, one ought to consider the KTP in both sides of the eq 4 containing different concentrations of defects (e.g., $K_{1-x}TiOPO_{4(1-x/8)} \rightarrow K_{1-y}TiOPO_{4(1-y/8)} + ((y-x)/2)K_2O$) created according to the reaction (2). But, the weight change corresponding to their formation is rather small, and it has been omitted in reaction 4. Additional experiments are necessary to determine the form of the phosphorus and potassium species in the gas phase. However, it is evident that the rate of decomposition depends upon the pressure and the exact composition of the ambient atmosphere. It should be mentioned that stable compounds between TiO_2 and P_2O_5 are unknown. Hence, potassium oxide plays an important role providing stability to the crystalline framework of the triple oxide $KTiOPO_4$. Therefore, a deficiency of potassium oxide in the crystalline lattice of KTP can promote, at some threshold, the destruction of the crystalline lattice as a whole. We speculate that reaction 4 is a substantially deeper stage of the reaction 2 suggested by Morris et al.[7] and it occurs when the volatilization of potassium oxide and the concentration of defects have exceeded some limit for KTP.

The maximum weight loss in reaction 4 at temperature t and in the limit of infinite time $\tau = \infty$ is equal to $\Delta m(t,\infty) = 59.64\%$. Assuming that overall reaction 4 occurs, the degree of KTP decomposition at time t at a given temperature can be calculated utilizing thermogravimetric (TG) data according to the ratio

$$\alpha(t,\tau) = \Delta m(t,\tau)/\Delta m(t,\infty) \quad (5)$$

Kinetic data were collected in isothermal regime using a TG DuPont-9900 instrument. Most of the experiments were done in the flow of dry nitrogen. Several experiments completed in air showed a slower velocity in the weight change corresponding to the increase in melting point temperature (i.e., increase in the stability relative to the liquid) of KTP in an air atmosphere compared to an inert atmosphere.[5] Platinum sample holders were used and the typical mass of a given specimen was approximately 100 mg. A "jump" routine with a heating rate of more than 100 °C/min was used to achieve the desired temperature. Nonetheless, it was not possible to reach isothermal conditions instantly as is necessary for an ideal experiment. This is illustrated in Figure 3 which presents the typical, original TG data. Moreover, the first minutes of the temperature and mechanical equilibration of the TG balance resulted in a shift of the zero point. To obtain useful kinetic information, the data were smoothed and corrections were made for dead time and balance shift. Figure 4 depicts experimental results collected at several temperatures which have been converted utilizing expression 5 to the degree of decomposition. Each point represents the averaged value from three independent runs. The time of each run was 900–1000 min.

The points shown in Figure 4 form upward curved lines and evidently cannot be described using acceleratory rate equations. In general, some sigmoid rate equation with very short induction and acceleratory periods or some deceleratory rate equation can be used to fit the experimental data. As a rule, kinetic equations contain two parameters: a rate constant, k, and an index of reaction, n.[9] The constant, k, depends on temperature and contains the energetic and configuration characteristics of a reaction path. The index, n, depends on the kinetic regime and the particle shape and size distribution. Sometimes, a third parameter, such as the b factor in the Taplin equation[9] or the reactant to product molar volumes ratio in the Carter equation,[10] is necessary. However, these dimensionless factors are normally near unity and at small degrees of reacted fraction, as is the case with our experiment where α is less than 0.1, can be omitted from consideration without decrease in the precision of the experimental data description.

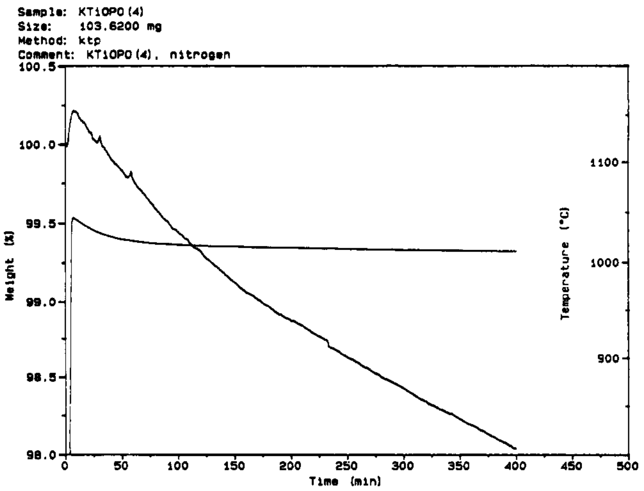

Figure 3. Weight change of KTP powder sample in a nitrogen atmosphere (left) and the temperature ramp (right) are shown.

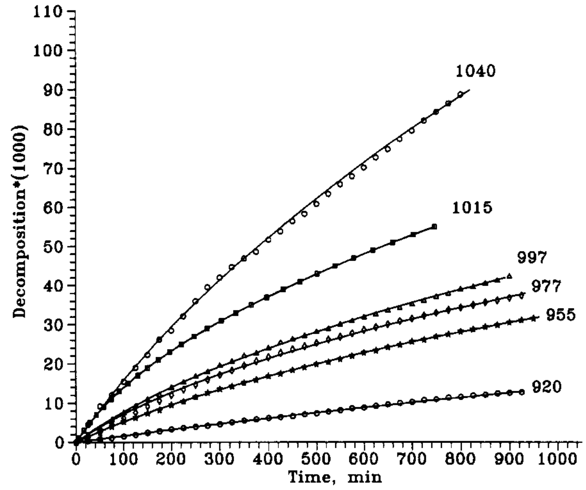

Figure 4. Experimental points for the fraction of the decomposition. The temperature of the experiment is shown for each set of points. The solid lines represent a fit according to the Ginstling–Brounshtein equation.

In the analysis of the experimental data, the two parameters k and n were considered free variables. In this approach, k can have any value depending on temperature, but the parameter n ought to remain independent of temperature, and, moreover, correspond to the physical model for the equation under consideration. Only two equations were found which fit the entire data set with correlation coefficients better than 0.995: the

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[9] Taplin, J. H. *J. Am. Ceram. Soc.* **1974**, *57*, 140.
[10] Carter, R. F. *J. Chem. Phys.* **1961**, *35*, 1137.

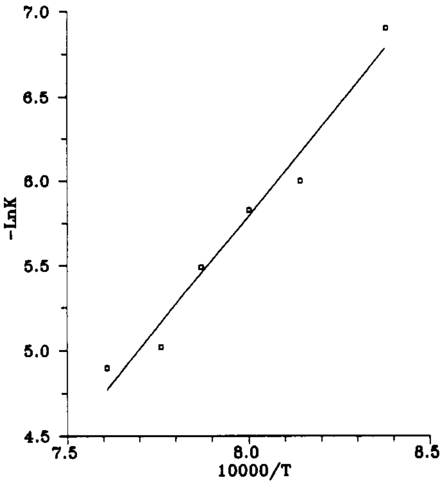

Figure 5. Arrhenius plot for $KTiOPO_4$ decomposition process.

Table II. Ginstling–Brounshtein Fit of KTP Decomposition at Different Temperatures

T, K	$10^4/T$	10^7k	*n*	$-\ln k$	correlation coefficient
1313	7.61	30.01	0.68	4.90	0.9989
1288	7.76	7.25	0.67	5.02	0.9999
1270	7.87	4.51	0.67	5.49	0.9998
1250	8.00	3.23	0.67	5.83	0.9994
1228	8.14	2.71	0.67	6.00	0.9999
1193	8.38	1.10	0.67	6.90	0.9993

Avrami–Erofeev equation[11] and the Ginstling–Brounshtein equation.[12] However, the Avrami–Erofeev fit can be discarded immediately because of the fact that the values of the parameter *n* depend on temperature and are less than unity, which conveys no physical meaning. The results of the fit according to the Ginstling–Brounshtein equation:

$$(1 - 2/3\alpha) - (1 - \alpha)^n = k\tau \qquad (6)$$

are presented in Table II. The value of *n* is unique for all temperatures and is remarkably close to the theoretical value of $^2/_3$. The theoretical curves of decomposition of KTP utilizing the parameters from Table II are depicted by the solid lines in Figure 4. Values for *k* at different temperatures map a straight line in Arrhenius coordinates with satisfactory accuracy (Figure 5). The apparent activation energy, *E*, was determined to be equal to 2.3 ± 0.2 eV.

The micrographs of separate KTP grains after completion of TGA are shown in Figure 6. Figure 6.1 shows a KTP grain containing flakes of the decomposition product covering the uppermost facet and dark spots on a side face of the microcrystals. One can suppose that these dark spots are nucleation centers at the latest stage of their development. They are observed as a result of the slower growth rate of the nucleus on this facet compared with the upper facet. Moreover, the micrograph documents that the decomposition process develops on the surface of the microcrystals and progresses into the bulk of the microcrystals, which is consistent with the kinetic model of the process. Figure 6.2 shows another microcrystal in a later stage of decomposition where one can see the overall shell of covering product. X-ray data together with EDAX analysis indicate that the composition of this shell is predominantly titanium dioxide (rutile). Therefore, the macroscopic kinetic description of the decomposition process, based on diffusion in equal sized particles, corresponds to the microscopic observation of the phenomena.

The energy for the evolution of potassium oxide from KTP and the formation of potassium vacancies according to reaction 2 was estimated to be equal to 3.3 ± 0.3 eV.[7] This value exceeds the apparent activation energy for reaction 4, which would indicate that the creation of these vacancies is not the limiting stage for the overall decomposition process 4. On the other hand, the potassium vacancies, which appear to be the most natural explanation for the formation of the nucleation centers on the atomic level, are present in microcrystals as a result of the synthesis procedure. The observed decomposition of KTP, developing on a surface of a crystal, gives a reasonable explanation to the surface deterioration of seed crystals.[6]

Some practical consequences follow from these results. Because high temperature promotes the decomposition reaction 4, temperatures below 900 °C are required when synthesizing KTP in air. Under these conditions, the dense ceramic can be sintered using the KTP powder prepared according to some low temperature method. A necessary prerequisite for any KTP ceramic technology that takes advantage of a premelting temperature region for agglomeration and densification for KTP will require that the surface of the ceramic be protected by a rather thick layer of KTP powder. The dependence of the high-temperature decomposition rate and activation energy on the low-temperature route used to synthesize the starting materials is not understood. To understand the relationship between the concentration of K vacancies generated at low- and high-temperature decomposition processes, similar experiments on hydrothermally grown KTP and KTP prepared by other means are necessary.

Another significant problem arises apart from the synthesis temperature. Some methods of film deposition, magnetron sputtering for example, are inevitably associated with elevated temperatures near the target. Even with a cooled support for the target, high temperatures occur at the working surface of the target during the sputtering procedure when the target itself is a thermal insulator. KTP is a good dielectric and a poor heat conductor.[2] Consequently, the temperature gradient through cross sections of a target during magnetron sputtering employing a single-target approach is extremely sharp. The temperature at the surface can become rather high while it remains quite moderate in the inner region of the target. This leads to the decomposition of the upper, working layer of the target and causes its chemical composition to change. At the same time, the low temperature of the bulk prevents the diffusion of components to the surface resulting in the absence of steady conditions for the deposition process even after rather long sputtering times, thus reproducible sputtering conditions are unattainable. Methods to overcome this problem could utilize a composite target. Another alternative would be to use a multitarget scheme with separate sources of constituent species. Laser ablation would also appear to be a more favorable approach rather than single-target magnetron sputtering in order to avoid the intense heating of the entire sputtered surface. Finally, if crystalline films of KTP are desired, any procedure involving heat

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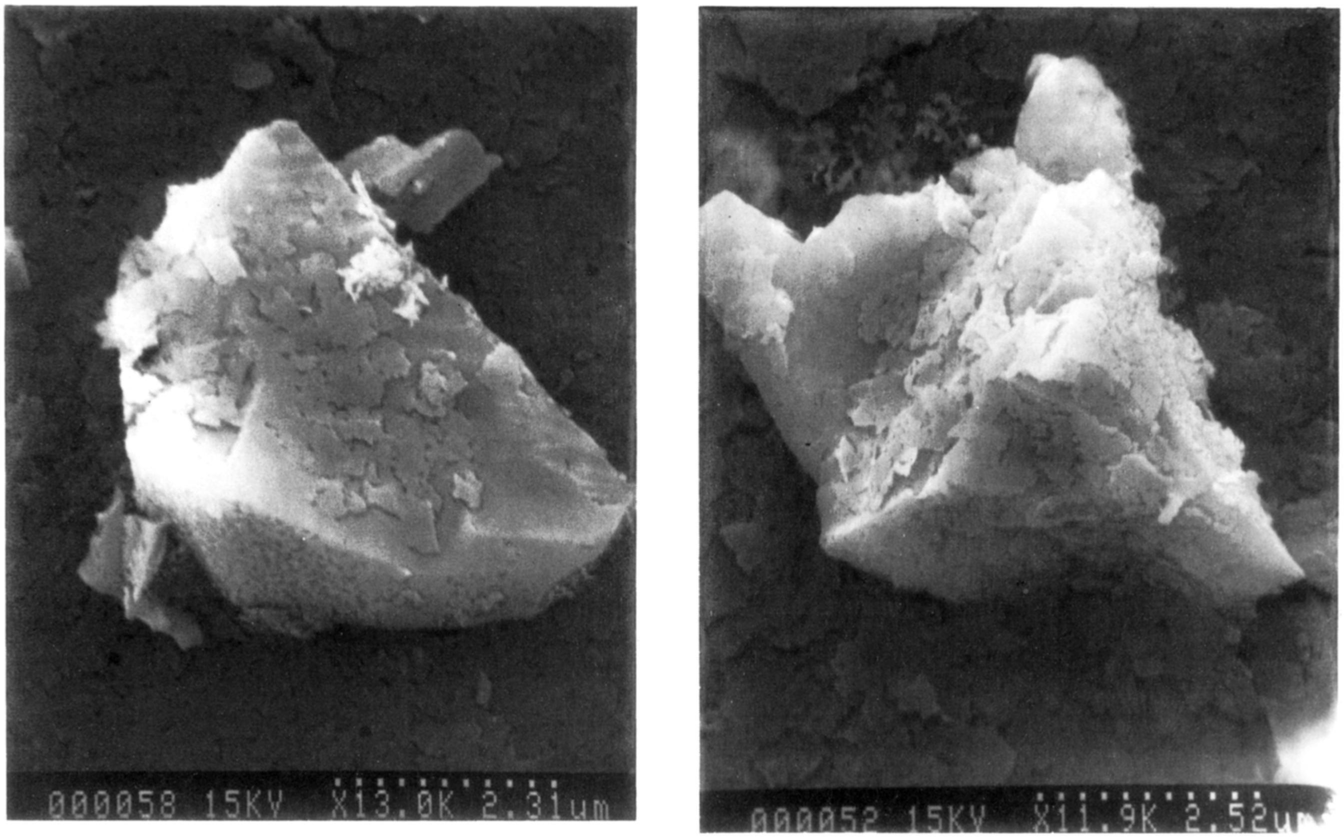

Figure 6. (1) KTP microcrystal at early stage of decomposition. (2) KTP microcrystal at later stage of decomposition.

treatment to improve the crystallinity of a deposit must not require high temperatures. A high-temperature anneal would ultimately lead to the destruction of the film or to the generation of nucleation centers, which would act as light scatterers and reduce the film's transparency.

Conclusions

It has been shown that potassium titanyl phosphate, $KTiOPO_4$ or KTP, vaporizes incongruently at elevated temperatures and that it decomposes losing both potassium and phosphorus. Kinetic analysis of decomposition curves has shown that the decomposition of KTP is limited by a diffusion process. The apparent activation energy of the decomposition was found to be equal to 2.3 ± 0.2 eV. The high-temperature behavior of KTP can be used to explain the need to renew the surface of a seed crystal before initiation of crystal growth and should be taken into account for any KTP ceramic technology or method of KTP thin film deposition.

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