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The thermal expansion and stability of $KTiOAsO_4$ and related compounds [1]

Z. Zhong [a], P.K. Gallagher [a,*], D.L. Loiacono [b] and G.M. Loiacono [b]

[a] *Department of Chemistry and Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210 (USA)*
[b] *Crystal Associates, Inc., Waldwick, NJ 07463 (USA)*

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Abstract

$KTiOAsO_4$ and related compounds are of interest because of their electro-optical properties. The thermal stability of the material is important both for its potential use as a device and in determining suitable conditions for its crystal growth. The stabilities and melting points of $MTiOAsO_4$, where M is K, Rb or Cs, and selected combinations thereof, have been investigated in oxygen and nitrogen using simultaneous thermogravimetry–differential thermal analysis (TG–DTA). The melting temperatures were observed to correlate with the ionic radius of M^+.

The materials are highly anisotropic and the thermal expansion of $KTiOAsO_4$ is reported over the temperature range from −170 to 950°C based on thermodilatometry (TD) of an oriented single crystal. The second order phase transformation at 861°C was much more evident in TD than in DTA.

INTRODUCTION

The compounds, $KTiOPO_4$ (KTP) and its isomorphs, have received considerable attention for second harmonic generation (SHG). The analogous arsenate compound KTA has shown particular promise because of its higher figure of merit and electro-optical coefficients combined with an increased stability at higher powers [1].

Single crystals have been grown from molybdate and tungstate fluxes [2]. Knowledge of the decomposition temperatures and phase equilibria are essential for this process. The melting temperatures, decomposition temperatures, and any $solid_1$–$solid_2$ phase transformations are of particular

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* Corresponding author.

[1] Dedicated to Hans Georg Wiedemann. It is a pleasure for PKG to take part in honoring an old friend and respected colleague who has contributed so much to thermal analysis over many years.

relevance. Simultaneous TG–DTA techniques are used herein to study these phenomena in both oxygen and nitrogen. Oxidation reduction processes associated with the arsenic ion should introduce into these equilibria a dependence on the partial pressure of oxygen.

The crystal structure is orthorhombic at room temperature (point group mm^2, space group $Pna2_1$ (C^9_{2v}) $Z = 8$) [3, 4]. The unit cell is composed of chains of very slightly distorted AsO_4 tetrahedra sharing oxygen ions with somewhat more distorted TiO_6 octahedra. The M^+ ions fill voids in this structure.

Such a structure should have a highly anisotropic thermal expansion. In fact, cracking along the *c* axis has been a problem during crystal growth. This has been attributed to differences in thermal expansion between the crystal and the platinum suspension wires [2]. Consequently, the thermal expansion of an oriented single crystal of $KTiOAsO_4$ is measured over a wide temperature range from −170 to 950°C using TD.

EXPERIMENTAL PROCEDURES AND RESULTS

Single crystals of $MTiOAsO_4$ (where M is K, Rb or Cs) were grown by the high temperature solution (HTS) method from tungsten based solvents, as previously reported [2]. Typical crystal growth parameters were, initial growth temperature 950–910°C, temperature lowering rate of 2°C per day, and seed rotation rate of 30 rev min^{-1}. For the mixed crystals, the initial melt composition was prepared at a 1:1 mole ratio: however, X-ray diffraction analyses showed that the crystal compositions were $K_{0.5}Rb_{0.5}TiOAsO_4$ and $K_{0.85}Cs_{0.15}TiOAsO_4$. The crystal grown from the $Rb_{0.5}Cs_{0.5}TiOAsO_4$ composition was not analyzed. Samples of these crystals were crushed and lightly ground in an agate mortar prior to thermal analysis. A cube approximately 0.5 cm on edge was carefully cut, oriented by X-ray, and polished from a single crystal of $KTiOAsO_4$ for the thermal expansion measurements.

Simultaneous TG–DTA measurements were performed using a Seiko Model 320 System. Nominally 15 mg samples were heated at 10°C min^{-1} in flowing oxygen or nitrogen at approximately 100 ml min^{-1}. Typical curves are presented in Fig. 1 for $KTiOAsO_4$. The melting and decomposition temperatures were measured from the extrapolated onsets of the processes and are summarized in Table 1 for all of the materials.

The thermal expansion measurements used the Perkin-Elmer System 7 TMA module. The sample was heated at 2°C min^{-1} in a slow flow of helium. The data were collected in two separate experiments covering different ranges of temperature. The first covered the low temperature range from −170 to 160°C and the second the range from 30 to 950°C. Data were collected for each of three crystallographic directions. The data are

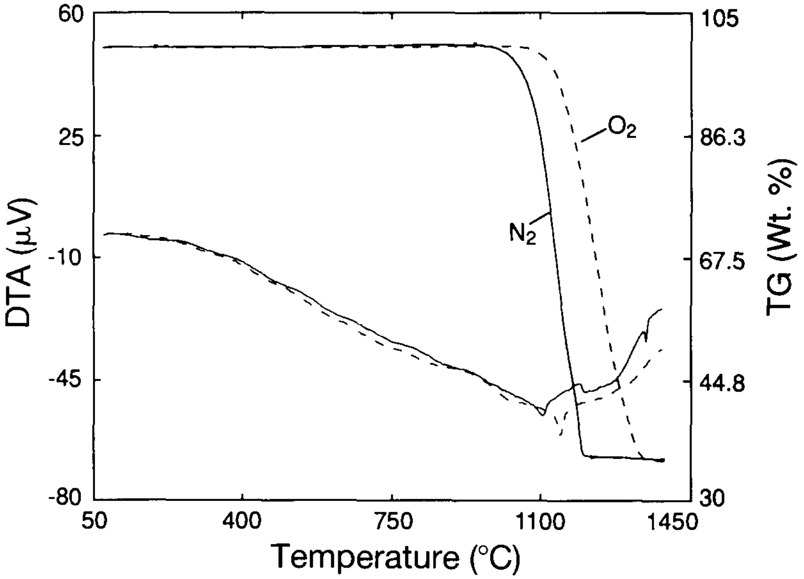

Fig. 1. Simultaneous TG-DTA curves for $KTiOAsO_4$ at 10°C min^{-1}.

TABLE 1

Decomposition and melting temperatures for alkali substitutions in $MTiOAsO_4$ (extrapolated onset temperatures in oxygen and nitrogen)

M	Oxygen		Nitrogen	
	Dec./°C	Melt./°C	Dec./°C	Melt./°C
K	1156	1137	1080	1088
K, Rb	1164	1114	1095	1071
Rb	1158	1092	1085	1063
K, Cs	1147	1095	1088	1082
Rb, Cs	1140	1062	1078	1029

presented in Fig. 2 without correction for the small amount of thermal expansion due to the fused quartz holder.

The change in slope associated with the second order ferroelectric transformation near 861°C is evident, particularly in the *c* axis data. Hence, the data were fit in two separate temperature regimes, before and after this transition. The fit of $\Delta L/L_{298}$ to third order polynomials as a function of temperature is summarized in Tables 2 and 3. The second order polynomial describing the linear coefficient of thermal expansion can be derived by simple differentiation of these third order polynomials.

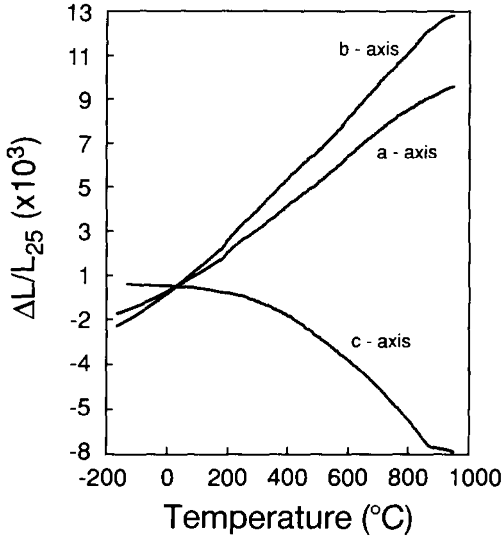

Fig. 2. Thermal expansion for single crystalline $KTiOAsO_4$ at 2°C min^{-1} in helium.

TABLE 2

A fit to the thermal expansion of $KTiOAsO_4$, over the temperature range −170 to 800°C: $\Delta L/L_{298} = a + bT + cT^2 + dT^3$, where T is the temperature in kelvin

Axis	a	b	c	d
$\parallel A$	-1.5420×10^{-3}	2.20972×10^{-6}	1.12511×10^{-8}	-4.6042×10^{-12}
$\parallel B$	-2.5298×10^{-3}	5.98544×10^{-6}	9.66804×10^{-9}	-3.6037×10^{-12}
$\parallel C$	-4.0622×10^{-4}	3.51577×10^{-6}	-5.8902×10^{-9}	-2.1710×10^{-12}

TABLE 3

A fit to the thermal expansion of $KTiOAsO_4$ over the temperature range 900–950°C: $\Delta T/L_{298} = a + bT + cT^2 + dT^2$, where T is the temperature in kelvin

Axis	a	b	c	d
$\parallel A$	6.78380×10^{-1}	-1.7512×10^{-3}	1.51895×10^{-6}	-4.3709×10^{-10}
$\parallel B$	-1.3986×10^{-0}	3.4169×10^{-3}	-2.7609×10^{-6}	7.44309×10^{-10}
$\parallel C$	1.95081×10^{-1}	-5.4428×10^{-4}	4.87860×10^{-7}	-1.4574×10^{-10}

Figure 3 shows an indication of the degree of fit, in this case, for the a-axis data. Every thirtieth datum point is indicated to enhance the legibility. Again the data are uncorrected for the very small expansion of the sample holder.

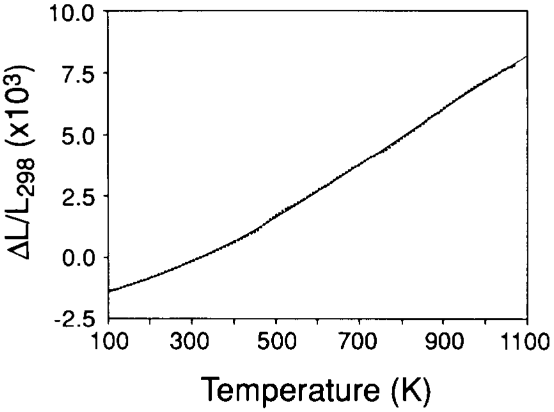

Fig. 3. Thermal expansion of $KTiOAsO_4$ along the *a* axis at 2°C min^{-1}. The thin line represents the fit using the parameters in Table 2.

DISCUSSION

The stability of $KTiOAsO_4$ in oxygen is greater than in nitrogen by approximately 100°C as determined by the onset of mass loss in Fig. 1. Table 4 is a summary of the calculated mass losses based upon various products. The observed final mass (37 mass %) is considerably less than that predicted by the vaporization of arsenic(III) oxide and oxygen alone (52.5 mass %). It is however more than that predicted by the formation of TiO_2 as the only residue (33.0 mass %).

This suggests the presence of some ill-defined potassium titanate approaching the composition $K_2Ti_{10}O_{21}$. This is not inconsistent with the phase diagram presented in Fig. 4 [5]. The residue at that point would be in the two phase field of $K_2Ti_5O_{11} + TiO_2$ and very near the pure TiO_2 boundary. The phase diagram also shows that the incorporation of arsenate into the simple potassium titanate compound raises the melting point nearly 200°C.

A strong minimum in the DTG curve occurs near the mass loss associated with the complete loss of arsenic but prior to the loss of potassium. The specific details or sequence of the loss of oxygen, arsenic,

TABLE 4

Mass loss calculations for $KTiOAsO_4$

Compound	Mass loss/%	Compound	Mass loss/%
$KTiOAsO_4$	100.0	$K_{0.4}TiO_{2.2}$	40.8
$KTiO_{2.5}$	52.5	observed	37.0 ± 0.2
$K_{0.667}TiO_{2.333}$	46.0	TiO_2	33.0

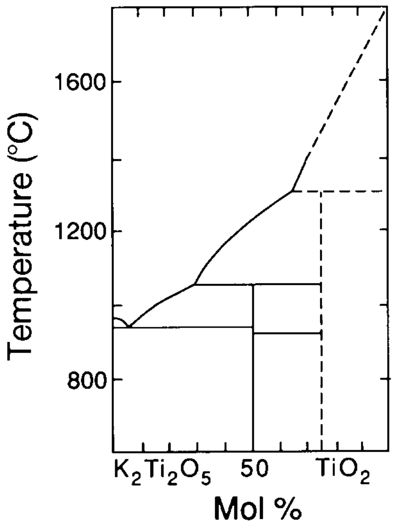

Fig. 4. The partial phase diagram for the system K_2O–TiO_2.

and potassium from $KTiOAsO_4$ cannot be established without further X-ray diffraction work or evolved gas analysis.

The incongruent melting point of KTA at about 1130°C is clearly evident in the DTA curve shown in Fig. 1. The ferroelectric transition with an onset around 861°C, which is pronounced in earlier dielectric measurements [1], is marginally detectable in the DTA trace. This transition appears to be of

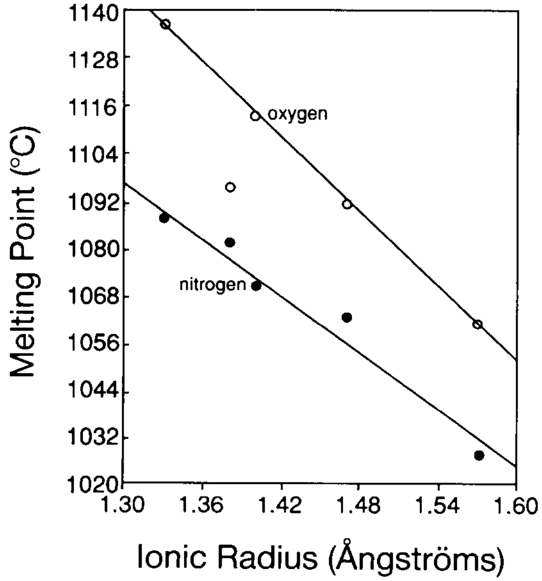

Fig. 5. Melting temperatures of $MTiOAsO_4$ compounds as a function of the average ionic radius of M^+.

second or higher order, generating only a step in the baseline as a result of the change in heat capacity without a change of enthalpy. It is best determined through dilatometry as is shown later.

The melting temperatures in Table 1 show a correlation with the average ionic radii of the M^+ ion as shown in Fig. 5. The two data points for mixed but adjacent ions fit well; however, the point for the $K_{0.85}Cs_{0.15}$ compound in oxygen has a significantly lower melting temperature than would be predicted solely on the basis of their average ionic radii.

The thermal expansion behavior is similar to that of other ferroelectric materials such as $LiNbO_3$ [6]. A ferroelectric phase transition reported at 880°C, which is pronounced in earlier dielectric measurements, is marginally detected in the DTA data presented in Fig. 1. The transition appears to be of second or higher order, generating only a small step in the baseline as a result of a change in heat capacity without a change in enthalpy. The transition is better defined in the thermal expansion curve taken parallel to the *c* axis. The onset appears at 861°C in agreement with a value of 852°C recently reported [7].

If a single domain single crystal were desired, it would be necessary to impose the electrical field around 900°C and maintain it during cooling to near room temperature. Subsequent heat treatments would be limited to below 850°C in order not to depole the crystal.

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