Thermochimica Acta, 214 (1993) 1–7
Elsevier Science Publishers B V , Amsterdam

Applications of Thermal Analysis to the Study of Inorganic Materials

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Abstract

Three examples are selected from the author's current work to illustrate the important role that thermoanalytical techniques play in the characterization of inorganic materials and their processing. The first example deals with the crystal growth, phase equilibria, and defect structure of lithium niobate. This is a prominent material used in electro-optical devices.

The second example deals with the relatively new electro-optical material, $KTiOAsO_4$. Its thermal stability and expansion will be discussed. Some information is also included on the ferroelectric transition temperature and the melting point.

The final topic is an application of thermomagnetometry to study the thermal decomposition of solid solutions and physically mixed oxalates of nickel and cobalt in an inert atmosphere. The magnetic transition temperature is used to establish whether the metal initially formed is an alloy or mixture of pure metals.

1. INTRODUCTION

Thermal analysis is a collection of relatively simple, fast, and versatile techniques. In some respects the term "analysis" is unfortunate, in that it tends to limit the potential investigator's thinking to chemical analysis. The usefulness of thermoanalytical techniques, however, extends well beyond that boundary to include the measurement of physical properties and, even more importantly, into the domain of materials processing.

Although the current major use of thermal analysis is in the area of plastics, polymers, and other organic materials; its roots are in earth sciences, metallurgy, and inorganic materials. These applications continue strong today and the dominance by organic materials is not due to any decrease in activity on the part inorganic applications. They have continued to increase, but the fields of polymers, plastics, and biotechnology have undergone enormous growth.

This paper is intended to call attention to the continued use and importance of thermal analysis in the area of inorganic materials by selecting three relatively recent examples from the author's work.

This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992

2. LITHIUM NIOBATE

The electro-optical properties of $LiNbO_3$ in conjunction with its relatively high thermal stability and transparency in the wave length region of solid state lasers make it of great interest for devices. One such use is as an optical switch. If suitable light guides are formed in the material and electrodes properly placed, then the optical beam can be diverted from one path to another by an electrical impulse. It is imperative that these optical light paths produce very little absorption or scattering in order not to diminish the signal. To this end the devices are made from single crystal, single domain specimens so that there is no scattering by grain boundaries or domain walls. Consequently the ability to grow large flawless, homogeneous, single crystals of this material is of great importance.

The phase diagram for this system is shown in Fig. 1[1]. Three aspects of this diagram are critical to the specific application: a) the compound, lithium niobate, has a wide range of lithium deficiency, i.e. $Li_{1-x}NbO_3$; b) the stoichiometric compound melts incongruently and, therefore, crystals grown from the melt must be precisely at the congruent concentration to remain uniform in composition during growth; and c) there is a ferroelectric phase transformation within the single phase region that has a steep dependence of the transition temperature on lithium concentration. The latter point provides the basis of an analytical method for determining the lithium concentration.

This transition is second order and demands careful DTA work with the frequent use of temperature standards, such as the melting point of gold, to establish the exact transition temperature as a function of composition. The nature of the DTA curve is indicated in Fig. 2 and the calibration curve is presented in Fig. 3 [2]. Through the use of Fig. 3 and DTA curves measured for specific portions of the melt and resulting crystal, it was possible to establish the congruent composition, 48.45 wt% Li_2O, with high precision. Since the DTA analysis is fast, simple, and accurate, it is well suited for quality control of both the incoming feedstock for growth and of the product.

To make the single crystal also a single domain it is necessary to cool the crystal from above the ferroelectric transition temperature down to well below that temperature in an electrical field. Subsequent processing or use must not raise the temperature above the transition point lest it depolarize and form multiple domains. The usefulness of the material, however, depends on the ability to produce the appropriate light guides. This is achieved by diffusing TiO_2 in a prescribed pattern to produce carefully controlled regions having a different refractive index. The substitution of Ti^{4+} into the lattice creates cation vacancies. These in turn lower the ferroelectric transition temperature to a point near that required to diffuse the Ti within a reasonable time. Consequently, the DTA study of the creation of cation vacancies by various substitutions and their subsequent effect on the transition temperature and phase equilibria was of considerable technological as well as scientific interest [3].

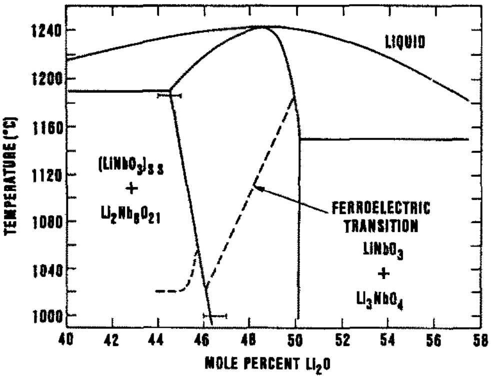

Figure 1

Phase Diagram of $LiNbO_3$ [1].

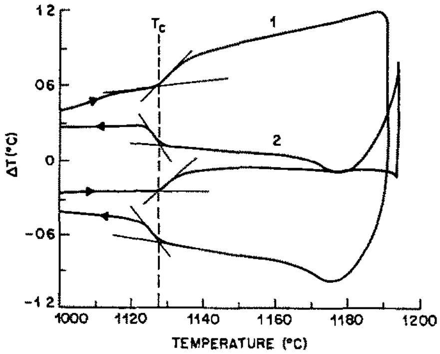

Figure 2

DTA Curves for two samples of a crushed single crystal of $LiNbO_3$[3].

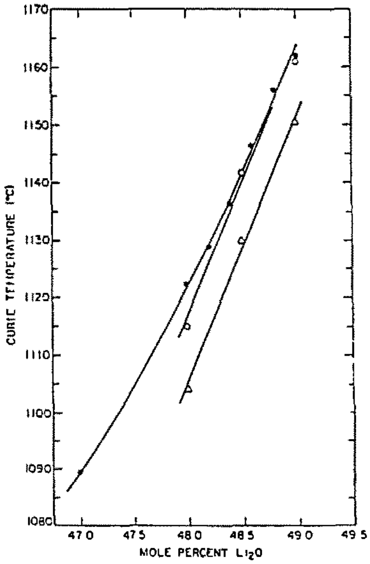

Figure 3

Curie Temperature of $LiNbO_3$ as a Function of the Lithium Concentration [2].

3. POTASSIUM TITANYL ARSENATE

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 [4]. Single crystals have been grown from molybdate and tungstate fluxes [5]. Simultaneous TG/DTA curves are presented in Fig. 4 for a crushed single crystal of KTA provided by Crystal Associates heated at 10°C min^{-1} in oxygen and nitrogen [6].

The stability in oxygen is greater than in nitrogen by approximately 100°C as determined by the onset of weight loss. The extent of weight loss, 37 wt%, is greater than that predicted by the vaporization of arsenic(III) oxide and oxygen, 47.5 wt%. It is. however less than that predicted by the formation of TiO_2 as the only residue, 33.1 wt%. This suggests the presence of some ill-defined potassium titanate approaching the composition $K_2Ti_{10}O_{21}$. A strong minimum in the DTG curve occurs near the weight loss associated with the complete loss of arsenic but prior to the loss of potassium.

The incongruent melting point of KTA, at about 1130°C, is clearly evident in the DTA curve shown in Fig. 4. The ferroelectric transition with an onset around 850°C, which is pronounced in earlier dielectric measurements [4], is marginally detectable in the DTA trace. This transition appears to be of second or higher order generating only a step in the base line 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 crystal structure is orthorhombic at room temperature (point group mm2, space group $Pna2_1$ Z=8). 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 [5]. A single crystal was provided by Crystal Associates which had been carefully oriented and machined to form a cube approximately 1 cm on edge with the major axes perpendicular to the cube's faces.

Expansion along each direction was measured at 2°C min^{-1} in a flow of helium using a fused quartz holder. The results are depicted in Fig. 5 for the three axes [6]. Table 1 summarizes the fit to the thermal expansion over the temperature range from 100 to 800°C. This range was selected to be well above the problems associated with reaching a uniform heating rate and well below the ferroelectric transition temperature that is clearly evident in Fig. 5 at about 865°C. Similar to $LiNbO_3$, the weak

Table 1
A fit to the thermal expansion of single crystal $KTiOAsO_4$ over the range of temperature from 100 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	-4.2282×10^{-3}	8.3375×10^{-6}	4.4265×10^{-9}	-6.3682×10^{-13}
$\parallel$ B	1.8806×10^{-3}	-1.3044×10^{-5}	2.9518×10^{-8}	-1.1838×10^{-11}
$\parallel$ C	-1.9912×10^{-3}	9.2168×10^{-6}	-1.5123×10^{-8}	2.3623×10^{-12}

second order phase transition is most evident in the thermal expansion curve taken parallel to the c-axis [7]. Also, the magnitude of the thermal expansion along the c-axis is small and goes through a maximum as a function of temperature.

4. THERMAL DECOMPOSITION OF MIXED NICKEL-COBALT OXALATES USING THERMOMAGNETOMETRY (TM)

The thermal decomposition of metal oxalates falls into two general categories, those which undergo reduction and those which do not. The alkali, alkaline earth, rare earth, and most stable transition metals do not reduce and generally decompose via carbonate formation with the concurrent evolution of carbon monoxide. The carbonates subsequently decompose at higher temperatures evolving carbon dioxide to form the appropriate oxide. Many of the transition metals are more easily reduced and in an inert atmosphere will form the metal in a single decomposition step. They evolve only carbon dioxide at that time.

Both nickel and cobalt are in the latter category. They also have stable divalent ions in aqueous solution which have virtually identical ionic radii. When oxalate ion is added to such a mixed solution of nickel and cobalt ions, a solid solution of the relatively insoluble oxalate dihydrate precipitates at room temperature. Since the charge and solid state ionic radii are so similar there is a complete range of solid solution and very little change in the lattice constants with composition.

As a result of the similarity between the two oxalates the following questions arise: a) does the solid solution decompose as a single entity or as separate oxalates and b) is the product an alloy or a mixture of the metals? Because of the very close similarity between the x-ray diffraction patterns of cobalt and nickel metals or oxides, it is difficult to answer these questions using this technique.

Conventional TG should discriminate between the decomposition of individual versus a collective decomposition and thereby answer the first question. Unfortunately, TG would not differentiate between the formation of the alloy or a mixture of metals, since this is not reflected in the simple weight loss curve. The application of a small magnetic field gradient, however, will convert TG to TM and should suffice to distinguish between these products. The difference in the magnetic transition temperature, T_c, between pure nickel and cobalt is great. The T_c across the solid solution (face centered cubic) varies smoothly from 1121°C for cobalt to 361°C for nickel [8].

The TG and TM curves measured in argon at 10°C min^{-1} for a solid solution and physical mixture of nickel and cobalt oxalate dihydrates having a nickel to cobalt ratio of three are presented in Fig. 6. These sets of data are taken from a much more extensive study [9]. The TG curves were run to 600°C while the TM curves were measured to 800°C.

The notable distinction in the shapes and temperatures of the dehydration curves between the solid solutions and physical mixtures serves to indicate that the mixed oxalates decompose separately and the solid solutions behave as a single entity. The relative proportions of the weight losses indicate that the cobalt oxalate dihydrate dehydrates first. This was verified by measuring the dehydration temperatures of the individual

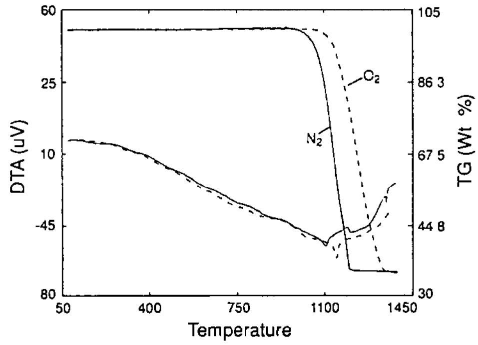

Figure 4

Simultaneous TG/DTA Curves for $KTiOAsO_4$ at 10°C Min^{-1} [6].

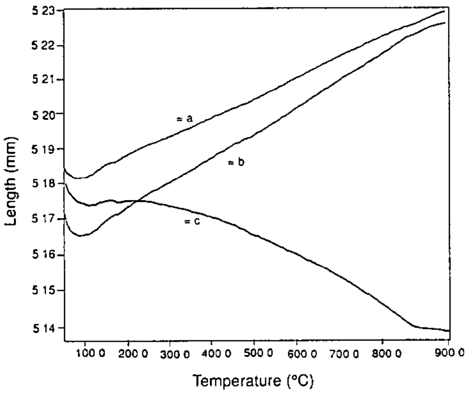

Figure 5

Thermal Expansion for Single Crystalline $KTiOAsO_4$ at 2°C Min^{-1} in He [6].

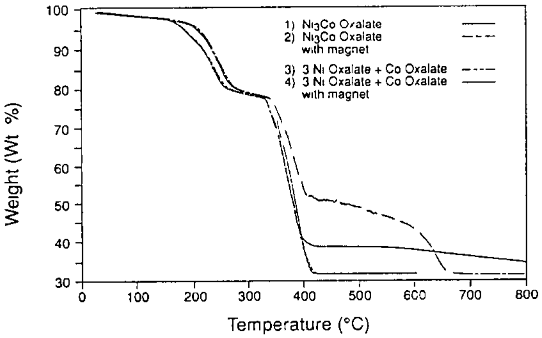

Figure 6

TG and TM Curves of Co-precipitated and Mixed Oxalates of Cobalt and Nickel [9].

oxalates. These distinctions are more clear when looking at the DTG curves. Other samples across the entire range of nickel to cobalt ratios showed the same behavior [9].

The T_c for the alloy, 75 At% Ni and 25 At% Co is about 630°C [8]. This agrees very well with the extrapolated end point of the magnetic attraction for the TM curve of the solid solution in Fig. 6. Clearly a relatively homogeneous alloy is formed directly during the thermal decomposition of the solid solution of oxalates. The TM curve for the physically mixed oxalate exhibits two features which substantiate that the individual metals are formed initially during the thermal decomposition.

The level of weight loss for the physically mixed materials at 450°C is substantially greater, consistent with the nickel being in an non-magnetic state at this temperature, i.e., pure nickel with a T_c of only 361°C. Secondly the magnetic transition temperature of the product is very broad extending from about 600 to well above 800°C. This is consistent with the individual metals having reacted to a limited degree producing a very heterogeneous composition and, hence, broad transition. Again, similar behavior was observed across the entire system [9].

5. CONCLUSIONS

The choice of the above examples was made to indicate that thermal analysis is playing a major role in the new wave of inorganic as well as organic materials. It is also intended to reveal how thermoanalytical techniques can be used to study phase and defect equilibria and the more subtle aspects of solid state reactivity. A great many other selections could have been made had space and time permitted. Some of these would have been in such important areas as superconductors and semiconductors, catalysis, composites, etc. The thermoanalytical techniques themselves are conceptually very simple. The skill and ingenuity comes in recognizing their use and adapting them to the problems at hand.

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