THERMAL ANALYSIS OF $KNBO_3$ SINGLE CRYSTALS

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Abstract: This study Ferroelectric ceramics have been synthesized from powders formulate from individual oxides also called mixed oxide process. The thermal studies were carried out by means of thermal techniques such as TGA, DTA, etc. The DTA curve shows two dips or valleys at temperatures of 70˚C and 1080˚C. These valleys indicate the absorption of energy. The reason for this is not clear here. But, at temperature upto 100˚C the crystal shows endothermic behaviour, while above 100˚C, the behaviour is exothermic upto 1000˚C. After 1000˚C the crystal shows the endothermic behaviour again with a valley at near 1080˚C.

Key Words: **- Thermal techniques, endothermic behaviour , single crystals, orthorhombic.**

I. INTRODUCTION

Hirohashi Junji et.al.[1]studied the controllability of specific domain structures in $KNbO_3$ single crystals was investigated by electric poling to several different orientations at room temperature. By applying electric field to the direction corresponding to the differential direction between the original and intended spontaneous polarization directions (differential vector poling method), 60˚-, 90˚-, and 180˚- domain pairs were successfully fabricated under control in $KNbO_3$.

Milata M. et. al.[2]studied the obtaining of the high quality $KNbO_3$ single crystals is difficult both due to a complicated phase diagram of the solution K_2O–Nb_2O_5 and due to reduction processes taking place during the growth of crystals. Using the TiO_2 as oxidizer during the growing process enable to obtain transparent and colourless crystals. The exponential absorption edge was observed for the crystal doped with iron. The reduction process causes the blue colouration of the crystals. The impurity optical absorption band is associated with electron transitions between the donor impurity band and the conduction band.

Shichijyo Shiro et.al.[3] studied 90˚ -domain structure was fabricated using electrical poling in ferroelectric birefringent $KNbO_3$ crystal. The refraction and reflection characteristics of the light at the boundary of the 90˚-domain structure were investigated.

Wang Ying et.al.[4] was worked on Potassium niobate ($KNbO_3$) powders with the orthorhombic structure and was successfully synthesized through the hydrothermal reaction of Nb_2O_5 and KOH at 200˚C. The morphology of $KNbO_3$ powders changed from rod-like to cubic particles when the potassium hydroxide (KOH) concentrations was in the range of 6.25–15 M. Particularly, when the KOH concentration was 7.5 M and the amount of Nb_2O_5 was 0.02 mol, dodecahedral crystalline was found in the precipitations.

Lu Zheng [5]has observed Localized reversal of patterns formed by ferroelectric domains on the naturally grown surface in an iron-doped potassium niobate (Fe: $KNbO_3$) single crystal and discussed the mechanism of forming this domain structure.

Adachi M.[6] Potassium niobate (KN) single crystals were successfully grown from a melt with potassium enriched composition 51.2 mole % K_2CO_3 using the TSSG technique. Colorless and crack-free crystals up to 27 × 27 × 10 mm 3 in size are reproducibly grown using a platinum crucible of 50 mm in diameter and 50 mm in height. The crystal was allowed to grow laterally from around 30 h to obtain the cross section desired. The growing crystal was then lifted up above the melt surface or lifted intermittently at the rate of about 0.5 mm/h, while the melt was cooled. Cracking occurred at the phase transition temperatures of 435 and 225˚C. Slow cooling fairly eliminated the cracking at the both phase transition points.

Baier-Saip J.A. et.al.[7]the influence of grain size on the phase transitions of ferroelectric $KNbO_3$ was studied by micro Raman spectroscopy. It was found that the three transitions observed are not sharp for small particles (w50 mm). The transition temperatures depend on the size and all particles show hysteresis. From these experiments he obtained some evidence that in small particles monodomains of the rhombohedral and orthorhombic phases coexist in a range of temperatures.

Makovec Darko et.al.[8] studied sintering of $KNbO_3$ ceramics was achieved by using small additions of TiO_2. This improved densification can be explained on the basis of high-temperature chemical reactions in the system. X-ray diffractometry and electron microscopy were used in combination with diffusion-couple experiments in order to elucidate the chemical reactions between $KNbO_3$ and TiO_2. TiO_2 reacts with $KNbO_3$ forming $KNbTiO_5$, and a low concentration of Ti incorporates in the $KNbO_3$ structure resulting in the formation of oxygen vacancies and, consequently, in an improvement in the densification. At 1037 °C eutectic melting between the $KNbO_3$ and the $KNbTiO_5$ further improves the densification of the $KNbO_3$ ceramics.

Wada Satoshi [9] the engineered domain configuration was induced into potassium niobate ($KNbO_3$) crystals, and the piezoelectric properties were investigated as a function of domain size. First, single-domain treatment was investigated. Finally, the engineered domain configurations were induced into $KNbO_3$ crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these $KNbO_3$ crystals with the engineered domain configurations showed much higher values than those of the single-domain crystal. Moreover, the piezoelectric properties increased with decreasing the domain sizes of the engineered domain configuration.

Evans D. R.[10]studied optical and electrical measurements have been made on a new codoped potassium niobate crystal ($KNbO_3$: Fe, Ag) that yields a significant enhancement of the photorefractive and photovoltaic effects when compared with the published results for singly doped potassium niobate crystals. The codoped Ag impurity enters the K site, rather than the typical Nb site, thus changing the local field in the lattice. An enhanced trap density is likely the cause of the increased photorefractive counter propagating two-beam coupling efficiency.

Hirohashi Junji[11] studied a new electric poling concept called the `embryonic nucleation method' to $KNbO_3$, 1-mm-thick uniform periodically poled $KNbO_3$ (PPKN) with domain inverted period of 35.5 μm and an interaction length of 10 mm has been successfully fabricated by applying only 300 V/mm without the generation of unwanted domains. SHG using PPKN fabricated by this method was demonstrated and 100 mw second-harmonic laser generations at a wavelength of 532 nm was obtained from 1 W pumping without photorefractive damage at approximately 40˚C.

Hirohashi Junji [11]studied the controllability of specific domain structures in $KNbO_3$ single crystals was investigated by electric poling to several different orientations at room temperature. By applying electric field to the direction corresponding to the differential direction between the original and intended spontaneous polarization directions (differential vector poling method), 60˚-, 90˚-, and 180˚-domain pairs were successfully fabricated under control in $KNbO_3$.

Wada Satoshi et.al.[12] studied the engineered domain configurations were induced into $KNbO_3$ crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these $KNbO_3$ crystals with the engineered domain configurations showed much higher values than those of the single-domain crystal. Moreover, the piezoelectric properties increased with decreasing the domain sizes of the engineered domain configuration.

II. EXPERIMENTAL DETAILS

Thermal analysis (TA) means the analysis of a change in a property of a sample, which is related to an imposed temperature alteration. Thermal analysis generally covers three different experimental techniques: Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC). Generally all thermal analysis instruments are made in such a way that simultaneous TGA and DTA studies in the temperature range 100 - 1500 K, and DSC measurements in the range 100 - 1000 K can be performed. Photograph of TGA - DTA equipment is shown in Fig. II.1 and the TGA - DTA curves are shown in Figs. II.2 and II.3. For all experiments a selection of crucibles are available (platinum, gold, aluminum, quartz) and the measurements can be done in a flow of different gases. The basic principle in TGA is to measure the mass of a sample as a function of temperature. This, in principle[13], simple measurements is an important and powerful tool in solid state chemistry and materials science. The method for example can be used to determine water of crystallisation, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis.

TGA-DTA plays a central role in the strategy outlined for early evaluation of the solid state forms available to pharmaceutical new chemical entities. Understanding of the solid state forms becomes more difficult when individual samples present as mixed forms, especially when it is not immediately recognized that the samples represent a mixture. In this study, TGA-DTA, in combination with light microscopy and powder X-ray diffraction, provided immediate evidence that samples represented mixed solid state forms. The initial assessment was made using as little as 5 mg of sample. Hygroscopicity challenges provided further proof for mixed forms. To make a definite assignment of the solid state forms present, isolation of pure phases of the suspected individual forms was necessary. Success of this testing strategy is illustrated using an example of mixed salt stoichiometry[14] and mixed hydration states. A hierarchy is suggested for efficient isolation efforts when a complex mixture of solid state samples is present.

Many thermal changes in materials (e.g. phase transitions) do not involve a change of mass. In DTA one instead measures the temperature difference between an inert reference and the sample as a function of temperature. When the sample undergoes a physical or chemical change the temperature increase differs between the inert reference and the sample, and a peak or a dip is detected in the DTA signal. The technique is routinely applied in a wide range of studies such as identification, quantitative composition analysis, phase diagrams, hydration-dehydration, thermal stability, polymerisation, purity, and reactivity.

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. In the particular case of carbon nanotubes, the weight change in an air atmosphere is typically a superposition of the weight loss due to oxidation of carbon into gaseous carbon dioxide and the weight gain due to oxidation of residual metal catalyst into solid oxides.

Fig.II.1: TGA - DTA Instrument.

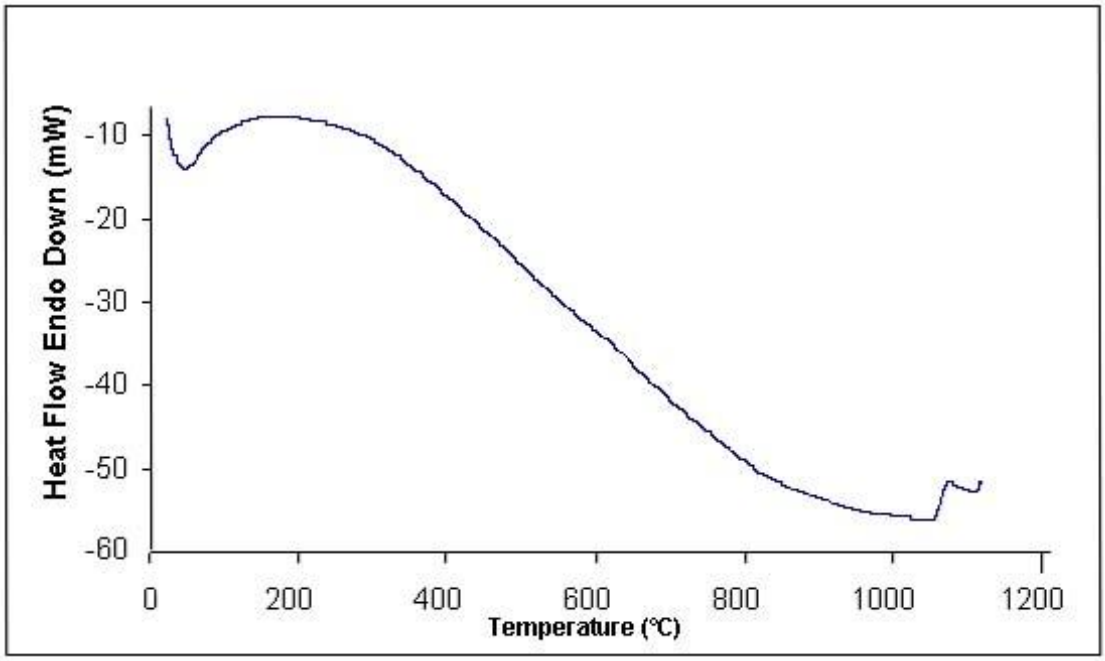

Fig.II.2: TGA - DTA curve for heat flow (mW) Vs temperature.

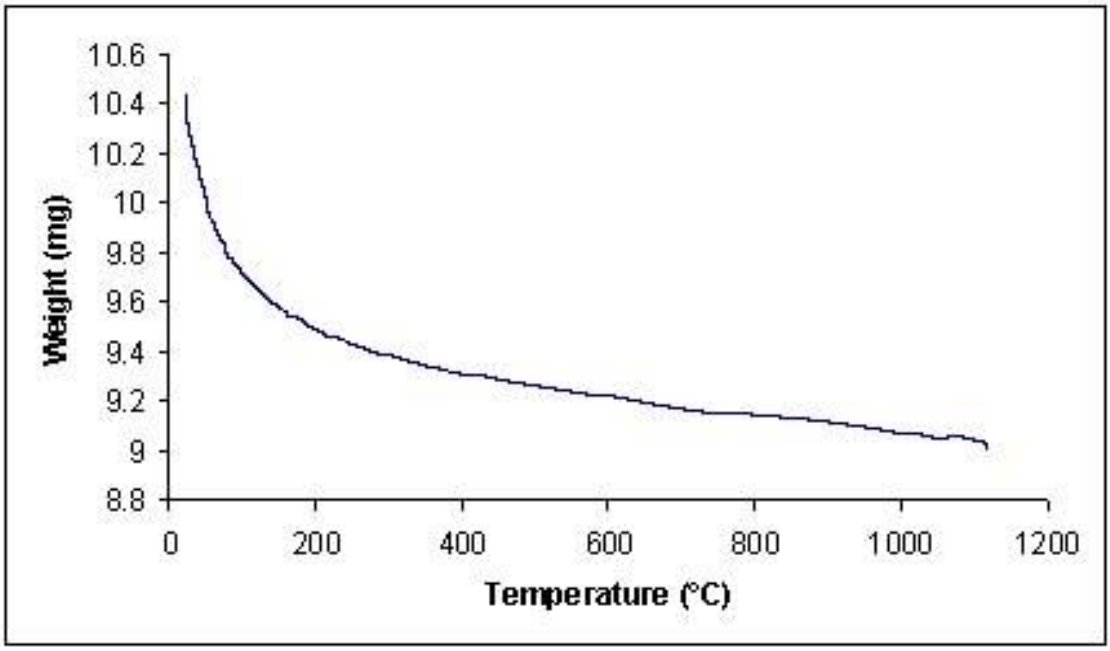

Fig.II.3: TGA - DTA curve for weight (mg) Vs temperature.

III Findings and Conclusions

Thermal analysis

The thermal studies were carried out by means of thermal techniques such as TGA, DTA, etc. The DTA curve shows two dips or valleys at temperatures of 70˚C and 1080˚C. These valleys indicate the absorption of energy. The reason for this is not clear here. But, at temperature upto 100˚C the crystal shows endothermic behaviour, while above 100˚C, the behaviour is exothermic upto 1000˚C. After 1000˚C the crystal shows the endothermic behaviour again with a valley at near 1080˚C.

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