

# THERMAL STUDY OF KNBO<sub>3</sub> SINGLE CRYSTALS

<sup>1\*</sup>Atul R.Khobragade, <sup>2</sup>Bhupendra Singh

<sup>1\*</sup> Raje Dharmarao College of Science, Aheri, *Gondwana* University, Gadchiroli. State- Maharashtra, India

<sup>2</sup>Dept. Of Physics, Maharishi University of Information and Technology, Lucknow.

**Abstract:** This study Ferroelectric ceramics have been synthesized from powders formulate from individual oxides also called mixed oxide process. From the pattern of DSC, it is roughly found that the possibility of phase transition. First peak occurred at about 73°C and the second one at about 225°C. From this it is concluded that the sample transform to tetragonal phase at the temperature of about 225°C. It is seen that the thermogram shows two valleys, one at 73°C and the other at 225°C. The valley at 73°C clearly corresponds to the valley in the DTA curve obtained at 70°C.

**Key Words:** - Ferroelectric ceramics, thermogram, phase transition, single crystals, tetragonal.

## I. INTRODUCTION

Hirohashi Junji et.al.<sup>1</sup> studied the controllability of specific domain structures in KNbO<sub>3</sub> 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<sub>3</sub>.

Milata M. et. al.<sup>2</sup> studied the obtaining of the high quality KNbO<sub>3</sub> single crystals is difficult both due to a complicated phase diagram of the solution K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> and due to reduction processes taking place during the growth of crystals. Using the TiO<sub>2</sub> 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.<sup>3</sup> studied 90°-domain structure was fabricated using electrical poling in ferroelectric birefringent KNbO<sub>3</sub> crystal. The refraction and reflection characteristics of the light at the boundary of the 90°-domain structure were investigated.

Wang Ying et.al.<sup>4</sup> was worked on Potassium niobate (KNbO<sub>3</sub>) powders with the orthorhombic structure and was successfully synthesized through the hydrothermal reaction of Nb<sub>2</sub>O<sub>5</sub> and KOH at 200°C. The morphology of KNbO<sub>3</sub> 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<sub>2</sub>O<sub>5</sub> was 0.02 mol, dodecahedral crystalline was found in the precipitations.

Lu Zheng <sup>5</sup> has observed Localized reversal of patterns formed by ferroelectric domains on the naturally grown surface in an iron-doped potassium niobate (Fe: KNbO<sub>3</sub>) single crystal and discussed the mechanism of forming this domain structure.

Adachi M.<sup>6</sup> Potassium niobate (KN) single crystals were successfully grown from a melt with potassium enriched composition 51.2 mole % K<sub>2</sub>CO<sub>3</sub> using the TSSG technique. Colorless and crack-free crystals up to 27 × 27 × 10 mm<sup>3</sup> 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.<sup>7</sup> the influence of grain size on the phase transitions of ferroelectric KNbO<sub>3</sub> 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.<sup>8</sup> studied sintering of KNbO<sub>3</sub> ceramics was achieved by using small additions of TiO<sub>2</sub>. 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<sub>3</sub> and TiO<sub>2</sub>. TiO<sub>2</sub> reacts with KNbO<sub>3</sub> forming KNbTiO<sub>5</sub>, and a low concentration of Ti incorporates in the KNbO<sub>3</sub> structure resulting in the formation of oxygen vacancies and, consequently, in an improvement in the densification. At 1037 °C eutectic melting between the KNbO<sub>3</sub> and the KNbTiO<sub>5</sub> further improves the densification of the KNbO<sub>3</sub> ceramics.

Wada Satoshi <sup>9</sup> the engineered domain configuration was induced into potassium niobate (KNbO<sub>3</sub>) 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<sub>3</sub> crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these KNbO<sub>3</sub> 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.<sup>10</sup> studied optical and electrical measurements have been made on a new codoped potassium niobate crystal (KNbO<sub>3</sub>; 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<sup>11</sup> studied a new electric poling concept called the 'embryonic nucleation method' to KNbO<sub>3</sub>, 1-mm-thick uniform periodically poled KNbO<sub>3</sub> (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<sup>11</sup> studied the controllability of specific domain structures in KNbO<sub>3</sub> 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<sub>3</sub>.

Wada Satoshi et.al.<sup>12</sup> studied the engineered domain configurations were induced into KNbO<sub>3</sub> crystals by the control of the temperature and the electric-field along the [001] c direction. The piezoelectric properties of these KNbO<sub>3</sub> 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

The lack of information on the domain structures in KNbO<sub>3</sub> is probably because of the difficulty in growing good single crystals that are not highly twinned. Moreover, the crystals with plate like habit, suitable for the domain studies are not easily obtained. We have grown these single crystals, following the method of Wood (1951) with some modifications K<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> were taken in the molar composition 1.2:1 and the dry materials were grounded together in a mortar and packed into a 50 cc. flat bottomed platinum crucible. The crucible with its charge was introduced in the furnace.

Another method, potassium carbonate and niobium pentaoxide were used in mortar composition 1.2:1.0. Another grade niobium pentaoxide has been used. Potassium carbonate was dried at 300°C for two hours before its use. This particular composition was selected following Reisman et.al., and Miller can indeed be expected to give good results for the reason that it is always desirable to effect nucleation from the melt, as rich in KNbO<sub>3</sub> as possible.

Another method, by taking dopant in required mixture is as follows by S. G. Ingle<sup>13</sup>. The dopant Al<sub>2</sub>O<sub>3</sub> was added to the mixture of K<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>.

The materials were mixed thoroughly by growing them together in the mortar for a sufficiently long time (4 to 5 hrs) and mixture packed in a 50 ml flat bottom platinum crucible. The crucible with its charge was covered with a lid and introduced in a furnace up to 1100°C. The soaked period was 24 hrs. The soaked time was expected to set the on this temperature melt in an equilibrium state. The temperature of the crucible was measured by platinum - platinum rhodium thermocouple. The platinum crucible was adjusted in an inclined position.

After soaking the mixture cooled slowly at the rate of 14-17°C per hour up to 840°C. Then the crucible is reheated up to 1000°C and kept there for 18 hrs. A sufficiently nucleation and growth must have occurred during this interval. The eutectic temperature is reached at 840°C and if the cooling would have continued up to 840°C, complete crystallization of KNbO<sub>3</sub> would have taken place. It is known however, that the crystals so obtained are small. This is not surprising, as, when the nucleation takes place simultaneously at various places in the liquid the small crystallites grow independently of each other. Since they start with no knowledge of each other. They have different orientations, and when they meet, they may not join to form a big single crystal. It is necessary for the growth of a large single crystal that stray nucleation should be reduced to a minimum. Deshmukh and Ingle hence thought of an alternative procedure which results in large crystals<sup>14</sup>.

In the method followed, the cooling is stop at 840°C. The crucible is reheated to a temperature just below 1000°C, and kept at the temperature for yet another soaking period of 18 hours. The reheating is expected to re-dissolve the number of small crystals that might be nucleated initially as a result of stray nucleation. The crystallites might have been nucleation. The crystallites might have been nucleated at different times in the cooling process, and as the cooling approached 840°C, numbers of crystallites of different sizes must have been present. In the reheating process, the smaller crystallites dissolve rapidly, while the larger crystallites are also attached and get reduced in size gradually. At a temperature just below 1000°C, the liquid us temperature for the composition used, the charge in the crucible is expected to be in a completely molten state, expect for a very few crystallites that remain scattered in liquid.

An equilibrium is reached between them are the rest of the melt during a soaking period of 18 hrs. When cooling is now started slowly at the rate of 30-35 hrs till the room temperature was reached, the small crystallites serve as seeds are favoured, as the growth of the crystal is dendritic and quite rapid. The chances of stray nucleation are consequently considerably reduced, and the large single crystals are observed. The crystal blocks separated from flux was found covered at the top by a thick crystalline layer projecting from the walls of the crucible. (i.e.CO<sub>2</sub> is evaporated from the mixture). A thin layer of small crystals was also found to be growing out of the thick layer. Crystal plates could also be obtained on the bed of flux.

Inclined position of the crucible is found to be helpful to the crystal, as the diffusion rates are higher at the walls than in liquid, and therefore conditions at the walls are more favorable to the growth of crystals.

The crystal plates found on the bed of the flux are mostly white. Some of them are colorless. The size of the colourless plates range from 2 mm to 50 mm on edge length. The thickness is about 0.4mm. These crystals plates usually show quite simple twinning, and are very good for dielectric as well as domain studies. The white crystal plates are larger in area and smaller in thickness (of the order of 0.1mm.), very fragile and highly twinned usually showing curvature. The large single crystals are in the form of transparent greenish colour. The crystal can be cleared very easily into very thin crystal flakes that appear nearly colourless and their conductivity is quite low of the order of 10<sup>-9</sup>(Ohm-cm)<sup>-1</sup>.

The rate of cooling is an important parameter in any crystals growth. In general, the crystals growth at low rate of cooling are expected to be more perfect with less strains, since random thermal gradient effects are non considerably reduced. At the low cooling rates, the impurities get time to adjust themselves more favorably in the crystal structure, and the strains in such crystals are correspondingly less. In addition to all these arguments in favoured of the lower cooling rates, one has to balance the thickness of the crystal grown with the attendant cost problem and more importantly the mechanism of crystal growth. The changed rates of cooling can produced drastic changes in the crystal growth. The mechanism of the growth may change, and the twinning habit and the crystal growth habits may also change. Indeed, the whole crystal texture changes by changing a single simple looking parameter, namely the cooling rate. Therefore, in the present investigation the main emphasis was on the study of the changes produced in the crystal textures a result of the changes in the cooling rate. The cooling rates of the order of 60°/hour were used by Ingle, when he developed the technique which has been the basis for the present work. He had found that crystal surfaces, particularly the small

crystals found on the flux bed show dendritic mechanism of growth. It could not be ascertained then if the whole crystal had grown following the same mechanism. Therefore, it was one of the objects of the present investigation to verify this point also.

We, therefore, changed the rates of cooling from 60°/hr to the various lower values, coming down to as low as 10°/hrs. The main finding of these experiments is that below 35°/hr the dendritic growth is generally completely suppressed. There is no sharp transition from dendritic growth to the layer growth as the cooling rates are reduced. The layer growth is found to be caused both by natural kinetics factors and the defects factors. The various facets of the layer growth have been studied<sup>15</sup> extensively.

We have carried out experiments to see the effect of dopants on the crystals growth mechanism and the crystal textures. Aluminum ions produced by using the known amount of Al<sub>2</sub>O<sub>3</sub> produced some interesting effects on the domain structures. No change was observed on the mechanism of the crystal growth<sup>16</sup>.

### III. FINDINGS AND CONCLUSIONS

#### DSC studies

In these studies, the experimental sample and the reference sample are simultaneously heated in a furnace, and the difference in the power required to keep the two samples at the same temperature is noted as a function of temperature. If the experimental sample is requiring more power than the reference sample to be maintained at particular temperature, it means that the experimental sample is absorbing energy at that temperature. The excess energy required is shown in mW versus temperature. A typical curve is shown in Fig. III.1 as obtained on an instrument at VNIT, Nagpur. The heating rate was 10° per min. and the weight of experimental sample was 12.10mg. The measurement of the difference in heat flow to sample and reference, which are heated (or cooled) together in a controlled temperature program. The heat flow path at the DSC sensor is well defined and reproducible. The DSC curve shows the peaks at the temperature of about 73°C and 224°C. The sharp nature of valley shows that the crystal is not dirty or a disorder ferroelectric.

#### Advantages

- Direct measurement of temperature difference with differential thermocouple.
- Direct measurement of temperature with thermocouple at the reference side.
- Area thermocouple contact.
- Low influence of convection and radiation (depending on design), because heat transfer is dominated by conduction on metallic construction parts of the sensor.
- Highly repeatable baselines.
- Precise calibration possible (for temperature and for enthalpy changes).
- Suitable for combination with TG in STAs.
- Accurate determination of heat of transitions and reactions (enthalpy changes).
- Accurate specific heat determination.
- Fast heat exchange for short time constant of differential signal changes

#### Disadvantages

- Relatively small sample weights recommended (for homogeneous heating of the materials).
- Restrictions at very high temperature (available metallic construction Materials).
- Careful sample and crucible positioning is necessary.
- Crucible lids necessary to cover sample surface from surrounding (could restrict solid-gas reactions).

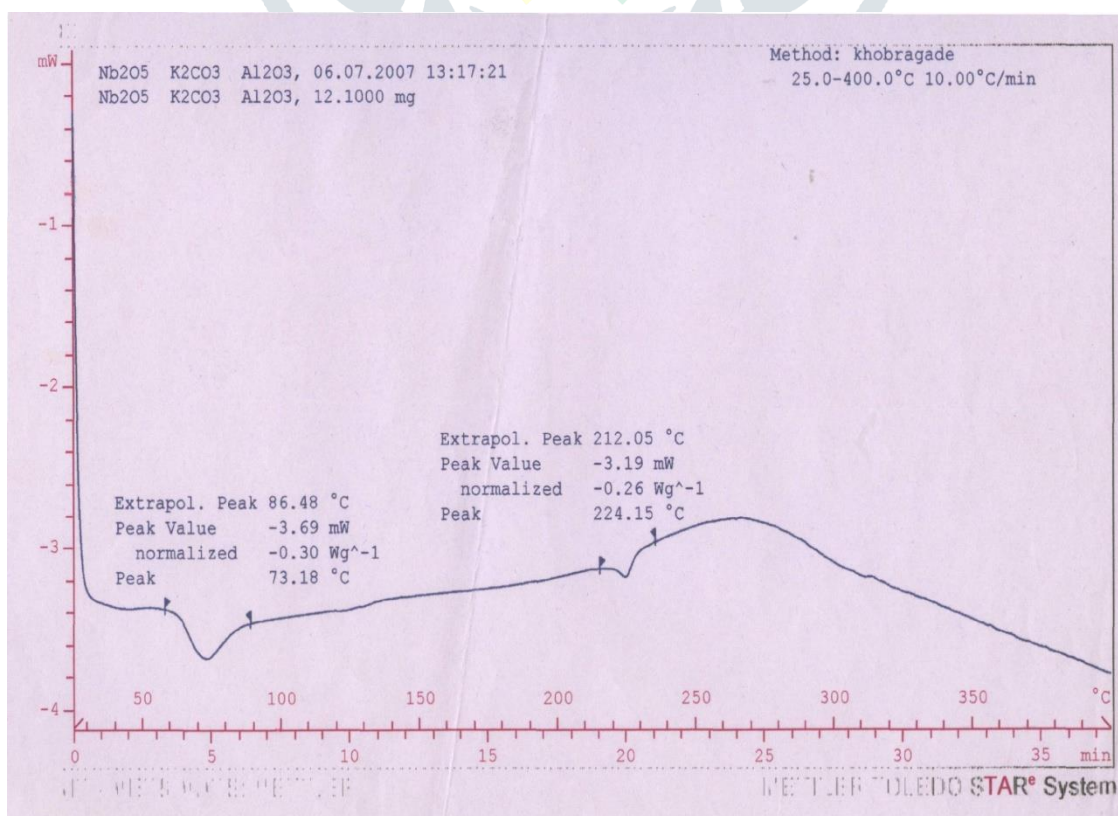


Fig. III.1: DSC curve for mW Vs temperature.

From the pattern of DSC, it is roughly found that the possibility of phase transition. First peak occurred at about 73°C and the second one at about 225°C. From this it is concluded that the sample transform to tetragonal phase at the temperature of about 225°C. It is seen that the thermogram shows two valleys, one at 73°C and the other at 225°C. The valley at 73°C clearly corresponds to the valley in the DTA curve obtained at 70°C.

#### IV ACKNOWLEDGEMENT

Thanks to R.T.M. university Nagpur to providing Labs of Laxmi narayanan Institute of Technology ,Nagpur.

#### REFERENCES

- [1] Hirohashi Junji, Yamada Kazuhiro, Kamio Hiroyuki and Shichijyo Shiro Japanese Journal of Applied Physics No. 2, Vol.38(2004)559-566.
- [2] Milata M., Wójcik K. and Zieleniec K. Institute of Physics, University of Silesia, Ul. Uniwersytecka 4, PL-40-007 Katowice, Poland.
- [3] Hirohito Junji , Yamada Kazuhiro , Kamio Hiroyuki , Masao Uchida, and Shichijyo Shiro Mitsui Chemicals, Inc., 580-32.
- [4] Wang Ying, Zhiguo Yi. , Yongxiang Li., Qunbao Yang, Dong Wang Ceramics International (22 July, 2006).
- [5] Lu Zheng and Xiao Min Journal of Applied Physics Issue 7, Vol. 76(October 1, 1994) 4451-4453.
- [6] Adachi, M.; Fujita, N.; Norimatsu, Y.; Karaki, T. Ferroelectrics, Number 2, Vol. 334(2006) 91-96.
- [7] Baier-Saip J.A., Ramos-Moor E., Cabrera A.L., Solid State Communications 135 (2005) 367–372.
- [8] Makovec Darko, Pribosic Irena, Drogenik Miha Ceramics International (2006).
- [9] Wada Satoshi, Muraoka Kazuma, Kakemoto Hirofumi, Tsurumi Takaaki and Kumagai Hirohiko Japanese Journal of Applied Physics No. 9B, Vol. 43(2004) 6692-6700.
- [10] Evans D. R., Cook G., Carns J. L., Saleh M. A., Basun S. A., Seim J. M., and Mizell G. J. Optics Letters, Vol. 31, Issue 1, pp. 89-91.
- [11] Hirohashi Junji, Yamada Kazuhiro, Kamio Hiroyuki and Shichijyo Shiro Japanese Journal of Applied Physics No. 2, Vol.43(2004)559-566.
- [12] Hirohashi Junji, Yamada Kazuhiro and Shichijyo Shiro Japanese Journal of Applied Physics No. 2, Vol. 43(2004) 559-566.
- [13] Wada Satoshi, Muraoka Kazuma, Kakemoto Hirofumi, Tsurumi Takaaki and Kumagai Hirohiko Japanese Journal of Applied Physics , No. 9B, Vol. 43(2004) 6692-6700.
- [14] Ingle, S.G. and Mishra, M.B. Ind.J. Pure and Appl.Phys. 16 (1978)1030.
- [15] Ingle, S.G. Ph.D. Thesis, ‘Studies in some ferroelectric properties of KNbO<sub>3</sub> Single crystals’ Nagpur Uni. (1971).
- [16] Katpatal, A.G. and Deshmukh, K.G. Ind. J.Pure and Appl.Phys. 14 (1976) 66.