Supplementary Document To: Optical crystallographic Study of Piezoelectric $K_xNa_{1-x}NbO_3$ (x = 0.4, 0.5 & 0.6) Single Crystals using Linear Birefringence

1. Crystal Growth, Compositional and Orientation Determination -

Figure 1(a) shows the optical image of as grown crystals (x = 0.5) embedded in the re-solidified flux. By successive boiling and treating by ultrasonic waves in water, crystals were separated from flux. Crystal with a cubic geometry were found to have maximum dimensions of about 6 mm X 6 mm X 2 mm. Figure 1(b) shows one of the crystal (x = 0.5) having planer dimensions of about 5 mm X 5 mm. After compositional homogenization by annealing at 1000°C, energy dispersive X-ray analysis (EDX) was performed to confirm the composition of crystals. Figure 2 shows the atomic mole % of Na and K ions in the crystals of three batches (x = 0.4, 0.5 and 0.6). For optical birefringence study, crystals with higher transparency were chosen from each batch of x = 0.4, 0.5 and 0.6 respectively.

Figure 1 Optical images showing (a) as grown crystals in KF – NaF matrix (b) One of the large size crystals.

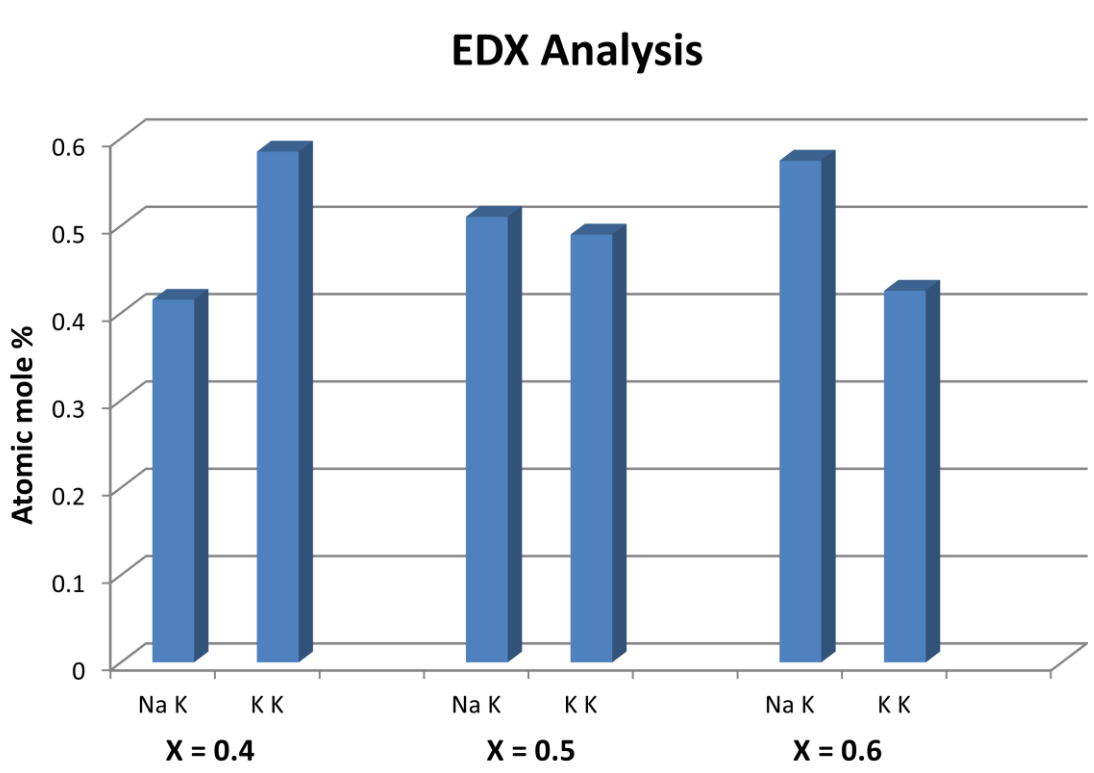

Figure 2 Energy dispersive X-ray (EDX) analysis performed on crystals intended to have composition x = 0.4, 0.5 and 0.6.

Figure 3 shows x-ray diffraction pattern obtained for one of the major faces of a crystal (x = 0.5), confirming these crystals to be $\{100\}_{pc}$ oriented. This observation was further confirmed by electron backscattered diffraction analysis (EBSD) performed on two opposite major faces of these crystals.

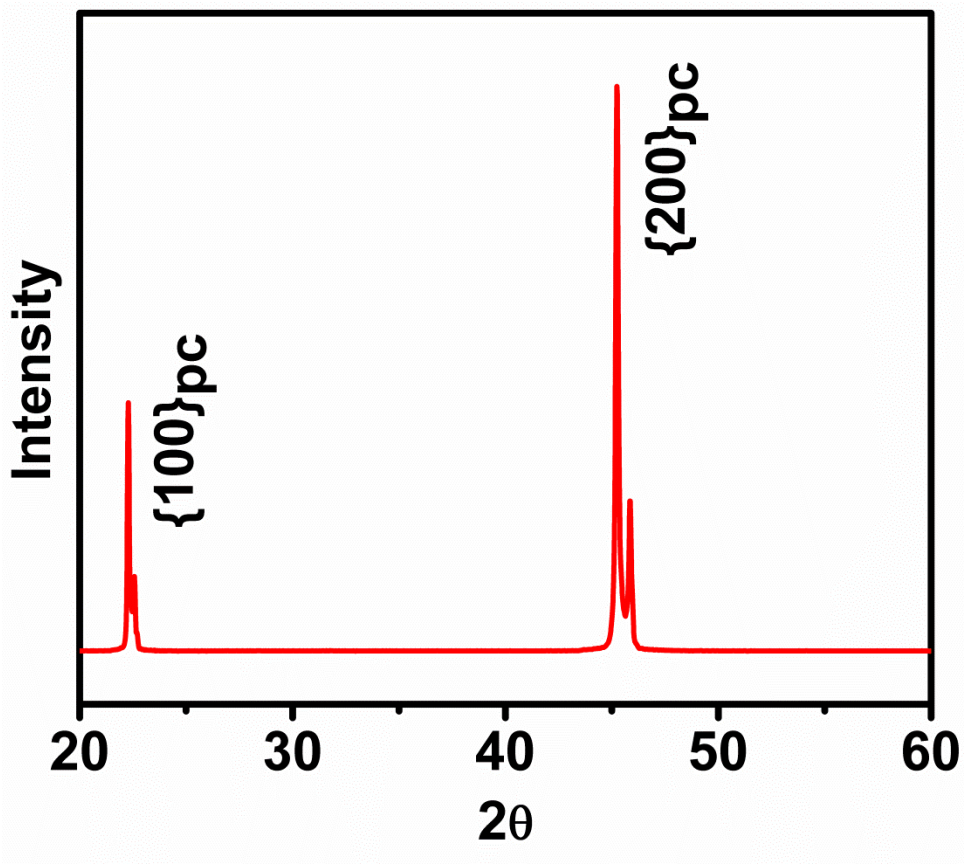

Figure 3 x-ray diffraction pattern showing the presence of only {100} family peaks.

2. Birefringence Measurements –

Figure 4 shows the schematic diagram of the Metripol birefringence measurement system.[1]

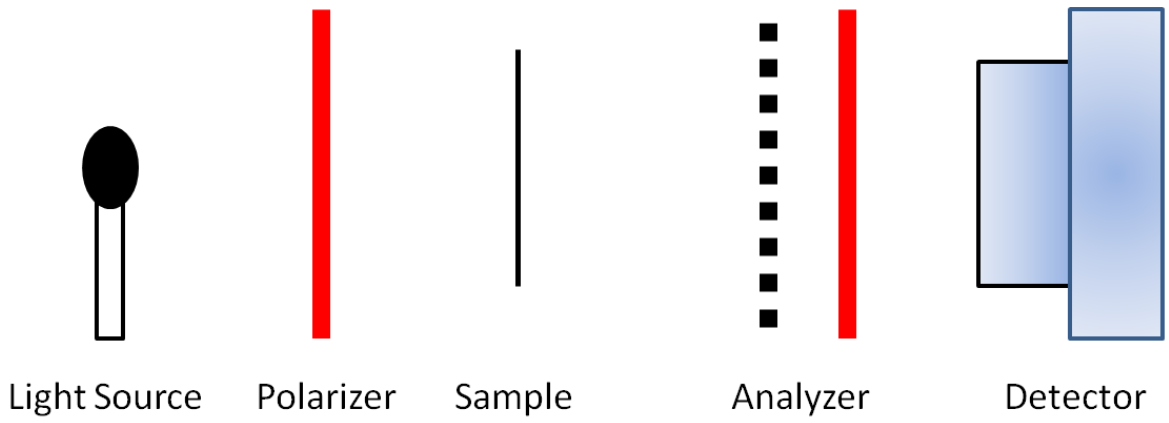

Figure 4 Schematic diagram of Metripol birefringence measurement system.

It consists of a monochromatic light source, a rotating polarizer followed by a sample stage. The transmitted light is allowed to go to the circular analyzer followed by a CCD detector. Intensity measured at each pixel of detector is given by Equation 1.[1]

$$I = I_o/2[1 + Sin(2\alpha - 2\varphi)Sin\delta]$$

Or

$$I = \frac{1}{2}I_o + \frac{1}{2}I_o\ Sin\delta\ Cos2\varphi\ Sin2\alpha - \frac{1}{2}I_o\ Sin\delta\ Sin2\varphi\ Cos2\alpha \quad (1)$$

Where I_o and φ are the transmittance of the sample and the angle between the minor axis of the indicatrix with an arbitrary coordination axis, respectively. δ is the phase difference introduced by the crystal to the transmitted light ray. To determine the values of all three components I_o, |Sinδ|, and φ, the intensity of the transmitted light is measured for different values of the rotation angle α which the polarizer makes from a fixed reference.

Least square fitting method is used to determine the three parameters of interest, according to equation (2)[1]

$$y(x) = a_o + a_1 Sinx + a_2\ Cosx \quad (2)$$

On comparing it with equation (1), "a" parameters are found to be

$$a_o = \frac{1}{2}I_o$$
$$a_1 = \frac{1}{2}I_o\ Sin\delta\ Cos2\varphi$$
$$a_2 = \frac{1}{2}I_o\ Sin\delta\ Sin2\varphi \quad (3)$$

If the polarizer is stepped through N steps in the process of collecting data, "a" parameters can be given as in equation (4).

$$a_o = \sum_{i=1}^{N} \frac{1}{N} y_i$$

$$a_1 = \sum_{i=1}^{N} \frac{2}{N} y_i \, Sinx_i$$

$$a_2 = \sum_{i=1}^{N} \frac{2}{N} y_i \, Cosx_i \qquad (4)$$

Values for two parameters of interest ǀSinδǀ and φ can be determined from values of parameters "a" according to equation (5).[1]

$$|Sin\delta| = \frac{\sqrt{(a_1^2 + a_2^2)}}{a_o}$$

$$\varphi = \frac{1}{2} arcSin\left(- \frac{a_2}{\sqrt{(a_1^2 + a_2^2)}} \right) \qquad (5)$$

3. Determination of Orientation Histogram –

To obtain the orientation histograms for three (x = 0.4, 0.5 and 0.6) compositions at different temperatures, φ false color images were obtained from an area of about 2.5 mm X 1.9 mm. Each of these images consisted of about 1.39 million (1360 X 1024) pixels, each representing a value of φ between 0^o – 180^o. Each histogram was created using these 1.39 millions φ values with the bin size of 1^o.

4. Reference -

1. A. M. Glazer, J. G. Lewis and W. Kaminsky, *Proceedings: Mathematical, Physical and Engineering Sciences*, 1996, **452**, 2751-2765.