Material Science Research India Vol. **13**(1), 14-20 (2016)

High Temperature XRD of Phase Transition in Piezoelectric $PbNb_2O_6$ across its Curie Temperature

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http://dx.doi.org/10.13005/msri/130103

(Received: June 09, 2016; Accepted: June 21, 2016)

ABSTRACT

Orthorhombic phase of lead metaniobate ($PbNb_2O_6$) is piezoelectric with a high Curie temperature (>570°C) with high potential of wide use in important high temperature applications that cannot be covered by the popular piezoelectric materials based on BT and PZT. Difficulty of preparing it in pure phase hindered full characterization and wide use of this long known piezoelectric material. Here, $PbNb_2O_6$ pellets have been prepared in pure orthorhombic phase and first characterized by room temperature TEM and XRD techniques, with a satisfying agreement of the two results. Next, we carried out high temperature x-ray diffraction study of its ferroelectric to paraelectric phase transition on heating across the Curie temperature, and also traced the cooling path. On heating the sample to 590°C and cooling back, there is a significant increase of cell volume.

Keywords: Piezoelectric materials, Orthorhombic $PbNb_2O_6$, Tetragonal $PbNb_2O_6$, Curie Temperature, Ferroelectric Phase Transition, TEM, High Temperature XRD, Rietveld Refinements.

INTRODUCTION

Piezoelectric materials are finding increasing utilization as sensors, actuators, ultrasonic imaging devices, and in many other commercially profitable applications. For applications in critical areas like Fast Breeder Reactors and exhausts of rockets and vehicles, piezoelectric materials with high Curie temperature[1] are essential. Among the few materials in different stages of development for higher temperature piezoelectric devices, less work has been done on the old but inadequately studied piezoelectric material[2] of lead metaniobate ($PbNb_2O_6$ or PN). Room temperature structure of PN can be[2-4] either rhombohedral or orthorhombic. Only the latter is ferroelectric with piezoelectric properties, attractive because of attractively high Curie temperature[5] (> 570°C). Fewer studies on PN, in spite of this high Curie temperature, have been basically due to the problem of preparing, by quenching[6], the piezoelectric form (the meta-stable orthorhombic structure) in pure phase. Subsequently, various aspects have not been re-studied in modern times. We decided to investigate with high temperature (HT) x-ray diffraction (XRD) the structural changes during ferroelectric to paraelectric phase transition on heating across the Curie temperature and trace the cooling path also, of orthorhombic $PbNb_2O_6$, characterized at room temperature by XRD and TEM (Transmission Electron Microscopy). We have optimized preparation steps[3] including the quenching (Q) step, and prepared pure orthorhombic phase of PN, to be called PNOQL, with L denoting the supplier (Loba) of Nb_2O_5 used in the preparation.

MATERIALS AND METHODS

Sample Preparation

Pellets from starting chemicals of PbO and Nb_2O_5 with 2% extra weight of PbO (to compensate

for feared loss of Pb during firing) have been calcined first for 3.5 h 1050°C, and then at 1290°C for 1 h. The 3rd firing (about 5 h) at 1270°C has branched into quenched (PNOQ or PNOQL)[7] and slow-cooled (PNS) samples.

HT XRD study

Using Cu K_α radiation with α_1 = 1.54056 Å and α_2 = 1.54439 Å, generator voltage = 40 V, tube current = 30 A, scan step size = 0.02, and scan step time = 0.50 s, x-ray powder diffraction has been carried out (Figs. 1-5) at different temperatures on PNOQL sample: 30°C, 550°C, 570°C and 590°C. After soaking at 590°C for about 1hour, the powdered sample has been cooled back, and XRD has been taken again at 30°C. Rietveld refinements[3] have next been done, as depicted in Figs. 1 & 3-5, to extract lattice parameters, given in Table 1, and a pictorial representation (Fig. 2).

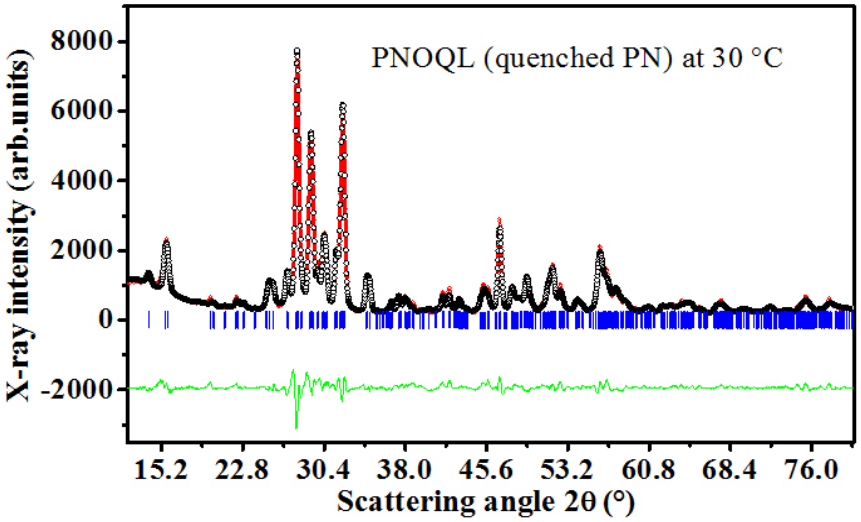


Fig. 1 Open circle symbols (black), giving XRD data for PNOQL at 30°C, fit closely the Rietveld refined plot (the continuous red curve in the main graph). Their difference is shown by the continuous curve in the smaller-sized graph (green in color). The vertical bars (blue color) in the main graph are the calculated peak positions.

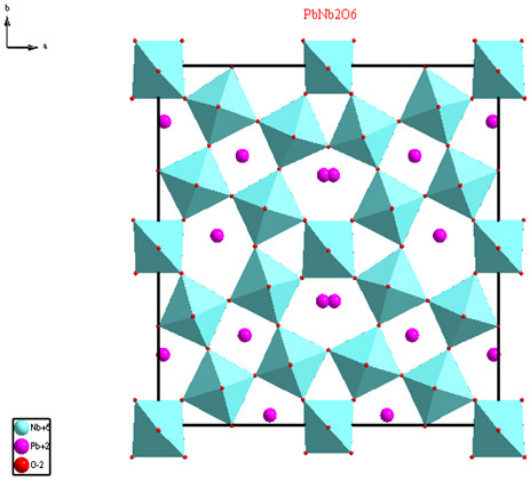


Fig. 2: Pictorial view of the orthorhombic $PbNb_2O_6$ structure in PNOQL

TEM examination

Practically the same inter-layer separation (d) (in table[8] 2) has been obtained by Transmission Electron Microscopy (Fig. 6, d(TEM)), and by x-ray, d(XRD), for the orthorhombic $PbNb_2O_6$ sample at room temperature.

RESULT AND DISCUSSION

The temperature variation of lattice parameters (a, b and c) of the orthorhombic PNOQL sample, from room temperature (RT) to 590°C and return to RT, has been shown graphically in Fig. 7. This matches well with the original work of Francombe and Lewis[9]. As the temperature is raised from 30°C to ~ 550°C, the lattice parameter 'a', indicated by open circle, increases (from 17.6515 Å to 17.7587 Å) and the lattice parameter 'b', indicated

by open rectangle, decreases (from 17.9484 Å to 17.7875 Å) so that the two approach a common value beyond ~ 570°C, the temperature for transition from orthorhombic to tetragonal structure[9-10]. This corresponds also to the Curie temperature, above which piezoelectric and ferroelectric properties disappear to pave the way for a paraelectric phase. Plot of (b-a) vs. temperature in Fig. 8 also shows a decrease of (b-a) towards zero. Over the temperature range 30°C to 590°C the 'c' parameter, indicated by open down triangle, increases linearly (from 3.8734 Å to 3.9228 Å). Unit cell volume is seen in Fig. 9 to increase rapidly with temperature in the orthorhombic phase, and only slightly above Curie temperature. The powdered sample has been heated from 30°C to 590°C, soaked at 590°C for about 1hour and then cooled down to 30°C. Parameters a, b and c have been re-measured by XRD at 30°C. The values of lattice parameters increase slightly after this 590°C cycling (with soaking at the high temperature) of the

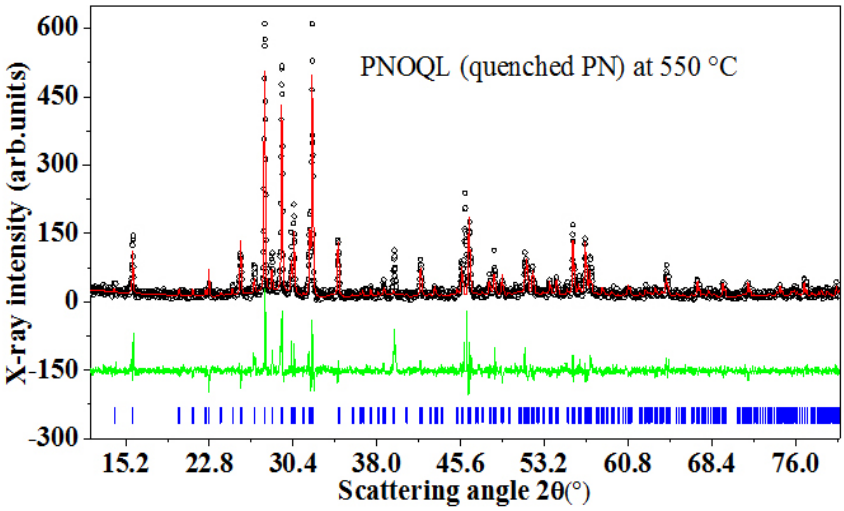


Fig. 3: Open circle symbols (black), giving XRD data, for PNOQLat 550°C, fit well the Rietveld refined plot

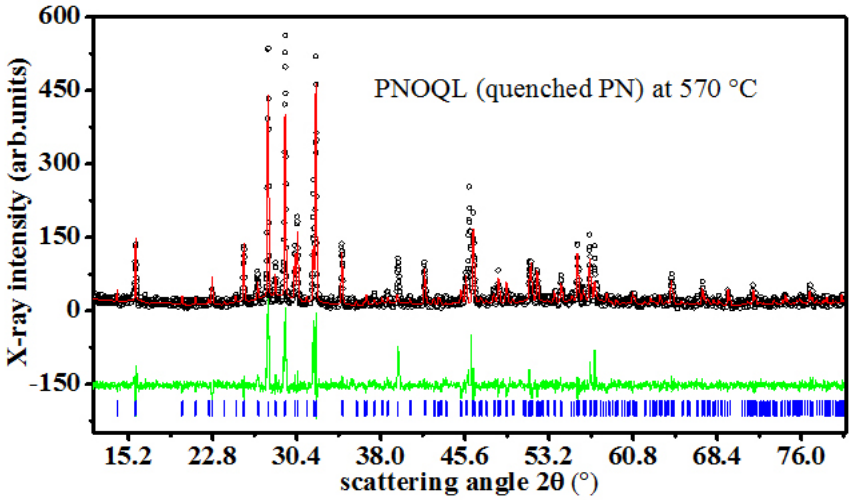


Fig. 4: Open circle black symbols, giving XRD data for PNOQL at 570°C, fit well the Rietveld refined plot

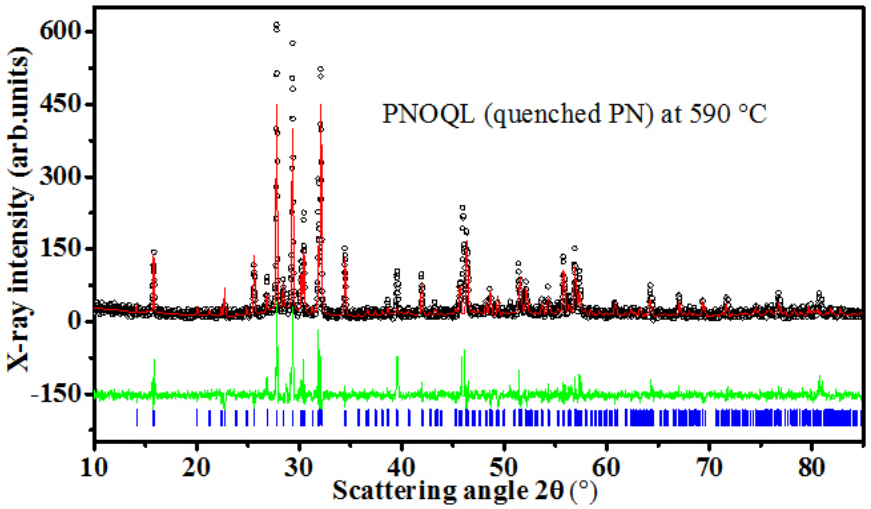
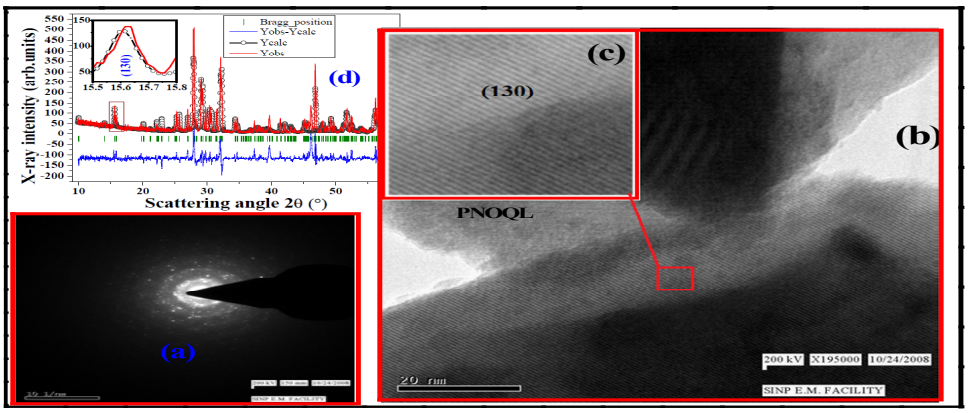


Fig. 5: Open circle symbols (black colour), giving XRD data for PNOQL at 590°C, fit well the Rietveld refined plot



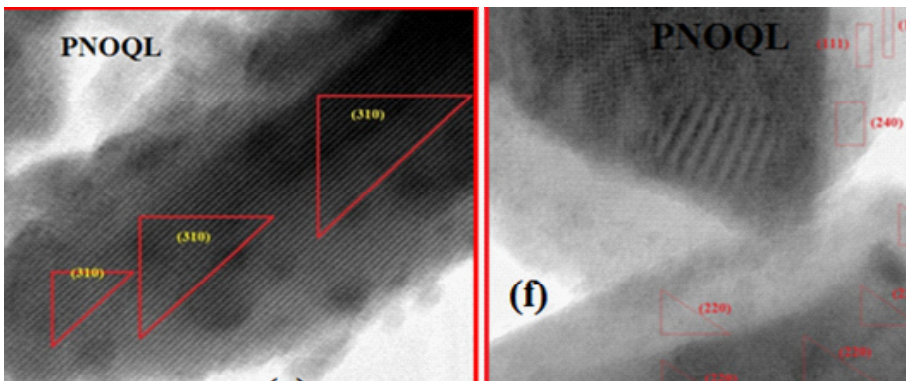


Fig. 6: TEM diffraction pattern (a) and images of different atomic planes of PNOQL sample (b, c, e and f) and inset view of XRD (d). It shows <130> planes in (b) and (c), <310> plane in (e), and <111>, <020>, <240> and <220> planes in (f)

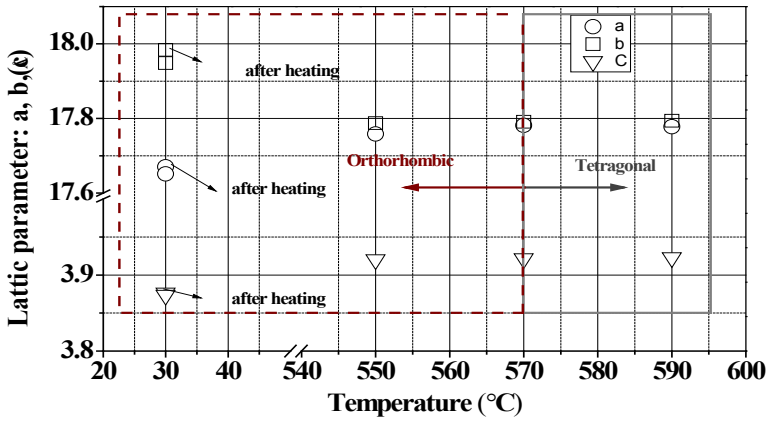


Fig. 7: Graphical representation of the variation of lattice parameters a, b, and c with temperature cycling

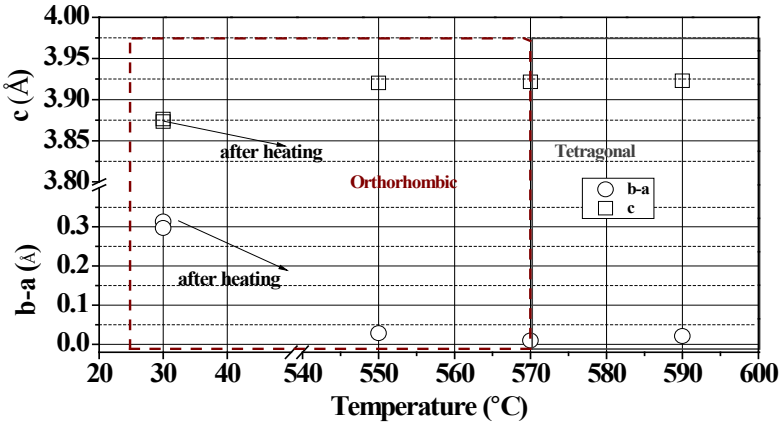


Fig.8: Variation of the difference (b – a) and c with temperature

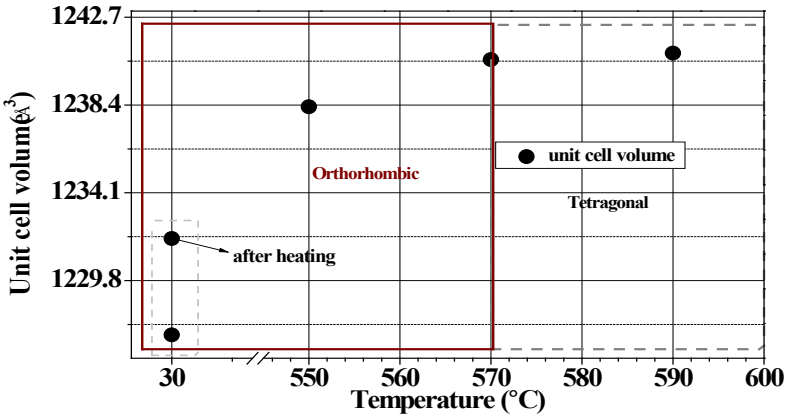


Fig. 9: Variation of unit cell volume (V) of $PbNb_2O_6$ with rise in temperature from 30°C to 590°C as calculated from present XRD results. On heating the sample to 590°C and cooling back, there is an increase of volume.

samples: a (~ 0.107%), b (~ 0.198 %), and c (~ 0.078 %) with Fig. 7 showing the value after the heating (cycle) by the upper point with same symbol.

Lattice dimension measured by TEM from different spots of the orthorhombic $PbNb_2O_6$ sample match the averaged value measured by x-ray diffraction, confirming the correctness of both characterizations. The high temperature structure is tetragonal. Electrical[11] and thermal[12] techniques showed the Curie temperature to be above 570°C. Below Curie temperature, a < b < c, and the sample is ferroelectric with piezoelectric properties.

Loss of piezoelectric properties[11,12] above this temperature is accompanied by increase of a, and decrease of b, to make a = b, as indicated in our (b-a) vs. T plot. Unit cell volume is seen to increase rapidly with temperature in the orthorhombic phase, and only slightly above Curie temperature. It is a new observation that room temperature cell volume increases on heating the sample to 590°C and cooling back to room temperature.

Table 1: Lattice parameters of $PbNb_2O_6$ as a function of temperature (orthorhombic below Curie temperature and tetragonal above)

Temperature (°C)	a (Å)	b (Å)	c (Å)	$\alpha = \beta = y$ (°)	Unit cell volume (Å3)
30(before)	17.651(5)	17.948(4)	3.873(4)	90.00	1227.145
550	17.758(7)	17.787(5)	3.920(2)	90.00	1238.317
570	17.781(5)	17.791(3)	3.921(7)	90.00	1240.624
590	17.778(1)	17.793(7)	3.922(8)	90.00	1240.939
30(after)	17.670(5)	17.984(1)	3.876(4)	90.00	1231.865

Table 2: Comparison of inter-planar separations, d, of orthorhombic $PbNb_2O_6$ sample, as found by Transmission Electron Microscopy (TEM) and X-Ray Diffraction (XRD)

Sample Name	d_{TEM} (Å) (TEM)	d_{XRD} (Å) (XRD)	Plane	2θ or Bragg's angle (°)
PNOQL	5.5878	5.5770	310	15.88
(Orthor hombic	5.6244	5.6629	130	15.62
$PbNb_2O_6$)	3.75695	3.6904	111	23.02
	4.0003	3.9463	240	22.20
	6.2894	6.2889	220	14.06
	9.1141	8.9688	020	9.85

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