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Short communication

Thermal characterization of piezoelectric and non-piezoelectric Lead Meta-Niobate

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ABSTRACT

Powerful tools like Differential Scanning Calorimetry (DSC) and DTA seem to be under-utilized for the emerging materials for high temperature piezoelectric sensors, while thermal aspects of such piezoelectric phase change are also of theoretical interest. Curie temperature of Lead Meta-Niobate ($PbNb_2O_6$ or PN) is 570 °C, much higher than that for widely used lead zirconate titanate, making PN potentially more attractive at high temperatures. However, the only specific heat measurement for PN appears to be the 2–25 K study by Lawless, leaving the Curie temperature region unexplored. For PN, piezoelectricity is possible for the meta-stable orthorhombic structure only. So, we prepared pure phase orthorhombic PN by quenching (Q) and the rhombohedral PN by slow-cooling (S). We report for the first time, to our knowledge, DSC across the Curie temperature for Q and S types of PN. We find clear and interesting DSC signals at the Curie temperature in heating and cooling graphs for quenched (Q) $PbNb_2O_6$ only and none for the slow-cooled (S) $PbNb_2O_6$.

1. Introduction

Curie temperature of the widely used piezoelectric material, lead zirconate titanate cannot be improved above 380 °C. Synthesis and phase identification of the piezo-electric phase of Lead Meta-Niobate ($PbNb_2O_6$) [1–13] is difficult, as a few competing phases and compounds tend to form during the preparation. But, it has an attractively higher Curie temperature of 570 °C [14–16]. Present DSC [17–19] for identification of this phase has been very rewarding. Earlier DSC on piezoelectric materials has been limited to a few materials like $BaTiO_3$ [20] and $[Bi_{0.5}(Na_{1-x}K_x)_{0.5}]TiO_3$ [21]. The piezoelectric $PbNb_2O_6$ is known to change from orthorhombic to tetragonal phase on heating across the Curie temperature of 570 °C. The stable forms of $PbNb_2O_6$ are believed to be rhombohedral (at low temperature) and tetragonal (at high temperature). The latter is transformed, usually by quenching, to the meta-stable orthorhombic structure, often described as an orthorhombic distortion of the tetragonal structure. This orthorhombic distortion of the atomic positions of $PbNb_2O_6$, in fact, creates a polar axis paving the way for ferroelectric and piezoelectric behavior. Slow-cooling leads to the rhombohedral structure, which is non-piezoelectric.

2. Experimental outline

Instead of wet chemical routes [22,23], a purely solid-state reaction route has been utilized in our work. Simple steps like making all firings in palletized form to provide intimate contact and fine grinding plus re-palletizing at each step for more uniform mixing, have resulted in good quality samples also from this non-wet route. Pellets from starting chemicals of PbO and Nb_2O_5 with 2% extra weight of PbO (to compensate for known Pb loss 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 (PN_Q) and slow-cooled (PN_S) samples. Powder X-ray diffraction patterns for these samples, taken at IACS, Kolkata-32, India, are shown in Figs. 1 and 2. For the DSC runs in a Seiko DSC 6200 set-up, the heating has always been kept at 5 °C/min, as higher rates mask finer features of the DSC plot. Dimensions of each disc-like pellet sample have been measured by a digital caliper. Then by finding its mass in an electronic balance, the real density of the pellet has been calculated. This has been done for several pellets of PN_Q sample.

3. Results and discussion

XRD pattern of the quenched sample, PN_Q, in Fig. 1 matches well with the best reported orthorhombic patterns for piezoelectric samples [11,13,14,24,25]. Rietveld analysis [26] showed $a = 17.659$ Å, $b = 17.951$ Å and $c = 3.8717$ Å, implying a theoretical density of 6.416 g/cm^3. Our samples achieved up to 81.2% of the

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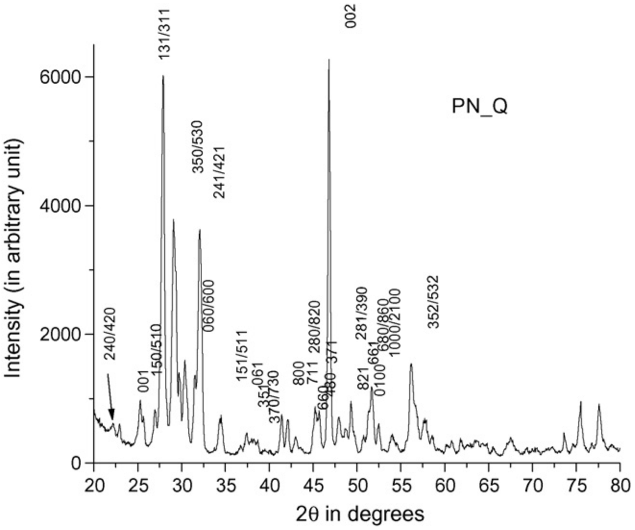

Fig. 1. XRD pattern of powdered PN_Q, $PbNb_2O_6$ sample that has been quenched to room temperature after sintering at 1270 °C. The peaks have been indexed, considering the orthorhombic phase.

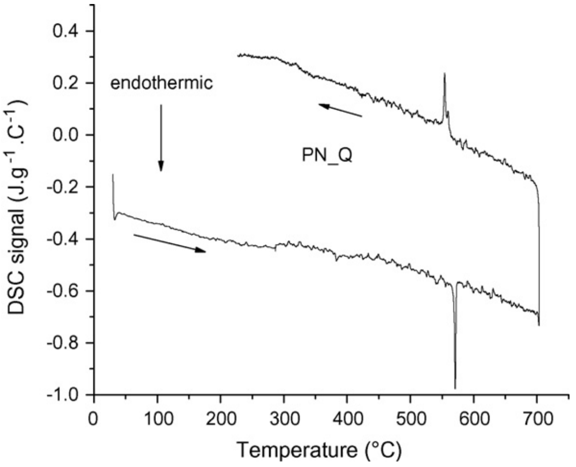

Fig. 3. DSC signal vs. temperature graphs for heating and cooling branches for PN_Q, $PbNb_2O_6$ sample that has been quenched (Q) to room temperature after sintering at 1270 °C. The observed minimum (during heating) and maximum (during cooling) are related to Curie temperature as clarified in Fig. 5 and the text.

theoretical density, the average being 79.5%. Main XRD peaks for rhombohedral symmetry in $PbNb_2O_6$ are known [9] to be at 2θ values 28.7° for the (1 1 3) line and 29.4° for the (3 0 0) line. So, 28.711° and 29.454° peaks for our slow-cooled sample in Fig. 2, prove the slow-cooled sample to be rhombohedral. This pattern is clearly different from that for the quenched sample. The difference of the two samples shows up more dramatically in DSC studies in the next section. Our observed need for quenching to get orthorhombic distortion in the room temperature sample is in agreement with most authors, Lee and Kimura [4] for example, although some earlier papers did not mention the quenching step clearly. Obtaining [1] orthorhombic phase without quenching is not understood.

In our DSC runs, typically ~25 mg sample has been taken in a miniature platinum (Pt) crucible (~180 mg) on one of the two heaters. A similar Pt crucible in empty state on the other heater served as the standard for the differential measurement. A follow-up blank run of these two empty crucibles has provided the background correction. This last run, in view of a small difference in mass of the two platinum crucibles, has also measured the specific heat of platinum, roughly reproducing the value 0.033 cal g^{-1} K^{-1} in 20–500 °C range, reported in [27]. This is encouraging, although phase transition temperatures rather than specific heat values have been of interest in the present work. Our results have been presented (in Figs. 3–5) as heat flow per unit mass per °C change of temperature (derived from the DSC signal given in μW unit) vs. temperature (°C) graphs. We prepared two sets of quenched samples under same preparation conditions. DSC output file for the first set sample (one used in Figs. 3 and 5) gives the minimum at 570.60 °C, while it is 570.57 °C in the same compound (sample) from the second preparation in a second DSC run. A phase change, which absorbs heat during heating and shows a dip, must reject heat during cooling and give a peak. This is observed in Figs. 3 and 5, confirming the correctness of the measurements. The maximum (in the cooling branch) for the first set sample (one used in Figs. 3 and 5) appears at 553.83 °C, while it is at 554.07 °C in the same sample from the second preparation in the second DSC run. Practically same or close results, for the heating and cooling branches, on repeating the DSC run with a second preparation of the sample indicate the high overall accuracy of the data. In the presentation of the DSC results in the next paragraph, we limit ourselves to the first set sample and result up to first decimal place. The maximum possible error in

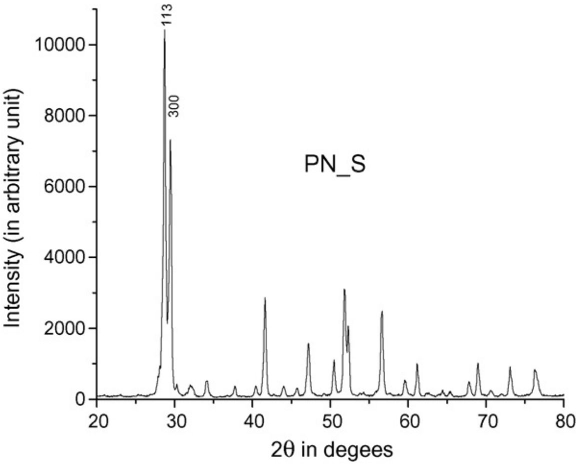

Fig. 2. XRD pattern of powdered PN_S, $PbNb_2O_6$ sample that has been slow-cooled in about 15 h to room temperature after sintering at 1270 °C. The pattern matches the published rhombohedral pattern, and the two main rhombohedral peaks have been indexed.

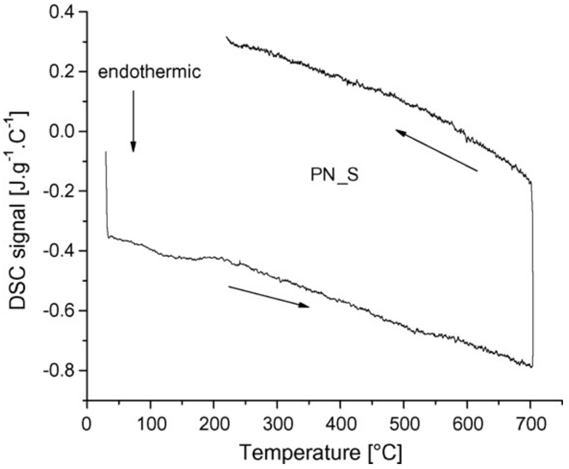

Fig. 4. DSC signal vs. temperature graphs for heating and cooling branches for PN_S, $PbNb_2O_6$ sample that has been slow-cooled (S) in about 15 h to room temperature after sintering at 1270 °C. Neither any minimum during heating nor any maximum during cooling has been observed for this slow-cooled rhombohedral sample.

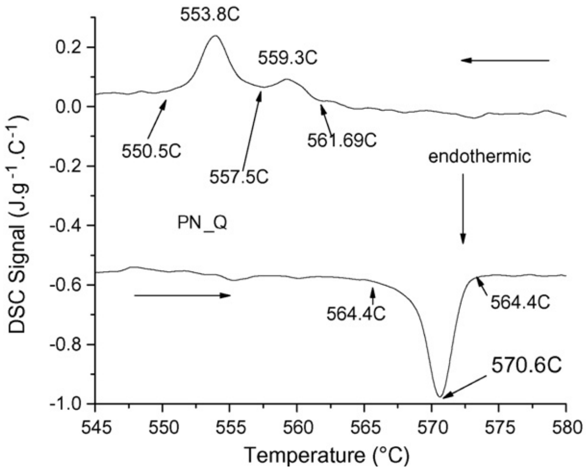

Fig. 5. A magnified view of the heating and cooling branches of our DSC signal vs. temperature graph for PN_Q, $PbNb_2O_6$ sample that has been quenched to room temperature after sintering at 1270 °C. The 570.6 °C minimum during heating correspond to piezoelectric orthorhombic to non-piezoelectric tetragonal phase transformation. The 553.8 °C maximum shows the reverse transformation during cooling. Other details are given in the text.

present DSC determination of the temperature of the minimum or maximum is less than 0.05 °C.

Most prominent feature of the heating graph for the quenched $PbNb_2O_6$ in Figs. 3 and 5 is a minimum at 570.6 °C, which is [28] the Curie temperature of the compound. The same feature has been recorded during cooling, expectedly, as a maximum, but at a slightly reduced temperature of 553.8 °C. Such a DSC dip at the Curie temperature on heating (the minimum at 127.6 °C) and the corresponding peak at a slightly lower temperature during cooling (the maximum at 125.3 °C) have been observed [20] earlier for $BaTiO_3$. This hysteresis in DSC signal in $BaTiO_3$ was observed also by us. However, to our knowledge, ours is the first record in case of $PbNb_2O_6$ compound, of the total observations across the Curie temperature of DSC minimum and maximum. Another interesting observation in the cooling graph of PN_Q is a smaller peak (maximum) at 559.3 °C, just before the main maximum at 553.8 °C. Since this feature of double maxima is not well-known, it is shown more clearly in Fig. 5 While the origin of two second maxima is not clear, it is noted that in the internal friction measurement on KDP crystal, Huang et al. [13] observed a separate peak due to domain wall movement, in addition to the peak at the Curie temperature. The two phenomena appear to be related and the domain wall movement in $BaTiO_3$ has been studied by various authors [29]. Still, no definite conclusion on this point can be drawn without further work. Most important is the fact that slow-cooled $PbNb_2O_6$ (PN_S) does not show (Fig. 4) any DSC dip or peak during identical heating and cooling steps. We have already found this PN_S sample to be of rhombohedral structure that does not support ferroelectricity and piezoelectricity. This confirms that the dip (during heating) and peak (during cooling) in DSC of the quenched $PbNb_2O_6$ are linked to orthorhombic structure and the transition at the Curie temperature.

4. Conclusion

Differential Scanning Calorimetry (DSC) measurement of specific heat is seen to be a novel but easy test of the formation of the correct orthorhombic piezoelectric phase in Lead Meta-Niobate ($PbNb_2O_6$). Working with pure orthorhombic and pure rhombohedral samples, we get enthalpy change at the Curie temperature, only for the orthorhombic $PbNb_2O_6$. The strength of the DSC signal should be related to the fraction of orthorhombic phase in case of a multi-phase sample. Present work appears to be the first reporting of DSC data on orthorhombic and rhombohedral Lead Meta-Niobate.

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