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## TEM sample preparation of lead containing ceramic materials

*(Work performed in collaboration between LJU and STU)*

With advanced TEMs the quality of the electron-transparent sample has become one of the major limiting factors for quantitative investigations on the nanometer scale [1]. A widespread choice of techniques are available for sample preparation, however Ar ion milling is still one of the most commonly used techniques, as it has been for several decades [2]. One of the reasons for such broad use is its applicability to a majority of solid materials [3], although it can introduce significant artifacts [4, 5]. The most frequently observed damage is an amorphous surface layer on the specimen [6, 7]. Additionally, structural, compositional and topographical changes can appear and influence the TEM studies [3]. The energy incorporated by the ion beam during the ion-milling process causes a huge raise of the local sample temperature. According to Kim and Carpenter [2], temperatures between 200°C and 400°C can be reached easily at the specimen surface and may cause severe changes leading to misinterpretation of the results. The heating effects are most intense just before the perforation of the specimen. By cooling the specimen using liquid nitrogen, the thermal effects during the ion-milling process can be effectively reduced [8].

Many ion-milled perovskite ceramic oxides do not exhibit undesirable damage effects. However, as shown by Barber [8], some Pb-based compounds develop surface layers during the ion-milling process. We have studied the influences of different transmission electron microscopy (TEM) specimen preparation techniques on the chemical composition of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  -  $\text{PbTiO}_3$  (PMN-PT) single crystals [9]. Two different TEM specimen preparation techniques were applied, such as (i) classical grinding and dimpling followed by standard ion-milling and (ii) tripod polishing without and with additional ion-milling, to prepare specimens of the single crystalline PMN-PT material.

(i) TEM samples were prepared using classical grinding and dimpling followed by the standard ion-milling technique as already described by Barna and co-workers [6]. Specimens were first mechanically polished (grinding and dimpling) down to a thickness of  $\sim 16 \mu\text{m}$ . Afterwards, one specimen was Ar ion milled at an accelerating voltage of 4 kV and an ion beam incidence angle of  $10^\circ$  to perforation in a *Bal-Tec RES 010* (*Balzers*) without sample cooling (sample SP1a in Table 1). Two samples

were Ar ion-milled in a *Gatan Precision Ion Polishing System* (PIPS) at accelerating voltages of 4 kV (without cooling the specimen) (sample SP1b in Table 1) and 2.5 kV while cooling the specimen with liquid nitrogen (sample SP1c in Table 1).

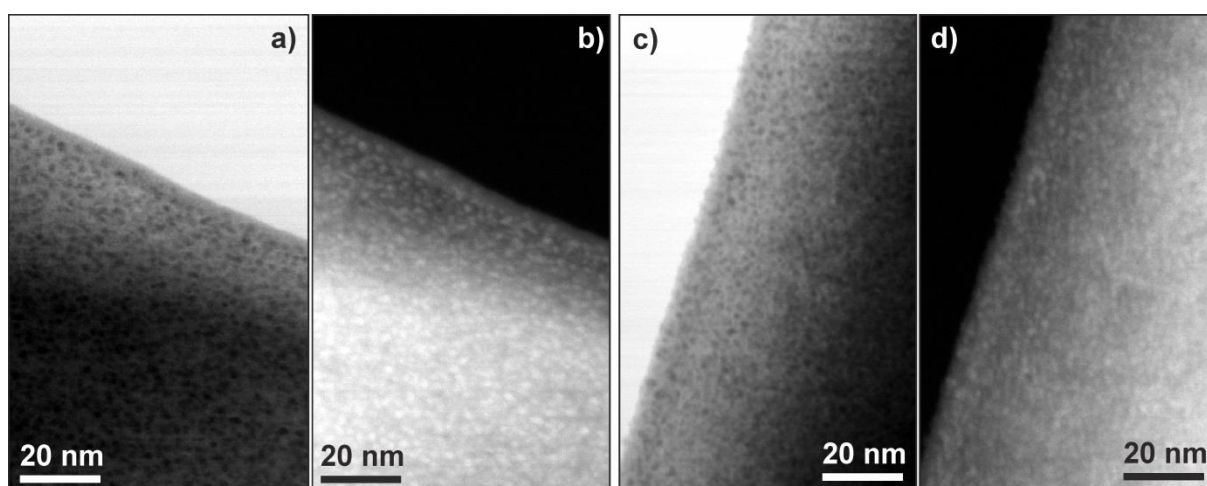
(ii) To avoid possible damage caused by ion-milling, further electron transparent lamellae were prepared by tripod polishing following the procedure proposed by Voyles et al. [10] in an automatic tripod polisher using the *Allied Multiprep System*. The PMN-PT specimens were cut into slabs of ~1.5 mm wide and 2 mm long and attached to a pyrex specimen holder using *Crystal Bond* thermoplastic wax. The specimen was first polished using a diamond-lapping film (DLF) with 15- $\mu\text{m}$  grain-size to provide a planar surface. For further polishing, DLFs with grain sizes of 6, 3, 1, 0.5, and 0.1  $\mu\text{m}$  were used. A final polishing step was performed on a polyurethane cloth using a silica solution with 50-nm sized particles (*Allied Colloidal Silica Suspension*) to remove the scratches from the polished surface. During every polishing step, the specimen surface was regularly observed under the optical microscope to ensure all scratches were removed. Prior to polishing the other side, the sample was removed from the pyrex holder by heating the polishing block on a hot plate. Then the specimen was turned upside down and glued onto the pyrex specimen holder again. The specimen was thinned down to a thickness of 200  $\mu\text{m}$  using a 15- $\mu\text{m}$  DLF. A wedge angle of  $5^\circ$  was introduced, which makes the specimen more robust to handle. The specimens were polished down further to thicknesses of 70, 50, 30, 10  $\mu\text{m}$  using 15-, 6-, 3-, 1- $\mu\text{m}$  DLFs, respectively. Subsequently, final polishing was performed with 0.5- $\mu\text{m}$  DLF and 50-nm colloidal silica to thin the sample to electron transparency (sample SP2a in Table 1).

Two wedge-shaped specimens were additionally thinned in a PIPS at 1.8 kV for 15 minutes (sample SP2b in Table 1) and in a low-energy ion-milling and polishing system (Model 1010, E.A. Fischione Instruments Inc., U.S.A.) at 0.5 kV for 10 minutes (sample SP2c in Table 1). During the ion-milling process these specimens were cooled using liquid nitrogen.

**Table 1.** Investigated TEM samples and conditions used for their preparation

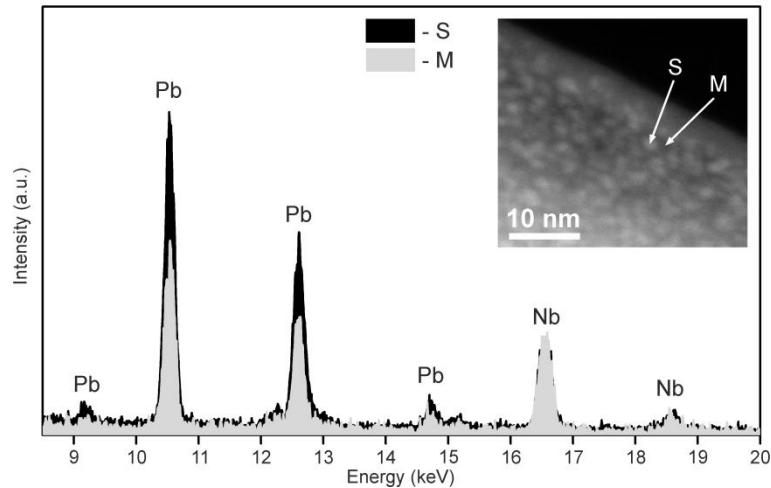
Type/name of the	Technique used for TEM sample preparation	Energy used for ion-beam thinning and polishing	L-N <sub>2</sub> cooling
SP1a	Grinding, dimpling, ion-milling	4 kV, Bal-Tec	No
SP1b	Grinding, dimpling, ion-milling	4 kV, PIPS	No
SP1c	Grinding, dimpling, ion-milling	2.5 kV, PIPS	Yes
SP2a	Tripod polishing	No thinning	No
SP2b	Tripod polishing, ion-milling	1.8 kV, PIPS	Yes
SP2c	Tripod polishing, ion-milling	0.5 kV, Fischione	Yes

In Figure 1, BF- and ADF-STEM images of PMN-PT samples prepared by classical grinding and dimpling followed by ion milling are shown. The samples were ion-milled using Bal-Tec (Fig. 1a, b) (sample SP1a in Table 1) and the PIPS (Fig. 1c, d) (sample SP1b in Table 1) at 4 kV. During ion-milling the samples were not cooled. ``Spotted`` looking structure is clearly visible in both samples.



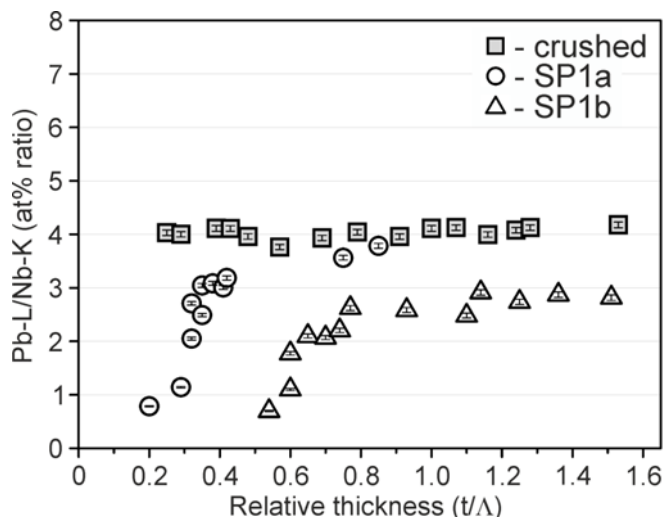
**Figure1:** (a, c) BF- and (b, d) ADF-STEM images of samples prepared by grinding, dimpling and ion-milling at 4 kV without L-N<sub>2</sub> cooling using Bal-Tec (a, b) (sample SP1a in Table 1) and the PIPS (c, d) (sample SP1b in Table 1).

EDX measurements showed that the brighter spots (in ADF images) are enriched in lead (Pb) compared to the surrounding areas (Fig. 2).

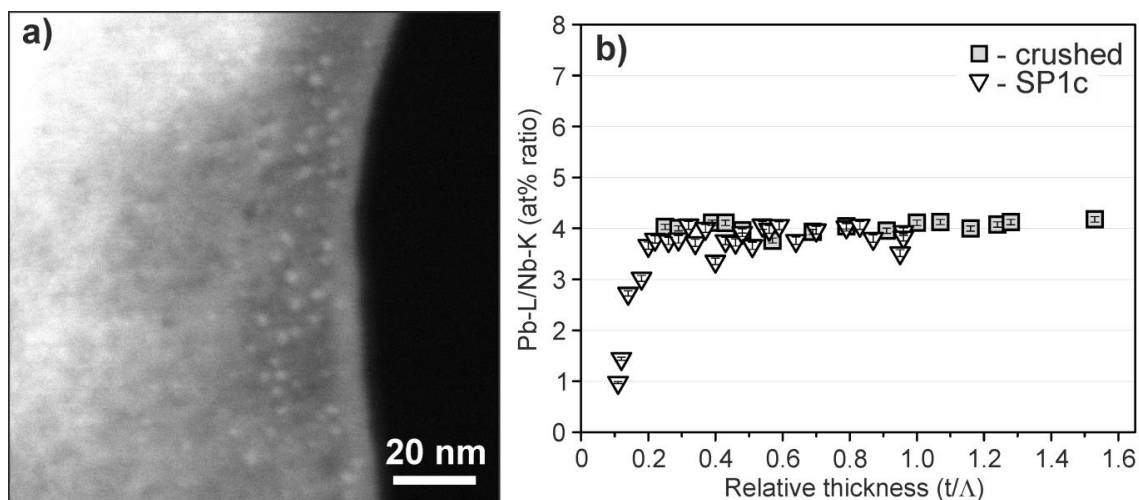


**Figure 2:** EDX spectra acquired from a bright spot (S) and from the matrix (M) from a sample ion-milled in Bal-Tec at 4 kV without using L-N<sub>2</sub> cooling (sample SP1a in Table 1).

EDX line-scan measurements were performed in both samples shown in Fig. 1 from the edge of the sample towards thicker regions. The Pb-L/Nb-K at% ratio was calculated at every measured position and plotted against the relative specimen thickness that was determined from EELS. For comparison results measured from crushed sample are plotted on the same graph (Fig. 3). As visible from the graph, in the crushed sample the composition stays unchanged, while in both ion-milled samples the chemical composition is dramatically changed due to loss of lead from PMN-PT, which becomes more dominant closer to the specimen edge. An additional sample, ion-milled by using PIPS at lower ion-beam energy (2.5 kV) while cooling the sample with L-N<sub>2</sub>, shows highly reduced irregularities (Fig. 4).

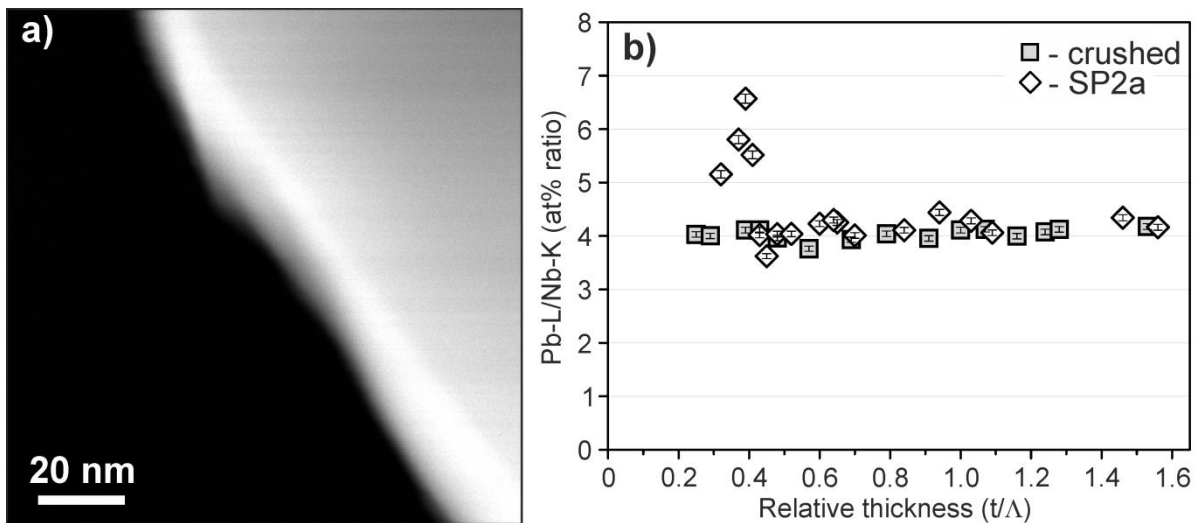


**Figure 3:** Pb-L/Nb-K at% ratio measured from the samples prepared by grinding, dimpling and ion milling using the Bal-Tec (sample SP1a in Table 1) and the PIPS (sample SP1b in Table 1) at 4kV without cooling. For comparison the data measured from the crushed sample are plotted.

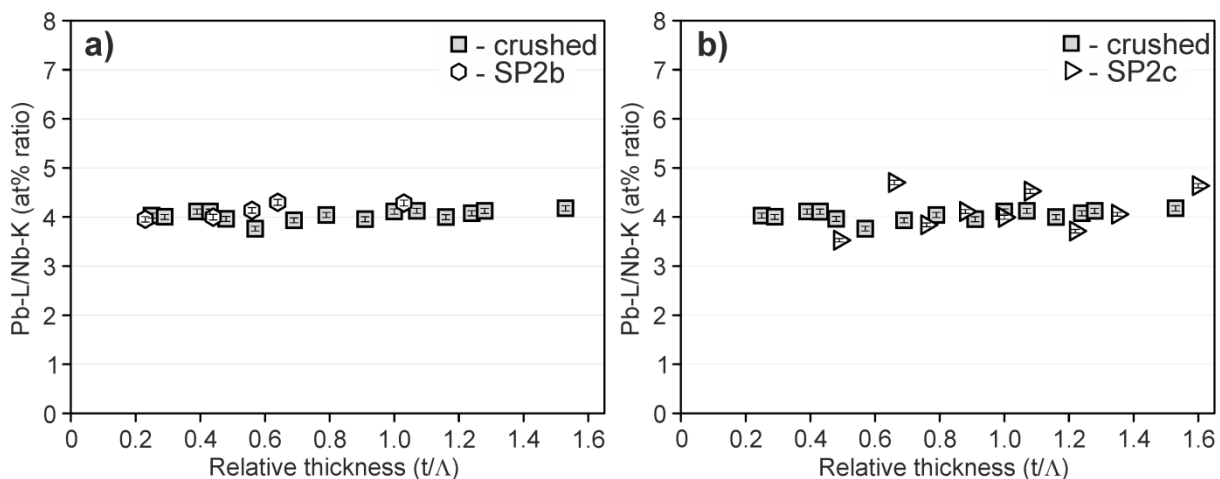


**Figure 4:** (a) ADF-STEM image of sample prepared by grinding, dimpling and ion-milling at 2.5 kV in PIPS while cooling the sample (SP1c in Table 1). (b) Pb-L/Nb-K at% ratio determined from the EDX line-scan measurements compared to the data acquired from crushed sample (sample SP1a in Table 1).

Mechanically thinned and tripod-prepared PMN-PT samples show a completely homogeneous structure. However, based on EDX line-scan measurements, there is an increase in Pb close to the specimen edge (Fig. 5). Finally, tripod prepared samples that were ion-milled using the PIPS at 1.8 kV while cooling the sample with L-N<sub>2</sub> (sample SP2b in Table 1) and using the Fischione ion milling system (Model 1010) at 0.5 kV (sample SP2c in Table 1) do not show considerable changes of chemical composition for different thicknesses (Fig. 6).



**Figure 5:** (a) ADF-STEM image of a sample prepared by tripod polishing (sample SP2a in Table 1). (b) Pb-L/Nb-K at% ratio measured from a tripod prepared sample (sample SP2a in Table 1) compared with a crushed sample (sample SP1 in Table 1).



**Figure 6:** Pb-L/Nb-K at% ratio from samples prepared by tripod polishing followed by ion milling at low energies using (a) the PIPS (sample SP2b in Table 1) and (b) the Fischione (sample SP2c in Table 1), compared with the values obtained from crushed sample (sample SP1 in Table 1).

We have shown that for lead-containing ceramic materials (such as PMN-PT) a combination of tripod polishing and short ion-milling at low accelerating voltages while cooling the sample with L-N<sub>2</sub> is the most suitable preparation technique.

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