

# Aqueous tape casting of the $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.3\text{PbTiO}_3$ ceramic films: production optimization and properties

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Received: date / Accepted: date

**Abstract** The  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.3\text{PbTiO}_3$  ceramic films were prepared using the water-based tape casting method. Two main components of the slurry are water and solids. The concentrations of other chemicals, the surfactant and binder, are at the level of 1 wt. %. Both binder and surfactant are eco-friendly polymers. Additional chemicals are not required. The optimal concentration of surfactant determined through viscosity measurements. The density of the ceramics was studied as a function of the concentration of water and binder. The density is nearly independent of amount of water despite a wide range of values of concentration. This independence is a powerful tool to cast using different techniques. The density substantially depends only on binder concentration. The polymers removal protocol of the cast films was optimized using thermogravimetric analysis. As a result, the translucent ceramic films with a relative density of 98 % and thickness of 70  $\mu\text{m}$  were prepared. The permittivity, remnant polarization and pyrocurrent measurements, along with the scanning electron microscopy, prove the high density of the ceramics.

**Keywords** Tape casting · PMN-PT · dielectric properties · ferroelectric properties

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## 1 Introduction

Tape casting is one of the most popular wet-shaping manufacturing technologies of ceramic films in large areas. The thickness of the layer can be as small as 175 [1], 75 [2], and even 10  $\mu\text{m}$  [3]. After drying, the films can be laminated, debonded and sintered [4, 5, 6, 7]. Non-aqueous tape casting requires different organics like alcohols, ketones, oils as a solvent. Despite short evaporation time [8, 9, 10, 11], these liquids has environmental and safety issues. The aqueous tape casting is the eco-friendly alternative [12]. The progress of the aqueous tape casting of the recent decades reveals several branches of the tape casting process modification. The polymer-derived ceramics production is based on the pyrolysis of the polymers into amorphous ceramics with further sintering. This approach is suitable for non-oxide ceramics like SiC, AlN, oxide ceramics and mixed non-oxide ceramics, like SiCNO [13]. The ceramics with the artificial porosity are used as the membranes. Several approaches like freeze casting, phase-inversion, partial sintering and sacrificial pore formers [14] develops the porosity.

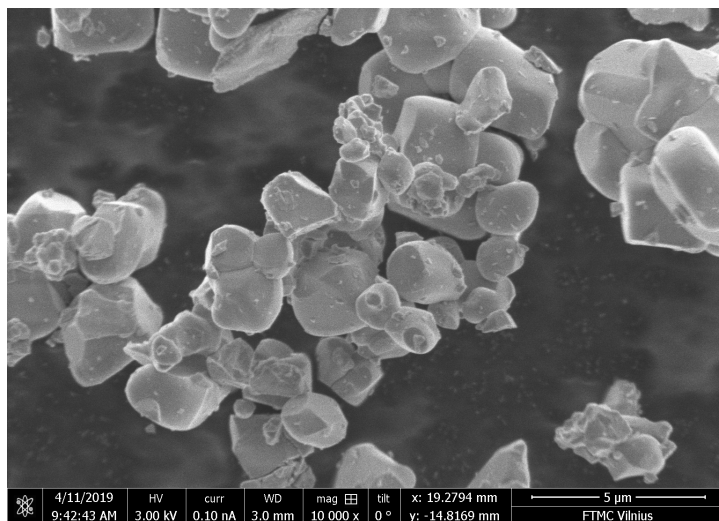
Tape casting is one of the main ferroelectric film manufacturing technologies [15]. Piezoelectric, pyroelectric and other properties of the ferroelectrics became the driving force of the interest [16]. Wide range of the applications of the ferroelectrics includes multilayered capacitors and energy storage [17, 18], biomaterials [19], piezoelectric actuators [20] or sensors [21].

This research is motivated by several reasons. Despite the significant progress, the works devoted to water-based tape casting of the ferroelectrics are still rare [22, 23, 24]. The method requires a list of different chemicals and reagents, like plasticizers, defoamers, binders and surfactants. Very few researchers successfully applied the technique with the reduced number of organics (only binder and surfactant) [25, 26]. This reduction should also benefit the densities of the ceramics, which is a critical parameter for ferroelectrics [27, 28, 29].

In the present work,  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  (PMN-0.3PT) films were produced by eco-friendly aqueous tape casting method using only two organic chemicals. Although PMN-PT solid solutions are not lead-free, there are several advantages of PMN-PT usage in the particular work. It is well-investigated, does not require a high calcination temperature, and highly sensitive to defects. Due to this, the direct comparison of the measured properties of the films with data presented in literature allows developing the quality control of the produced samples. The main parameters of the preparation were optimized. The dielectric and ferroelectric properties of the prepared ceramic films were studied. Further on, the developed procedure is prospective for application to lead-free ceramics.

## 2 Materials and methods

Commercially available by American Elements PMN-0.3PT powder was used for the preparation of the films. Scanning electron microscopy of as received



**Fig. 1** Scanning electron microscopy of the  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  powder

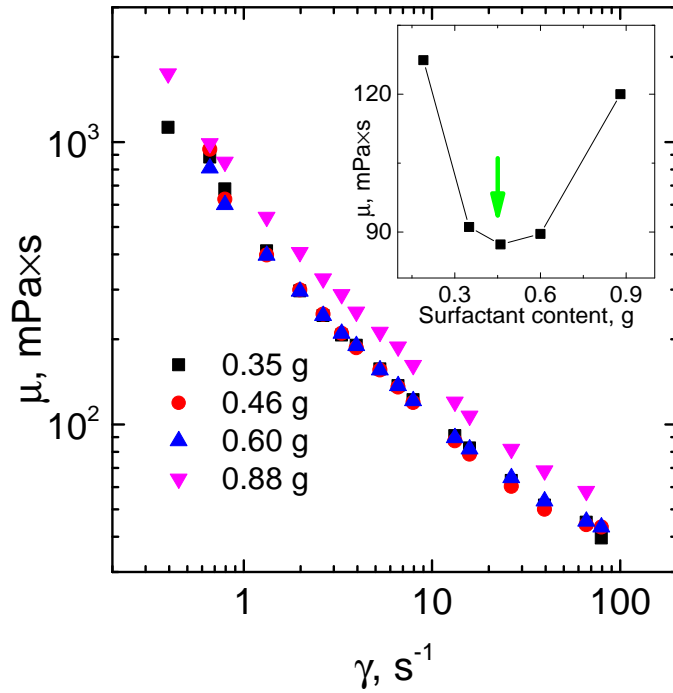
PMN-0.3PT shows that the average grain size is lower than  $5 \mu\text{m}$  (see Figure 1). A solution of an ammonium salt of an acrylic polymer in water, Displex AA4040 (BASF) was used as a surfactant. Its density is  $1.16 \text{ g/cm}^3$  at  $20^\circ\text{C}$ , solid content  $\approx 45\%$ . Luvitec K 90 powder by BASF, a water-soluble polyvinylpyrrolidone (PVP) was used as a binder. The approximate molecular weight is 1400 kDa. Since the material is hygroscopic, it was kept in a vacuum before use.

THINKY ARE-250 mixing machine was used to make a homogeneous suspension. It is a non-contact mixer that has mixing and defoaming functions. A rotational viscometer Viscotech Myr VR 3000 with an adapter for small sample volumes was used for the viscosity measurements. Dielectric properties were measured using an LCR HP4284A meter. For the measurements above the room temperature, a homemade furnace was used. The silver paste was applied as electrodes. Densities of the ceramics were measured through Archimedes method using deionized water. AixacCT TF2000 analyzer equipped with 4 kV voltage supply was used for ferroelectric hysteresis and pyrocurrent coefficient measurements.

### 3 Results and discussion

#### 3.1 Slurry preparation

Several suspensions were tested for the determination of the optimal concentration of surfactant. They consisted of 33.5 g of PMN-0.3PT, 5 g of deionized water and variable amounts of the surfactant (0.19 – 0.88 g). The volume content of the solids is 45.5 %. The dependencies of the viscosity ( $\mu$ ) of the slurries



**Fig. 2** Viscosity of the slurries with different surfactant content as a function of the shear rate. Inset: the comparison of the viscosities of the slurries at the shear rate of  $\gamma = 13.2 \text{ s}^{-1}$ .

on the shear rate ( $\gamma$ ) at a constant temperature of  $22 \text{ }^\circ\text{C}$  are presented in Figure 2. The viscosity decreases as the shear rate rises that proves the desired shear-thinning behaviour.

The dependence of the  $\mu$  versus the surfactant loading is presented in Figure 2 (inset). The slurry with the lowest concentration (0.19 g) was not stable to be measured in the whole range of  $\gamma$ . However, it was possible to measure at the selected rate of  $13.2 \text{ s}^{-1}$  for the comparison. The dependence demonstrates a minimum of the viscosity. At low surfactant concentration, the polymer molecules absorb onto the surface of the solids. That decreases the concentration of agglomerated powder and, as a result, reduces the viscosity of the suspension. When all agglomerates are separated, the viscosity is the smallest. At the same time, the surface of the solid particles absorbs the maximum possible amount of the surfactant. After the system reaches the optimum, the polymer excess into the suspension. Due to multiple cross-linking effects, the viscosity increases [30,31]. This behaviour is typical for the tape casting slurries, in particular  $\text{Al}_2\text{O}_3$  [32],  $\text{AlN}$  [11,33],  $\text{BaTiO}_3$  [34], *etc.* loaded suspensions. According to Figure 2 (inset), the minimal viscosity of the slurry achieved with the surfactant content of 0.46 g, or 0.0137 g per 1 gram of solid content (highlighted with arrow).

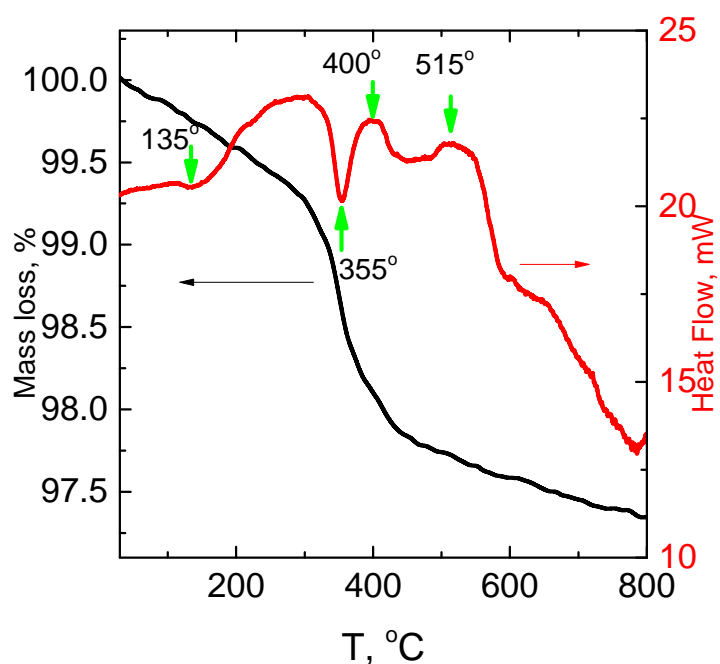


Fig. 3 Thermogravimetric analysis and differential scanning calorimetry of the green tape.

The solid PVP binder was dissolved directly in the slurry, and after mixing and defoaming, the obtained suspensions were cast using the homemade doctor blade technique. The doctor blade height was 0.25 mm. Two series of samples were prepared. The first series made with variable binder loading and a fixed water/solids ratio of 19 wt. %. The second made with a fixed binder/solids ratio of 1.37 wt. % and variable water content.

### 3.2 Thermal treatment

The thermal treatment of the prepared green tapes consists of two stages: polymer removal and calcination. The polymer removal stage is critical since multiple imperfections and defects like cracks or bubbles appear if the gas evacuation rate is lower than the polymer decomposition rate.

Figure 3 presents the thermal analysis of the green tape. Several stages of polymer removal were reported [35,36]. At lower temperatures, the polymers with a low molecular mass start to decompose. The peaks in the DSC curve at 135, 400, and 515 °C corresponds to the Dispex decomposition [37]. According to [37], the mass loss due to Dispex degradation observed up to 599 °C. The decomposition of the binder is associated with a noticeable thermal effect at 355 °C with a corresponding mass loss of 1.5 %. The PVP fully decomposes at 407-450 °C [38,39]. As a result, the polymer removal stage is set as a linear

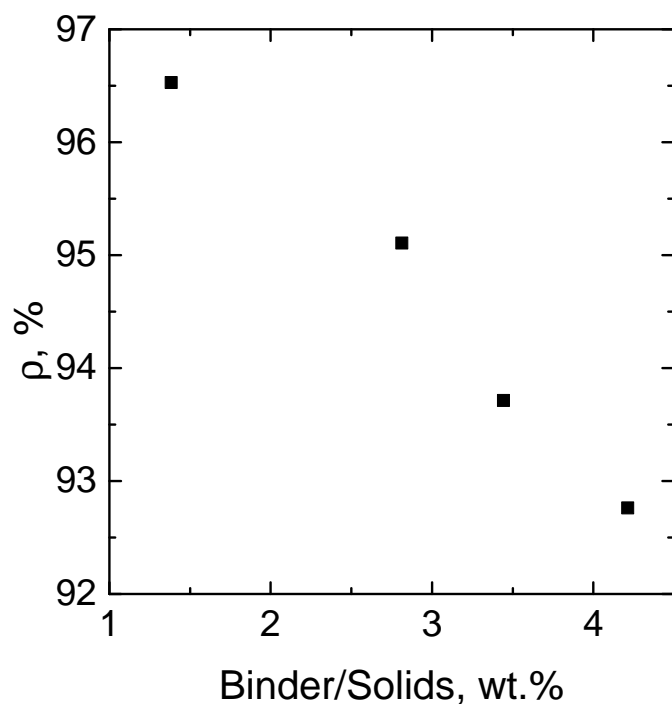


Fig. 4 The dependence of the relative density on the binder/PMN-0.3PT ratio.

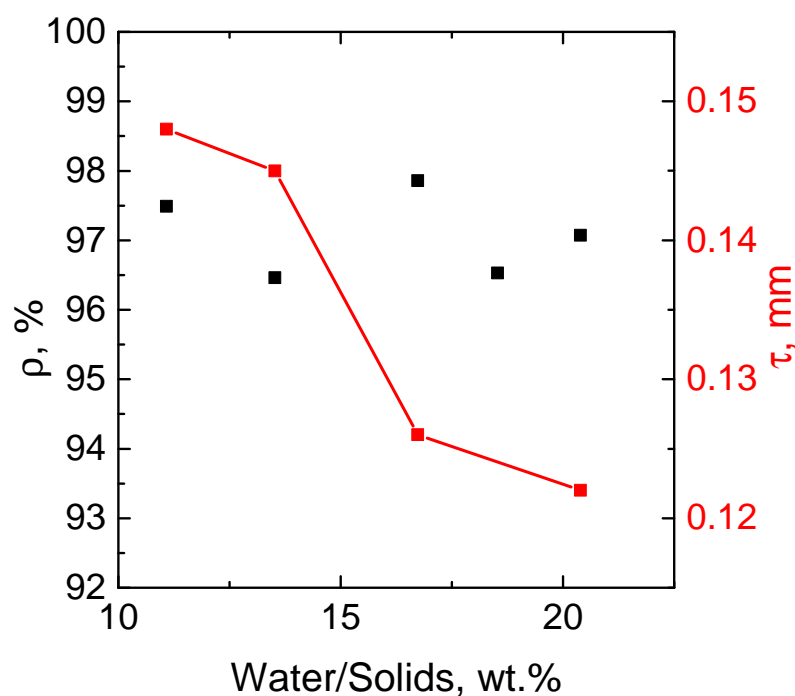
increase of the temperature up to  $600\text{ }^{\circ}\text{C}$  with a rate of  $0.5\text{ }^{\circ}\text{C}/\text{min}$ , followed by two hours of isothermal treatment.

After the polymer removal stage, the temperature increased up to  $1200\text{ }^{\circ}\text{C}$  with the rate of  $2\text{ }^{\circ}\text{C}/\text{min}$ . The solid content was isothermally calcined at  $1200\text{ }^{\circ}\text{C}$  for 5 hours on the platinum substrate in the double-walled closed crucible. The mixture of PbO and  $\text{PbZrO}_3$  was used to develop the Pb-rich atmosphere.

### 3.3 Density of films

The density of both calcined ceramics and green tapes depends on many factors. The major one is the concentration of components of the slurry. The increase of the content of the binder improves the mechanical properties of the green tapes but reduces their density [40,32,12].

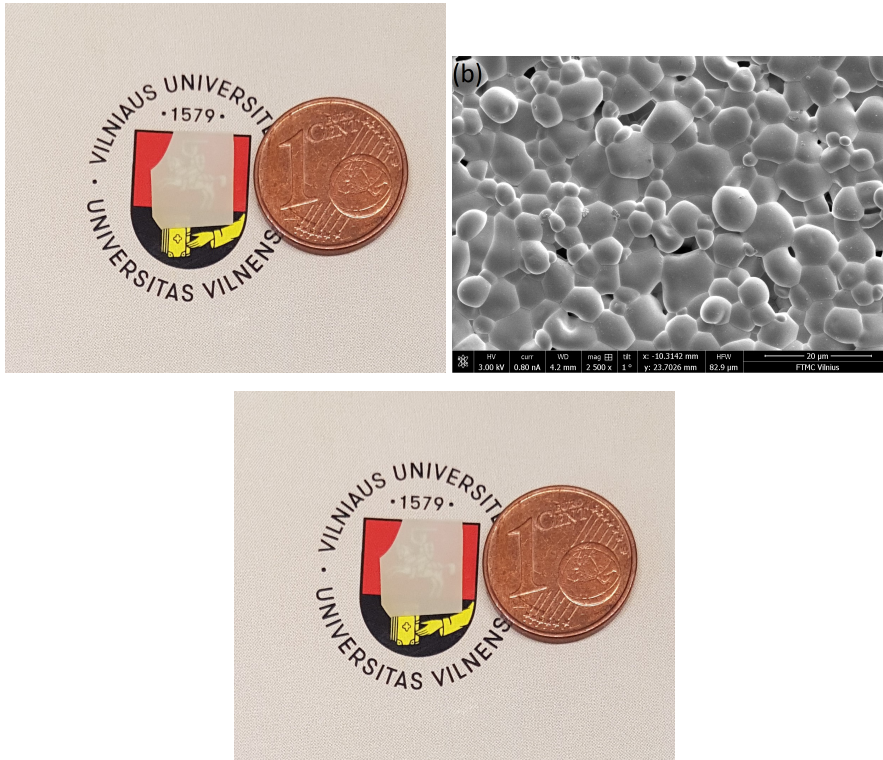
The dependence of the relative density on the binder/solids ratio is studied. The water/solids ratio kept on the level of 19 wt. %. The results are presented in figure 4. The density of the calcined films depends on the binder amount and reaches up to 97 % for the sample with minimal binder loading. **Scanning electron microscopy demonstrates the impact of density on the morphology of samples (Figure 6, a,b).** Further increase of the binder



**Fig. 5** The dependence of the relative density and thickness of the calcined films on the water/PMN-0.3PT ratio.

concentration leads to a very rapid rise of the viscosity of the slurry, which makes the slurry not suitable for casting.

The dependence of the relative density on the water/solids ratio is also studied. The binder/solids ratio kept on the level of 1.37 wt. %. The results are presented in figure 5. The water loading drastically changes the concentration of the solids in the slurry. However, the final density of the ceramic films does not depend on the water content. The final densities of the films are in the range of 96-98 %. Independence is attributed to complete and relatively slow water evaporation. The capillary shrinkage effects start acting upon the solvent removal. As a result of this action, the compaction of solids appears similar after the complete removal of water. At the same time, the films from more diluted slurries should be thinner (see figure 5). Although the collected data is not enough to characterise the reduction of thickness in details, the general tendency is clear. Such independence of the density in mentioned limits may be useful to variate the viscosity of the slurry and the thickness of films for the different casting techniques.



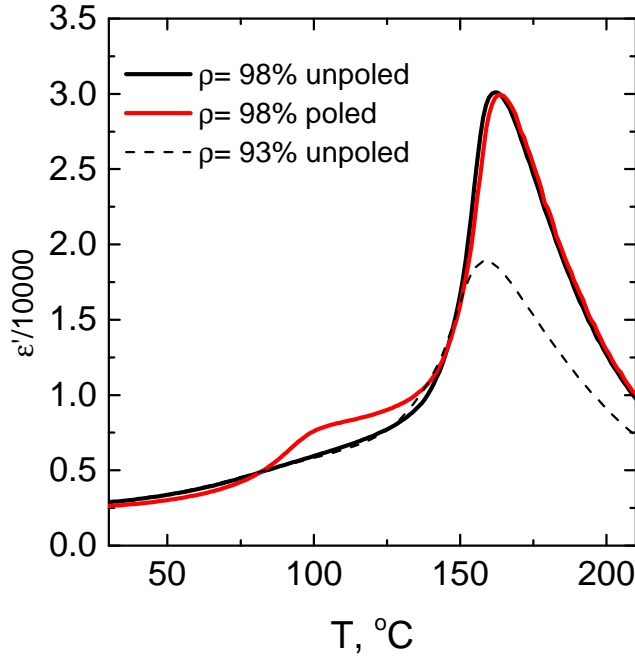
**Fig. 6** Scanning electron microscopy of the calcined ceramics with the density of 98 % (a) and 93 % (b). Photo of the calcined ceramics.

### 3.4 Dielectric and ferroelectric properties

The sample with the highest density of 98 wt. % was selected for further study. The dielectric permittivity of the poled and unpoled sample measured as a function of temperature (Figure 7). The sample with  $\rho = 93$  wt. % was measured for comparison. The permittivity of poled and unpoled sample goes through the maximums at 164 °C. This anomaly is related to the ferroelectric/paraelectric phase transition. The corresponding value of the dielectric permittivity is  $\epsilon = 31000$  and 19000 for 98 % and 93 samples, respectively. The permittivity of the synthesized films is high in comparison with uni-axially pressed and sintered samples: 32000 [41], 24000 [42], spark plasma sintering 15500 [43] and single crystal's 35000-60000, depending on crystallographic direction [44]. The poled sample demonstrates the additional anomaly close to 100 °C. This anomaly is related to another phase transition, from the Tetragonal to Rhombohedral phase [45].

The P-E hysteresis loop and the pyrocurrent coefficient of the calcined films are studied (see Figure 8). The remnant polarization is  $P_r = 28.2 \mu\text{C}/\text{cm}^2$  at room temperature. That is close to the  $P_r$  of the single crystal of 22.8-



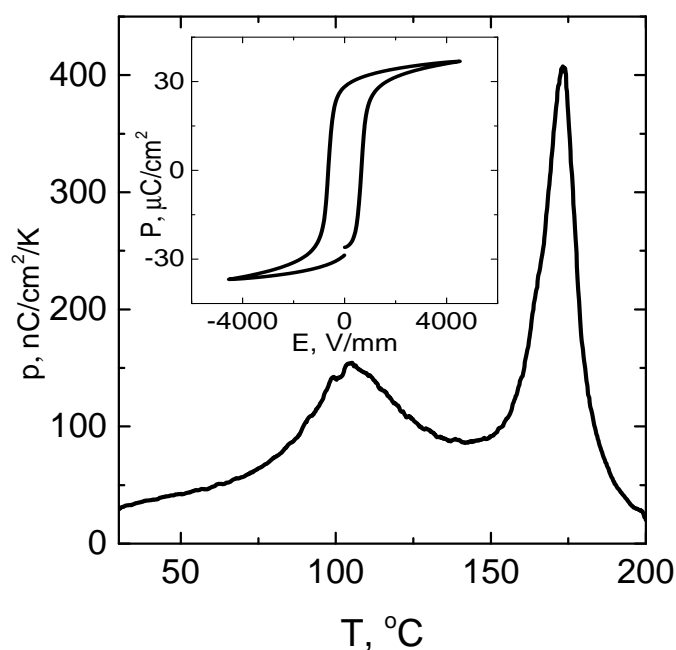


**Fig. 7** The dielectric permittivity of the calcined ceramic films. The measurement frequency  $\nu = 1.21$  kHz.

$33.3 \mu\text{C}/\text{cm}^2$ , depending on the crystallographic direction [46]. The pyroelectric coefficient at room temperature is  $\approx 25 \text{ nC}/\text{cm}^2/\text{K}$ , and it linearly increases with temperature up to  $75 \text{ }^\circ\text{C}$ . The increase followed by a peak of  $150 \text{ nC}/\text{cm}^2/\text{K}$  at  $100 \text{ }^\circ\text{C}$ , which is related to the FE-FE phase transition (Tetragonal-Rhombohedral). A second huge peak of  $410 \text{ nC}/\text{cm}^2/\text{K}$  observed at the temperature of  $175 \text{ }^\circ\text{C}$ . The peak is related to the transition to the paraelectric Cubic phase. The difference of the transition's temperatures with data presented in literature [47] attributed to the possible defects, as both transition temperatures are higher than in [47], which would not be possible according to the PMN-PT phase diagram.

#### 4 Conclusions

We report on the water-based ceramic films preparation method. The main preparation parameters (surfactant, binder, and water amounts) are optimized. Two main components of the slurry are water and solids. The concentration of other chemicals is comparatively low: the binder content is lower than 5 wt.%, and the optimal concentration of the surfactant is 1.37 wt.%. Both used chemicals are eco-friendly. The surfactant Dispex is non hazardous, according to BASF. The binder polyvinylpyrrolidone is used in the food production in-



**Fig. 8** The pyroelectric coefficient of the ceramic film as the function of temperature. Inset: the ferroelectric hysteresis at room temperature

dustry (E1201). No additional chemicals, like plasticizers or defoamers, are used.

As a result, highly dense (up to 98 %) translucent ceramic films with thickness down to  $70 \mu\text{m}$  (see Figure 6) are prepared. The dielectric permittivity, polarization and pyroelectric coefficient of the ceramic films are investigated. Above room temperature, the sample undergoes two phase transitions at 100 and  $175 \text{ }^\circ\text{C}$ . The dielectric permittivity and polarisation are high in comparison to the ceramics, synthesized using other methods (spark plasma sintering, uniaxial pressing, *etc.*). That proves the high density of the sample.

**Acknowledgements** This work is supported by the Research Council of Lithuania (Project No. S-LLT-20-4). PK is supported by H2020-MSCA-IF-2018 project 836816 TURANDOT.

This is a post-peer-review, pre-copyedit version of an article published in Journal of Electroceramics. The final authenticated version is available online at: <http://dx.doi.org/10.1007/s10832-021-00240-z>.

## Data availability

Data sharing not applicable to this article as all raw data were generated by the authors

## Conflict of interest

The authors declare that they have no conflict of interest.

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