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Seeding effects on crystallization and microstructure of sol-gel derived PZT fibers

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Dense and fine micro-structured lead zirconate titanate (PZT) fibers were successfully fabricated by sol-gel process from lead acetate dehydrate, zirconium normal butoxide, and titanium isopropoxide. An addition of perovskite seed particles (2 wt%) can lower the formation temperature of the perovskite phase and a single-phase perovskite PZT fiber can be obtained by heat-treating the precursor fiber at 500°C. Crystallization of perovskite phase was improved with the seed content. The diffraction peaks of (200) and (002) in the PZT fiber with 6 wt% seed was better split than in the PZT fiber without seed, which indicates that the tetragonality of PZT fiber was increased by adding seed particles. Seed particles also affected microstructure development of the PZT fibers. © *2000 Kluwer Academic Publishers*

1. Introduction

Lead zirconate titanate, PZT, and long fibers are attractive for actuator and sensor applications in composite materials because they provide increased anisotropy and specific strength over monolithic PZT ceramics as well as excellent flexibility. Many researchers have tried to fabricate the PZT fibers by extrusion, [1, 2] impregnation, [3] and sol-gel process [4–7]. Although extrusion can provide meter length fibers with various cross-sectional geometries, it has disadvantages: diameters of the fibers are limited to approximately 100 μm and it is hard to yield fine grain and high density, and produce fibers with cross-sectional dimensions below critical flaw sizes.

The sol-gel process is the most promising one, as it can meet the demands mentioned above, i.e., dense, homogeneous micro-structured and mechanically strong PZT fibers. Several research works have been made to develop PZT fibers by the sol-gel process. Yoshikawa *et al*. [5] fabricated fine-scale PZT fibers using a spinning methodology and applied the method to polarize fibers in a continuous manner and investigated dielectric and mechanical properties of the fibers. Kitaoka *et al*. [7] developed single-phase perovskite lead lanthanum zirconate titanate, PLZT, fibers 5–200 μm in diameter and 20 cm in length to apply the fibers to optical modulating devices.

Since an addition of perovskite seed particles causes an increase in the number of nucleation sites for the pyrochlore-to-perovskite phase transformation, using seeds would reduce the temperature at which the perovskite phase appears. In this regard, the effect of perovskite seeds has been extensively studied in the fields of sol-gel derived ferroelectric thin film applications [8–10]. However, there have been no attempts to fabricate PZT precursor fiber with perovskite seeds. In this study, perovskite PZT seed particles were added in amorphous gel fibers to prepare dense and fine-grained PZT fibers at low temperature. The crystallization behavior of the PZT precursor fibers was investigated using X-ray diffraction and Deferential scanning calorimetry (DSC) analysis. Seeds effect on microstructure development are also discussed.

2. Experimental procedure

Two different types of PZT fibers were prepared. These were PZT fibers with and without seed particles. The starting materials used to prepare the precursor fiber were lead (II) acetate dehydrate, $Pb(CH_3COO)_2$ (High Purity Chemical Co., Japan), titanium iso-propoxide (Nakarai Chemical Co., Japan) and zirconium n-butoxide (High Purity Chemical Co., Japan). The atomic ratio of the starting solution was $Pb : Zr : Ti = 1 : 0.52 : 0.48$. No excess lead was introduced in the 52/48 PZT composition. The sol-gel process for precursor fibers in this study is illustrated in Fig. 1. Lead solution was prepared by dissolving lead acetate dehydrate in 2-methoxyethanol. Titanium isopropoxide and zirconium n-butoxide were mixed in isopropyl alcohol. The solution of Pb, and the solution of Ti and Zr were mixed and refluxed at 60°C. In the case of fibers with seed particles, 2, 4, and 6 wt% of PZT seed particles (Sakai Chemical Co., Sakai, Japan) were added to the mixed solution with Pb, Ti, and Zr. The solution was hydrolyzed by adding acetic acid, CH_3COOH, for catalyst and water, and then, condensed by refluxing at 60°C for 24 h. In order to control the viscosity of the precursor solution, isopropyl alcohol, which was involved in the solution, was removed from the solution through evaporation. Viscosity of some of the solutions increased gradually.

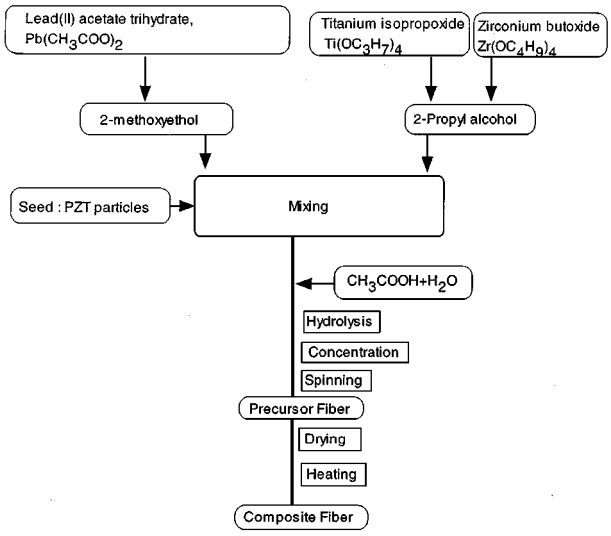

Figure 1 Flowchart of sol-gel process for the precursor PZT fibers.

The solution was then spun to the precursor fiber by inserting the end of a wire into the viscous solution and pulling it upward quickly by hand under 45% relative humidity. The resulting precursor fibers were aged and dried at room temperature for 24 h with 30–60% relative humidity. Then, the gel fibers were put in a platinum crucible and heat-treated with $PbZrO_3$ powder in air at various temperatures. The heat treatment was carried out at temperatures ranging from 500 to 1000°C with a heating rate of 10°C min^{-1}. The holding time at the desired temperature was fixed at 2 h. After a designed heat treatment the fibers were cooled to room temperature in the furnace.

The crystalline phase of the PZT fiber was identified by X-ray powder diffractometry (RU-200B, Rigaku Co. Ltd., Japan). Deferential scanning calorimetry, (DSC, DSC8270, Sinkuu-rikou, Japan) was carried out on PZT precursor fibers to investigate the crystallization behavior. The microstructures of the PZT fibers were observed by scanning electron microscope (SEM, JSM-6320FK, JEOL, Japan).

3. Results and discussions

PZT precursor fibers 15 to 150 μm in diameter and below 20 cm in length were successfully fabricated. The surface of the precursor fiber was very smooth. Fig. 2 shows the X-ray diffraction patterns of seeded (2 wt%) PZT fibers heat-treated at 300°C, 500°C, 700°C, 800°C and 1000°C. All of the precursor fibers were amorphous prior to heat treatment. At 300°C, three small diffraction peaks were detected at $2\theta = 32$, 36, and 52°. An amplified trace, Fig. 2 inset, showed a small and broad peak at $2\theta = 29°$ that corresponds to a poorly crystallized pyrochlore phase, and also a sharp peak at around $2\theta = 31°$, along with a diffraction peak at $2\theta = 32°$. The sharp diffraction peak at $2\theta = 31°$ can be assigned to the perovskite (110) diffraction peak. Thus, it is considered that the perovskite phase starts to appear at 300°C. Three diffraction peaks at $2\theta = 32$, 36, and 52° appear to be due to metallic lead. The appearance of metallic lead is in accordance with the result by Kitaoka *et al.* [7]. They observed the precipitation of metallic lead, and discussed that it resulted from the reduction of lead ions by carbonaceous species that are produced by acetate decomposition, because they introduced 10% of excess lead to the precursor solution. Although why metallic lead appeared in this study is not clear, this phenomenon is often observed in sol-gel derived PZT fibers or films.[4, 11, 12].

The seeded precursor PZT fiber completely transformed to a single-phase perovskite when it was heat-treated at temperature as low as 500°C. As is evident in Fig. 2, at 500°C, only the perovskite phase was detected, and there were no unwanted peaks, which would

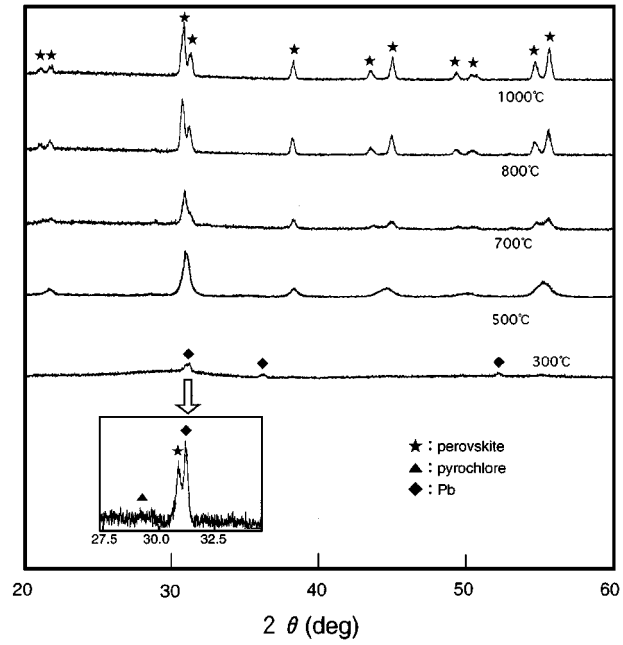

Figure 2 X-ray diffraction patterns of seeded (2 wt%) PZT fibers heat-treated at 300°C, 500°C, 700°C, 800°C and 1000°C, respectively. The inset is an amplified pattern of the fiber heat-treated at 300°C.

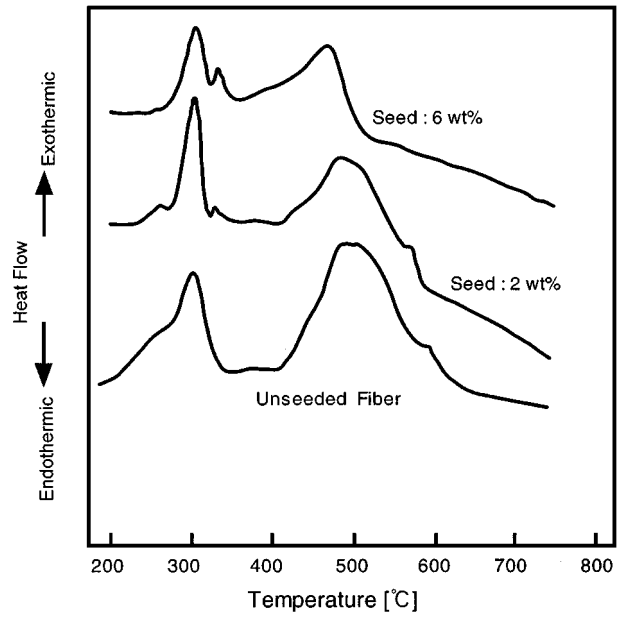

Figure 3 DSC curves of the PZT precursor fibers with 2 and 6 wt% of seed particle; the measurements were conducted in air at a heating rate of 10°C min^{-1}.

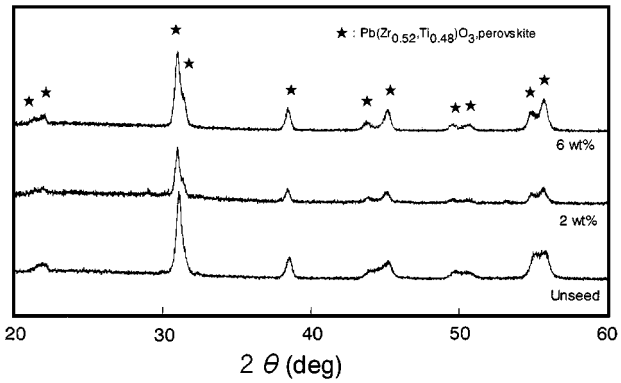

Figure 4 X-ray diffraction patterns of the unseeded and seeded (2 and 6 wt%) PZT fibers heat-treated at 700°C for 2 h.

be attributed to pyrochlore or other impurity phases. According to other reports, the pyrochlore-to-perovskite transformation of sol-gel derived PZT fiber usually starts between 500 and 550°C, and single-phase perovskite PZT fiber can be obtained at above 700°C [7, 9]. By adding seed particles in the precursor solution, it was found that the crystallization temperature from pyrochlore to perovskite was significantly lowered. In addition, crystalline perfection and crystallite size increased as the heat-treatment temperature was raised up to 1000°C, although a single-phase perovskite can be obtained at 500°C. In particular, the extent of crystallization largely changed between 500 and 700°C; the splitting of diffraction peaks at around $2\theta = \sim 32^\circ$, $\sim 45^\circ$ and $\sim 56^\circ$ was confirmed.

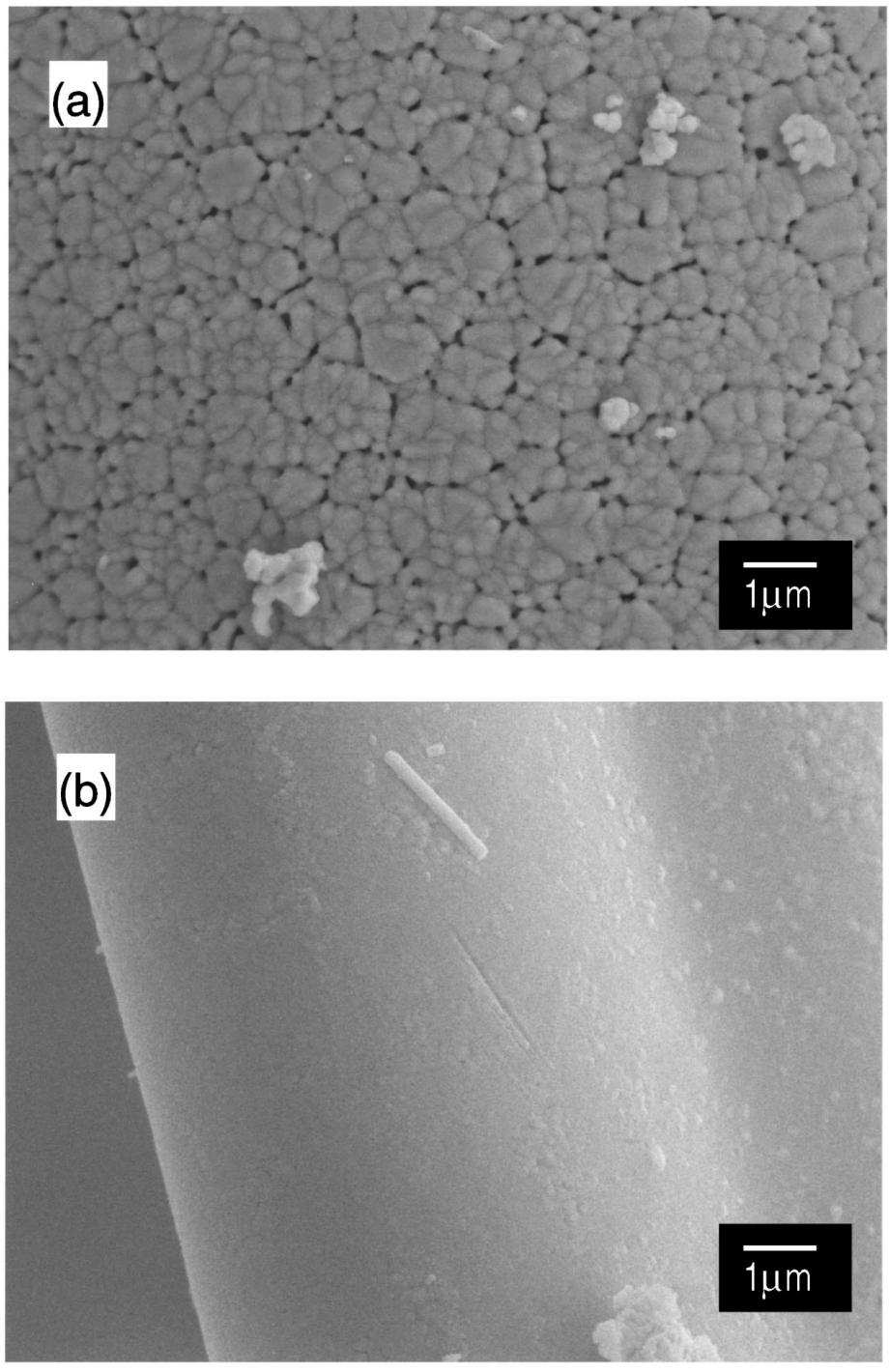

Figure 5 SEM photographs of the unseeded and seeded (2 wt%) PZT fibers heat-treated at 800°C for 2 h.

Fig. 3 shows DSC curves of the PZT precursor fibers with 2 and 6 wt% of seed particle at a heating rate of 10°C min^{-1}. For comparison, the DSC curve of the PZT fiber with no seed is also shown in Fig. 3. In the DSC curves, two big exothermal peaks around 300 and 500°C and one small exothermal effect at 580°C were observed for the unseeded PZT fiber. The first exotherm at 320°C is independent on the amount of seeds. Therefore, this first part of the thermal behavior was attributed to the evaporations of acetate and isopropyl alcohol derived from the starting materials and from oxidative decomposition of the organic ligands primarily to CO_2 and H_2O [7, 13]. The position of the second exotherm varied with seed content. The second exotherm at around 500°C gradually shifted to a lower temperature as the seed content increased. The exotherm is observed at 500°C for the unseeded fiber and at 490°C, and 470°C for the seeded (2 wt% and 6 wt%) PZT fibers, respectively. It seems that the second exotherm at around 500°C is due to the crystallization of perovskite phase, [14] because the seeded PZT fiber (2 wt%) heat-treated at 500°C for 2 h consisted only of perovskite phase (see Fig. 2b). These results are not in accordance with Kitaoka *et al*. and with Selvaraj

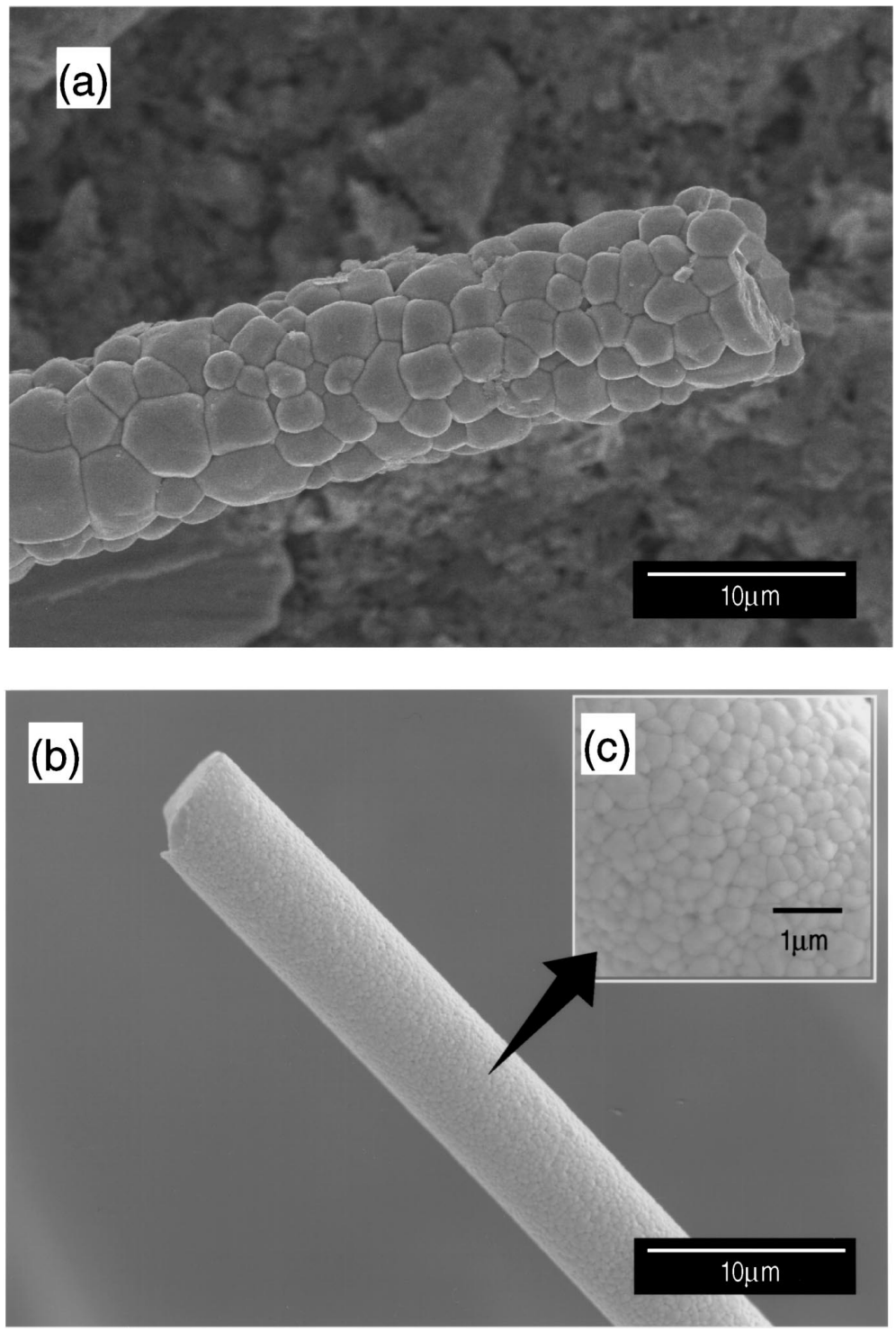

Figure 6 SEM photographs of the unseeded and seeded (2 wt%) PZT fibers heat-treated at 1000°C for 2 h.

et al. [4, 7]. They reported the crystallization temperature of perovskite phase was ∼570°C and single-phase perovskite could be obtained at above 800°C. It can be thus inferred that the perovskite seed particle can lower the crystallization temperature of the PZT fiber. At about 600°C, another shoulder appeared in all of the fibers, and the small third exotherm in the seeded (6 wt%) PZT fiber was observed at lower temperature than in the unseeded PZT fiber, indicating that this behavior also can be correlated with the development of the perovskite phase.

To investigate the extent of crystallization of the PZT fibers, X-ray diffraction patterns were studied. In Fig. 4, the X-ray diffraction patterns of seeded (2 and 6 wt%) PZT fibers heat-treated at 700°C for 2 h are given, along with the pattern of the unseeded PZT fiber. All the fibers exhibit perovskite tetragonal phase. The seeding effect on the crystallization of the PZT fiber appeared clearly in this study. As evident in the 2θ range of 43°–45° and 55°–57°, in the unseeded PZT fiber, the diffraction peaks of (200) and (002), as well as of (112) and (211), which are known to be very sensitive to the variation of perovskite crystal structure, were ambiguous in comparison with the seeded fibers. This observed result means that the tetragonality, c/a, of the unseeded fiber is not so good when heat-treating the unseeded fiber at 700°C for 2 h. On the other hand, the diffraction peaks of (200) and (002) in the seeded fibers were better split than in the unseeded PZT fiber. The crystallization of perovskite phase in the seeded fibers proceeded better the unseeded one, and it was further improved with increasing the seed content up to 6 wt%.

All of the precursor fibers prior to heat treatment were amorphous and consisted of weak-boned agglomerates, and the primary particle size was a few nano-meters. The fibers transformed to stable perovskite structure at different temperatures, depending on the content of seed particles. It is expected that the transformation of PZT from amorphous to perovskite phase accompanies an abrupt grain growth. Microstructure development of each PZT fiber, therefore, is significantly affected by the transformation behavior. SEM photographs of the unseeded and seeded (2 wt%) PZT fibers heat-treated at 800°C for 2 h are shown in Fig. 5. From the X-ray diffraction pattern, both fibers completely transformed to a single-phase perovskite after the heat treatment at 800°C for 2 h. The unseeded PZT fiber (Fig. 5a) shows typical vermicular grain structure: several micrometer-sized agglomerates composed by small grains and large voids that are mainly distributed between the agglomerates. This typical vermicular structure is often observed in alumina ceramics [15, 16]. This phenomenon can be explained by the smaller number of perovskite nuclei in the unseeded PZT fiber. On the other hand, the seeded PZT fiber (Fig. 5b) shows more homogeneous microstructure with no pores and small grain size comparing to that of the unseeded PZT fiber.

SEM photographs of the unseeded and seeded (2 wt%) PZT fibers heat-treated at 1000°C for 2 h are shown in Fig. 6. Similar to the fiber that was heat-treated at 800°C, the seeded PZT fiber exhibited a fine and homogenous microstructure, as shown in Fig. 6b and c. The grain size of the seeded PZT fiber (about 500 nm) was one tenth of that of the unseeded PZT fiber (about 3 to 5 μm). The seeding effect on microstructure development as well as the transformation was obvious in the PZT fiber.

4. Conclusions

Polycrystalline PZT fibers were successfully fabricated by sol-gel process and a perovskite seed particle addition. The seed particles accelerated the crystallization of the amorphous PZT precursor fibers. A single-phase perovskite PZT fiber can be obtained at temperature as low as 500°C. The crystalline perfection increased with increasing seed content. The seeded PZT fiber heat-treated at 1000°C consisted of homogeneous and sub micrometer-sized grains. The microstructure was much finer in the seeded PZT (2 wt%) than in the unseeded one. It was found that dense and homogeneous microstructure could be obtained by dispersing the perovskite seeds into the precursor PZT fiber.

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