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Stability and single crystal growth of lead scandium niobate and its solid-solution with lead titanate under hydrothermal conditions

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The stability of the lead scandium niobate (PSN) and its solid solution with lead titanate (PSNT), both with the perovskite structure, was investigated in a platinum capsule under hydrothermal conditions. The perovskite solid solution of PSNT decomposes in water at 640 °C, which results in the transformation to the tetragonal structure after the treatment. In KOH solutions, the PSNT powder was partially dissolved, it results in the precipitation of Pb_2ScNbO_6 powders with the perovskite structure, and the growth of both lead oxide (massicot) and $K_4Ti_3O_8$ needle crystals at the top of the capsule. In contrast, single crystals of both PSNT or PSN were grown in KF solutions at the top of the capsule by hydrothermal treatments at 600 °C with a temperature gradient of 40 °C. In both cases a deficiency of the scandium content achieves the stabilization of the pyrochlore structure of the grown crystals. *© 2000 Kluwer Academic Publishers*

1. Introduction

Lead zirconate titanate (Pb(Zr, Ti)O_3; PZT) ceramic plates are widely used as ultrasonic transducers in medical devices particularly in echocardiography analysis. To obtain high sensitivity and broad band-width, however, it is necessary that these piezoelectric materials have a high electromechanical coupling factor, k, and a low acoustic impedance, Za. Thus, much effort to improve both properties in PZT ceramics have been examined in detail, but no appreciable improvement in the properties of polycrystalline PZT ceramics has been reported in the past two decades [1]. A solid solution between lead scandium niobate ($Pb(Sc_{0.5}Nb_{0.5})O_3$; here after abbreviated as PSN) and lead titanate ($PbTiO_3$; PT) with a composition near to the morphotropic phase boundary, was recently found to have excellent piezoelectric properties [2, 3]. Niobium-doped lead scandium titanate ceramics ($Pb[(Sc_{0.5}Nb_{0.5})_{0.575}Ti_{0.425}]O_3$, here after abbreviated as PSNT) have the largest electromechanical coupling factor k of all relaxor-lead titanate binary ceramic systems so far reported.

Another route to improving the sensitivity and bandwidth of ultrasonic transducers is the employment of single crystals, which generally have superior properties compared to polycrystalline ceramics, if the appropriate axis is utilized. Crystals of PSN or PSNT should be grown by the solution technique, because PSN melts incongruently at 1425 °C [4]. Recently, high quality single crystals of PSN or PSNT were grown by means of the flux method using a PbO or a mixture of PbO and B_2O_3 as a flux, at a temperature of 1200 °C [5–9]. Under these conditions commonly a further release of PbO by evaporation is often produced, and has an important influence on the single crystal growth of both type of ceramics (PSN or PSNT). In contrast, the hydrothermal method is an alternative method, in which the growth proceeds without evaporation of PbO. The hydrothermal reaction is normally conducted in sealed autoclaves, and at lower temperatures than those employed by the flux method. Therefore, hydrothermal crystal growth offers the advantage of high yields of good quality single crystals, with less thermal strain.

In general, for the crystal growth under hydrothermal conditions, a solute should be stable and dissolve in a solvent to achieve the growth process. Until now, the growth of piezoelectric single crystals has been studied under hydrothermal conditions for PT and PZ [10], $PZ_{1-X}T_X$ [11] and PMN [12]. Fluoride mineralizers have been determined as successful solvents for crystal growth, because they exhibit good characteristics for dissolution and transport of the solutes such as Pb, Ti, Zr, Mg or Nb. However, no results have been reported on the hydrothermal treatment of PSN and PSNT. Hence, the present work, we focusses our attention on the stability of PSN and PSNT ceramic powders in KF solutions under hydrothermal conditions, as well as, to investigate the possibility of single crystal growth of both ceramics under these conditions.

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2. Experimental

The starting powders were the piezoelectric ceramics PSN ($Pb(Sc_{0.5}Nb_{0.5})O_3$) and its solid solution with lead titanate (PSN/PT = 58/42) obtained by solid state reaction at 1200 °C. Previous X-ray diffraction analyses conducted on both powders indicate that the structure was all of the perovskite type.

Initial evaluations were conducted using solutions of 35 wt % KOH and distilled water. The mineralizers (solvents for hydrothermal crystal growth) were KF and CsF solutions with concentrations in the range of 25–45 wt %,. The mineralizer was injected into a platinum capsule with outside diameter 3.0 mm, thickness 0.2 mm and length 50 mm. The amount of the solution was determined in order to balance the pressure outside and inside the capsule during hydrothermal treatment. 50 mg of each starting powder was weighed and poured into the capsule, the capsule was then welded by shut with an electric arc.

The sealed capsule was placed in a test-tube-type pressure vessel made of Stellite-25, and then water as a pressure medium was pumped into the vessel. The vessel was heated by an electric furnace. Temperature measurements were conducted by two chromel-alumel thermocouples, placed on the wall of the vessel at the positions corresponding to the top (cool growth zone) and the bottom (hot dissolution zone) of the capsule. The experiments were conducted at a controlled temperature of 600 °C ± 2 °C at the growth zone, with a temperature gradient between the growth and solubility zones of 40 °C ± 2 °C. The pressure inside the vessel was adjusted to 100 MPa by releasing water from the vessel during heating. The vessel was held at the reaction temperature and pressure for 120 h.

At the conclusion of each run, the vessel was cooled down to room temperature by removing the furnace. The capsule was cut open, and the solid contents were washed with distilled water by successive decanting. X-ray powder diffraction was used for phase identification of the reaction products. Morphological observations of the grown crystals were conducted by using an optical microscope and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer.

3. Results and discussion

3.1. Stability of PSNT ceramics in water and various mineralizers

Initial attempts to evaluate the stability on PSNT ceramics were carried out by the using various solutions (sodium and potassium hydroxide, sodium chloride, potassium and cesium fluorides, and water), with the aim of selecting the most suitable mineralizer for the crystal growth. The X-ray diffraction pattern of the PSNT powder hydrothermally treated in pure water at 640 °C for 120 h is shown in Fig. 1. Under these conditions the perovskite phase was the main constituent in the residual powder, although a small amount of lead oxide (PbO, massicot) was also produced during the treatment. A compositional variation due to the release of lead is mainly represented by the separation of the broad peak observed at a 2θ angle of approximately 45° (Fig. 1). Thus, the X-ray diffraction pattern of the residual powder indicates that the structural transformation from the rhombohedral-tetragonal mixture to the tetragonal structure has occurred [3, 13].

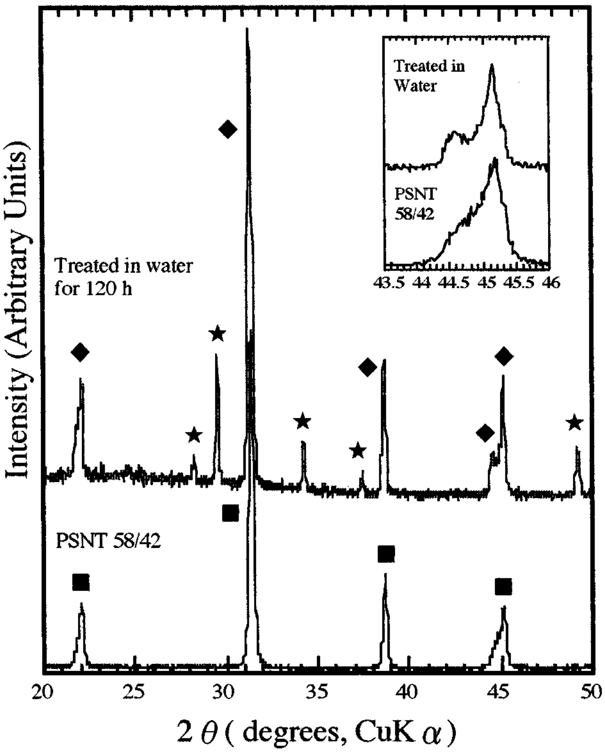

Figure 1 X-ray diffraction patterns of (a) perovskite PSNT (PSN/PT = 58/42) and those of (b) the remainder powders after hydrothermal treatments in pure water at 640 °C for 120 h. (■) Perovskite PSNT powders (PSN/PT = 58/42), (◆) Perovskite PSNT tetragonal, (★) PbO Massicot.

The alkaline mineralizer (KOH) has been used to prepare precursor piezoelectric PMN ceramics by low temperature hydrothermal treatment [12], while KF was used in the hydrothermal single crystal growth of $Pb(Ti, Zr)O_3$ [11]. Therefore, the stability of the PSNT powder was evaluated using both mineralizers. When the original powder was treated in a KOH 35 wt % solution, it was partially dissolved into the mineralizer, and recrystallized at the top of the capsule to form needle white crystals and yellow platelets. The X-ray diffraction patterns of these crystals are shown in Fig. 2, and were satisfactorily matched to the $K_4Ti_3O_8$ and PbO (massicot) phases, respectively. Furthermore, the X-ray diffraction pattern of the powder found at the bottom of the capsule was indexed to Pb_2ScNbO_6 with a perovskite structure. According to the microstructural observations (Fig. 3), some traces of the $K_4Ti_3O_8$ were crystallized on the surface of the Pb_2ScNbO_6 crystals.

On the other hand, in the KF solution (35 wt %), bulky single crystals were grown at the top of the capsule surrounded by a great amount of fibrous crystals (Fig. 4a). The position where the small fibers were found in the capsule indicates that these crystals were grown faster than the bulky crystals, which were commonly grown as an agglomerate amongst small fibrous crystals. From the analysis of the X-ray diffraction pattern of the fibrous crystals, these were successfully matched with

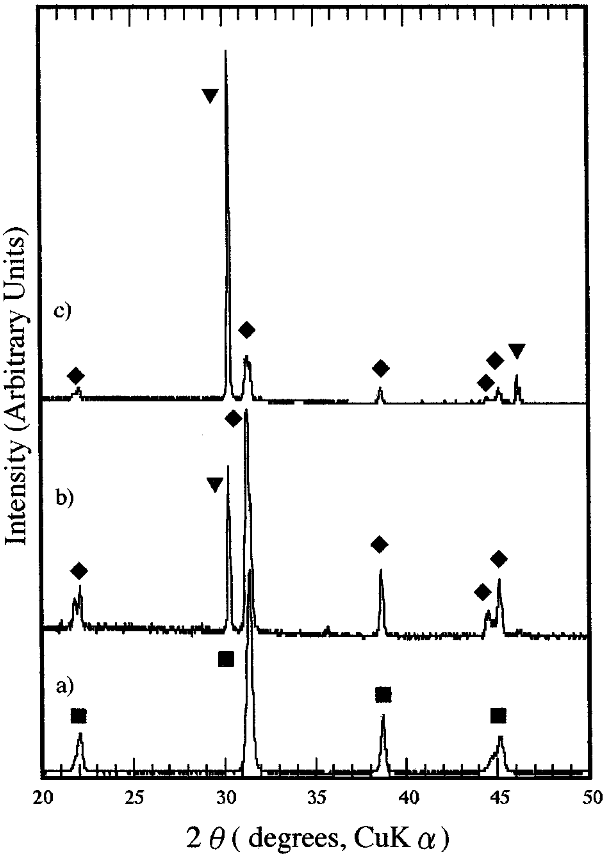

Figure 2 X-ray diffraction patterns of (a) perovskite PSNT (PSN/PT = 58/42) and those of (b) the remainder powders at the capsule bottom, and (c) needle crystals formed along the capsule after hydrothermal treatment in a solution of 35 wt % KOH at 640 °C for 120 h.

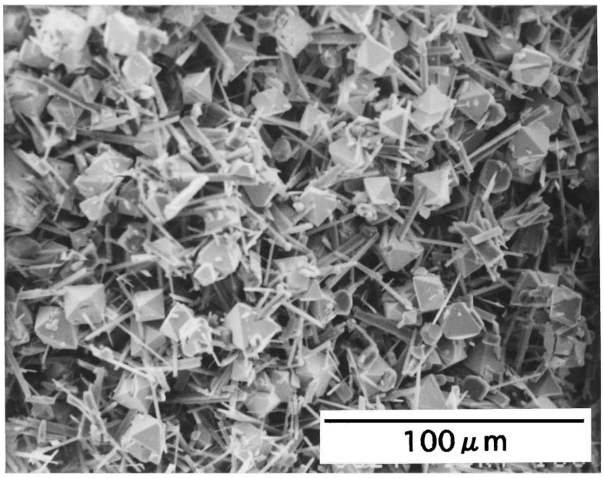

Figure 3 SEM micrograph of Pb_2ScNbO_6 powders remaining at the bottom of the capsule after hydrothermal treatment in a solution of 35 wt % of KOH for 120 h.

the pattern for $K_4Ti_3O_8$. The X-ray diffraction pattern of the bulky crystals is given in Fig. 5b. This pattern resembles that for $Pb_2Ti_2O_6$ with the pyrochlore structure. Using 35 wt % CsF solution as the mineralizer, only bulky crystals with the pyrochlore structure (Fig. 5c) were grown at the top of the capsule. In contrast with the treatments conducted in KF solutions, no needle-like crystals were produced in the CsF solution. Complete transportation of the raw powder initially poured into the capsule did not occur in either mineralizer. In most of cases a small amount of powder corresponding to Pb_2SnNbO_6 was remained at the bottom of the capsule. Energy dispersive X-ray analysis conducted on the bulky crystals (Fig. 4b) showed that the principal constituents were lead, titanium and niobium, with a trace of potassium as an impurity. Though the amount of niobium in the grown crystals is greater than in the raw powder, the amount of scandium is reduced in the grown crystals. The compositional change may result in the formation of the crystals with the pyrochlore phase, grown in both KF and CsF solutions.

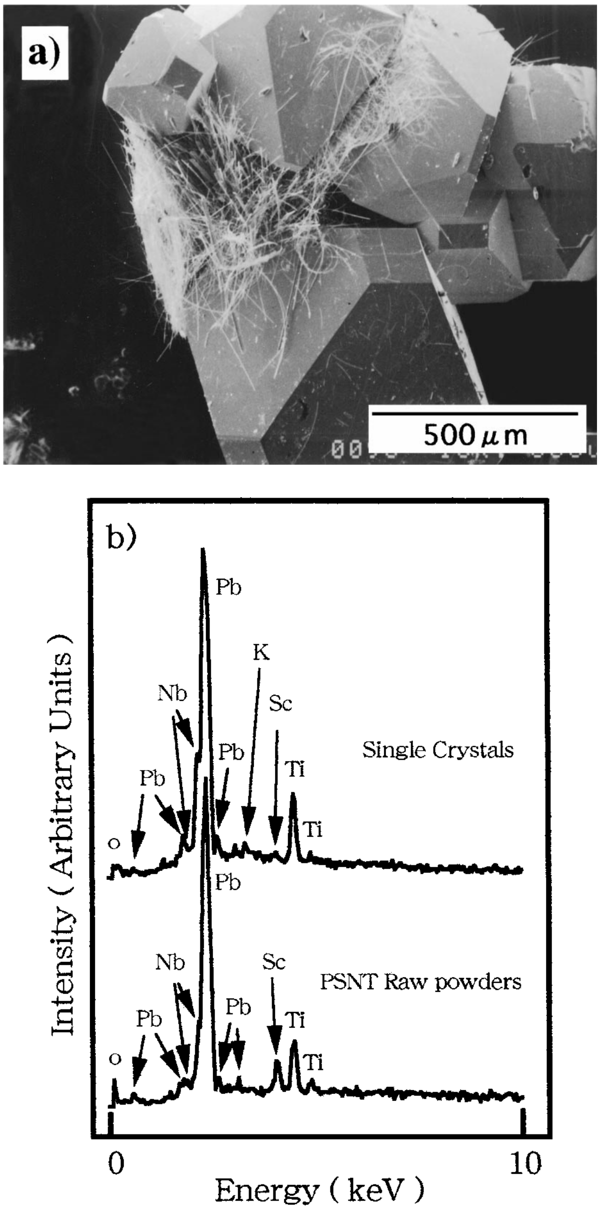

Figure 4 (a) SEM micrograph of the single crystals grown at the top of the capsule in 35 wt % KF solution at 600 °C for 120 h and (b) the respective EDS spectrum.

From these results, it can be concluded that alkaline or fluoride mineralizer may achieve further dissolution of the PT phase rather than the limited solubility of the PSN phase. In the KOH solution, $K_4Ti_3O_8$ and PbO were formed by the hydrothermal reaction of KOH and PT. Moreover, the hydrothermal treatment in fluoride solutions causes the preferential formation of the pyrochlore structure, which is due to the B′ cation

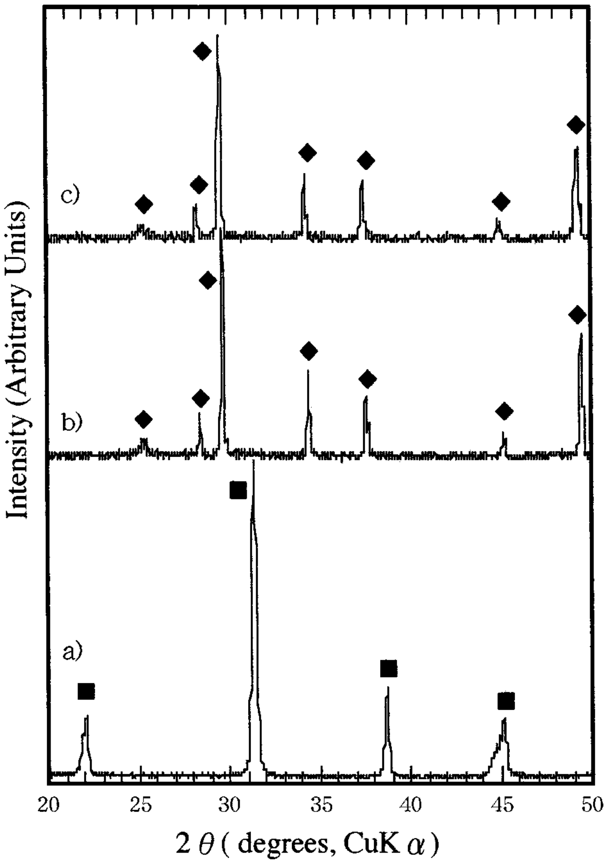

Figure 5 X-ray diffraction patterns of (a) the perovskite PSNT (PSN/PT = 58/42) and those of the $Pb_2Ti_2O_6$ single crystals grown in 35 wt % fluoride mineralizer of (b) KF and (c) CsF under hydrothermal conditions at 600 °C for 120 h. (■) Perovskite PSNT powders (PSN/PT = 58/42), (◆) Pyrochlore.

(scandium) deficiency from the ideal perovskite structure, $Pb(B'B'')O_3$.

3.2. Stability of PSN ceramics in fluoride solutions

Experiments aimed to evaluate the crystal growth and stability of PSN ceramic powder were only conducted using KF solutions (25 or 35 wt %). Under these conditions, a continuous transference of all the constituents resulted in the spontaneous nucleation and grown of PSN bulky single crystals at the top of the capsule, (Fig. 6a). The rate of growth of the PSN crystals was irrespective of the concentration of the mineralizer. In addition, a considerable amount of Pb_3O_4 (red) or PbO (massicot, yellow) were found along the capsule, when the powder was treated in KF solutions of 35 or 25 wt %, respectively. The X-ray diffraction patterns of the bulky crystals grown at 600 °C in 25 and 35 wt % KF solutions are shown in Fig. 7. There are no significant crystalline structure differences between the crystals grown in the two solutions. The X-ray diffraction patterns shown in Fig. 7 suggest that the structure of the crystals resembles that of the pyrochlore $Pb_{1.83}$ $(Zn_{0.29}Nb_{1.71})O_{6.39}$.

Semiquantitative analyses of the compositions determined for the bulky single crystals, grown at 600 °C in a 35 wt % KF solution, and that of the raw powder, are shown in Fig. 6b. From the EDS spectrum, one point that deserves emphasis is the amount of niobium detected in the grown crystals, which is greater than that determined in the original perovskite powder. This fact is attributed to the high solubility of lead in the KF solution, which promotes the easier formation of the lead oxide. A significant amount of scandium was detected in these crystals in comparison with that observed on crystals grown from the PSNT powder in the same solution. In addition, potassium was incorporated into the crystals as an impurity (Fig. 6b). The preferential formation of the pyrochlore structure in the grown crystals is expected to be due to a deficiency in the content of scandium. In general, the deficiency of the amount of scandium in crystals grown from both perovskite PSNT and PSN in KF mineralizer at hydrothermal conditions is due to the limited solubility of scandium under these conditions. The deficiency of scandium atoms in B′ positions stabilized the pyrochlore structure rather than the ideal perovskite $Pb(B'B'')O_3$.

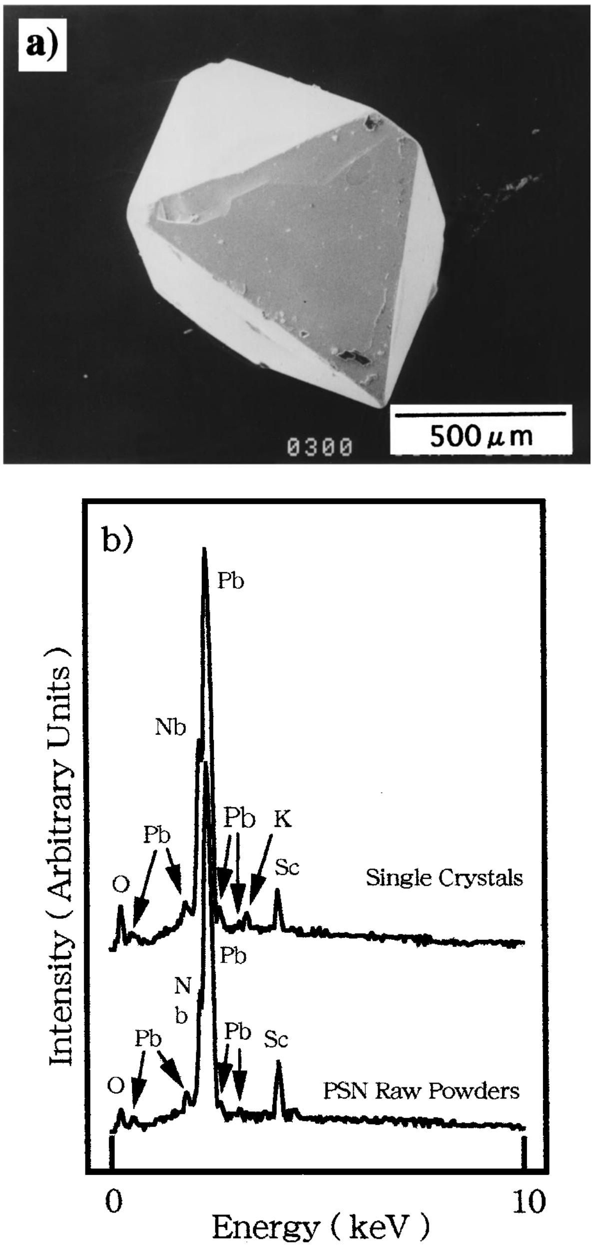

Figure 6 (a) SEM micrograph of the PSN single crystals grown at the top of the capsule in 35 wt % KF solution at 600 °C for 120 h and (b) the respective EDS spectrum.

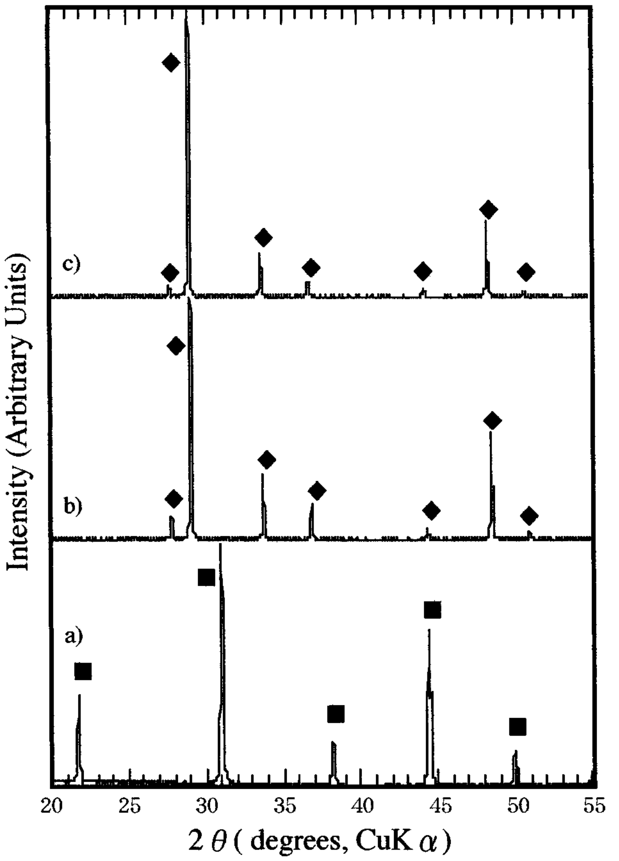

Figure 7 X-ray diffraction patterns of (a) the perovskite relaxor PSN and those of the single crystals grown under hydrothermal conditions at 600 °C for 120 h in (b) 35 wt % KF and (c) 25 wt % KF. (■) Perovskite PSNT powders (PSN/PT = 58/42), (◆) Pyrochlore.

4. Conclusions

The stability of PSNT powders with perovskite structure in various mineralizer solutions was investigated by hydrothermal treatments at 640 °C. The perovskite structure was decomposed in KOH and KF solutions under hydrothermal conditions. Likewise, the PSN perovskite structure was also not stable in KF solutions. In the KF solution, however, bulky single crystals with pyrochlore structure were grown from both of the perovskites, PSNT and PSN, by spontaneous nucleation at the top of the capsule under hydrothermal conditions at 600 °C. The preferential formation of the pyrochlore structure is mainly due to a deficiency of the B′ site cation of the ideal perovskite structure, Pb(B′B″)O_3.

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