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Raman Scattering Studies on Crystallization Process from Amorphous $PbTiO_3$

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Investigations have been made on the rapidly quenched amorphous $PbTiO_3$. It has been confirmed that the obtained state is really amorphous state by utilizing DTA and Raman spectroscopy. Effect on annealing has been examined and it has been found that samples crystallize at 500 ~ 550°C. Continuous change in Raman spectrum due to the structural relaxation has been clearly observed.

§1. Introduction

The soft-mode Raman spectroscopy is one of promising tools for investigating a disordered lattice state since the soft mode is a lattice mode and a sensitive probe of the lattice ordering. This paper reports investigations of the amorphous state of $PbTiO_3$ and the structural relaxation toward the crystalline state with special emphasis on the soft mode. No work has hitherto been made from this view point. A part of this study has already been reported in ref. 1.

§2. Sample Preparation

Amorphous samples of $PbTiO_3$ were prepared by a twin-roller quenching apparatus as shown in Fig. 1. The starting material (99.9% crystalline $PbTiO_3$ powder) was melted at about 1300°C in the Pt tube with the fine nozzle 0.3 ~ 0.5 mm in diameter. The melt was sprayed on the rollers rotating at 3000 rpm and was quenched. Obtained samples were flakes or ribbons of about 1 cm in length and 20 μm in thickness and were optically isotropic. The quenching rate is roughly estimated to be about 10^6 deg/sec as follows: for example, in a 1 cm long sample, since the surface velocity of the roller is about 8×10^2 cm/sec, the quenching time is given approximately by 1 cm/(8×10^2 cm/sec) $\simeq 1 \times 10^{-3}$ sec. The temperature difference between the initial melt and the final quenched state is estimated to be about 10^3 deg [the estimation of the final temperature is difficult, but it is said to be less than the crystallization temperature T_{crys} ($\simeq$500°C, see §3) at least qualitatively]. Thus, the quenching rate is given by 10^3 deg/(1×10^{-3} sec) = 1×10^6 deg/sec.

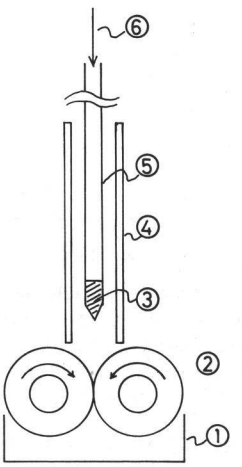

Fig. 1. The twin-roller quenching apparatus used. 1. Collector, 2. Steal roller (50 mmϕ), 3. Melt, 4. Heater (SILICONIT, DSP11), 5. Pt tube (10ϕ × 400 mm), 6. N_2-gas pressure.

§3. The Characterization of As-quenched Samples

It is important problem to determine whether thus prepared samples are really in the amorphous state or not.

First, X-ray measurements[2,3] were made by Uno and Ozawa and the first and second haloes characteristic of the amorphous state have been observed in as-quenched samples.

Second, the DTA curves were examined.[1] Figure 2 shows a typical result for the as-quenched sample together with that for the initial material. In the curve of the as-quenched sample, a sharp exothermic peak and a slight step anomaly (shown by T_g) are seen in the region 450 ~ 550°C instead of the endothermic anomaly at the Curie point ($\simeq$480°C) in the

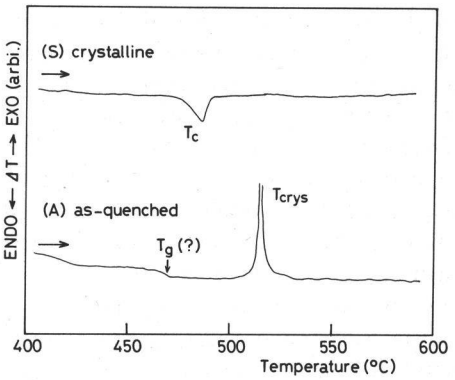

Fig. 2. Typical DTA curve on heating of the initial material (S) and the as-quenched sample (A). Curve (A) is obtained only in the first heating process and shapes at T_{crys} and T_g depend on each sample.

initial material. Generally speaking, the amorphous sample is in the thermodynamically non-equilibrium or metastable state and it tranforms to the stable crystalline state exothermically (The peak temperature is called a crystallization temperature T_{crys}). Non-existence of the Curie point indicates that the ferroelectric ordering does not exist in the as-quenched sample. The slight anomaly shown by T_g is supposedly the glass transition point, but we can not indicate it definitely, because this anomaly is very weak and different for each sample.

Third, the Raman spectrum from as-quenched samples were examined.[1] Figure 3 shows the result together with that from the initial material. The most significant difference between the two is the non-existence of the soft mode in the amorphous state. This is in accord with non-existence of the anomaly at T_c in the DTA curve of Fig. 2 (A). The soft mode is an external mode or a lattice mode, of which the frequency is low because of near cancellation of the long range and the short range forces; thus the occurrence of the soft mode is characteristic of crystal lattices. Non-existence of the soft mode is one of evidences that the lattice is disordered.

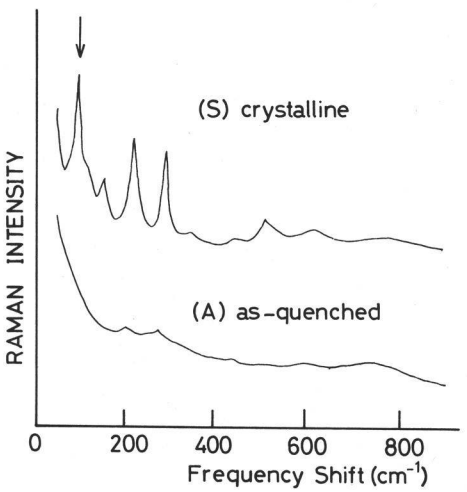

Fig. 3. Raman spectra from the initial material (S) and the as-quenched sample (A). Ferroelectric soft mode is shown by an arrow in (S).

These three facts, the diffraction pattern of X-ray, non-existence of T_c anomaly in DTA curve and non-existence of the soft mode in Raman spectrum establish that the as-quenched sample is not in an amorphous-looking ceramic or crystalline state, but in real amorphous state.

§4. Structural Relaxation Toward the Crystalline State

As described in §3, the samples are understood to crystallize exothermically at T_{crys}. The investigation on the state above T_{crys} were made. If the as-quenched state would transform to the crystalline state of paraelectric $PbTiO_3$ at T_{crys}, the room temperature Raman spectrum from the sample once heated up to T_{crys} would change to the crystalline pattern identical to that in Fig. 3 (S). The result for annealing effects is shown in Fig. 4. In this figure, (B), (C) and (D) are spectra from samples heated to $T_{crys}+25°C$ (540°C), $T_{crys}+175°C$ (690°C) and $T_{crys}+385°C$ (900°C) and cooled to room temperature, respectively. (A) and (S) are the same as those in Fig. 3. The spectrum (B) is much different from the spectrum (S), but is rather alike that of as-quenched sample (A), or spectral patterns do not change abruptly to that of the perfect crystalline state on passing through T_{crys}. The structure of the sample just after the crystallization seems not to become completely ordered crystalline state yet. It is fairly disordered. A gradual relaxation is necessary to reach the perfect crystalline state. The soft mode appears as a shoulder in (B) and it shows narrowing and hardening when the relaxation proceeds through (C) and (D). Such a relaxation may include two mechanisms: first a recovery of ordering of atoms in a shorter range, and second a recovery of ordering whole over a crystal. The spectral pattern change around 600 cm^{-1} and the soft

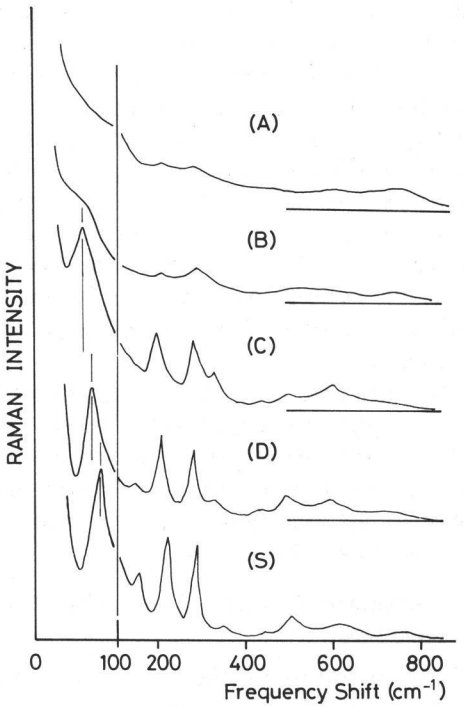

Fig. 4. Raman spectra from five samples. (A) ~ (S) are shown in the text. Thg frequency scale is changed at 100 cm^{-1}

mode hardening seen in Fig. 4 (B), (C) and (D) seem to be attributed to the former case (for example, recovery of the shape of TiO_6 group) and to the latter case, respectively.

The investigation on the state above T_{crys} was also made by the DTA. The samples which had been heated to a temperature below 900°C showed no heat anomaly of the ferroelectric transition at T_c, but those heated to above 900°C did show the heat anomaly at T_c. This suggests that the process of the recovery of ordering whole over the crystal has been completed when heated to above 900°C.

The measurements of dielectric constant were made.[2,4] The effect of annealing on the dielectric behavior also reflects the structural relaxation.[4]

References

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