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Broadband dielectric spectroscopy of PSN ceramics

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Abstract

The complex dielectric permittivity of ordered and disordered PSN ceramics was measured in the frequency range from 20 Hz to 3 GHz. The anomaly of dielectric permittivity is clearly seen in the region of 115 °C for ordered PSN at all measured frequencies. Disordered PSN exhibits typical relaxor behaviour with a huge frequency dispersion below 125 °C. Calculated distribution of relaxation times shows noticeable influence of polar clusters to the total dielectric spectrum of disordered PSN below 80 °C with the longest relaxation times edge diverging according to the Vogel–Fulcher law. In the case of ordered PSN, two almost not overlapping peaks in the distribution of relaxation times represent displacive lead motions at high frequencies and possible conductivity phenomena at low frequencies and high temperatures.

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1. Introduction

$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) belongs to the family of mixed oxide systems with perovskite $A(B'_xB''_{1-x})O_3$ structure. Due to the high dielectric, piezoelectric, electrostrictive responses[1] and relaxor behaviour PSN attracts both fundamental and technological interest. In contradiction with most documented relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) which remain cubic down to the liquid helium temperatures[2] ordered PSN have a low-temperature rhombohedral ferroelectrics phase.[3] The another peculiar property of PSN is the different degree of ordering between Sc^{3+} and Nb^{5+} ions which can be controlled by thermal treatment.[3–5] In addition, it has been shown that lead vacancies suppress the relaxor-to-ferroelectric transition[5] and such PSN with Pb vacancies exhibit usual relaxor behaviour. The chemically ordered PSN should be a classical ferroelectric however a weak relaxation of dielectric permittivity was observed in it.[4] The ordering between Sc^{3+} and Nb^{5+}, so-called B-site ordering influences physical properties of PSN. Such influence has been studied extensively in last decade by different techniques. It can be regarded as consisting of a regular alternations of B′ and B″ cation planes which are perpendicular to the ⟨1 1 1⟩ direction. The phase transition is characterized by cooperative motions of Pb and Sc/Nb atoms in this direction.[4] More recent X-ray diffuse scattering studies of disordered PSN have been interpreted in terms of ferroelectric and antiferroelectric ordering induced by size difference between the Sc^{3+} and Nb^{5+} ions however these authors assumed an antiparallel displacement of Pb and Sc/Nb ions to the ⟨1 1 0⟩ direction. Studies on structural and dielectric properties on PSN with different degree of ordering showed that chemical ordering yields to a non-spatially homogeneous material constituted of disordered and ordered phases and the phase transition temperature of the disordered phase is lowered with the presence of an ordered phase.[6] Studies on the X-ray, neutron diffraction and differential scanning calorimetry measurements[5–8] supported this observation with the phase transition temperature ∼106 °C of disordered and ∼73 °C of ordered phases. The existence of Pb positional fluctuations in the paraelectric phase is typically considered as a formation of polar clusters. The investigation performed on disordered PSN by neutron diffraction experiments revealed the occurrence of diffuse scattering around some of the Brag peaks[8] similar to the observed for PMN.

It is well known that polar clusters play a major role in the dielectric response of relaxor materials at low frequencies. Our purpose was to examine the dielectric permittivity of both ordered and disordered PSN ceramics in a wide frequency range because in previous studies the dielectric response was investigated only at low frequencies (up to 1 MHz). Obtained dielectric

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spectra were analyzed by the distribution of relaxation times function.[9]

2. Experiment

The samples for dielectric measurements were cut from bulk ceramics. The frequency range from 20 Hz to 3 GHz was covered by using HP 4284 precision LCR meter in low frequency (20 Hz–1 MHz) and Agilent 8714 network analyzer in high frequency (1 MHz–3 GHz) part. The silver electrodes were applied on the each sample to produce good electrical contact. The samples were annealed to 230 °C before each measurement to avoid memory effects. The measurements were performed in cooling cycle down to −25 °C with the temperature change rate 1 °C/min. monitored within 0.1 °C accuracy.

3. Results and discussion

The dielectric spectrum of ordered PSN shows anomaly with dispersion at about 115 °C temperature (Fig. 1). At low frequen-

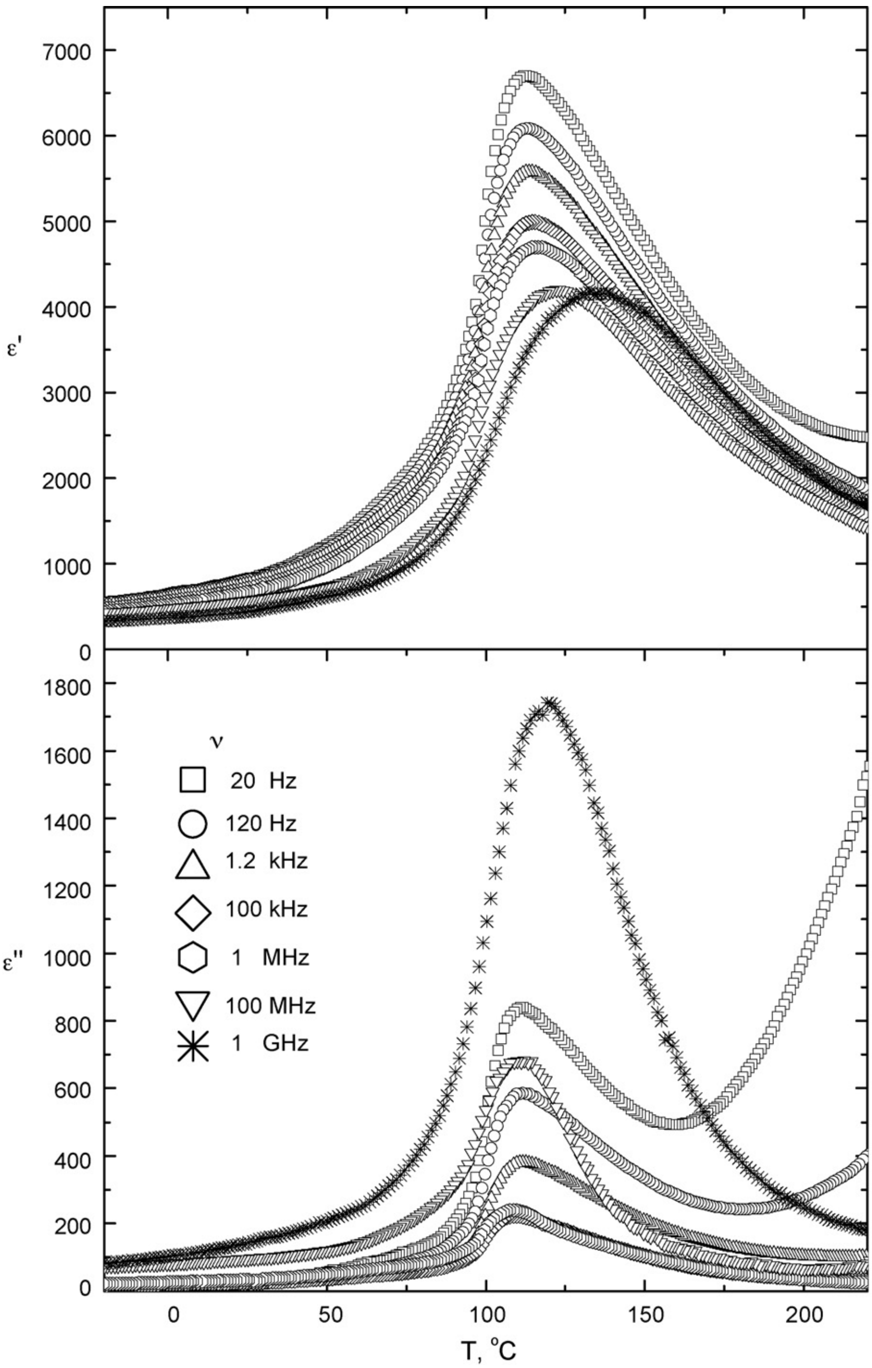

Fig. 1. Temperature dependence of real and imaginary parts of dielectric permittivity of ordered PSN at different frequencies.

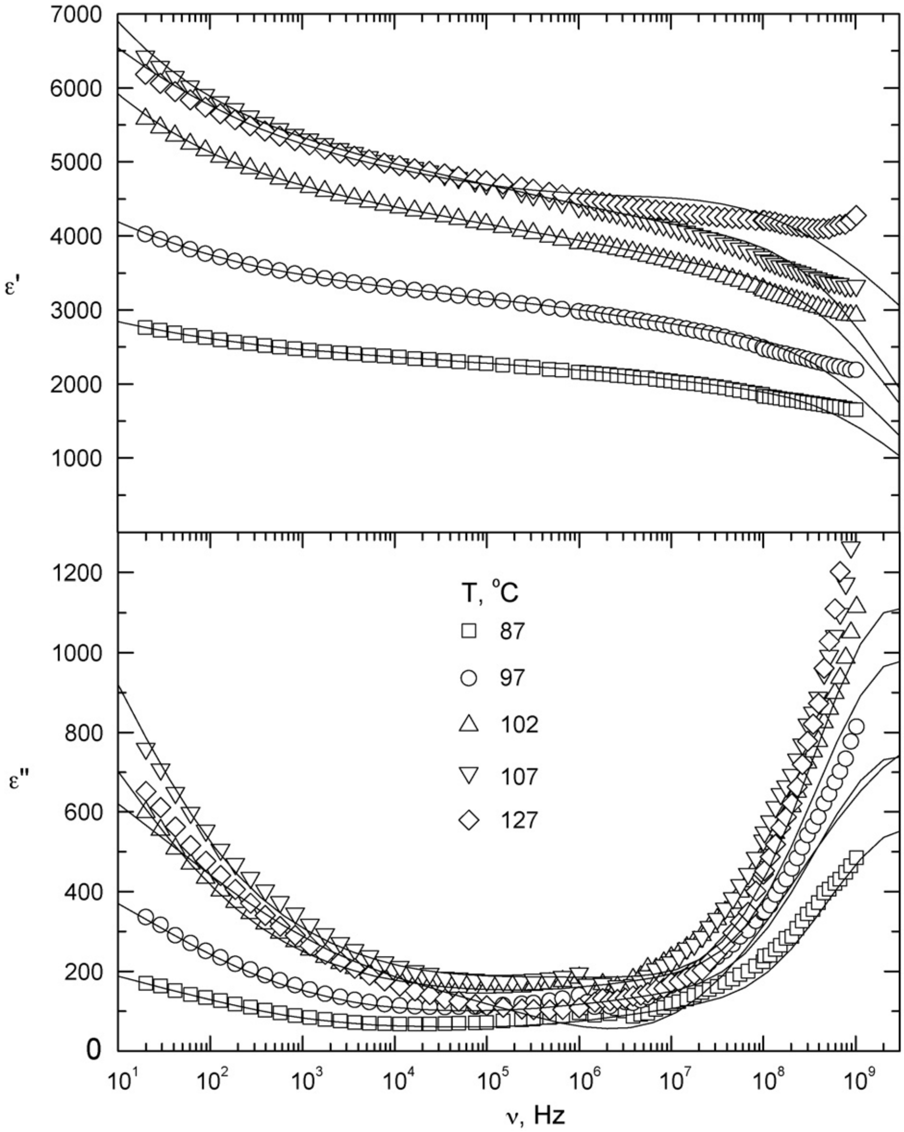

Fig. 2. Frequency dependence of real and imaginary parts of dielectric permittivity of ordered PSN at different temperatures. The solid lines are distribution of relaxation times fits.

cies below 1 MHz the increase of real and even more imaginary parts of dielectric permittivity can be observed. This increase is similar to dielectric dispersion typically observed in conducting materials. In contrast to the observation of other authors[6,7] the main dispersion region is shifted about 20 °C towards higher temperatures. From frequency dependences (Fig. 2) two dispersion regions can be distinguished: one below several kilohertz obviously caused by conductivity phenomena and another one arising from displacive motions of Pb ions.

The disordered PSN shows different behaviour of dielectric spectrum. As can be seen from temperature dependences in Fig. 3, maxima of real and imaginary parts of dielectric permittivity shift to the higher temperatures with increasing frequency. Such behaviour is typically attributed to the relaxor ferroelectrics and coincides with works of other investigators.[5–7] Frequency dependences of ε' and ε'' broadens anomalously below 105 °C temperature and moves of our spectral range on cooling (Fig. 4).

One of mostly important points in analyze of dielectric spectra is to estimate the distribution of relaxation times. Formulas like Cole–Cole are able to describe the dynamics of materials only with symmetrical distribution of relaxation times. The more realistic idea is to treat the relaxation time distribution as a sum of independent Debye-like processes.[9] This method allows us to extract the relaxation time distribution without any a priori assumptions and to take into account the influence of each relaxator into total dielectric spectrum of material. Calculated distribution of relaxation times for ordered PSN (Fig. 5) clearly show two different processes taking contribution to the dielectric permittivity of this material. The short relaxation times maximum stays nearly stable at approximately 10^{-11} s. The long relaxation times part slightly broadens with increasing the

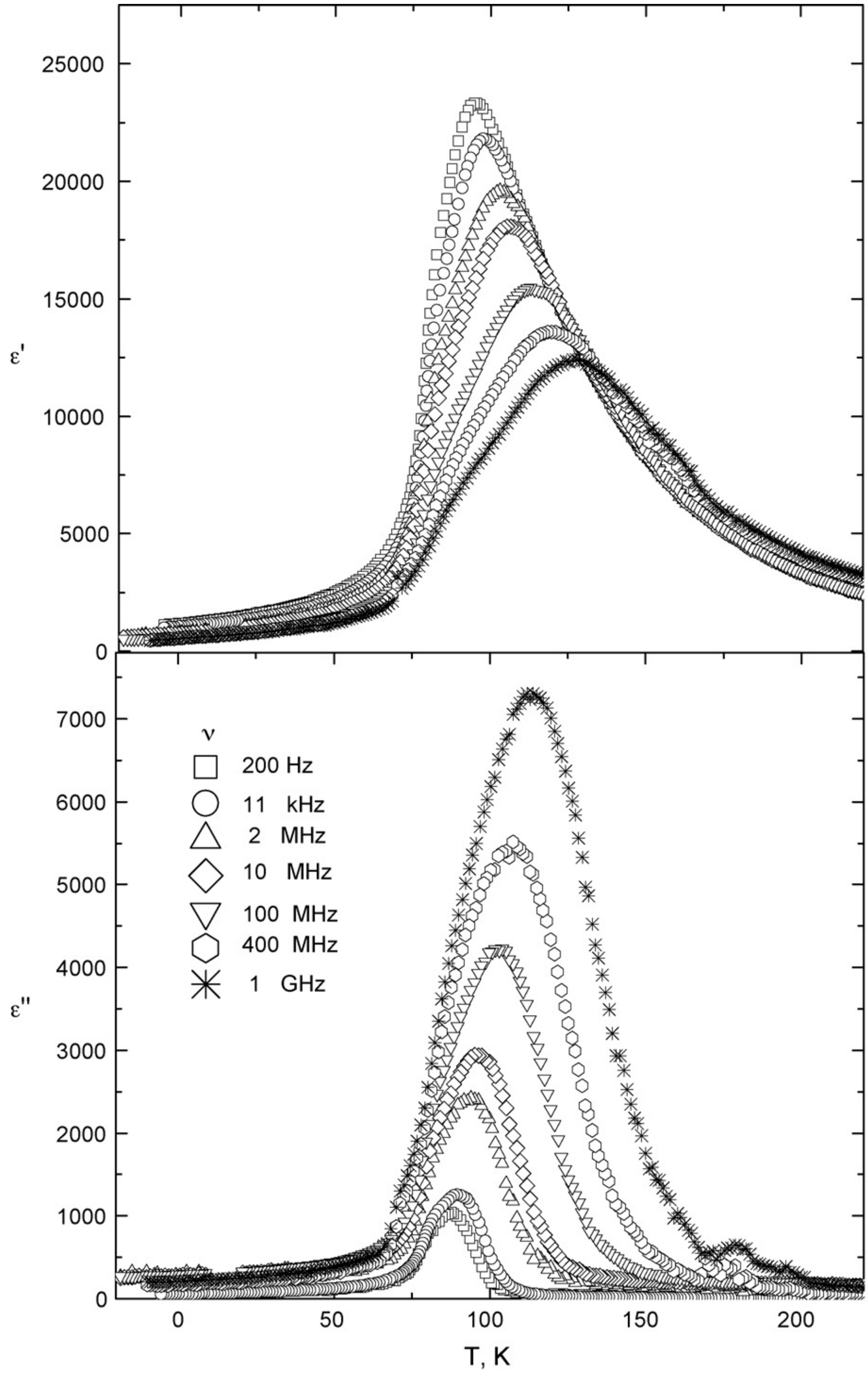

Fig. 3. Temperature dependence of real and imaginary parts of dielectric permittivity of disordered PSN at different frequencies.

temperature. Such behaviour coincides with a prediction made above that short relaxation times part is caused by ordering of the Pb ions while long relaxation times part obviously is influenced by conductivity effects. The distribution of relaxation times of disordered PSN (Fig. 6) differs totally from the ordered one. It broadens continuously to the longest relaxation times with decreasing of the temperature. The splitting into two parts is caused by the relaxation of individual Pb atoms and polar clusters and can be observed only below 80 °C. This behaviour is different from PMN where the contribution of the glassy matrix and polar clusters to the distribution of relaxation times is much more clearly pronounced.[10] The behaviour of longest edge of the distribution of relaxation times shows nonexponential character and can be fitted by empirical Vogel–Fulcher relationship rather well (insert in Fig. 6). It follows that the freezing of polar clusters occurs at lower temperature than observed phase transition of

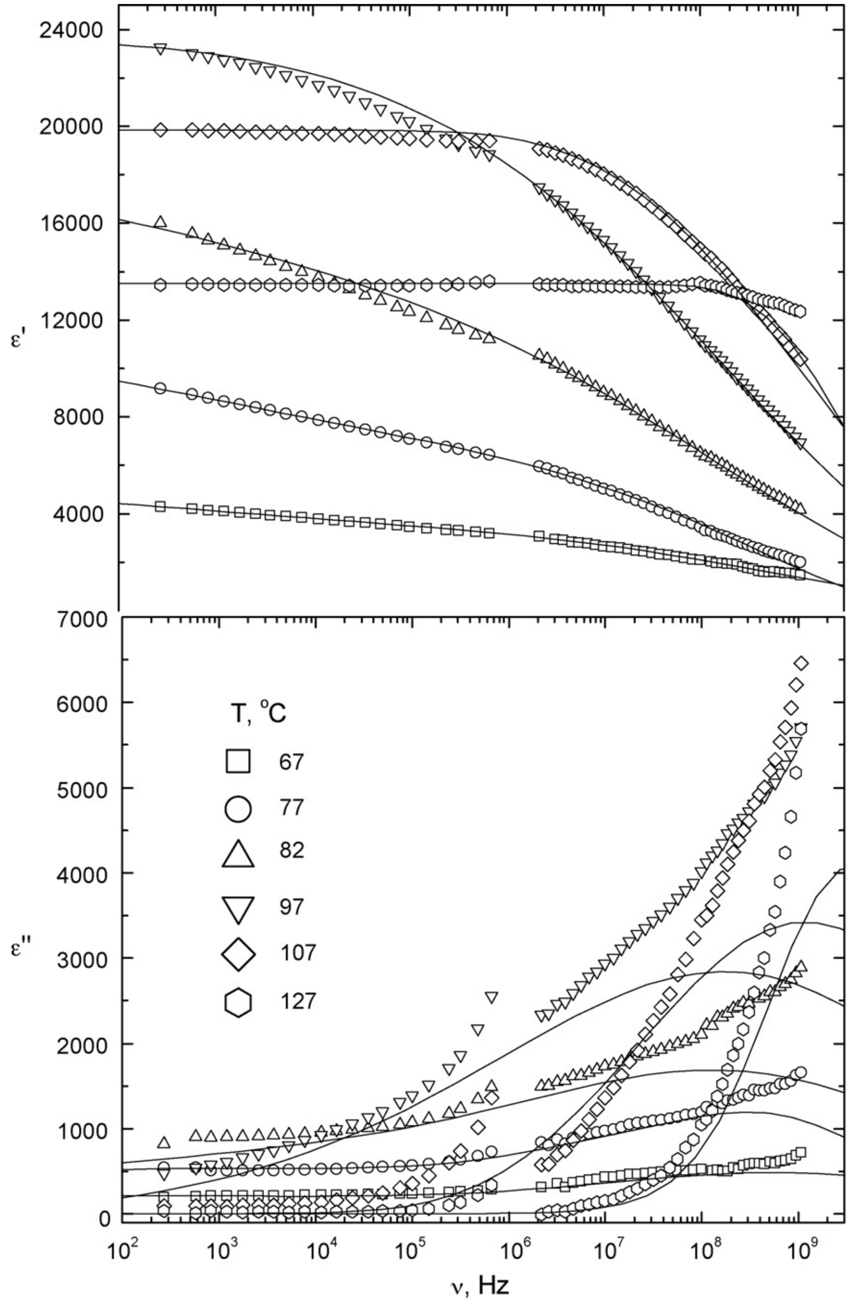

Fig. 4. Frequency dependence of real and imaginary parts of dielectric permittivity of disordered PSN at different temperatures. The solid lines are distribution of relaxation times fits.

disordered PSN. Surprisingly this temperature (∼69 °C) coincides rather well with the second anomaly observed for partially disordered samples.[6,7]

4. Conclusions

In case of ordered PSN, dielectric anomaly in the region of ∼115 °C has been observed. The frequency dependencies of the real and imaginary parts of dielectric permittivity show that relaxation time do not change very much with temperature. In disordered PSN the dielectric spectrum is diffuse and typical for ferroelectric relaxors. Two main contributions to the dielectric spectrum of ordered PSN can be clearly distinguished. The low frequency anomaly can be caused by conductivity phenomena of oxygen vacancies. The disordered PSN shows a huge dispersion of dielectric permittivity and a broad distribution of relaxation times. The contribution of polar clusters to the total dielectric spectrum can be distinguished below 80 °C. The behaviour of longest relaxation times edge in distribution of relaxation times of disordered PSN diverges according to the Vogel–Fulcher law with a freezing temperature 69 °C which is obviously related with a transformation into rhombohedral phase.

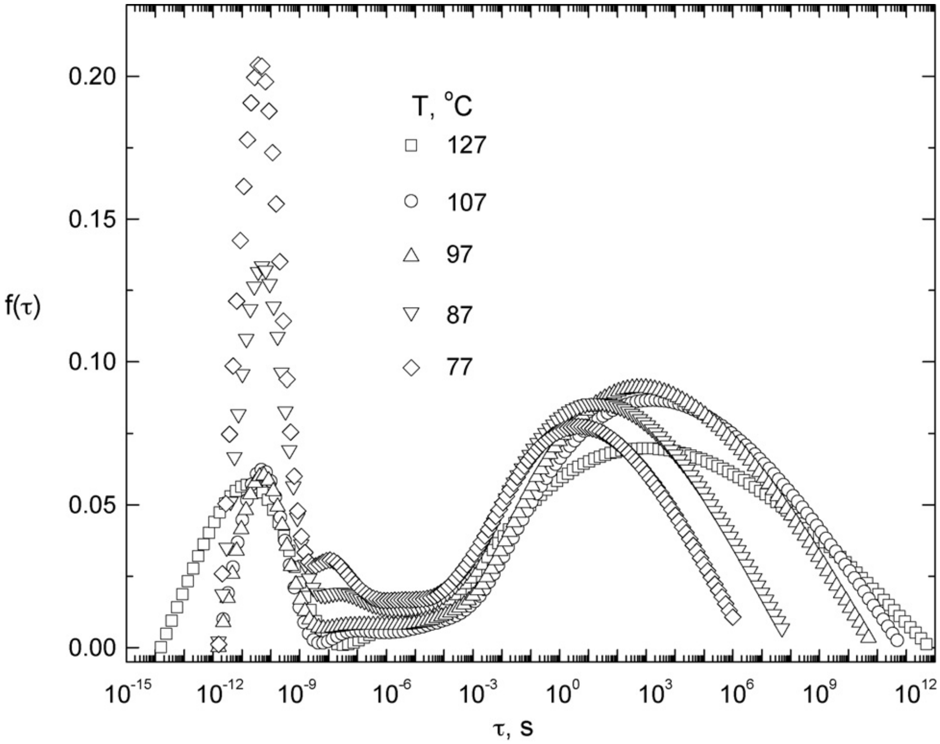

Fig. 5. Relaxation time distribution function $f(\tau)$ of ordered PSN at different temperatures.

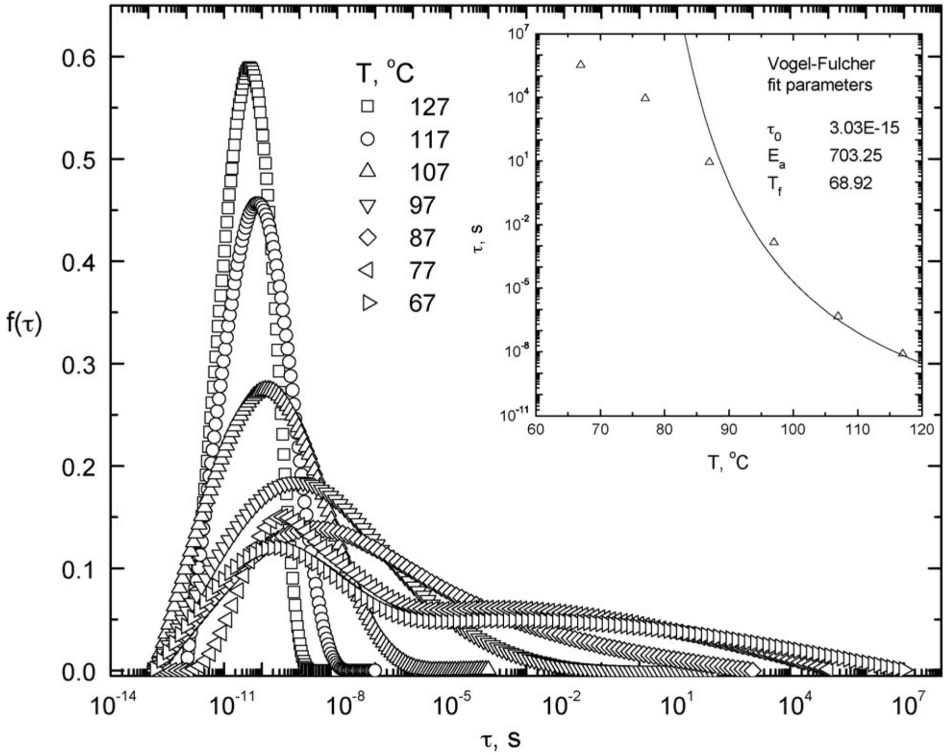

Fig. 6. Relaxation time distribution function $f(\tau)$ of disordered PSN at different temperatures. *Inset*: the Vogel–Fulcher fit to the behaviour of longest relaxation times edge.

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