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CRYSTAL GROWTH, STRUCTURE AND DIELECTRIC PROPERTIES OF FERROELECTRIC MIXED $Pb_2ScTa_xNb_{1-x}O_6$ SINGLE CRYSTALS

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Single crystals of a solid solution of the two ferroelectric compounds Pb_2ScTaO_6 (PST) and Pb_2ScNbO_6 (PSN) have been prepared by the high temperature solution method. They had the chemical formula $Pb_2ScTa_{0.48}Nb_{0.52}O_6$ (PST-PSN). X-ray diffraction analysis showed a perovskite type structure with a lattice parameter a = 4.0803 Å. The dielectric constant and dielectric losses were measured in temperature range -55 to 325 ^oC. At a 10 kHz measurement frequency, three peaks were observed at 15, 80 and 190 ^oC, corresponding to the phase transitions of PST, PST-PSN and PSN single crystals respectively.

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1. Introduction

Complex perovskite ferroelectric relaxors $A(B'_xB''_{1-x})O_3$ with heterovalent B-site ions exhibit relaxor behaviour, and the study of these materials is of both fundamental and technological interest [1,2]. PST and PSN are ferroelectric at room temperature, but exhibit a structural displaced transition to the paraelectric phase at higher temperatures. In PST, this transition takes place at 25 ^oC and in PSN at 85 ^oC [3,4]. The system PSN makes an order-disorder transition at the B sites near 1280 ^oC [5, 6]. According to a dielectric study, the ordered state was found to be ferroelectric,with disordering introducing the relaxor nature [6,7].

The purpose of the present work was to study the dielectric behaviour of mixed single crystals of PST-PSN.

2. Experimental details

The growth of mixed PST-PSN crystals was carried out by the high temperature solution growth method. Polycrystalline Pb_2ScTaO_6 and Pb_2ScNbO_6 perovskite structures were synthesized by the solid state reaction of stoichiometric amounts of [PbO (99.999%), Sc_2O_3 (99.99%), Ta_2O_5 (99.99%)] and [PbO (99.999%), Sc_2O_3 (99.99%), Nb_2O_5 (99.99%)] respectively. They were then further annealed for 48 h. in air. The starting material was a 75% PST and 25%PSN mixed powder, which was mixed with the flux (PbO: PbF_2: B_2O_3=0.75: 0.24: 0.01) in a 10:1 ratio.

A platinum crucible of diameter 45mm and height 120mm, covered with a platinum lid, was used in the crystal growth experiments. The temperature elevation rate was 60 ^oC/h in the range from

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room temperature to the growth temperature of 1250 °C. The single crystals were obtained at a cooling rate of 0.3 °C/h, in temperature interval 1250 to 950 °C, and a temperature gradient which did not exceed 10 °C/cm during the crystal growth experiment. The obtained crystals had a relatively large volume, of 1 to 1.5 cm^3. The {001} planes were flat and well shaped. X-ray diffraction analysis established a perovskite structure, *Pm3m*, with a cell parameter of 4.081 Å.

The examined samples had thicknesses of 0.68, 1.20 and 1.10mm for PSN, PST-PSN and PST crystals respectively. Silver electrodes were attached onto two opposite polished surfaces of the crystals. Furthermore platinum fibers were attached to the electrodes, allowing measurements over a wide temperature range. The dielectric measurements were done with a Hewlett-Packard 4275A RLC-measurement bridge, over the temperature range -55 to +200 °C for PST and PST-PSN crystals, and from room temperature to 325°C for PSN crystals, at frequencies of 10 kHz, 100 kHz and 1 MHz. The relative error of the measurement bridge was about 3% over the whole frequency range.

3. Results and discussion

The temperature dependence of the dielectric constant of a mixed PST-PSN crystal, measured at a frequency of 10 kHz, is shown in Fig. 1, where it is compared with those of PST and PSN crystals. The phase transition temperature of the mixed crystal is at 80°C, while for PST and PSN crystals it is at 15 °C and 190 °C respectively.

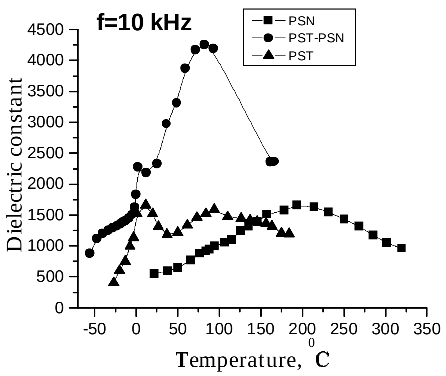

Fig. 1. Temperature dependence of the dielectric constants of PSN, PST-PSN and PST crystals at a frequency 10 kHz.

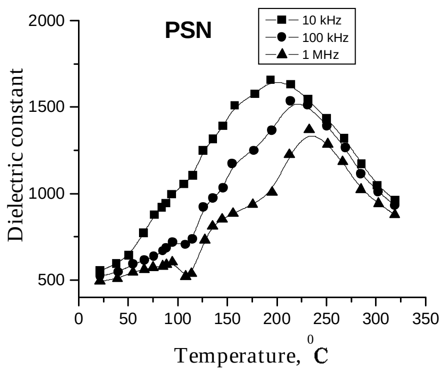

Fig. 2. Temperature dependence of the dielectric constant of PSN crystals at frequencies of 10 kHz, 100 kHz and 1 MHz.

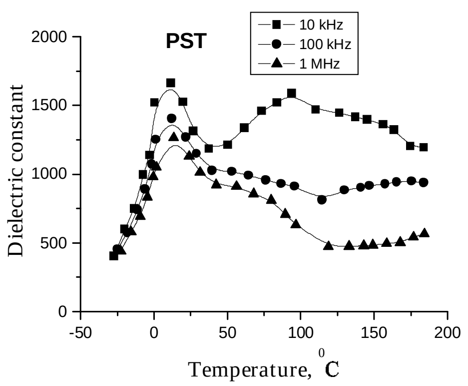

Fig. 3. Temperature dependence of the dielectric constant of PST crystals at frequencies of 10 kHz, 100 kHz and 1 MHz .

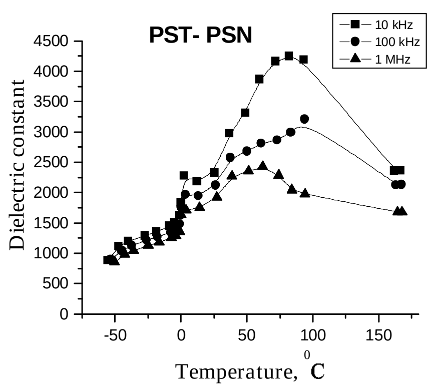

Fig. 4. Temperature dependence of the dielectric constant of PSN crystals at frequencies of 10 kHz, 100 kHz and 1 MHz.

With increasing measurement frequency, the temperature of the phase transition of PSN crystals moves to the higher temperatures (Fig. 2). At frequencies of 10 kHz, 100 kHz and 1 MHz it corresponds to 190 °C, 215 °C and 230 °C respectively. At the same time, the maximal value of ε decreases, as does the width of the temperature peak. For PST crystals (Fig. 3), a frequency shift of the phase transition temperature is not seen, but as for the PSN crystals the maximum value of ε decreases with increasing frequency. A clear tendency of the influence of the measurement frequency upon the PST-PSN crystals phase transition temperature cannot be seen in Fig. 4. At frequencies of 10 kHz, 100 kHz and 1 MHz, the phase transition of these crystals can be seen at temperatures of 80, 95 and 60 °C respectively. The decrease in the values of ε of these crystals with increasing frequency at the phase transition temperature remains the same as in the cases of PST and PSN crystals. Apparently, in order to examine the frequency dependence of the dielectric behaviour of the mixed crystals, measurements at frequencies lower than 100 kHz must be performed.

The dependence of the dielectric behavior of the mixed crystals upon their preliminary temperature treatment was also examined. For this purpose, PST-PSN crystals were initially heated from -55 to +170 °C, and after their cooling they were repeatedly heated from -50 to +325 °C. The temperature dependence of the dielectric constant for the initially heated (curve 1) and for the repeatedly heated (curve 2) PST-PSN mixed crystals, at a frequency of 10kHz, is shown in Fig. 5.

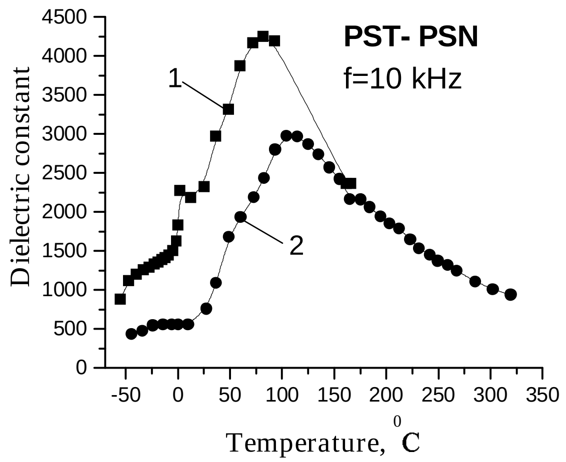

Fig. 5. Influence of the preliminary temperature treatment on the temperature dependence of the dielectric constant of PST-PSN crystals, at a frequency of 10 kHz.

Repeated heating of the crystals not only reduced the values of ε throughout the whole examined temperature range, but also shifted the phase transition temperature in relation to that of the initially heated crystal, by 40 °C towards higher temperatures. This tendency remained at frequencies of 100 kHz and 1 MHz. The initial heating of the mixed crystals changed the functional dependence of ε(T) at 15 °C, which is the phase transition temperature of the PST crystals (Fig. 4). At temperatures from -55 to +15 °C, ε(T) is an increasing function whereas from +15 to +25 °C it has a constant value. As a result of the temperature treatment, this observed effect disappears (Fig. 5).

4. Conclusions

Single crystals of mixed Lead Scandium Tantalate Niobate with the composition $Pb_2ScTa_{0.48}Nb_{0.52}O_6$ have been prepared using the high temperature solution growth method by spontaneous crystallization. X-ray phase analysis established the presence of a perovskite like phase belonging to the *Pm3m* space group, with a lattice constant of a = 4.0803 Å. The dielectric constant and dielectric losses have been investigated in the temperature range -55 to 325 °C, at three different frequencies of 10 kHz, 100 kHz and 1 MHz.

The results of the present investigations on mixed PST-PSN crystals can be useful in the production of capacitor materials for electronics.

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