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DIELECTRIC BEHAVIOR OF Sn DOPED AND ANNEALED FERROELECTRIC LEAD SCANDIUM TANTALATE SINGLE CRYSTALS

D. Kaisheva[*], D. Doshkova, B. Mihailova[a], M. Gospodinov[b]

South West University "Neophit Rilski", 66 Ivan Mihailov Street, 2700 Blagoevgrad, Bulgaria.
[a]Central Laboratory of Mineralogy and Crystallography, Bulgarian academy of Sciences, Acad. G. Bonchev Street, Building 107, 1113 Sofia, Bulgaria.
[b]Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.

The growth conditions of undoped Pb_2ScTaO_6 (PST) and Pb_2ScTaO_6 doped with Sn (PST:Sn) ferroelectric single crystals, produced by the high temperature solution method, were optimized. Elemental analysis of the doped crystals revealed their composition – $Pb_{1.89}Sn_{0.11}ScTaO_6$. X-ray diffraction analysis showed a perovskite type structure with a *Pm3m* space group and a lattice parameter a = 4.0749 Å. The influence of thermal treatment (annealing) and doping effects on the dielectric constant, dielectric losses and the real part of the conductivity have been investigated in the temperature range –30 to 200^{o}C, and in the frequency range 10 kHz to 1 MHz. The values of the dielectric constant of the PST crystals remained the same after thermal annealing, whereas they decreased after Sn doping in the phase transition temperature range of the PST single crystals. The real part of the conductivity rose with increasing temperature for all samples investigated.

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1. Introduction

Complex lead-based oxides with the general formula Pb(B′, B″)O_3 where B′ = Sc^{3+} and B″ = Ta^{5+} belong to the perovskite family and exhibit a ferroelectric-paraelectric phase transition with relaxor behaviour. These materials show low-frequency dielectric dispersion, a high electrostriction coefficient and switchable pyroelectric and piezoelectric properties [1-4]. $PbScTaO_6$ crystals are of special interest for various practical applications in pyroelectric detectors, electromechanical devices, capacitors, ultrasonic and medical devices, and as materials for information data storage [5]. It has been shown that the state of ordering of the two B site cations in the perovskite structure can be modified by suitable thermal treatment (annealing in different atmospheres) [6] and doping with different elements [7].

In the present paper, the influence of the annealing treatment in air and doping with Sn on the dielectric constant, dielectric losses and AC conductivity of PST single crystals will be discussed and analysed.

2. Experimental details

Pure polycrystalline perovskite Pb_2ScTaO_6 was synthesized by the solid state reaction of stoichiometric amounts of PbO (99.999%), Sc_2O_3 (99.99%), and Ta_2O_5 (99.99%), and further

[*] Corresponding author: darinakaisheva@yahoo.co.uk

annealing for 48 h. at 1150°C in an oxygen atmosphere. Undoped and Sn doped PST single crystals were grown by the high temperature solution growth method, using $PbO/PbF_2/B_2O_3$ flux (PbO: PbF_2: B_2O_3 = 0.75: 024: 0.1). The flux was mixed with the PST powder and SnO_2 in a 10:1 ratio (in the case of Sn-doped PST, the ratio was PST:SnO_2 = 0.9:0.1) and annealed at 1230 °C for 24 h. in air. The temperature was then reduced to 950 °C, and crystals with a typical size of 5×5×3 mm were obtained. EDAX analysis established 3.4 vol.% of Sn in the PST crystals.

For the dielectric measurements, the crystals were cut into flat-parallel plates, and silver electrodes were deposited on their opposite sides. The thicknesses of the samples were 1.100, 1.085 and 1.750 mm, respectively for the non-annealed PST, the annealed PST and the PST:Sn crystals. The dielectric measurements were made using a Hewlett-Packard 4275A RLC bridge, over a wide temperature range (-30 to +200 °C) and at 10 kHz, 100 kHz and 1 MHz frequencies.

3. Results and discussion

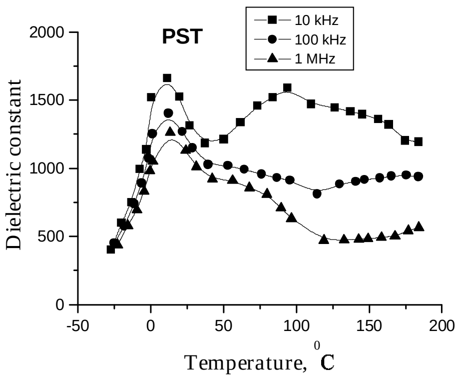

Fig. 1. Temperature dependence of the dielectric constant of PST crystals at frequencies of 10 kHz, 100 kHz and 1 MHz .

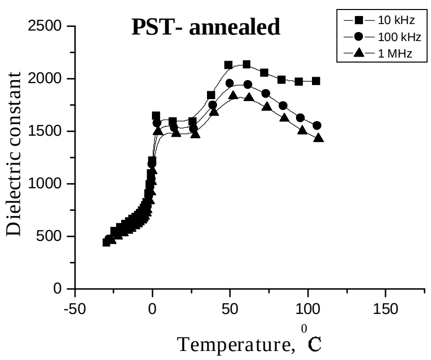

Fig. 2. Temperature dependence of the dielectric constant of annealed PST crystals at frequencies of 10 kHz, 100 kHz and 1 MHz.

Figure 1 shows the temperature dependence of the dielectric constant, ε, of the non-annealed PST crystal at 10 kHz, 100kHz and 1MHz frequencies. For all frequencies investigated, at a temperature of about 15 °C, we can see a clearly defined maximum in the dependence ε(T). The size of this diminishes with increasing frequency. It is evidence that at this temperature there is a ferroelectric to paraelectric phase transition for non-annealed PST crystals. However, annealing and doping can shift the maximum of the temperature dependence in the dielectric constant, as can be seen from a comparison of Figures 2 and 3.

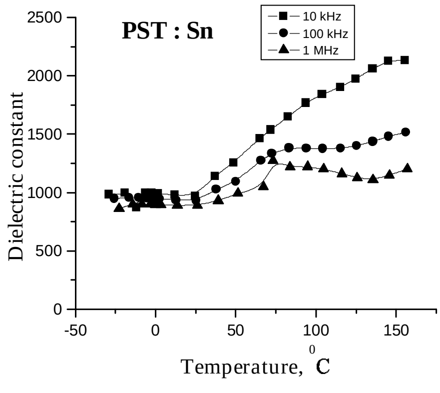

Fig. 3. Temperature dependence of the dielectric constant of PST:Sn crystals at frequencies of 10 kHz, 100 kHz and 1 MHz.

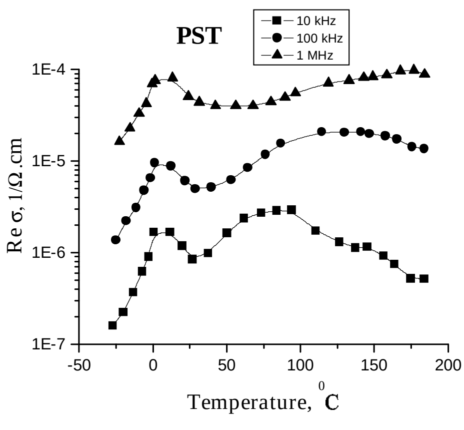

Fig. 4. Temperature dependence of the real part of the conductivity of PST crystals at frequencies of 10 kHz, 100 kHz and 1 MHz .

Annealing of the crystals (see Fig. 2) leads to a shift of the phase transition to higher temperatures. In the temperature range of 0 °C to 30 °C, the values of the dielectric constant remain constant. After that, ε increases with increasing temperature up to 65°C, for all measurement frequencies. Then the dielectric constant decreases up to the highest temperature range examined.

Doping with Sn (see Fig. 3) completely changes the dependence of ε(T) in comparison with non-annealed and annealed PST crystals. From -30 to +30 °C, the dielectric constant of the PST:Sn remains constant (approximately 1000). At higher temperatures, it starts to increase. A strong increase can be seen at the lowest frequency (10 kHz). At the highest temperature examined, the values of the dielectric constant for PST:Sn crystals are: 2200, 1500 and 1100 at 10 kHz, 100 kHz and 1 MHz frequencies, respectively.

Sn^{2+} has the same electron configuration of the outer shell as Pb^{2+}. Thus, Sn^{2+} and Pb^{2+} are supposed to have a similar affinity to form lone pair electron and similar interactions with the nearest oxygen atoms. However, Sn^{2+} and Pb^{2+} have different ionic radii. Therefore, doping with Sn should change substantially the tolerance factor of the perovskite, and the crystal lattice should be destroyed in the vicinity of the incorporated Sn atoms, thus affecting the ferroelectric properties

Annealing of PST crystals and doping with Sn lead to a significant decrease in the values of the dielectric losses. At a 10 kHz measurement frequency, this is valid in the temperature range -30 to +80 °C. At 1MHz frequency, it is valid from -75°C to the highest temperature examined. The values of the dielectric losses, tan(δ), for the annealed PST crystal and the PST:Sn crystals are approximately the same through the whole examined temperature range, while at 10 kHz frequency they increase from 0.03 (at -30 °C) to 0.14 (at 155 °C).

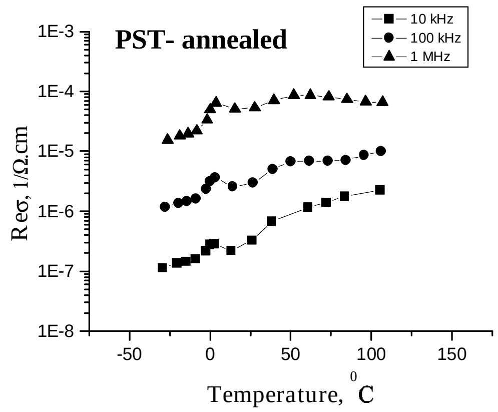

Fig. 5. Temperature dependence of the real part of the conductivity of annealed PST crystals at frequencies of 10 kHz, 100 kHz and 1 MHz .

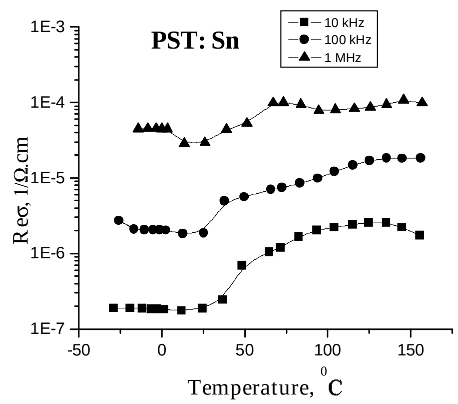

Fig. 6. Temperature dependence of the real part of the conductivity of PST:Sn crystals at frequencies of 10 kHz, 100 kHz and 1 MHz .

Figs. 4, 5 and 6 present the temperature dependences of the real part of the conductivity (Reσ) for non-annealed, annealed and doped with Sn PST single crystals, respectively. As shown, when the frequencies increase the Reσ values become larger for all crystals. For non-annealed and annealed PST crystals, there is a maximum at the temperature of the phase transition for all frequencies. However, this maximum is only very weakly present for the annealed PST crystal. At a frequency of 10 kHz, the conductivity of the non-annealed PST crystal remains larger in comparison with annealed and Sn-doped crystals, over the temperature range of -30 to +80 °C. At higher frequencies, the Reσ values increase with increasing temperature, for all samples.

4. Conclusions

Lead scandium tantalate single crystals doped with Sn have been prepared using the high temperature solution growth method, by spontaneous crystallization. The values of the dielectric constant of PST crystals stay the same after thermal annealing, whereas they decrease after Sn-doping in the phase transition temperature range of the PST single crystals. After that, the values of the dielectric constant of PST crystals become larger after thermal annealing as well as after doping with Sn. Furthermore, the annealing and doping effects can shift the phase transition to the higher temperatures. The conductivity, Reσ, increases with increasing temperature for all investigated samples.

The results presented on the influence of thermal annealing and Sn doping on the dielectric properties of PST ferroelectric crystals can be used to explain the relaxor behaviour of such materials, and for the optimisation of their properties in the desired direction.

Acknowledgements

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