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Growth of ferroelectric Pb_2ScTaO_6 single crystals in oxygen and hydrogen atmospheres, and investigation of their dielectric properties

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Pb_2ScTaO_6 single crystals are obtained by a high-temperature solution growth method, using a flux of composition $PbO:PbF_2:B_2O_3$=0.85:0.13:0.02. The crystal growth process is performed in the temperature range 1200 °C – 900 °C, in two steps with different gas atmospheres during the low temperature step. The dielectric measurements are performed in the frequency range 10 kHz – 1 MHz and the temperature range minus 40 °C to 60 °C. It is found that crystals prepared in oxygen and mixed oxygen/hydrogen atmosphere conditions possess more relaxor type behavior, with a diffuse ferroelectric phase transition at a lower temperature. Moreover the frequency dependence of the dielectric properties is stronger in these crystals.

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1. Introduction

The relaxor ferroelectrics with perovskite $AB^IB^{II}O_3$ type structures, such as lead scandium tantalate Pb_2ScTaO_6 (PST) crystals, are a broad class of materials in which the chemical disorder of the B^I and B^{II} sites positioning causes relaxor behavior [1]. B-site ordering in such complex perovskites has attracted considerable interest, due to the strong effects on the dielectric properties [2]. PST has been used for B-site structural ordering investigations, where the degree of ordering could be modified by thermal annealing following sintering at high temperature, allowing studies of the relationship between the structural order and ferroelectric properties [1-4].

In this paper, the influence of oxygen and a mixed oxygen/hydrogen atmosphere during the crystal growth process on the dielectric permittivity and dielectrical losses of PST crystals is reported.

2. Experimental

Single crystals of Pb_2ScTaO_6 were prepared by the high-temperature solution growth method (HTSG), using a flux with a composition ratio by weight of $PbO:PbF_2:B_2O_3$=0.85:0.13:0.02.

Single phase Pb_2ScTaO_6 (PST) material was synthesized preliminary from stoichiometric quantities of PbO, Sc_2O_3 and Ta_2O_5. Platinum crucibles with a volume of 250 ml and a Pt lid, which semi-hermetically seal the crucible, were used for the growing process. The synthesized material and the flux were mixed in a proportion of 1:5 and heated to 1200 °C at a rate of 50 °C/h. At that temperature, the mixture was kept for 48h, for soaking. After the soaking, a cooling program was commenced. The cooling process was performed in the temperature range 1200 °C – 900 °C in two steps: from 1200 °C to 950 °C in air, with a cooling velocity of 1 ^{0}C/h and from 950 °C to 900 °C. Two different gas atmospheres were used: (i) 100% oxygen atmosphere (PST:O_2) and (ii) 80% oxygen and 20% hydrogen atmosphere (PST:H_2). The cooling velocity from 950 ^{o}C to 900 ^{o}C temperature range was 0.3 °C /h. After the cooling, the flux was decanted from the crucible and the PST crystals were extracted from the walls and bottom of it. The crystals obtained had a cubic habit and a typical crystal size of 8×8×8 mm^3. The crystals were aligned along the (100) direction. The chemical composition was determined by electron microprobe analysis, with a Cameca Microbeam SX 100 electron probe microanalyser.

For dielectric measurements, samples with dimensions 8×8×0.7 mm were prepared and Ag electrode contacts were made on the surfaces. The dielectric properties were measured as a function of temperature and frequency, using a HP 4275 Precision LCR multi-frequency bridge meter with a relative error of 2 %. The applied voltage was 1 V. For temperature measurements, a custom-made

cryostat was used. The dielectric permittivity and dielectric loss were measured in the frequency range 10 kHz - 1 MHz at temperatures between 60 °C and minus 40 °C.

3. Results and discussion

The dielectric permittivity was measured as a function of temperature, to evaluate the diffuseness of the paraelectric to ferroelectric phase transition. The temperature dependences of the dielectric permittivity at different frequencies for PST grown in the air, PST:O_2 grown in an oxygen atmosphere and PST:H_2 grown in a mixed oxygen/hydrogen atmosphere are shown in Figs. 1 to 3 respectively.

As seen from Fig. 1, the phase transition for crystal samples, grown in air, occurred at 16-20 °C, depending on the frequency. The behavior of the dielectric permittivity of PST:O_2, however, is significantly different. The phase transition is shifted to lower temperatures. The broad maximum near -11°C to 0.5 °C at 10 kHz, 40 kHz, 100 kHz, 1 MHz, with a well- pronounced diffuse character as well as a substantial frequency dispersion of the dielectric permittivity' indicates unambiguously that the PST grown in an oxygen atmosphere is a relaxor ferroelectric.

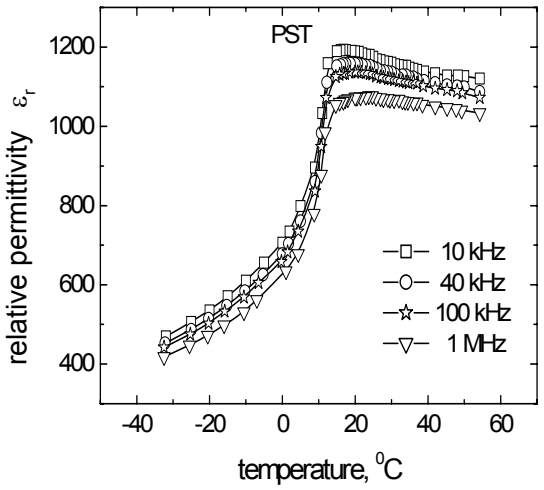

Fig.1. Temperature dependence of dielectric constant at different frequencies for PST crystals.

With increasing frequency, the phase transition is shifted to the higher temperatures, and the dielectric constant values decreased, which is also typical for relaxor ferroelectrics. The strong dielectric dispersion at the temperatures below the phase transition temperature indicates that PST:O_2 strongly affects the dielectric permittivity behavior and modifies the type of the phase transition.

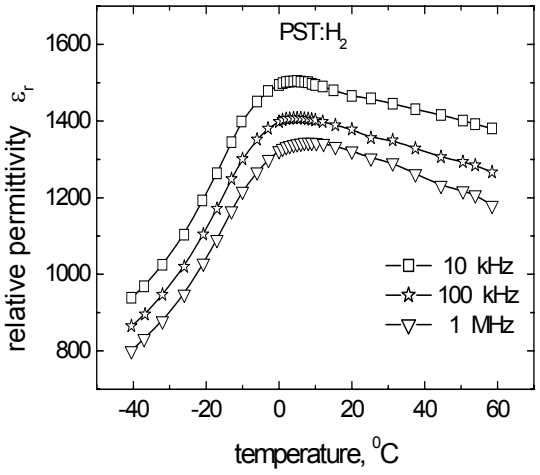

Fig. 2. Temperature dependence of dielectric constant at different frequencies, for PST:O_2 crystals.

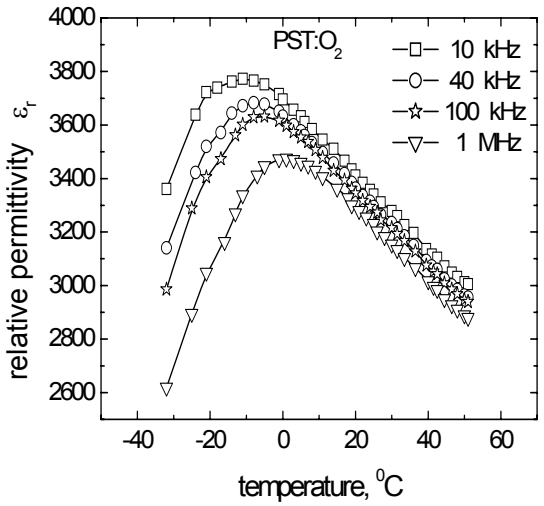

Fig. 3. Temperature dependence of dielectric constant at different frequencies for PST:H_2 crystals.

The dependence of the dielectric permittivity on the temperature at different frequencies, for crystals grown in mixed oxygen/ hydrogen atmospheres, is similar to that of crystals grown in an oxygen atmosphere. The phase transition temperature was from 2°C to 7°C. With increased frequency, T_m (the temperature of maximum permittivity) is shifted to higher temperatures, and the magnitude of the dielectric constant maximum was reduced. Such behavior is characteristic of relaxor ferroelectrics [5].

The dielectric losses (tan δ) dependence for PST:O_2 crystals is quite different from those of PST grown in air, as seen in Fig. 4.

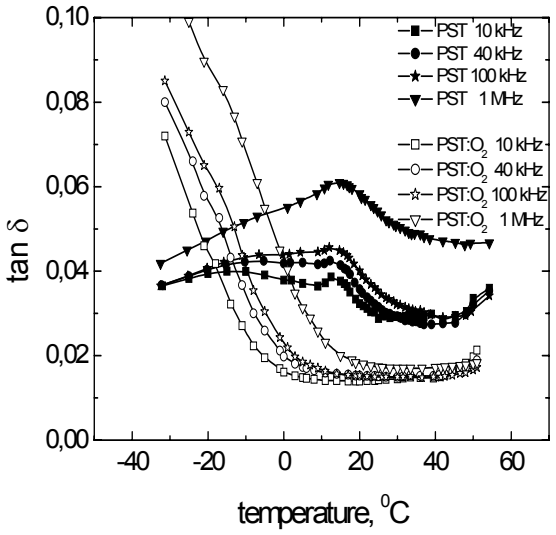

Fig. 4. Temperature dependence of the dielectric losses, tan δ, at different frequencies for PST and PST:O_2 crystals.

The tg δ values increase with increasing frequency, which is also characteristic for the relaxors. PST:H_2 samples grown in a mixed oxygen/hydrogen atmosphere show a similar behavior to those grown only in an oxygen atmosphere.

The observed dielectric non-linearity of the samples annealed in oxygen and in an oxygen/hydrogen atmosphere is probably due to the domain wall dynamics and/or to the interface boundaries [6-8]. Structural and optical studies are under way, in order to clarify the observed behavior of the dielectric properties of PST crystals prepared under different conditions.

4. Conclusions

The presented results indicate that PST crystals, grown by a HTSG method in different atmospheres (pure oxygen and an oxygen/hydrogen mixture) show quite different dielectric behavior than the samples, grown in air. The temperatures of the ferroelectric phase transition are lower, the dielectric constant values are higher and the frequency dependence of the dielectric properties is stronger than for PST grown in air.

These experimental results show that by using the appropriate temperature and gas atmosphere conditions during the PST crystal growth, the chemical disorder can be tuned and crystals with more or less relaxor-type behavior can be prepared.

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