TEMPERATURE DEPENCECE DIELECTRIC
BEHAVIOR OF Ge DOPED LEAD SCANDIUM TANTALALATE FERROELECTRIC

Mr. CHANDRA KR.DIXIT¹ and Mr. A.K. SRIVASTAVA²

¹Department of Physics Feroze Gandhi Institute of Enng. & Technology
Raebareli -229001 U.P
²Central Laboratory of Material Science, Kamla Nehru Institute of Physical & Social Sciences Sultanpur -228001 U.P
Email: ckparadise@gmail.com

ABSTRACT

The doped of Pb₂SeTaO₆ with Ge ferroelectrics, produced by high temperature solution method. We measure dielectric constant, dielectric loss and conductivity in the temperature range -30⁰C to 200⁰C and frequency range 10 kHz, 100 kHz and 1 MHz. The value of dielectric constant of the PST crystal remained the same after thermal annealing whereas they decreased after Ge doping in the Phase Transition temperature range of PST single crystal. All sample investigated for conductivity with increasing temperature.

KEY WORDS: Dielectric loss, Dielectric constant, conductivity, ferroelectrics.

1. INTRODUCTION

Complex lead-based oxides with the general formula Pb (B⁺,B”⁺)O₃ where
B⁺=Sc³⁺ and B”⁺=Ta⁵⁺ 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 properties[1-4]. Pb₂SeTaO₆ crystal are of special interest for various practical applications in pyroelectrical detectors, electrochemical 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 perovksite 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 Ge in the dielectric constant, dielectric loss and ferroelectric
conductivity of PST single crystals will be discussed and analysed.

2. EXPERIMENTAL

Pure crystalline perovskite Pb₂ScTaO₆ was synthesized by the solid state
reaction of stoichiometric amounts of PbO (99.999%), Sc₂O₃ (99.99%) and
Ta₂O₅(99.99%) and further annealing for 48 h.at 1150°C in an oxygen
atmosphere. Undoped and Ge doped PST single crystals grown by the high
temperature solution growth method using PbO/PbF₂/B₂O₃ flux (PbO:
PbF₂:B₂O₃=0.75 :0240.1).The flux was mixed with the PST powder and GeO₂ in
a 10:1 ratio in the case of Ge-doped PST, the ratio was PST:GeO₂=0.9:0.1) and
annealed at 1230°C for 24h. 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 Ge 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
thickness of the samples was 1.100, 1.085 and 1.750 mm, respectively for the
non-annealed PST, the annealed PST and the PST: Ge crystals.

The dielectric measurements were made using a Hewlett-Packard 4275A
RLC bridges, over a wide temperature range (-30 to +200°C) and at 10 kHz,
100 kHz and 1 MHz frequencies.
3. RESULT 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 PST crystals at Frequencies of 10 KHz, 100 kHz and 1 MHz
Figure 1 shows the temperature dependence of the dielectric constant, $\varepsilon$ of the non-annealed PST crystal at 10 kHz, 100 kHz and 1 MHz frequencies. For all frequencies investigated, at a temperature of about 15°C, we can see a clearly defined maximum in the dependence $\varepsilon(T)$. 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 fig.2 and fig.3.

![Fig. 3: Temperature dependence of the dielectric constant of PST crystals at frequencies of 10 KHz, 100 kHz and 1 MHz](image-url)
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, $\varepsilon$ increases with increasing temperature up to 65°C, for all measurements frequencies. Then the dielectric constant decreases up to the highest temperature range examined.

Doping with Ge (see fig.3) completely changes the dependence of $\varepsilon(T)$ in comparison with non-annealed and annealed PST crystals. From -30 to +30°C, the dielectric constant of the PST: Ge 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: Ge crystals are: 2200, 1500 and 1100 at 10 kHz, 100 kHz and 1 MHz frequencies, respectively.
Annealing of PST crystals and doping with Ge lead to a significant decrease in the values of the dielectric losses. At a 10 kHz measurements frequency, this is valid in the temperature range -30 to +80°C at 1 MHz 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-Ge 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 annealed PST: Ge crystals at frequencies of 10 kHz, 100 kHz and 1 MHz

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

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

The results presented on the influence of thermal annealing and Ge 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.

5. REFERENCES


ACKNOWLEDGEMENTS

This work was partially supported by the Department of Science & Technology New Delhi also and Indian Institute of Technology Kanpur U.P.