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Phase transitions and electrical properties of High-Pressure High-Temperature treated bismuth oxide based material

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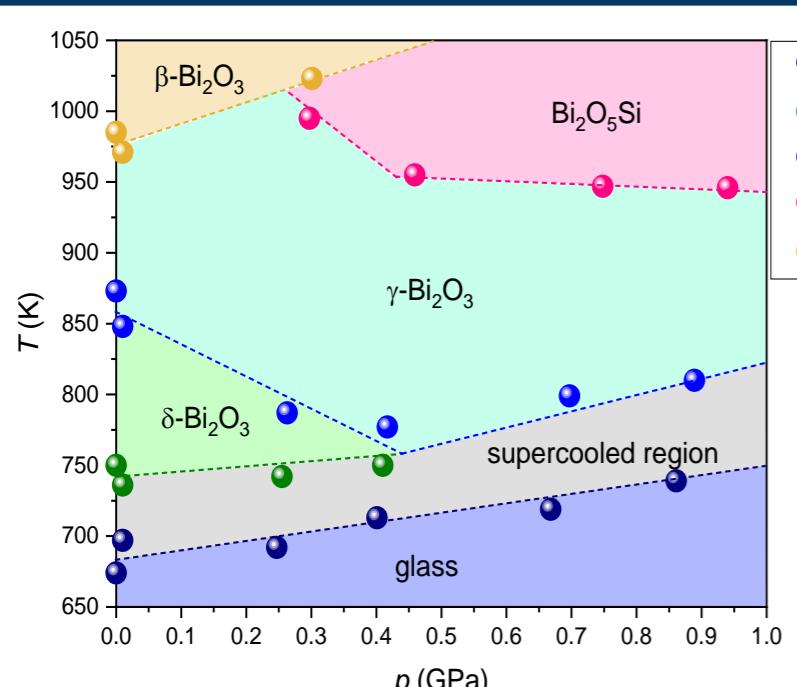
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1. Introduction

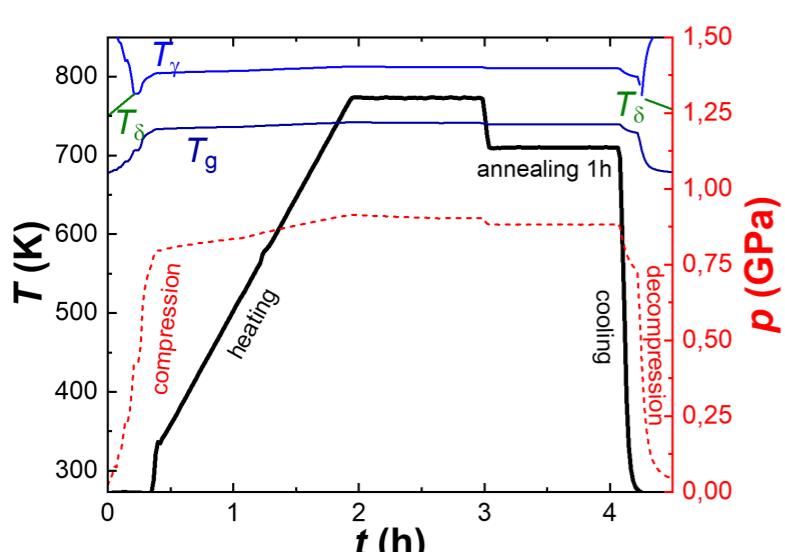
HPHT (high pressure high temperature) annealing slightly below the glass temperature (T_g) at pressure of just 1 GPa may lead to unusual properties, that are preserved after decompressing. In IHPP PAS there are HPHT processors operating at pressures up to 2.2 GPa at temperatures up to 1600°C with volumes up to 1 dm³⁽¹⁾. In our previous studies⁽¹⁾ HPHT treatment of electron conducting glassy materials lead to simultaneous increase of electrical conductivity of 1-2 orders of magnitude and reduction of activation energy.

Bismuth Sesquioxide is a polymorphous material exhibiting properties of either an oxygen (super)ionic conductor or a semiconductor⁽²⁾. It is potential candidate for use in Solid Oxide Fuel Cells due to δ -Bi₂O₃ superionic conductor properties⁽²⁾⁽³⁾. Previously properties of bismuth oxide (III) have been studied either at near atmospheric pressure or on already crystalline material⁽⁴⁾. Aim of this study was to observe whether HPHT treatment of Bi₂O₃ based glass could improve it's electrical properties.

2. Phase transitions

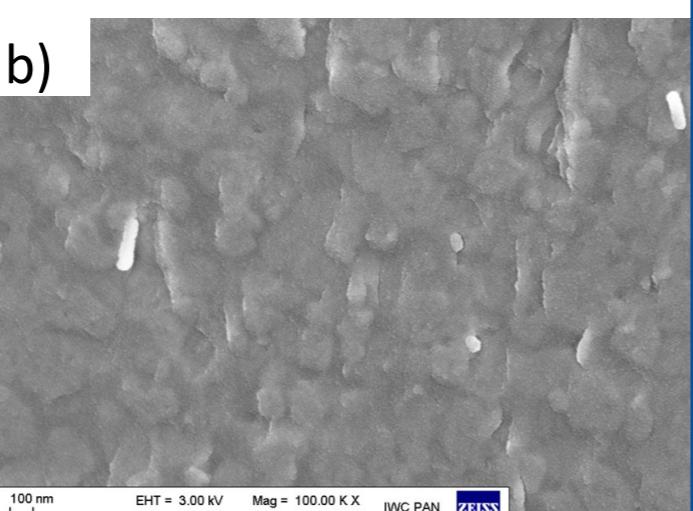
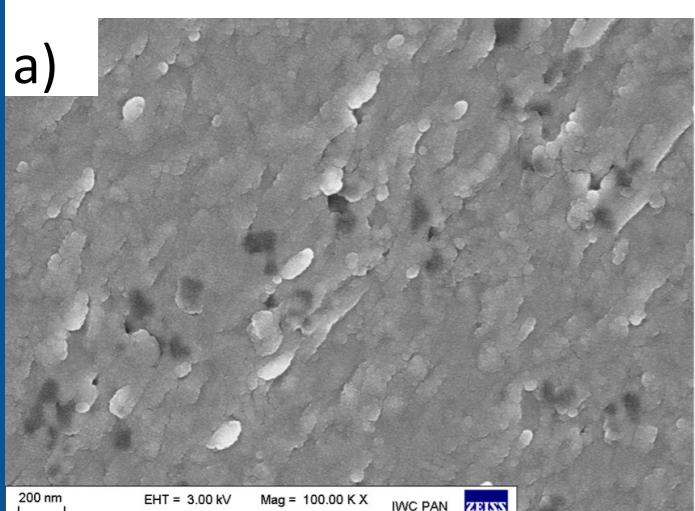


(Differential) Thermal Analysis at different pressures was utilized in conjunction with ex-situ X-Ray Diffraction to identify phase transitions. Based on those results P - T map of phase transitions was proposed.

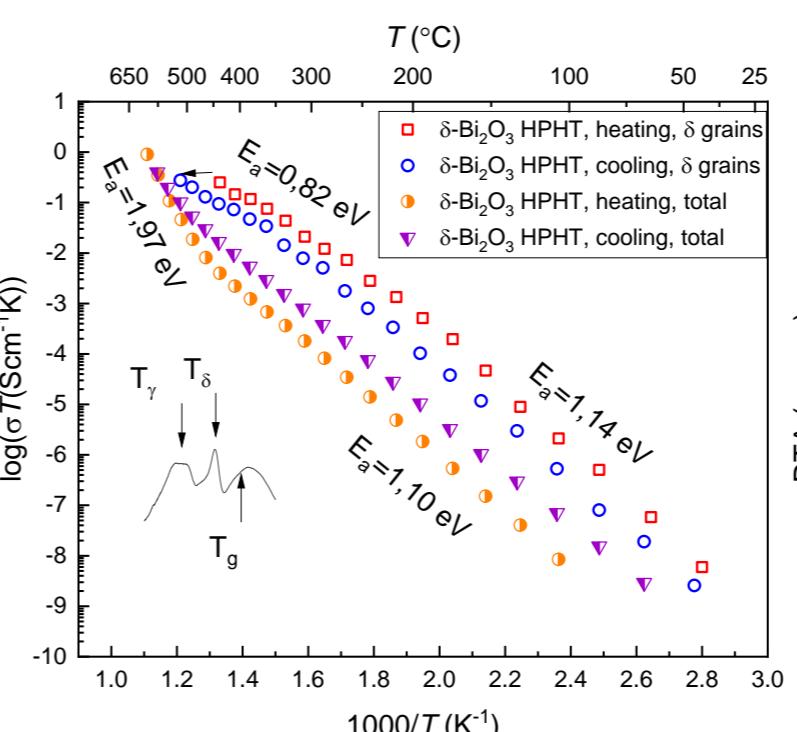
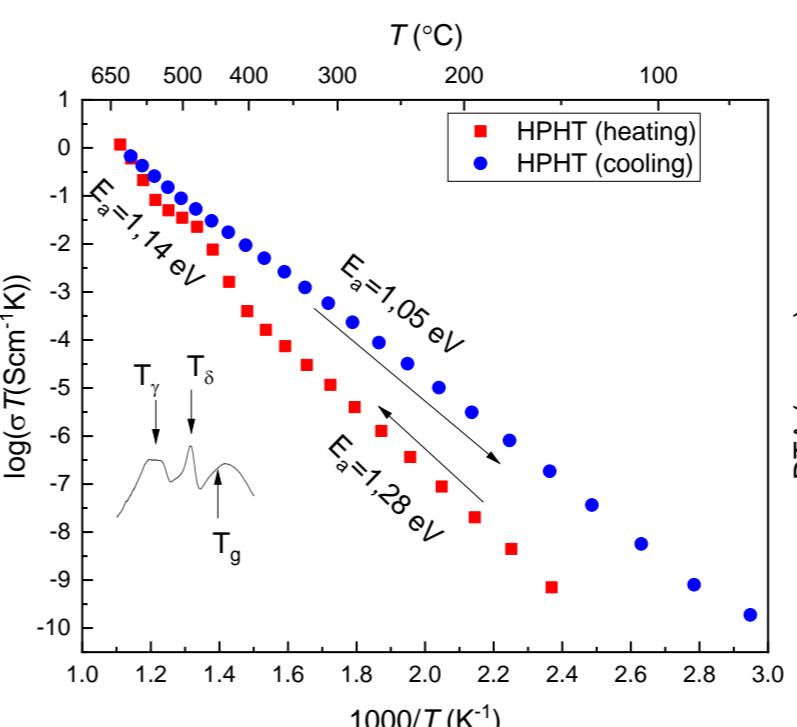


HPHT treatment was performed on glass ternary system and on thermally nanocrystallized at atmospheric pressure (HT) δ -Bi₂O₃.

Scanning Electron Microscopy was performed on material a) before and b) after HPHT.



3. Electrical properties



Electric conductivity was measured with Impedance Spectroscopy.

Two HPHT treated samples were compared:

1. Glass Bi₂O₃, HPHT treated for 1h at 250 MPa.

2. Nano δ -Bi₂O₃ further HPHT treated at 800MPa.

HPHT treated glass formed nanocomposite consisting of δ -Bi₂O₃ and Bi₂O₅Si with γ -Bi₂O₃ admixture embedded in SiO₂-Al₂O₃ glassy matrix.

In HT nano- δ -Bi₂O₃ phase conductivity of δ grains was clearly distinguishable from conductivity of whole sample.

In both cases further thermal treatment permanently increased total conductivity of the samples.

However, intra-grain conductivity of nano- δ -Bi₂O₃ was reduced.

4. Conclusions

- P - T map of phase transitions was obtained and utilized for HPHT treatment of selected crystalline phase (δ -Bi₂O₃).
- HPHT treatment allowed for better separation of polarization processes in nanocomposites containing δ -Bi₂O₃ grains and for easier determination of intragrain O²⁻ conductivity.
- The values of O²⁻ conductivity equal to: $4 \cdot 10^{-3}$ S/cm (grains of δ phase) and $4.5 \cdot 10^{-4}$ S/cm (total) at quite moderate temperature (600°C) are very promising from applications point of view.

5. Acknowledgments

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6. References

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