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Electronic structure and chemical segregation process induced by redox conditions in PbHfO3 single crystal.

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The miniaturization of electronic devices initiated by the discovery of the transistor has spawned the need for the development of advanced materials to build new electrical circuits responsible for storing energy. A high energy storage density is required in modern practical applications, such as hybrid or electric cars, and is offered by antiferroelectric materials. Representatives of this type of material include lead zirconate PbZrO3, silver niobate AgNbO3, and lead hafniate PbHfO3 [1, 2, 3]. The first two materials are well-studied in terms of electrical, structural, and electronic properties compared to the latter. The use of lead hafnate PbHfO3 for application purposes is mainly based on studies of polycrystalline ceramics. This significantly limits the possibility of conducting a reliable analysis of physical properties reserved for single crystal materials.

The aim of our research was to grow $PbHfO_3$ single crystals. Initial electronic structure analyses performed using standard XPS showed interesting changes in the Pb/Hf ratio (Figure 1). To obtain a detailed analysis of the ion segregation on the PbHfO3 surface, synchrotron radiation investigations were needed. The electronic structure studies were carried out in the temperature range RT - 250 C. This range takes into account two phase transition temperatures [2]. The changes in the shape of the electronic states of the Pb4f and Hf4f core lines and the valence band were associated with the segregation processes of the crystal components in the surface layer. The changes in the chemical composition ratio Pb/Hf indicate the migration of PbO complex along the easy diffusion path with increasing temperature.

A detailed analysis of Pb4f, O1s, and Hf4f and the valence band indicates a redistribution of the atomic arrangement in the surface layer in accordance with ionic diffusion from the bulk material. In particular, resonance photoemission studies have revealed a contribution of the *d* electrons of lead and hafnium atoms to the valence band structure in the phase transition region.

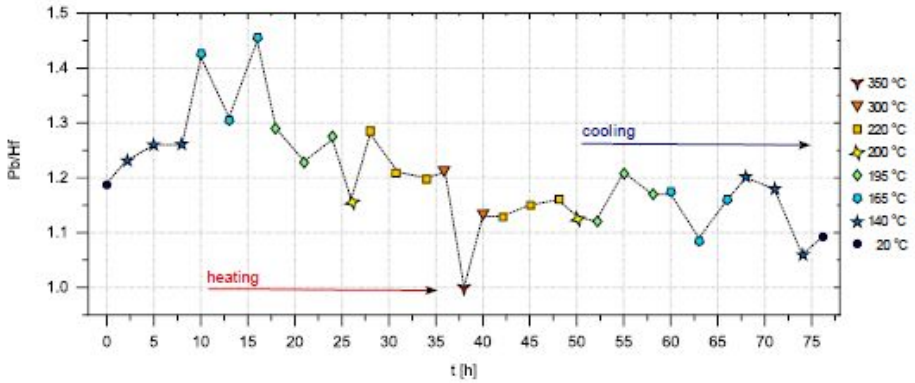

Figure 1. The changes of atomic concentration in the Pb/Hf ratio obtained for the *as grown* PbHfO3 single crystal in wide range of temperatures obtained from the XPS study.

References

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