of electronic properties. Since the simple experimental equipment mentioned above is probably available world wide and since the software is free of charge an unlimited use of the procedure we will teach here, seems possible.

[1] C. Huebschle, P. Luger, B. Dittrich, J. Appl. Cryst. (2007)40, 623-627.

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Properties of $BiFeO_3$ and $Bi_{0.7}La_{0.3}FeO_3$ nanopowders obtained by mechanosynthesis

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The search for materials exhibiting both electric and magnetic long-range order at room temperature, driven by the perspective applications in information storage and sensors, renewed the interest in $BiFeO_3$. At room temperature $BiFeO_3$ has rhombohedrally distorted cubic perovskite cell (R3c) [1] and the antiferromagnetic properties are related to G-type ordering with a cycloid modulation (62 nm) apparent down to 5 K [2]. Due to the due to long-range spin arrangement one may expect the magnetic properties of $BiFeO_3$ to be size-dependent. We expected that the decrease in the particle size below the periodicity of cycloid modulation will modify considerably the magnetic properties. Recently nanosize powders (obtained by glycine combustion synthesis) were reported to exhibit ferromagnetic hysteresis loops at room temperature [3]. We studied the magnetic properties of $BiFeO_3$ and $Bi_{0.7}La_{0.3}FeO_3$ nanosize powders produced by mechanical synthesis from respective oxides at room temperature. In $Bi_{0.7}La_{0.3}FeO_3$ the ferroelectric Curie temperature T_C is close to the magnetic Néel temperature ($T_N \approx$ 640 K) [4], whereas $T_C \approx$ 1100 K for $BiFeO_3$. The nanopowders were prepared by mechanically triggered room temperature synthesis from commercially available oxides Bi_2O_3, Fe_2O_3, La_2O_3 (99% purity from Aldrich) in a SPEX 8000 Mixer Mill. The batch contained ～6g of the oxide powders in stoichiometric ratio. The weight ratio of the stainless steel balls to the oxidesamounts to 2:1. The process was controlled by XRD and the powder was characterized by TEM. Magnetic properties were measured with Oxford Instruments Ltd. MagLab 2000 magnetometer in the temperature range 2 - 350 K. The temperature variation of the magnetization was measured in zero field cooling (ZFC) and field cooling (FC) experiments, whereas the magnetization loops were recorded at constant temperature with magnetic field applied step by step. The powders obtained after 120 h milling of the oxides were found to exhibit rhombohedrally distorted perovskite structure and TEM observations show that the powder forms irregular 100-150 nm loosely packed agglomerates composed of oval 10-30 nm grains. The nanograins exhibit core-shell structure with crystalline core surrounded by a disordered shell (1-2 nm thick). Thermal treatment (1 h at 500℃) results in a disappearance of the shell and an increase in the grain size to 40-50 nm. BiFeO3 and $Bi_{0.7}La_{0.3}FeO_3$ nanopowders with core-shell structure of the grains were found to exhibit field-dependent $1/\chi(T)$ anomaly at ～8K in ZFC measurements. A continuous increase in values was observed on FC-measurements down to 2K. For annealed BiFeO3 powder (grains without disordered shell) a broad $1/\chi(T)$ anomaly at ～94K was found in ZFC experiments; for $Bi_{0.7}La_{0.3}FeO$ the anomaly was found to be shifted towards lower temperature. A continuous increase in χ value was observed in FC experiments down to 2K, whereas for $Bi_{0.7}La_{0.3}$ FeO_3 the χ values slightly change with temperature. To check whether the disturbance in the long-range cycloid spin arrangement in $BiFeO_3$ type multiferroics can result in an increase in magnetization and in a nonlinear field dependence of magnetization we studied the field dependences of magnetization M(H) for the prepared nanopowders. Magnetic hysteresis loops were observed at low temperatures for $BiFeO_3$ and $Bi_{0.7}La_{0.3}FeO_3$ nanograins both as-prepared and annealed. The magnetization loops were not really saturated which points to basic antiferromagnetic nature. We found that the annealing decreases considerably the magnetization. Moreover, the coercive field of $Bi_{0.7}La_{0.3}FeO_3$ was found to be higher than that of $BiFeO_3$. The improvement of magnetization in nanosize particles of $BiFeO_3$ and $Bi_{0.7}La_{0.3}FeO_3$ obtained by mechanical activation of respective oxides we would like to relate both to:

i) An incomplete rotation of the spins along the direction of the wave vector (62nm modulation length of the cycloid),

ii) An increase in the spin canting due to the strain extended by the grain shell (which gives rise to ferromagnetism).

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References

[1] P. Fischer, M. Po?omska, I. Sosnowska, M. Szyma?ski, J. Phys. C: Solid St. Phys. **13** (1980) 1931

[2] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, J. Phys. C: Solid State Phys. **15** (1982) 4835.

[3] R. Mazumder, P.S. Devi, D. Bhattacharya, P. Choudhury, A. Sen, M. Reja, Appl. Phys. Lett. **91**(2007) 062510.

[4] M. Po?omska, W. Kaczmarek, Z. Paj?k, phys. stat. sol (a) **23**(1974)567