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Application for beam time at ESRF – Experimental Method

Proposal Summary (should state the aims and scientific basis of the proposal):

The research will be devoted to study of local structure of ternary tellurides of the system Ge-Bi-Te, namely to compounds **$Ge_8Bi_2Te_{11}$, $Ge_2Bi_2Te_5$ and to $GeBi_2Te_4$.** The Sb containing analogy of these compounds ($Ge_8Sb_2Te_{11}$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$) have been widely studied and used as phase change memory materials (PCMM) in DVD and Blu-ray discs and also in electrical non-volatile memories (PC RAM) [1-6]. The local structure of these Ge-Sb-Te compounds was also studied several times (see, e.g. [1, 2, 7-10] and papers cited). The X-ray bands of Te and Sb are unfortunately overlapping and to distinguish between the positions and coordination of Sb and Te is difficult. Such data are important for determination of the occupation of individual crystal positions by specific atoms in cubic metastable crystals of Ge-Sb-Te system compounds and for explanation of fast crystallization processes in PCMM. The present model of the structure of some PCMM of Ge-Sb-Te system is based on X-ray diffraction that also cannot exactly distinguish between the Sb and Te positions. The Ge-Bi-Te system is isostructural with Ge-Sb-Te system [7, 11] and the Bi and Te atoms can be easily distinguished. Even more, the compounds of Ge-Bi-Te system, e.g. $Ge_8Bi_2Te_{11}$ belong according to our results to PCMM as well, similarly to $Ge_8Sb_2Te_{11}$ that is is already used in commercial Blu-ray discs with capacity of 100Gb.

The results of the EXAFS and XANES studies can help to improve the models of the structure and the crystallization of PCMM generally. The results of EXAFS measurements of these compounds can also help for understanding of the problem of easy doping (alloying) of PCMM in very broad composition regions without abrupt changes of their structure and properties. There is also further reason; several materials from Ge-Bi-Ch system, where Ch is for chalcogen, are plasmonic materials and topological insulators [12] that very promising materials and are studied also in our group. The results obtained can help to understand their structure and properties.

The aim of project is to obtain clear information about local structure of studied systems, to add new results for elucidation and future prediction of PCMM, to help understood fast crystallization of PCMM and, possibly, to improve the model of fast phase changes. They also connect the research of these materials with basic research of new topological insulators and plasmonic materials. The last ones can extend the work of optical elements to sub-wavelengths size. The results will deepen the understanding of the structural changes in PCMM-like plasmonics materials and in topological insulators.

Scientific background:

The proposer has extensive and long-time experience with study of structure and properties of chalcogenides including PCMM and many Bi chalcogenides [13]. The co-proposer (Dr. M. Krbal) worked for several years in France and Japan and used the synchrotron facilities of ESRF and of Japanese Spring8 for many years. He has also a good experience with interpretation of obtained data, with modelling and with theoretical calculations. The PCMM have been used for optical data storage and also for electrical storage (phase change random access memories, PCRAM) for mobile facilities. It is supposed that they will soon replace the "flash" memories being faster and having lower power consumption and lower sizes. The research of new materials and of basic properties of PCMM is still very intensive; the processes during writing and erasing are still not fully clear. The present proposal wants to contribute to their understanding.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) :

We plan to collect Ge, Bi, Te, K-edge XAS spectra for $Ge_8Bi_2Te_{11}$, $GeBi_2Te_4$ and $GeBi_4Te_7$ as deposited amorphous and crystalline thin films using a transmission mode at 10K (cryostat is required) and at room temperature. If Bi: K-edge is not possible to probe it because of high energy (90keV), Bi:L_1-edge (16.4keV) provides the same information and can be potentially measured using the Ge: K-edge setup. Due to different selection rules, using a fluorescence mode we plan to collect L_3 –edge XANES spectra of Bi and Te (4.3keV) to obtain complementary information about the structure (Bi:L_3-edge {13.42keV} can be collected in the transmission mode together with Bi:L_1-edge). Samples will be deposited on Al-foil using the flash-evaporation and the pulse laser deposition techniques. The part of the as deposited samples will be crystallized in Ar atmosphere. The samples on Al will be stacked to reach unit edge jump for each element. Laser re-amorphization is only possible for samples d < 40nm. In order to measure the re-amorphized material, it will be necessary to carry out the experiment in a fluorescence mode using a detector that enables us to collect Ge:K- Bi:K (Bi:$L_{1,3}$)- and Te:K(Te:$L_{1,3}$)- edges spectra (the HP-Ge detector?). Samples will be deposited on SiO_2 glass substrates. The thin films will be coated to prevent air oxidation when re-amorphized by laser pulses using a KrF laser.

Beamline(s) and beam time requested with justification :

We ask for beamlines: BM08 or BM23. We will need a sufficient energy to probe Ge:K-, Te:K-, Bi:K- edges of studied systems. **Time requested:** Initial set up including crystal settings, energy calibration, setting up detectors for transmission and fluorescence measurements and test measurements is expected to require about 240 minutes. To obtain good data quality using the transmission mode, the measurement will take about 30 min per a loop (1 EXAFS spectrum) – 18+6(Bi:L_3) 24 hrs. in total: both as-deposited and crystallized films measured at 10K and at room temperature. The measurements will require 2 cooling-heating loops-4 hrs. are estimated. Edge switching from Ge:K-edge to Te:K-edge and Bi:K-edge and Te:L_3 is considered to consume about to 3 hrs. The Te K-edges are expected to be measured at the same energy, Bi-L edge. The switch between the transmission mode to fluorescence mode will take about 1 hr. To collect a good data quality using the fluorescence mode we request 3 hrs. per one EXAFS spectrum 3x3x3=27 hrs. To be able to compare XANES spectra for as-deposited, crystallized and laser re-amorphized samples, we need to collect XANES spectra for as-deposited and crystalline samples. Each XANES spectrum requires 1 h: 18x1 = 18hrs.
We request: 4+24 +4+3+1+18+27+9 =72 hrs. in total 9 shifts.

Results expected and their significance in the respective field of research :

The Ge-Bi-Te compounds or alloys $Ge_8Bi_2Te_{11}$, $GeBi_2Te_4$ and $GeBi_4Te_7$ are perspective as PCMM, they can also serve as model materials. The study of their local structure, coordination of individual atoms etc. will help to elucidate the mechanisms and structural background of fast phase and structural changes. It will also help to predict new PCMM. The PCMM are perspective also as topological insulators and plasmonics materials with many perspective applications in sub wavelength optics, but still not very well understood.

References

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