# Final report of OTKA project PD 111756

In this project we aimed to study two material families: narrow band gap Mott insulators with lacunar spinel structure and semiconductors with strong spin-orbit interaction; both of which are promising for future applications in information technologies. Below the achievements of the project are described in details in two separate sections according to the material families.

The scientific results have been summarized in 17 manuscripts, so far, out of which **15 papers** have already been published in high rank international journals such as Nature Materials, Physical Review Letter, and Scientific Reports. Their **cumulative impact factor** is **87.1**.

**Scientific results related to lacunar spinel Mott insulators**

The lattice dynamics and charge excitations were studied in $GaV_4S_8$ and $GeV_4S_8$ by measuring their reflectivity from far-infrared to ultra-violet energy region at various temperatures from room temperature and down to 5 K [3, 10]. Additional Raman scattering experiments were performed on $GaV_4S_8$ [10]. Based on the selection rules we could assign the different optical phonon modes and compared their frequencies with ab-initio calculations. We also identified the phonon modes which are involved in the ferroelectric phase transition. Our experiments evidenced the redistribution of the spectral weight around the Mott gap upon the Jahn-Teller and the magnetic phase transitions [3]. We found that in $GaV_4S_8$ the size of the Mott gap determined from the optical spectroscopy is in agreement with that of deduced from the temperature dependence of the resistivity above the Jahn-Teller transition [9].

The temperature vs. magnetic field phase diagram of $GaV_4S_8$ was determined based on specific heat [9], magnetization [4, 9, 16], ac magnetic susceptibility [4] and electric polarization [9, 13] measurements. We identified an unusual Jahn-Teller phase transition, which gives rise to sizeable electric polarization due to the non-centrosymmetric crystal structure of $GaV_4S_8$ [9, 13]. We found that $GaV_4S_8$ is a multiferroic compound since several magnetic phases are detected in its polar phase [9, 13, 16]. Furthermore, the polar and magnetic order parameters are not independent of each other but they are strongly coupled and the magnitude of the ferroelectric polarization changes depending on the magnetic phases [9, 13]. Upon the magnetic phase transitions we observed slow relaxations, which together with the small critical fields indicated the rearrangement of large scale spin structures [4].

Using small angle neutron scattering (SANS) and magnetic force microscopy (MFM) we assigned the magnetic phases to a spin cycloidal, a magnetic skyrmion lattice and a ferromagnetic phase [2, 16]. While the cycloidal order, where the spins are rotated in a plane containing the modulation vector, has been well known, our experiment evidenced the existence of Néel skyrmion lattice in a bulk material for the first time. Néel skyrmions, which are hedgehog-like spin textures, possess non-trivial polarization pattern in $GaV_4S_8$ [13]. In a sister compound, $GaV_4Se_8$ we found an even richer magnetic phase diagram, which also includes several modulated magnetic phases, however, the magnetic order has not been fully determined [5].

In the grant application second harmonic generation (SHG) microscopy was planned to study the ferroelectric domain structure of lacunar spinels, however, due to the small size of the domains we used piezoresponse force microscopy (PFM) to image the polar domains of $GaV_4S_8$ [6]. We observed mechanically and electrically compatible lamellar domain patterns, where the lamellae are aligned parallel to the (100)-type planes with a typical spacing between 100 nm–1.2 $\mu$m. Since the magnetic pattern abruptly changes at the polar domain boundaries, we expect that the control of ferroelectric domain size in Néel skyrmion hosts can be exploited for the spatial confinement and manipulation of Néel-type skyrmions. Imaging of the polar domains has been extended to other lacunar spinel such as $GaV_4Se_8$ and $GaMo_4S_8$, where similar domain patterns were observed. We are working on the analysis and the publication of the results.

At room temperature we characterized the linear THz spectrum of undoped $GaV_4S_8$ crystals. We found that the refractive index is about 3.45 and the absorption has a moderate value of 50 $cm^{-1}$ around 1 THz. We studied the influence of intense electric fields in the THz frequency range by measuring the absorption spectrum of $GaV_4S_8$ pellets at various incoming beam intensities. Although we expected the generation of itinerant charge carriers up to about ~100 kV/cm we did not observe any changes in the THz spectrum. In the future electric field induced changes in the THz spectrum might be studied at low temperatures where higher contrast is expected as the temperature induced carriers are frozen out in this narrow gap compound.

**Scientific results related to semiconductors with strong spin-orbit interaction**

We measured the magnetic field induced changes in the reflectivity of BiTeI up to 34 T for various carrier concentrations.  When the Fermi energy was tuned close to the Dirac point, which is the crossing point of the spin polarized bands, a series of S-shaped features were observed in the relative reflectivity spectrum. These features were shifted with the magnetic field and they faded away as the carrier density was increased. Next, thin flakes (1-2 μm) of BiTeI were prepared by slicing single crystals. These thin flakes allowed us to measure the inter-Landau subband transition in transmission configuration. The infrared absorption spectrum clearly gives the position of the resonance lines without performing Kramers-Kronig transformation. We found that the excitation energies were increased as a square root of the magnetic field even in the high field range. Similar results were found for BiTeBr when the magneto-transmission was studied in thin slices. Our findings are in contrast to the expectation based on the Rashba model generally accepted to describe the band structure of the conduction band in BiTeI. Our results indicate that the energy-momentum dispersion can be described by V-shaped bands. A manuscript summarizing the above results is in preparation.

Since the bulk crystals are built up by Te-Bi-I triple layers bonded by van der Waals interactions, theoretically, it is possible to stabilize a single unit cell thick flake of BiTeI. Such a triple layer inherits the strong spin-orbit coupling of the bulk material and the Rashba type spin splitting, thus it could be a new building block for spintronics devices as source of spin polarized carriers. However, single unit cell thick BiTeI cannot be prepared by conventional exfoliation techniques successfully used to fabricate e.g. graphene. In collaboration with the group of Dr. Sz. Csonka and Dr. L. Tapasztó, we developed a new method where triple layer of BiTeI is exfoliated on epitaxial Au. Due to the strong bonding between Au-Te or Au-I large flakes of BiTeI triple layers are exfoliated as confirmed by STM and AFM. Our findings are summarized in a manuscript, which is submitted to NPJ 2D materials [1].

Beside the polar semiconductors, we studied the optical and magneto-optical spectra of another layered semiconductor, $MoS_2$ which also has strong spin-orbit interaction. The crystal structure of a single S-Mo-S layer breaks inversion symmetry, which lifts the spin degeneracy at the K-point of the Brillouin-zone. The bulk crystal structure is known to have two polytypes: 2H and 3R. In 3R-$MoS_2$ the layers are only stacked on the top of each other, however, in 2H-$MoS_2$ the neighboring layers are mirror images of each other, thus, bulk 2H-$MoS_2$ has inversion symmetry and the bands are spin-degenerate. We observed that the optical spectra of the two polytypes are markedly different, which was attributed to the different energy spectrum of the exciton states. Theoretical calculations showed that in the 3R polytype the hopping between the nearest neighbor layers is absent and the motion of the excitons is confined. Part of the experimental results has already been published [17].

**Other scientific results not directly related to the main goals of the project**

The spin excitation in several multiferroic compounds are also studied by means of THz spectroscopy in the duration of the project. These compounds simultaneously posses ferroelectric and magnetic order and the dynamics of the coupled order parameters results to novel optical phenomena. The most unusual is the directional dichroism which is the light absorption difference for counter-propagating beams.

Absorption and directional dichroism spectra are measured in $BiFeO_3$ [14], which is the only known room-temperature single phase multiferroics. Our results showed that among the several possible microscopic coupling mechanisms between the spins and the electric polarization, the so-called inverse Dzyaloshinskii-Moriya term is the most important [14, 15].

We studied the magnetization, the static polarization and the optical properties of $CaBaCo_4O_7$ [7, 12] and $CaBaFe_4O_7$ [11], which are members of a new family of multiferroic materials. While $CaBaCo_4O_7$ shows one of the largest magnetic order induced ferroelectric polarization, the multiferroic phase of $CaBaFe_4O_7$ arise close to room-temperature. In the THz excitation spectrum of $CaBaCo_4O_7$ we found a spin resonance, which shows directional dichroism close to 100% [12]. To describe the spin-wave excitations we developed a microscopic spin model, which predictes that magneto-striction is the dominant mechanism of the magnetoelectric effect in this compound [7]. By measuring the magnetization and the electric polarization in

$CaBaFe_4O_7$ we constructed the magnetic field vs. temperature phase diagram of this compound [11]. We revealed a sequence of magnetic phase transitions driven either by an external magnetic field or by the temperature, however, the details of the spin order are not fully understood.

Finally, we studied the spin excitations in $TbFe_3(BO_3)_4$ [8]. From the magnetic field dependence of the spin resonance energies we constructed a microscopic model to describe the spin order and its excitations, and we experimentally determined the coupling coefficients.

**Other impacts of the project**

In the course of the project 3 PhD students (Vilmos Kocsis, Dávid Szaller, Ádám Butykai) and 2 MSc students (Dániel Gergely Farkas, Bertalan Szigeti) were involved in the scientific research outlined above. Dániel Gergely Farkas prepared a TDK (available in Hungarian http://tdk.bme.hu/TTK) and an MSc thesis under the supervison of the PI. With the TDK he was awarded first place and received the award of the rector as well.

Budapest, 28th September 2017.

Sándor Bordács

**List of publications**


[1] B. Fülöp, Z. Tajkov, J. Peto, P. Kun, J. Koltai, L. Oroszlány, E. Tóvári, H. Murakawa, Y. Tokura, S. Bordács, L. Tapasztó, and Sz. Csonka
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arXiv preprint arXiv:1704.03621, submitted to Phys. Rev. Lett. (2017)

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*Optical conductivity in multiferroic $GaV_4S_8$ and $GeV_4S_8$: Phonons and electronic transitions*
arXiv preprint arXiv:1704.08602, accepted for publication in Phys. Rev. B (2017)

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Független idéző: 1 Függő idéző: 1 Összesen: 2

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Független idéző: 2 Függő idéző: 3 Összesen: 5

*For 2016 and 2017 impact factor calculated in 2015 is indicated.