Magneto-optical and magnetoelastic effects in multiferroic materials

PhD Thesis booklet

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Overview

Multiferroics permit the magnetic control of the electric polarization and electric control of the magnetization. These static magnetoelectric (ME) effects are of enormous interest: the ability to read and write a magnetic state current-free by an electric voltage would provide a huge technological advantage. For example, the dissipation in terms of Joule-heating is expected to be two-three orders of magnitude smaller as compared with the case of present state-of-the-art spin transfer torque magnetic random access memories (MRAM) [1, 2, 3]. The realization of room temperature memory devices based on magnetoelectric heterostructures [4] and the manipulation of magnetic domain walls by electric field [5] demonstrated that multiferroics are knocking on the door of daily applications.

Magnetoelectric effects can influence not only the static but also the dynamic properties of matter [6, 7]. One of the most interesting optical effects in a magnetoelectric medium is the optical directional anisotropy also called the one-way transparency. In such materials, where both the time reversal and the spatial inversion symmetries are violated, counter-propagating light beams passing through the medium can experience different indices of refraction giving rise to the optical directional anisotropy [8, 9]. This phenomenon, if realized at room temperature, would allow the development of optical diodes which transmit unpolarized light in one, but not in the opposite direction, also supplemented by the ability to switch the transmission direction with magnetic or electric fields.
Main objectives

The primary aim of my PhD work was to explore new ME multiferroic compounds which host strong coupling between the electric and magnetic degrees of freedoms. Therefore, I synthesized multiferroic crystals, such as CaBaFe$_4$O$_7$, CaBaCo$_4$O$_7$, Ba$_2$CoGe$_2$O$_7$, (Ca,Sr)$_2$CoSi$_2$O$_7$, Sr$_2$CoSi$_2$O$_7$ and LiCoPO$_4$, and investigated their static and dynamic magnetoelectric properties via the combination of magnetization, polarization, specific heat and optical transmission measurements. Besides the investigation of ME phenomena, I studied magneto-optical effects in multiferroic FeCr$_2$O$_4$ and CoCr$_2$O$_4$ crystals.

Scientific achievements

1. I participated in the development of a broadband magneto-optical spectrometer (photon energy range E=0.087-4.5 eV) which is capable of the high precision ($10^{-3}$ degree accuracy) measurement of the complex magneto-optical Kerr angle. I have investigated the on-site 3$d$ – 3$d$ transitions in a broad family of spinel oxides including NiCr$_2$O$_4$, MnCr$_2$O$_4$, CuCr$_2$O$_4$, CoCr$_2$O$_4$ and FeCr$_2$O$_4$ [IV]. In the last two compounds I have found strong magneto-optical Kerr-effect. The magneto-optical Kerr rotation and ellipticity observed in CoCr$_2$O$_4$ is the largest reported so far in magnetic semiconductors and insulators. I discussed the criteria of strong magneto-optical effects in insulating transition-metal oxide compounds and
the unique potential of tetrahedrally coordinated Co$^{2+}$ ions [IV,X].

2. I synthesized melt-grown crystals of the orthorhombic polar ferrimagnet CaBaFe$_4$O$_7$ with the optical floating zone technique. Based on the combined magnetization, calorimetric, and magnetoelectric (ME) measurements, I explored the $\mu_o H - T$ magnetic phase diagram of this material. Specific heat measurements revealed that a structural phase transition to a higher symmetry form of CaBaFe$_4$O$_7$ takes place at $T_3=380\,K$. I found a paramagnetic to ferrimagnetic transition at $T_{C1}=275\,K$ followed by a spin re-ordering transition at $T_{C2}=211\,K$. In addition, I investigated the ME properties below $T_{C2}$ with different orientations of the magnetic field. I observed a large linear ME coefficient of $\alpha_{xx} \approx 39\,\text{ps/m}$ as well as a gigantic field-induced polarization of $\Delta P=850\,\mu\text{C/m}^2$ for magnetic fields along the $c$ axis [IX].

3. I grew the type-I multiferroic easy-plane ferrimagnet CaBaCo$_4$O$_7$, the sister compound of CaBaFe$_4$O$_7$. I characterized the crystals with static magnetization and magnetoelectric measurements. I studied the magnon resonances in the far infrared photon energy range, and found two magnon branches. The lowest-energy doubly degenerate mode is a magnetoelectric resonance, i.e. it can be excited by both the electric and magnetic component of light, while the non-degenerate higher-energy resonance can be excited only by the electric field component of the light, thus it is an electromagnon. The magnetoelectric resonance realizes a nearly perfect unidirectional
light absorption, and the transparent/absorbing directions can be controlled by an external magnetic field. Furthermore, I measured the magnetic field dependence of the spin excitations in a broad magnetic field and energy region, which may provide valuable information for the construction of a microscopic spin model of CaBaCo$_4$O$_7$ [VIII].

4. I synthesized single crystals of the antiferromagnetic Sr$_2$CoSi$_2$O$_7$ with the floating zone technique and performed static magnetic and magnetolectric measurements in order to characterize these crystals. I investigated the optical directional anisotropy of this compound by means of far infrared spectroscopy. I measured the magnetic field dependence of the magnetic excitations over a broad magnetic field and energy region. I found that one of the magnon modes shows an almost perfect optical diode effect in high magnetic fields [VI].

5. I synthesized single crystals of LiCoPO$_4$ belonging to the orthorhombic Olivine material family. The crystal symmetry of LiCoPO$_4$ allows finite toroidal moment along the $z$ crystallographic axis, while neither ferroelectric, nor ferromagnetic orders are allowed. Instead the ferrotoroidal order emerges as a combination of an antiferroelectric and an antiferromagnetic order. I revisited the static magnetic and magnetolectric properties by means of magnetization and magnetic field induced polarization measurements. I found that the static magnetolectric susceptibility of LiCoPO$_4$ can be switched between two states when applying crossed $E_o$ electric and $H_o$ magnetic fields. For poling with $(+E_o,+H_o)$
or \((-\mathbf{E}_o, -\mathbf{H}_o)\) the magnetoelectric susceptibility is found to be positive, while it changed sign when \((+\mathbf{E}_o, -\mathbf{H}_o)\) or \((-\mathbf{E}_o, +\mathbf{H}_o)\) poling fields were used. I also investigated the optical magnetoelectric effects in LiCoPO$_4$ in the spectral range of magnon excitations. I found several magnetic resonances showing large remanent directional anisotropy persisting even after the removal of the poling fields. I proposed the concept of an optical magnetoelectric device, which could be written by electric field and read optically.

**List of publications**

Publications related to the thesis are typed in **bold face**.

I L. Demkó, G. A. H. Schober, V. Kocsis, M. S. Bahramy, H. Murakawa, J. S. Lee, I. Kézsmárki, R. Arita, N. Nagaosa, and Y. Tokura,
Enhanced infrared magneto-optical response of the nonmagnetic semiconductor BiTeI driven by bulk rashba splitting,

II Á. Butykai, Á. Orbán, V. Kocsis, D. Szaller, S. Bordács, E. Tátrai-Szekeres, L. F. Kiss, A. Bóta, B. G. Vértess, T. Zelles, and I. Kézsmárki,
Malaria pigment crystals as magnetic micro-rotors: Key for high-sensitivity diagnosis,
III G. Ceolin, Á. Orbán, V. Kocsis, R. E. Gyurcsányi, I. Kézsmárki, and V. Horváth,
Electrochemical template synthesis of protein-imprinted magnetic polymer microrods,

IV V. Kocsis, S. Bordács, D. Varjas, K. Penc, A. Abouelsayed, C. A. Kuntscher, K. Ohgushi, Y. Tokura, and I. Kézsmárki,
Magnetoelasticity in $ACr_2O_4$ spinel oxides ($A=$ Mn, Fe, Co, Ni, and Cu),

V D. Szaller, S. Bordács, V. Kocsis, T. Rööm, U. Nagel, and I. Kézsmárki,
Effect of spin excitations with simultaneous magnetic- and electric-dipole character on the static magnetoelectric properties of multiferroic materials,

One-way Transparency of Four-coloured Spin-wave Excitations in Multiferroic Materials,

VII T. Nakajima, Y. Tokunaga, V. Kocsis, Y. Taguchi, Y. Tokura, and T. Arima,
Uniaxial-Stress Control of Spin-Driven Ferroelectricity in Multiferroic $Ba_2CoGe_2O_7$,
VIII S. Bordács, V. Kocsis, Y. Tokunaga, U. Nagel, T. Rõõm, Y. Takahashi, Y. Taguchi, and Y. Tokura,

Unidirectional terahertz light absorption in the pyroelectric ferrimagnet CaBaCo$_4$O$_7$


IX V. Kocsis, Y. Tokunaga, S. Bordács, M. Kriener, A. Puri, U. Zeitler, Y. Taguchi, Y. Tokura, and I. Kézsmárki,

Magnetoelectric effect and magnetic phase diagram of polar ferrimagnet CaBaFe$_4$O$_7$,

Accepted for publication at PRB.

X V. Kocsis, S. Bordács, J. Deisenhofer, K. Ohgushi, Y. Kaneko, Y. Tokura, and I. Kézsmárki,

Strong magnetooptical effects in CoCr$_2$O$_4$ spinel oxide generated by tetrahedrally coordinated Co$^{2+}$ ions,

Submitted to PRB.
Bibliography


[2] M. Chin, “Ucla engineers develop new energy-efficient computer memory using magnetic materials,” december 2012. MeRAM is up to 1,000 times more energy-efficient than current technologies.


