

Optical, Dielectric, and Magnetoelectric Properties of Ferroelectric and Antiferroelectric Lacunar Spinel

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Lacunar spinels with a chemical formula of AM_4X_8 form a populous family of narrow-gap semiconductors, which offer a fertile ground to explore correlation and quantum phenomena, including transition between Mott and spin-orbit insulator states, ferro/antiferroelectricity driven by cluster Jahn-Teller effect, and magnetoelectric response of magnetic skyrmions with polar dressing. The electronic and magnetic properties of lacunar spinels are determined to a large extent by their molecular-crystal-like structure. The interplay of electronic correlations with spin-orbit and vibronic couplings leads to a complex electronic structure already on the single-cluster level, which—together with weaker intercluster interactions—gives rise to a plethora of unconventional correlated states. This review primarily focuses on recent progresses in the field of optical, dielectric, and magnetoelectric properties on lacunar spinels. After introducing the main structural aspects, lattice dynamics and electronic structure of these compounds are discussed on the basis of optical spectroscopy measurements. Dielectric and polarization studies reveal the main characteristics of their low-temperature ferro- or antiferroelectric phases as well as orbital fluctuations in their high-temperature cubic state. Strong couplings between spin, lattice, and orbital degrees of freedom are manifested in singlet formation upon magnetostructural transitions, the emergence of various multiferroic phases, and exotic domain-wall functionalities.

increasing attention because they offer a fertile ground for intriguing correlated and quantum states, such as a topological superconductor state,^[4] spin-orbit entangled molecular $J_{\text{eff}} = 3/2$ states,^[5,6] Néel-type skyrmions with polar dressing,^[7] molecular cluster orbital-driven ferroelectricity^[7–12] and antiferroelectricity,^[13] multiple multiferroic phases,^[7,9,14,15] and magnetic states confined to polar domain walls.^[14] Pressure-induced superconductivity,^[16] avalanche-like breakdown of the Mott gap, leading to a resistive switching,^[17] and colossal negative magnetoresistance^[18,19] further witness the complexity of these compounds.

The term lacunar refers to an important structural motif, namely, the lack of every second A-site ion with respect to the normal spinel structure, as described by the chemical formula $A\Box M_4X_8$ or simply AM_4X_8 . The regular alternation of voids (\Box) and cations on the diamond lattice formed by the A sites has two important consequences: 1) the inversion symmetry present in the cubic $Fd\bar{3}m$ spinel structure is lost and the symmetry is reduced to the noncentrosymmetric cubic $F\bar{4}3m$ and 2) the pyrochlore lattice of


the M sites develops a breathing, where smaller and larger corner-sharing M_4 tetrahedra alternate in a regular fashion. The breathing can be such strong that the M–M distance in the smaller tetrahedra is close to the interatomic distance of the corresponding elemental metal, as is the case for $M = \text{V}$.^[20] Correspondingly, the lacunar spinel structure can be described as two interpenetrating fcc networks. One network is formed of weakly linked M_4X_4 molecular units composed of interpenetrating M_4 and X_4 tetrahedra and the other consists of AX_4 units, as shown in **Figure 1a**. The weak electronic overlap between the M_4X_4 cubane units renders these compounds narrow-gap semiconductors.^[21]

The lacunar spinel structure is realized by a remarkably large number of compounds, including $3d$ (V, Ti), $4d$ (Mo, Nb), and $5d$ (Ta) transition metals in combination with $A = \text{Ga, Ge, Al}$, and $X = \text{S, Se, Te}$. Due to their molecular-crystal-like structure, the orbital scheme of the M_4 tetrahedra is often considered as a good starting point to describe the electronic structure of lacunar spinels.^[20,22–25] In fact, the tendency to form cluster orbitals is widely accepted for the V- and Mo-based compounds, such as $\text{GaV}_4\text{S}(\text{e})_8$ and $\text{GaMo}_4\text{S}(\text{e})_8$,^[20,22,26] where the uppermost partially occupied molecular orbital is a triply degenerate t_2 level,

1. Introduction

Cubic spinels with the chemical formula AM_2X_4 are unarguably one of the largest compound families, comprising a plethora of transition metal (M) oxides and chalcogenides.^[1–3] Lacunar spinels, being a populous subclass of spinels, have been attracting

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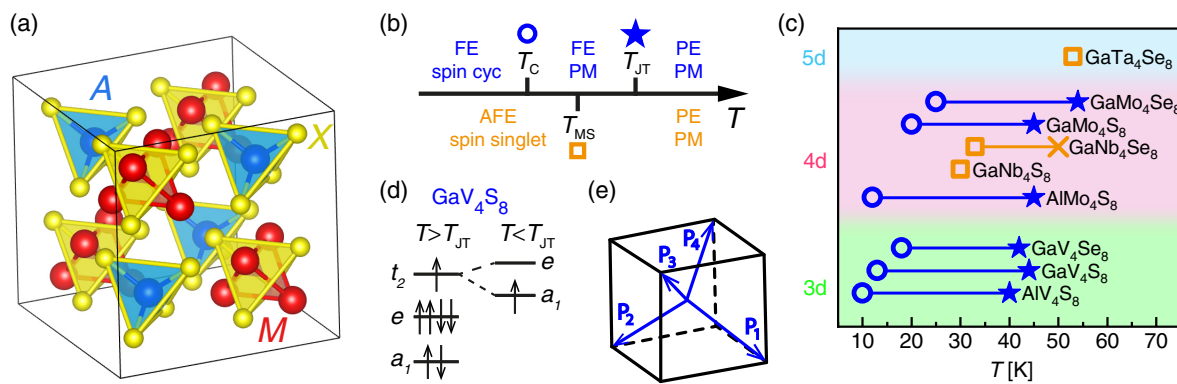


Figure 1. a) Cubic lacunar spinel structure at room temperature. b) Transition paths of spin 1/2 lacunar spinels showing distinct polar and magnetic order (PE, paraelectric; PM, paramagnetic). c) Transition temperatures of lacunar spinels with different transition metal clusters. Stars denote a structural and ferroelectric transition, circles a magnetic transition into a magnetic modulated phase, and rectangles a magnetostructural transition. The cross for GaNb_4Se_8 indicates a purely structural transition. d) Energy-level scheme of the molecular orbital of the V_4S_4 unit of GaV_4S_8 . e) Four polar directions (P_{1-4}) of rhombohedral lacunar spinels with respect to the cubic unit cell.

hosting a single unpaired electron and hole, respectively (see Figure 1d).

This orbital degeneracy is lifted by a cooperative Jahn-Teller distortion at T_{JT} , which reduces the symmetry to polar rhombohedral ($R3m$). Upon this ferroelectric/ferroelastic transition, all M_4X_4 units within a structural domain get distorted, elongated in $\text{GaV}_4\text{S}(e)_8$ and compressed in $\text{GaMo}_4\text{S}(e)_8$, along the same vertex of the M_4 tetrahedra (i.e., one of the cubic $\langle 111 \rangle$ -type axes), which also lowers their point-group symmetry to $3m$.^[20,26] Due to the lack of inversion in the parent cubic state, only four polar domain states can form.^[11,27–29] Their polarizations (P) span 109° with each other, i.e., there are no $\pm P$ domain states coexisting (see Figure 1e). These polar domains have been directly imaged by piezoelectric force microscopy in GaV_4S_8 ,^[28] GaV_4Se_8 ,^[14] and GaMo_4S_8 .^[11] The ferroelectric transitions can be categorized as order-disorder-type because the existence of local electric dipoles above T_{JT} and the dynamic Jahn-Teller effect associated with their fluctuations have been evidenced in GaV_4S_8 by dielectric studies.^[12,30–32]

In addition to the onset of ferroelectricity (FE), the rhombohedral distortion also affects the magnetic interactions. The overall exchange coupling, originally being antiferromagnetic in the cubic state, turns to ferromagnetic below T_{JT} .^[31,33,34] Moreover, the axial polar distortion generates a Dzyaloshinskii-Moriya interaction pattern that can stabilize cycloidal (cyc) modulations with propagation vectors perpendicular to the polar axis. In fact, the emergence of cycloidal spin order has been observed in these compounds below T_{C} . In finite magnetic fields, the cycloidal order can be transformed to a Néel-type skyrmion lattice (SkL) state and subsequently to a field-polarized ferromagnetic (FM) state.^[27,29,35] Importantly, the ferroelectric and the magnetic transitions are decoupled from each other, as shown in Figure 1b,c. The full list of transition temperatures is shown in Table 1.

As discussed earlier, the Jahn-Teller activity of the M_4 cluster leads to the onset of orbital-order-driven ferroelectricity below T_{JT} in $\text{GaV}_4\text{S}(e)_8$ and $\text{GaMo}_4\text{S}(e)_8$, followed by magnetic ordering at $T_{\text{C}} < T_{\text{JT}}$. However, although the M_4 clusters have the

Table 1. Jahn-Teller T_{JT} , magnetic T_{C} , and magnetostructural T_{MS} transition temperatures of lacunar spinels. The temperature marked by the asterisk most likely is a simple structural transition, which is not Jahn-Teller driven.^[36]

	T_{JT} [K]	T_{C} [K]	T_{MS} [K]	Low- T structure
AlV_4S_8	40 ^[26]	10 ^[26]		$R3m$ ^[26]
GaV_4S_8	44 ^[33]	13 ^[33]		$R3m$ ^[20]
GaV_4Se_8	41 ^[31]	18 ^[31]		$R3m$ ^[26]
AlMo_4S_8	45 ^[92]	12 ^[92]		$R3m$ ^[92]
GaNb_4S_8			31 ^[24]	$P2_12_12_1$ ^[13]
GaNb_4Se_8	50 ^{*,[36]}		33 ^[36]	$P2_12_12_1$ ^[37]
GaMo_4S_8	45 ^[20]	20 ^[20]		$R3m$ ^[20]
GaMo_4Se_8	54 ^[93]	25 ^[93]		$R3m$ ^[92]
GaTa_4Se_8			53 ^[36]	$P2_12_12_1$ ^[37]
CeV_4S_8	30 ^[76]		15 ^[76]	$Imm2$ ^[39]

same formal valency in $\text{GaNb}_4\text{S}(e)_8$ and $\text{GaTa}_4\text{S}(e)_8$ as in the compounds earlier and the main axis of distortion of the M_4 tetrahedra is also along one of the vertices, the symmetry lowering in these cases is realized via a single magnetostructural transition at T_{MS} , which lowers the cubic symmetry to orthorhombic (see Figure 1b,c).^[13,36,37] Specific to GaNb_4Se_8 , at first the face centering is lost by a transition from the $F43m$ parent state to the cubic chiral $P2_13$ state, followed by the loss of the cubic symmetry at T_{MS} .

In terms of the polar degrees of freedom, the low-temperature orthorhombic phase ($T < T_{\text{MS}}$) is antiferroelectric (AFE).^[13] Antiferroelectricity is realized by the nonzero polarization of individual distorted M_4X_4 clusters, ordering in an alternating fashion. The magnetostructural nature of the transition is best revealed in GaNb_4S_8 , where the quenching of spin degrees of freedom via spin-singlet formation at T_{MS} was evidenced by NMR spectroscopy.^[24,38] Similar to the materials with ferroelectric ground state, the fluctuation of local polar distortions has been observed already above T_{MS} , i.e., in the nominally cubic state.^[13,38]

We want to point out that the first lacunar spinel which was shown to become ferroelectric upon the structural transition was GeV_4S_8 ^[8]. However, in contrast to all aforementioned lacunar spinels, the highest molecular orbital level of the M_4 cluster in this compound is occupied by two unpaired electrons with total spin $S = 1$. This leads to a structural change to the polar orthorhombic space group $Imm2$ upon T_{JT} and an elongation and shortening of two opposite V-V bonds of the V_4 tetrahedra, respectively. Moreover, this compound also shows an additional structural change upon its antiferromagnetic ordering.^[22,39,40]

The intimate coupling between spin, orbital, and lattice degrees of freedom together with the competition/interplay of various types of interactions not only leads to the aforementioned fascinating magnetic and electric properties in lacunar spinels but also makes their microscopic description challenging. From the experimental side, this challenge can be addressed, in a first step, by studying the electronic structure and the lattice dynamics of these compounds by optical spectroscopy. The optical properties of lacunar spinels are summarized in Section 2. Systematic optical spectroscopy studies are of particular importance because of fundamental difficulties in modeling the electronic structure of lacunar spinels, requiring theoretical tools beyond standard density-functional theory calculations, such as cluster dynamical mean-field theory^[41] and quantum chemistry approaches.^[25] Splittings of optical phonon modes provide a sensitive probe of the symmetry lowering upon T_{JT} and T_{MS} ^[21,42], while broadband optical spectroscopy can follow reconstructions of the gap edge associated with these structural transitions.^[20]

As a next step, the cooperative behavior of polar constituents can be revealed by dielectric spectroscopy and domain imaging techniques. In particular, polarization measurements and dielectric spectroscopy provide valuable information about the nature of the polar state. Broadband dielectric spectroscopy over the Hz–THz range also enables the investigation of intriguing dipolar dynamics around the noncanonical polar or antipolar transitions of these materials, which are discussed in Section 3. Studies on the ferro-, and also the magnetoelectric polarization are summarized in Section 4. The investigation of the magnetoelectric phenomena can give insight into the coupling of orbital and lattice degrees of freedom to spins. The present review summarizes the progress achieved along these lines and discusses open questions and future directions.

2. Optical Properties

For theory it still remains a challenge to describe the electronic structure of the lacunar spinels. Based on a simple electron counting, one would expect metallic behavior due to the partial occupation of t_2 orbitals of M_4X_4 clusters. However, lacunar spinels are found to be semiconductors already in their high-temperature cubic state. Standard density-functional theory calculations on the DFT+ U level^[22,23,41,43–47] have failed to reproduce the finite gap of the cubic phase observed experimentally.^[17,21] Difficulties in the modeling of the electronic structure of the lacunar spinels arise from the interplay of various factors. The character of the M_4X_4 cluster orbitals, which governs the optical, dielectric, and magnetic properties, is determined by

a delicate balance between the Jahn-Teller instability of the clusters, vibronic interactions as well as spin-orbit and spin-lattice couplings. Moreover, the character of the cluster orbitals strongly affects the intercluster hopping. Therefore, reproducing the narrow-gap semiconductor nature of these compounds may require advanced theoretical approaches going beyond the usual density-functional theory schemes.

Broadband optical spectroscopy can provide a deep insight into the electronic band structure, especially when a series of compounds is systematically investigated, by probing the coupled density of states for electric dipole-active transitions. **Figure 2b,d,f** shows the room temperature broadband optical conductivity of GaV_4S_8 , GaV_4Se_8 , and GaNb_4S_8 up to $18\,000\text{ cm}^{-1} \approx 2.25\text{ eV}$, respectively, as obtained from reflectivity spectra via Kramers-Kronig transformation.^[21,32] An enlarged view of the low-energy optical conductivity (Figure 2a,c,e) reveals the temperature-induced evolution of electronic transitions located below $7000\text{ cm}^{-1} \approx 0.88\text{ eV}$. For all temperatures in the range of 10–300 K, the optical conductivity vanishes in the zero-frequency limit, which confirms the semiconducting nature of these lacunar spinels, already in the high-temperature cubic phase. In the spectral range between 2000 and 4000 cm^{-1} , the optical conductivity of these compounds exhibits a sudden increase, associated with the electronic band gap. The gap edge

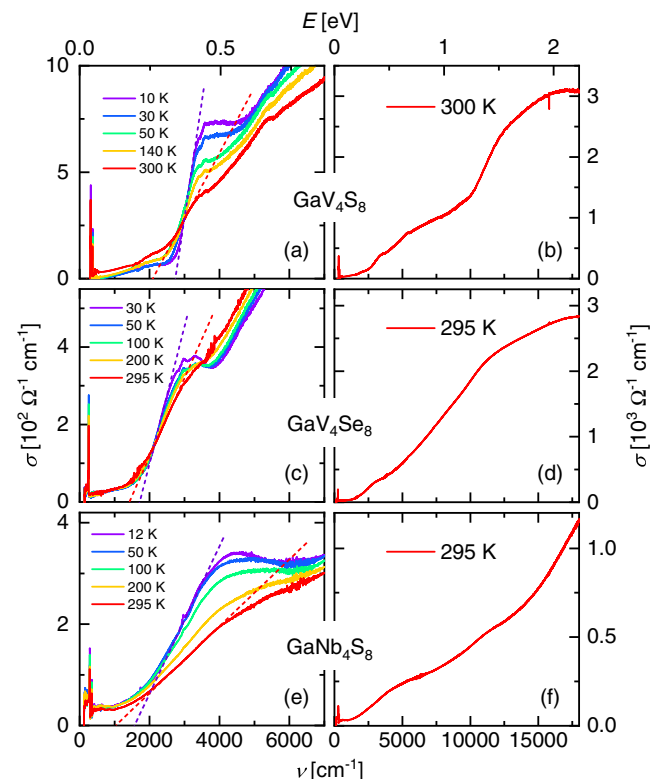


Figure 2. Frequency-dependent optical conductivity of a,b) GaV_4S_8 , c,d) GaV_4Se_8 , and e,f) GaNb_4S_8 for selected temperatures in the region of the band gap (left panels).^[21] Dashed lines indicate a linear extrapolation of the increase in the conductivity for determination of the gap energy. Corresponding broadband optical conductivity at room temperature (right panels). Adapted with permission.^[21] Copyright 2020, American Physical Society.

is manifested by a pronounced and sudden increase in the conductivity at low temperatures, which is continuously smeared out with increasing temperature. This temperature-dependent behavior has primarily been ascribed to orbital fluctuations in the high-temperature cubic phase.^[21,32] In fact, the dynamic Jahn-Teller effect, i.e., the dynamical breaking of cubic symmetry by local distortions, is a possible reason for the failure of DFT+*U* calculations to reproduce the narrow but finite gap in the high-temperature phase.

The size of the bandgap has been determined by a linear extrapolation of the optical conductivity to zero, as illustrated by dashed lines in Figure 2a,c,e. At room temperature, this procedure yields the following gap energies: 260 meV for GaV₄S₈, 175 meV for GaV₄Se₈, and 130 meV for GaNb₄S₈.^[21,32] These gap energies are in reasonable agreement with values previously reported based on resistivity measurements,^[23,33,48] characterizing the lacunar spinels as narrow-gap semiconductors. A systematic study, involving lacunar spinels with 3*d*, 4*d*, and 5*d* transition metal clusters,^[21] reveals that the charge gap is reduced from 3*d* to 5*d* compounds. With decreasing temperature the band gap increases gradually in all investigated compounds with tiny anomalies of the gap energies at the structural transitions.^[20] Though the values of the charge gap are not strongly temperature dependent, a considerable temperature-induced spectral weight transfer is observed in each compound near the gap edge, which may originate from the slowing down of the orbital fluctuations with decreasing temperature and the onset of static cooperative order upon the structural transition.^[21,32] In this scenario, vibronic interactions should be essential ingredients in describing the electronic structure of lacunar spinels. While these optical studies quantify the charge gap and its variation from 3*d* to 5*d* compounds, the determination of the electronic structure in the vicinity of the Fermi energy calls for theory support. A recent resonant inelastic X-ray scattering study implies that Ta₄ clusters in the 5*d* GaTa₄Se₈ may offer a realization of molecular $J_{\text{eff}} = 3/2$ states,^[5] indicating strong spin-orbit effects. In contrast, the structural transitions of several 3*d* and 4*d* lacunar spinels are well described by the simple orbital Jahn-Teller effect, implying a secondary role of spin-orbit coupling in these compounds.

The study of the infrared (IR) active phonon modes is often a highly sensitive tool to investigate changes in the crystal structure at the phase transitions.^[49–51] Generally, the number of the IR-active optical phonon modes can be determined by group theory based on the crystal symmetry and the occupied Wyckoff positions. For the high-temperature cubic phase of the lacunar spinels with space group $F\bar{4}3m$, six triply degenerate IR-active F_2 phonon modes are expected. Below T_{JT} and T_{MS} , the symmetry of the studied compounds is lowered to rhombohedral (GaV₄S₈, GaV₄Se₈) with space group $R3m$ ^[20] and orthorhombic with space group $P2_12_12_1$ (GaNb₄S₈),^[13] respectively. These symmetry lowering transitions should increase the number of IR-active zone center phonon modes to 21 and 141, respectively.

Far-IR reflectivity spectra of GaV₄S₈, GaV₄Se₈, and GaNb₄S₈ measured at room temperature and at 10 K are shown in Figure 3.^[21] These spectra reveal only a subset of the six IR-active phonon modes expected in the high-temperature cubic phase: four modes are visible in GaV₄S₈ (a) and three modes in GaNb₄S₈ (b) and GaV₄Se₈ (c), as shown in Figure 3. The

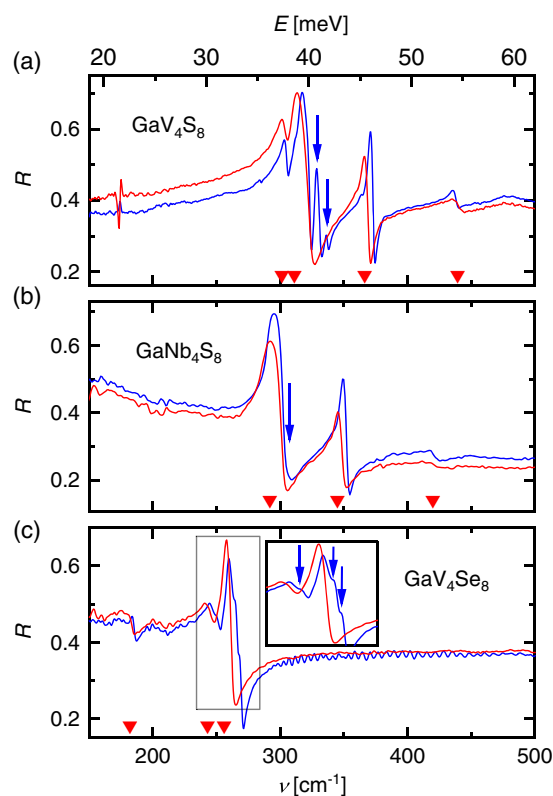


Figure 3. Frequency-dependent phonon reflectivity spectra of a) GaV₄S₈, b) GaNb₄S₈, and c) GaV₄Se₈ measured at room temperature (red curves) and at 10 K (blue curves).^[21] Red triangles indicate the mode frequencies at room temperature. Blue arrows indicate additional phonon modes appearing only below the structural transition temperature. Adapted with permission.^[21] Copyright 2020, American Physical Society.

remaining modes obviously have too low spectral weight to be detected by reflectivity measurements.

The room temperature mode frequencies, as indicated by the red triangles in Figure 3, are very similar for GaV₄S₈ (a) and GaNb₄S₈ (b). In contrast, the phonon eigenfrequencies of GaV₄Se₈ (c) are considerably lower, which can be explained by the mass ratio of S and Se. A systematic phonon study over a wide series of lacunar spinels, where *A*, *M*, and *X* atoms were sequentially changed, revealed that the modes observed in the high-temperature cubic phase can be assigned to vibrations of the ligands and the *A*-site ions.^[21] In other words, this implies that the vibrations of the tetrahedral *M*₄ units carry only a weak electric dipole moment. This is a surprising observation in the context of the widely accepted picture of the cubic-to-rhombohedral transition driven by the polar distortions of the *M*₄ clusters.

Although in the distorted state of these compounds again a subset of the expected modes are observed, the low-temperature phonon spectra allow to trace the symmetry lowering taking place at the structural transition. As indicated by the blue arrows in Figure 3, additional weak modes appear below T_{JT} and T_{MS} , indicating the cubic-to-rhombohedral and the cubic-to-orthorhombic structural phase transitions, respectively. The low number of additional phonon modes detectable upon the structural transition is in agreement

with the small deviations from the cubic structure, observed in these compounds.^[20,24] Though spin-lattice coupling plays an important role in the studied compounds, no anomalies in the phonon spectra have been detected at T_C .

3. Dielectric Properties

The investigation of lacunar spinels by dielectric spectroscopy is mainly motivated by the polar order detected in many of these materials as mentioned in Section 1.^[7,8,10–13,31] In recent years, unconventional mechanisms for the generation of polar order have come into the focus of interest. Such mechanisms often promote multiferroicity, especially the simultaneous ordering of spins and electrical dipoles, being of fundamental interest as well as relevant for applications in future electronics and spintronics.^[52] An interesting example is the ferroelectric order triggered by orbital ordering in various materials, including several lacunar spinels.^[7,8,53–56] As discussed in Section 1, the Jahn-Teller distortion of the M_4X_4 cubane units produces a dipole moment, and the collective ferro-type ordering of these local dipoles generates ferroelectricity. As these cubane units are weakly linked molecule-like entities, these lacunar spinels show analogy with molecular polar materials.^[57,58]

In general, at a polar phase transition pronounced anomalies are expected to occur in the temperature-dependent dielectric constant ϵ' (the real part of the dielectric permittivity). Therefore, aside of electrical polarization measurements (cf. Section 4.1), dielectric spectroscopy is an important tool for detecting polar phase transitions and the dipolar dynamics associated with the polar ordering and it can be used for characterizing the order of the transition. Investigating the polar dynamics allows, e.g., to distinguish between the two classical types of ferroelectricity, which can be of displacive or order-disorder nature.^[59,60] In the first case, the nonpolar high-symmetry structure, lacking electric dipoles even on the microscopic scale, transforms into a polar structure, where polarization arises from the displacements of ionic cores and/or the deformations of orbitals. In such materials, significant excitations associated with the dipolar dynamics are expected only in the optical range, e.g., the well-known soft-phonon modes. In contrast, in this class of ferroelectrics, ϵ' exhibits no significant frequency dependence within the typical frequency range of conventional dielectric spectroscopy (Hz–GHz) and, thus, the polar transition is manifested by an essentially frequency-independent peak in $\epsilon'(T)$.

In marked contrast, in order-disorder ferroelectrics, the polar order arises from the ordering of dynamically disordered permanent dipole moments that already exist above the ferroelectric ordering temperature. These dipoles can rearrange within multi-well potentials which leads to the typical spectral signatures of relaxational processes in the dielectric frequency range, both above and below the transition. Within the kinetic Ising model used to describe order-disorder ferroelectrics, a critical slowing down of this dipolar dynamics is predicted when approaching the ferroelectric transition from high or low temperatures.^[59,60] Moreover, the peak in $\epsilon'(T)$, also showing up at the transition in this class of ferroelectrics, becomes successively suppressed with increasing frequency.

While all these findings are well documented for conventional ferroelectrics,^[61–64] the dipolar dynamics and dielectric

anomalies associated with polar transitions are rarely investigated for ferroelectrics with unconventional ordering mechanisms.^[65,66] It is interesting to check, whether the aforementioned dielectric features of conventional displacive and order-disorder ferroelectrics can also be observed for such non-canonical polar materials.

Figure 4 shows three examples of the temperature-dependent dielectric constant of polar lacunar spinels, as measured at different frequencies in GaV_4Se_8 (a),^[31] GaV_4S_8 (b), and GaNb_4S_8 (c).^[13] To facilitate the comparison of the three materials, the temperature scale was normalized to T_{JT} . For GaV_4Se_8 and GaV_4S_8 , Figure 4 shows qualitatively similar behavior of $\epsilon'(T)$, while GaNb_4S_8 behaves markedly different. As mentioned in Section 1, in contrast to GaNb_4S_8 , both GaV_4Se_8 and GaV_4S_8 become ferroelectric at the Jahn-Teller transition. Both systems exhibit complex magnetic phase diagrams, including a skyrmion lattice phase^[7,9,29,31,33] and, notably, GaV_4S_8 was the first bulk material, where a Néel-type skyrmion lattice state was observed.^[7,27]

In previous studies,^[7,31] the orbital-driven polar order of these two compounds was evidenced by dielectric and polarization measurements (cf. Section 4.1 for the latter). As shown in Figure 4a,b, for both systems, $\epsilon'(T)$ exhibits a clearly pronounced peak at T_{JT} for each frequency. For GaV_4Se_8 , such a peak was also reported in the study by Fujima et al.^[9] for a single

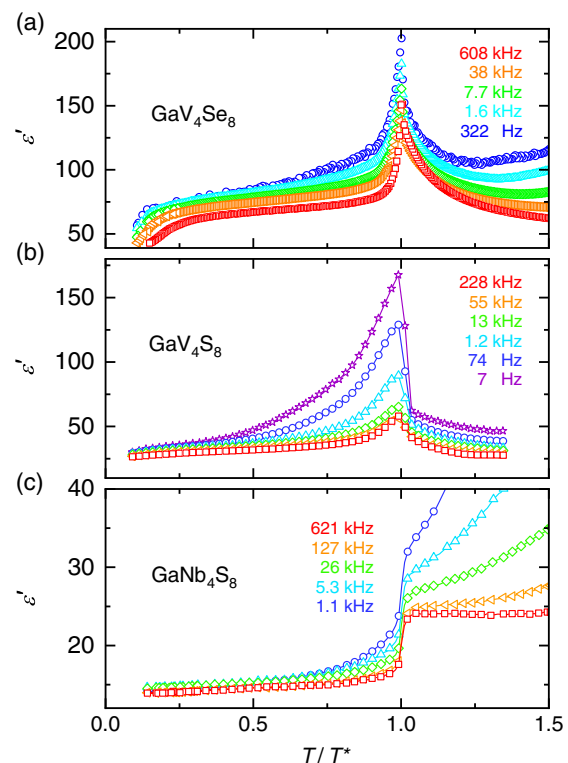


Figure 4. Temperature dependence of the dielectric constant of a) GaV_4Se_8 ^[31], b) GaV_4S_8 , and c) GaNb_4S_8 ^[13] for various frequencies with the temperature scale normalized to T^* , which represents T_{JT} for GaV_4Se_8 and GaV_4S_8 and T_{MS} for GaNb_4S_8 (see Table 1). (a) Adapted with permission.^[31] Copyright 2017, American Physical Society. (c) Adapted with permission.^[13] Copyright 2021, American Physical Society.

frequency. Dielectric anomalies associated with the polar ordering in GaV_4S_8 were also found in the study by Lal et al.^[67] For the latter compound, it was demonstrated^[7,33] that the peak in $\epsilon'(T)$ also persists for frequencies up to 2.5 GHz, thus excluding non-intrinsic, electrode-related effects in this region, which play no role at very high frequencies.^[65,68]

Both above and below T_{JT} , Figure 4a,b shows significant frequency dispersion of $\epsilon'(T)$ ^[7,31,33]. In particular, the peak amplitude reduces with increasing frequency, pointing to polar order of order-disorder ferroelectric nature.^[59,60] As discussed in detail in previous studies,^[7,31] at high temperatures (beyond the temperature range covered in Figure 4a,b) the frequency dispersion strongly increases and huge values of ϵ' are observed, which is due to nonintrinsic contributions. This is known to often arise from electrode effects in semiconducting samples such as the lacunar spinels and special care has to be taken to avoid misinterpretations in terms of intrinsic relaxation processes.^[65,68] At sufficiently low temperatures and especially below T_{JT} , intrinsic relaxational behavior, again typical for order-disorder ferroelectrics,^[60] leads to the observed dispersion.^[7,31] In GaV_4S_8 , pronounced relaxational dispersion effects were observed up to the THz range,^[30] which will be discussed in more detail later.

For GaV_4Se_8 , at the lowest temperatures, the classical signature of canonical relaxation processes in $\epsilon'(T)$ ^[65,69] shows up: a step-like decrease, which shifts to lower temperatures with decreasing frequency. The latter reflects the essentially thermally activated behavior of conventional relaxation dynamics,^[65,69] in contrast to the critical temperature dependence expected just below the polar transition.^[59,60] In the study by Ruff et al.,^[31] it was speculated that this relaxation could be due to a decoupling of orbital and lattice dynamics, which is affected by the onset of magnetic order. In contrast, the dielectric constant of GaV_4S_8 does not show any clear anomaly or relaxation step at the magnetic transition.

Overall, with a peak in $\epsilon'(T)$ that becomes suppressed with increasing frequency and significant relaxation dynamics, both GaV_4Se_8 and GaV_4S_8 reveal signatures of order-disorder ferroelectricity, where fluctuating dipoles already exist above the ferroelectric transition. As the polar and orbital dynamics in these materials are highly entangled, this also implies orbital fluctuations above T_{JT} , i.e., a dynamic Jahn-Teller effect, in accord with Raman- and IR-spectroscopic studies^[21,42] (cf. Section 2). As corroborated by polarization experiments (Section 4.1), these compounds are type-I multiferroics, where the magnetic and ferroelectric order develop independently.

As discussed in Section 1, in GaV_4Se_8 and GaV_4S_8 the dipole moments are essentially generated by the elongation of the M_4 clusters (with $M = \text{V}$ for these systems) along the crystallographic $\langle 111 \rangle$ direction. This is also the case for GaNb_4S_8 whose temperature-dependent dielectric constant is shown in Figure 4c.^[13] However, while in GaV_4Se_8 and GaV_4S_8 all M_4 clusters become distorted along the same cubic body diagonal, leading to parallel orientations of the dipole moments and macroscopic polarization, this is not the case for GaNb_4S_8 .^[24] Instead, here below T_{MS} the distortions arise along four different cubic body diagonals, leading to a noncollinear polar order with zero net polarization. As mentioned in Section 1, the resulting structure is compatible with antiferroelectricity, for which

markedly different dielectric behavior compared with ferroelectrics is predicted.^[70,71] Indeed, in contrast to GaV_4Se_8 and GaV_4S_8 , $\epsilon'(T)$ of this material (Figure 4c) does not show a peak at T_{JT} , but instead reveals an abrupt reduction below T_{JT} . This is in accord with the predictions^[70,71] and with findings for classical antiferroelectrics such as KCN or $\text{NH}_4\text{H}_2\text{PO}_4$.^[72,73]

In Figure 4c, significant frequency dispersion of ϵ' also shows up for GaNb_4S_8 , both above and below the transition. For elevated temperatures, beyond the region covered in Figure 4c, again huge values of ϵ' are reached pointing to nonintrinsic effects.^[65,68] However, in vicinity and below T_{MS} , intrinsic dipolar fluctuations seem to dominate. Again, due to the coupling of dipolar and orbital dynamics, this indicates a dynamic Jahn-Teller effect in this material, just as for GaV_4Se_8 and GaV_4S_8 . This is in accord with the finding of structural fluctuations even far above T_{MS} , based on nuclear magnetic resonance and X-ray diffraction experiments.^[13,38]

Relaxation processes are best analyzed in frequency-dependent plots of the dielectric loss, $\epsilon''(\nu)$, where they should lead to a peak when the angular frequency matches the inverse relaxation time.^[65,69] As a typical example, the ϵ'' spectra of GaV_4S_8 are shown in Figure 5a for various temperatures below T_{JT} . The observed relaxation peaks shift to higher frequencies with decreasing temperature, opposite to the usual behavior of

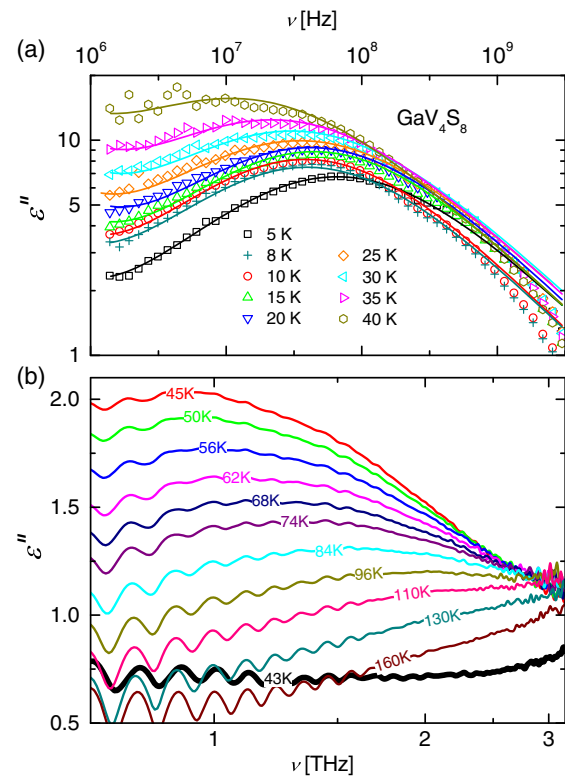


Figure 5. Dielectric loss spectra of GaV_4S_8 ^[30]. a) Spectra in the MHz—GHz frequency range for selected temperatures below T_{JT} . The lines show fits with the empirical Cole-Cole equation.^[74] b) Spectra at 0.5–3 THz shown for temperatures from 160 to 43 K, the latter being just below the Jahn-Teller transition at 44 K (bold line). Adapted with permission.^[30] Copyright 2015, American Physical Society.

thermally activated processes.^[65,69] Such an acceleration of the dynamics upon cooling just is in accord with the critical behavior expected below an order-disorder ferroelectric phase transition.^[59,60] The loss peaks can be reasonably well fitted by the usual empirical functions used to describe dipolar relaxation processes^[69,74] (lines in Figure 5a), providing information on the temperature-dependent mean relaxation time $\tau(T)$ discussed later.

Interestingly, for GaV_4S_8 , in the frequency range up to several GHz indications of intrinsic relaxation dynamics associated with dipolar motions were only found at $T < T_{JT}$ ^[7,30,33]. However, clear relaxational response at $T > T_{JT}$ was revealed in additional experiments performed at THz frequencies (Figure 5b).^[30] This implies that the corresponding relaxation time shifts by many decades when crossing the transition, which was ascribed to the first-order character of the orbital-ordering transition.^[30] As shown in Figure 5b, with decreasing temperature the relaxation peak shifts into the experimental frequency window and moves to lower frequencies. Such canonical temperature dependence is indeed expected for order-disorder ferroelectrics at $T > T_{JT}$ ^[59,60]. The peak amplitude continuously increases with decreasing temperature, which is related to the increase in $\epsilon'(T)$ expected for ferroelectrics. As shown in the study by Wang et al.,^[30] these spectra can be well fitted by the monodispersive Debye-relaxation function.^[69] While at 45 K the peak is well pronounced, it abruptly vanishes below the transition as documented by the loss curve at 43 K (bold line in Figure 5b), only 1 K below the phase transition. Here, the loss peak is shifted to lower frequencies, in accord with the low-frequency measurements, as shown in Figure 5a.

For GaV_4Se_8 and GaNb_4S_8 , the dielectric spectra also reveal the typical signatures expected for dielectric relaxation processes.^[13,31] Interestingly, in antiferroelectric GaNb_4S_8 , both below and above the Jahn-Teller transition relaxational behavior was detected in the low-frequency^[13] and the THz range as will be discussed later. For GaV_4Se_8 , at $T > T_{JT}$ nonintrinsic contributions prevent the detection of possible intrinsic relaxation processes in the low-frequency range, while THz measurements have not yet been performed in this system.

To quantify relaxational dynamics, usually relaxation times $\tau(T)$ are determined. They can be estimated from the frequency positions ν_p of the loss peaks via $\tau \approx 1/(2\pi\nu_p)$ and determined by fits of the spectra.^[65,69] Figure 6 shows the temperature dependence of τ of the three lacunar spinels discussed earlier and of GaMo_4S_8 and GeV_4S_8 , which will be treated in more detail later. Both above and below the Jahn-Teller transition, the relaxation times of these five systems partly differ by many decades and only some materials reveal common motifs as an increase in $\tau(T)$ when approaching the transition. These qualitative and quantitative differences could be expected in light of the different distortions of the cubane units found for most of these systems. However, even for GaV_4Se_8 and GaV_4S_8 with similar distortions, τ differs by more than a decade and its temperature dependence at the lowest temperatures is markedly different as discussed in more detail in the following paragraphs.

The triangles in Figure 6 show the temperature dependence of τ of GaV_4Se_8 . Here, the upright triangles represent the mentioned region of conventional temperature characteristics of

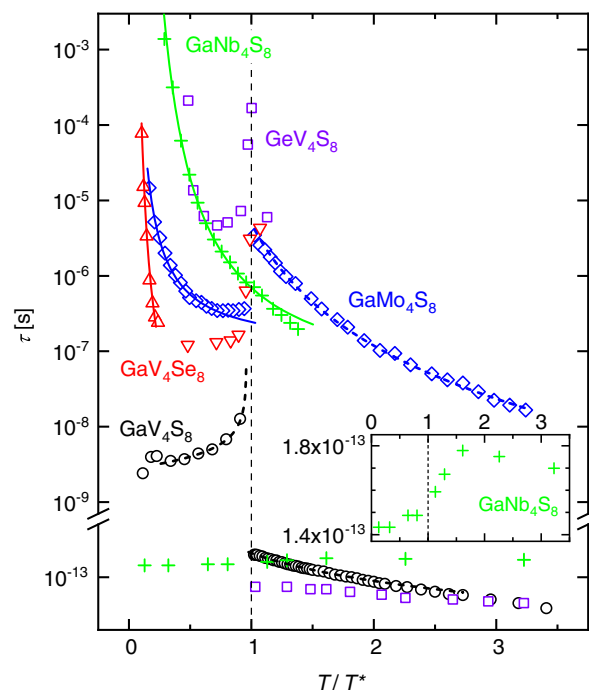


Figure 6. Overview of the temperature dependence of all relaxation times of dipolar relaxations found in lacunar spinels by dielectric and THz spectroscopy.^[12,13,30,31,77] The temperature scale is normalized to the T^* , which represents T_{JT} for each compound, except for GaNb_4S_8 where it represents T_{MS} (see Table 1). Solid and dashed lines represent fits of parts of the curves with Arrhenius or critical laws, respectively. The vertical dashed line indicates T^* . The inset shows an enlarged view of the GaNb_4S_8 fast-relaxation data.

the relaxation dynamics, already indicated by the steps in $\epsilon'(T)$ (Figure 4a). Indeed, in this region at $T < 9$ K, $\tau(T)$ can be well fitted by an Arrhenius law, with an energy barrier of 4.3 meV^[31] (solid line through the triangles). The inverted triangles in Figure 6 show unpublished $\tau(T)$ data at higher temperatures, approaching T_{JT} . The increase in $\tau(T)$, observed when approaching the transition, is consistent with the expectation for order-disorder ferroelectrics.^[59,60] The overall $\tau(T)$ curve at $T < T_{JT}$, exhibiting a minimum, could thus be explained by critical behavior being relevant close to the transition only, while at lower temperatures thermal activation gains in importance and finally dominates the dynamics (see Ruff et al.^[31] for an alternative explanation). As mentioned earlier, at $T > T_{JT}$, no information on the relaxation time of this system is available.

The temperature dependence of the relaxation time for GaV_4S_8 is shown by the circles in Figure 6, making obvious the huge jump of $\tau(T)$ at T_{JT} by about five decades (please note the break of the y-axis) when the relaxation dynamics shifts into the THz range above T_{JT} as discussed earlier (cf. Figure 5). Similar to the typical second-order transitions of order-disorder ferroelectrics,^[59–64] $\tau(T)$ increases when approaching the transition from both low and high temperatures and can be described by critical power laws, $1/(T - T_c)^\gamma$, in both cases (dashed lines).^[30] However, the ferroelectric transition in GaV_4S_8 reveals several noncanonical features as discussed in detail in the study

by Wang et al.^[30] The huge jump in $\tau(T)$ probably can be ascribed to the clear first-order character of the transition^[33] and the fact that it is driven by the orbital order; however, the detailed microscopic origin is far from being clarified. A close look at $\tau(T)$ of GaV_4S_8 at the three lowest shown temperatures reveals some anomalies. They reflect the successive transitions into the cycloidal (deceleration of τ) and the ferromagnetic state (acceleration of τ). In this respect, GaV_4S_8 behaves markedly different to GaV_4Se_8 , discussed earlier, exhibiting strong thermally activated relaxation dynamics in this low-temperature region. However, notably the increase in $\tau(T)$ when approaching T_{JT} from below qualitatively resembles the behavior of GaV_4Se_8 (inverted triangles). It seems interesting to measure the latter also in the THz range to check for a similarly strong acceleration of the relaxation dynamics when crossing T_{JT} .

The relaxation times of the antiferroelectric GaNb_4S_8 , deduced from the frequency-dependent dielectric data, are shown by the upper pluses in Figure 6. At $T < T_{JT}$ they can be fitted by an Arrhenius law (solid line). Interestingly, in contrast to GaV_4Se_8 and GaV_4S_8 , $\tau(T)$ of GaNb_4S_8 does not exhibit any marked anomaly or critical behavior close to T_{JT} . Instead, it only crosses over to a different temperature dependence, deviating from the Arrhenius fit. In the literature, information on dipolar fluctuations above and below the antiferroelectric phase transition is sparse. For antiferroelectric KCN, below the transition a relaxation process following Arrhenius behavior was observed, too.^[75] Similar to GaV_4S_8 (cf. Figure 5b), additional investigations of GaNb_4S_8 in the THz region revealed a fast relaxation process which, however, also persists below the Jahn-Teller transition, where it is superimposed by several sharp resonance excitations as will be reported in more detail in a future publication. Here, we only show its characteristic relaxation time, deduced from fits with the Debye formula (lower pluses in Figure 6), which appears in a similar range as for GaV_4S_8 . However, $\tau(T)$ for GaNb_4S_8 is only weakly temperature dependent and exhibits a heavily smeared-out anomaly across the transition at best (inset of Figure 6). Thus, this process seems rather unrelated to the dipolar fluctuations associated with the antipolar transition and its physical origin still has to be clarified.

Finally, we also briefly discuss the dielectric response of GaMo_4S_8 ^[12,76,77] and GeV_4S_8 , two more lacunar spinels whose dielectric properties have been investigated in detail. As mentioned in Section 1, in GaV_4Se_8 , GaV_4S_8 , and GaNb_4S_8 , the dipole moments essentially arise from a stretching of the M_4 tetrahedra along one of their vertices, accompanied by a shrinking of the opposite face, which reduces the point-group symmetry of these units to $3m$. Although the change in point group of the M_4 units in GaMo_4S_8 is the same, there the vertex-face distance of the tetrahedra shrinks and the face area increases. This is due to the different electron occupations of the molecular-like orbitals in the M_4 clusters.^[20] This structural distortion also generates a dipole moment^[10] and GaMo_4S_8 becomes ferroelectric upon the Jahn-Teller transition to a rhombohedral phase with switchable polarization below T_{JT} ^[11,12]. Thus, this lacunar spinel also is a type I multiferroic just as GaV_4Se_8 and GaV_4S_8 .

In a dielectric study of GaMo_4S_8 ^[12] complex relaxation dynamics was found. At $T < T_{JT}$ a single intrinsic relaxation shows up, exhibiting thermally activated temperature dependence at low

temperatures and a possible transition to critical behavior close to T_{JT} , as shown by the diamonds and corresponding fit line in Figure 6. At $T > T_{JT}$, two coupled intrinsic dipolar-orbital relaxation processes were identified and ascribed to relaxor-ferroelectric-like dynamics of nanoregions with short-range polar order and to the critical fluctuations of weakly interacting dipoles, as expected for order-disorder ferroelectrics.^[12] The relaxation times of the latter, which can be fitted by a critical law (dashed line), are shown by the diamonds at $T > T_{JT}$ in Figure 6. The relaxation behavior of GaMo_4S_8 above the Jahn-Teller transition markedly differs from that of GaV_4S_8 where the dipolar dynamics at $T > T_{JT}$ is much faster (circles in Figure 6). It seems likely that this is related to the mentioned differences in the structural distortions of the two lacunar spinels but the details are unclarified yet.

GeV_4S_8 was the first lacunar spinel whose dielectric properties were investigated in detail, revealing orbital-order-driven multiferroicity.^[8] In contrast to all the lacunar spinels treated earlier, it has two unpaired electrons with total spin $S = 1$ in the highest orbital level of the M_4 tetrahedra. This leads to a significantly different distortion of these units via an elongation and shortening of two opposite V-V bonds, respectively, and an overall symmetry change to the space group $Imm2$ upon T_{JT} .^[22,39,40] As first detected by Singh et al.,^[8] the behavior of the dielectric constant of GeV_4S_8 differs markedly from that of the compounds discussed earlier:^[76,77] below T_{JT} , $\epsilon'(T)$ strongly increases and a broad maximum develops several Kelvin below the transition. At the antiferromagnetic ordering a further structural transition takes place and $\epsilon'(T)$ is strongly suppressed,^[8] while the other ferroelectric systems do not exhibit significant anomalies at their magnetic transitions. An additional peak close to T_{JT} was detected in the study by Widmann et al.^[76] and suggested to indicate a possible decoupling of orbital and polar phase transition. A detailed dielectric study at audio and radio frequencies evidenced a relaxation process whose amplitude is strongly reduced above T_{JT} and in the antiferromagnetic phase.^[77] It was proposed to be due to the coupled orbital and dipolar fluctuations that are associated with the polar order.^[77] The corresponding relaxation times are shown by the upper squares in Figure 6 revealing a slowing down when approaching both the structural and the magnetic transition, the latter in contrast to the other lacunar spinels. Additional dielectric THz measurements were also performed for this compound, evidencing a number of different excitations.^[77] Among them is a Debye-like relaxation process that appears at $T > T_{JT}$. Its relaxation times are shown by the lower squares in Figure 6. This fast process reminds of the THz relaxation reported for GaV_4S_8 (lower circles in Figure 6), reflecting dipolar fluctuations related to the order-disorder ferroelectric transition.^[30] However, in contrast to GaV_4S_8 , below the Jahn-Teller transition the THz relaxation of GeV_4S_8 was reported to seemingly remain located in the THz regime while its character crosses over from relaxational to resonance-like.^[77] Therefore, there may be no close relation of this fast relaxation dynamics to the one detected below T_{JT} in the dielectric frequency range.

Overall, the aforementioned overview about the dielectric properties of five lacunar spinels, four of them being multiferroic, demonstrates that there is a large variation in the rather

complex dielectric response of these materials showing nonconventional, orbital-driven polar order. In fact, the dipolar moments in these compounds are in principle generated by the same mechanism, namely, a polar distortion of the molecule-like M_4 units. However, partly due to variations in the occupation of their electronic energy levels, these distortions qualitatively differ for most of these systems. Common to all investigated lacunar spinels is the occurrence of relaxational dynamics. This points to the order-disorder character of their polar transitions involving coupled dipolar and orbital fluctuations, consistent with a dynamic Jahn-Teller effect. A common motif of the relaxation-time curves shown in Figure 6 (except for the antipolar GaNb_4S_8) is the increase in the relaxation time when approaching the polar transition, which partly could be fitted by critical laws. This finding is in accord with the order-disorder scenario. At the lowest temperatures, thermal activation starts to dominate the coupled dipolar-orbital motions in all systems except GaV_4S_8 , leading to a more or less pronounced minimum in $\tau(T)$. Many open questions remain to be clarified concerning the partly huge differences in the relaxation times of these materials and, especially, the unusual many-decades jump of $\tau(T)$ that seems to arise at the transition of some of these nonconventional polar systems.

4. Ferro- and Magnetolectric Polarization

As shown in the previous section, a pronounced dielectric anomaly at T_{JT} hints to the onset of long-range polar order in various lacunar spinels. The emergence of ferroelectricity was directly evidenced by temperature and magnetic field-dependent polarization data, respectively, obtained via pyro- and magnetocurrent measurements, in GeV_4S_8 , GaV_4S_8 , GaV_4Se_8 , GaMo_4S_8 .^[7-9,11,31] Due to their spontaneous polarization and type-I multiferroic nature, these materials offer an ideal playground to investigate 1) novel magnetoelectric effects^[7-9,14,15,78,79] and 2) ferroelectric domain and domain-wall properties.^[11,14,27,28]

Singh et al.^[8] provided the first comprehensive study evidencing orbital-order-driven ferroelectric behavior and magnetoelectric coupling of a lacunar spinel, namely, GeV_4S_8 . Recently, the ferro- and magnetoelectric properties of the rhombohedral lacunar spinels GaV_4S_8 , GaV_4Se_8 , and GaMo_4S_8 have also been studied in detail. These compounds exhibit unique polar properties, such as the lack of inversion domains, full magnetic control of polar states (see Section 4.1), and Néel-type magnetic skyrmions dressed with polarization (see Section 4.2).^[7,9-11,14,31,78-80]

Ruff et al.^[7] provided a thorough characterization by magnetic susceptibility, specific heat, as well as magneto- and pyrocurrent measurements of the polar properties of GaV_4S_8 . Figure 7a shows typical temperature-dependent polarization data measured along the $\langle 111 \rangle$ -type axis. It is characterized by a sudden jump from zero to finite values below $T_{JT} = 44$ K followed by a moderate increase, which is typical for the order parameter of a first-order transition. The weak first-order nature of the ferroelectric transition was also corroborated by specific-heat measurements.^[33] Similar polarization results were also reported for GaV_4Se_8 , GaMo_4S_8 .^[9,11,14,31]

As shown in Figure 7a,b, a second increase in the polarization shows up at $T_C = 13$ K, as a result of an excess spin-induced polarization upon the magnetic ordering, indicating the presence

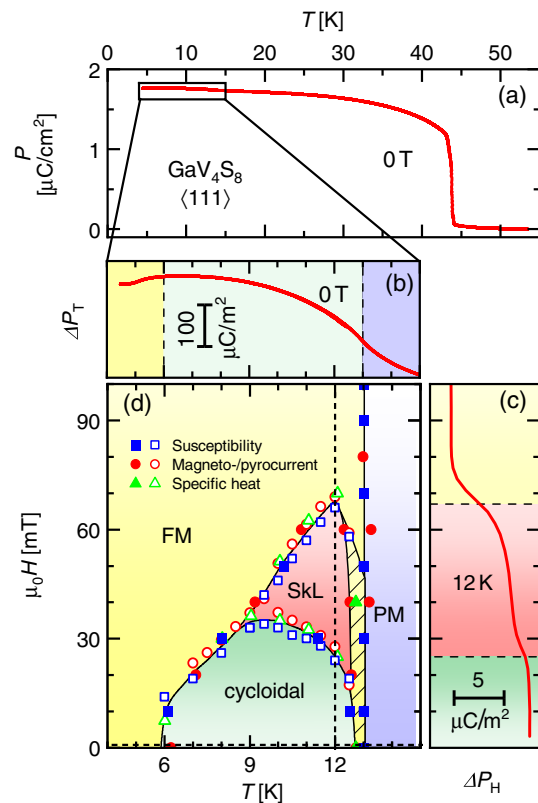


Figure 7. a) Temperature-dependent polarization of GaV_4S_8 . b) Temperature-dependent spin-induced polarization at 0 T observable in the temperature range marked by the box in (a). c) Magnetic-field-dependent spin-induced polarization at 12 K.^[7] d) Magnetic phase diagram of GaV_4S_8 .^[7] The horizontal and vertical dashed lines in (d) indicate the locations of (b) and (c), respectively. Adapted with permission.^[7] Copyright 2015, The Authors, published by American Association for the Advancement of Science.

of magnetoelectric coupling.^[7,9,14,31] The spin-induced polarization rises when entering the cycloidal spin state at T_C , and is somewhat reduced when entering the ferromagnetic state at 6 K. Interestingly, the magnetoelectric polarization distinguishes all the magnetically ordered states, i.e., the excess polarization has three distinct values in cycloidal, Néel-type skyrmion lattice, and ferromagnetic states (see magnetic phase diagram in Figure 7d), as shown in Figure 7c. This pioneering finding evidences that Néel-type skyrmions can also carry ferroelectric polarization,^[7] which may allow the electric control and readout of Néel-type skyrmions.

Spin-induced polarization was also observed in GaV_4Se_8 ^[9,14,31], which we discuss in detail in Section 4.2, on the basis of original data. In GaV_4S_8 , the skyrmions also carry electric polarization and the skyrmion lattice region in the phase diagram is strongly extended as compared with GaV_4S_8 , namely, it is stable down to zero Kelvin. The thermal and field stability ranges of the skyrmion lattice in GaV_4S_8 and GaV_4Se_8 have been studied in great details experimentally^[14,27,29,81] and theoretically.^[80,82-84] For the rhombohedral lacunar spinel GaMo_4S_8 , such a spin-induced polarization has been predicted by Nikolaev et al.^[79] but not yet observed, making this system also highly interesting.

From a more applied point of view, one important aspect of ferroelectrics is the control of the polarization by external stimuli, such as electric and/or magnetic fields. Despite the observation of polarization-dressed skyrmions and remarkable magnetoelectric couplings in these orbital-ordered ferroelectric systems, the on-demand control of the ferroelectric state remains a nearly uncharted territory in ferroelectric lacunar spinels. The control of the ferroelectric polarization by electric fields was first demonstrated and discussed in detail only for GeV_4S_8 .^[8] In case of the ferroelectric lacunar spinels with rhombohedral structure, the electric-field manipulation of polar domains was reported in GaV_4Se_8 and GaMo_4S_8 .^[11,14] So far, ferroelectric polarization control has not been demonstrated in case of the first reported Néel-type skyrmion host, GaV_4S_8 . Here, we choose GaV_4Se_8 to emphasize the feasibility of an electric-field control of magnetic skyrmions and to elucidate prospects for future investigations. In the following section, we describe the polarization switching by external magnetic and electric fields in this compound.

4.1. Electric and Magnetic Control of Domain States

As discussed in the introduction, the room-temperature cubic structure of lacunar spinels already lacks inversion symmetry.^[22,85] As a consequence, in compounds undergoing a

transition from the cubic state to the rhombohedral state ($R3m$), four polar domain states (P_1, \dots, P_4) can form with their polar axes pointing along the four cubic body diagonals ($[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, $[\bar{1}\bar{1}1]$), as shown in Figure 1b^[14,27,28]. A unique feature of this ferroelectric state is the lack of inversion domains ($-P_1, \dots, -P_4$). This polar-diode nature enables a peculiar control of the domain states by external fields. The application of an electric field ($+E_p$) along a polar axis, e.g., P_1 , promotes a single domain state, namely, the P_1 domain state (see Figure 8a), while an electric field of opposite sign ($-E_p$) equally favors the other three domains, P_2, P_3 , and P_4 (see Figure 8b), thus enforcing the creation of a polar multidomain state.

Figure 8c shows the manipulation of the ferroelectric polarization for GaV_4Se_8 by the application of various electric poling field (E_p) applied along the $[111]$ axis, demonstrating the electric control of the domain population. The polarization component parallel to the $[111]$ axis is derived from temperature-dependent pyrocurrent measurements (for experimental details, see Geirhos et al.^[14]). The temperature-dependent polarization resembles that of GaV_4S_8 (see Figure 7a).

It is interesting that a significant polarization of the order of $2\mu\text{C}/\text{cm}^2$ is observed below T_{JT} even without any poling field. This hints toward a natural preference on the domain state, P_1 in the present case, with its polar axis perpendicular to the

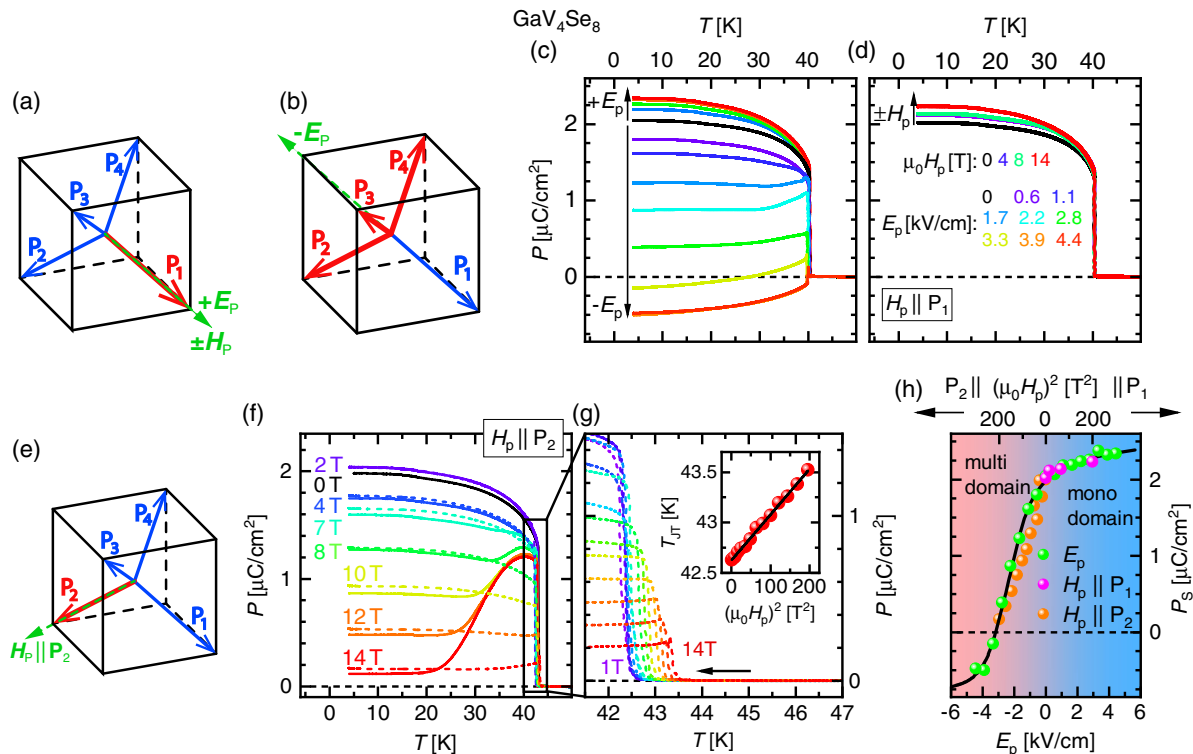


Figure 8. a,b) Schematic representations of the domain-selection process by electric and magnetic fields applied along the P_1 direction in the rhombohedral lacunar spinels. c,d) Temperature-dependent polarization of GaV_4Se_8 for various electric and magnetic poling fields applied along $[111]$ (P_1), respectively. e) Schematic representation of the direction of applied field used for the measurements shown in (f) and (g). f) Temperature-dependent polarization for various strengths of magnetic poling fields applied along P_2 measured during cooling (dashed lines) and heating (solid lines). g) Magnified view of the cooling curves in the area marked in (f) (additional fields included). The inset in (g) displays the magnetic field dependence of T_{JT} . h) Electric and magnetic poling field dependence of the saturation polarization P_s at 4 K. In all shown measurements, the polarization P was measured along P_1 .

planar metallic electrodes. Increasing the positive poling field E_p applied along the direction of P_1 up to 4.4 kV cm^{-1} leads to a slight enhancement and a saturation of the polarization to $P_{\text{mono}} \sim 2.3 \mu\text{C/cm}^2$. This saturation indicates the achievement of a polar monodomain state. Applying poling fields of opposite sign ($-E_p$) results in a gradual reduction of the macroscopic polarization with increasing strength of $-E_p$. This is due to the decreasing population of the P_1 domain state and the enhanced population of the other three domains, as sketched in Figure 7b. For $E_p = -4.4 \text{ kV cm}^{-1}$ the polarization measured along the [111] axis turns to a negative value, indicating that the volume fraction of the P_1 domain state is less than 50%. When the P_1 domain state is fully suppressed by negative poling electric fields, the polarization is expected to saturate to $P_{\text{mono}}/3 \sim -0.7 \mu\text{C cm}^{-2}$.

A direct comparison of the absolute value of polarization among different lacunar spinels is challenging, as either the relative populations of the four domains has to be known or a monodomain state has to be achieved. The polarization has only been measured on multidomain samples of GaV_4S_8 ^[7] and only estimated for GaMo_4S_8 ^[11]. The polarization in the monodomain state is only known for GaV_4Se_8 where the saturation value is $P_{\text{mono}} \approx 2.3 \mu\text{C cm}^{-2}$, as shown in Figure 7c and d. From theoretical analysis, polarization values calculated using a Berry phase approach are reported to be $2.43 \mu\text{C cm}^{-2}$ for GaV_4S_8 ^[10] and $\approx 3.1 \mu\text{C cm}^{-2}$ for GaMo_4S_8 ^[80]. Notably, the experimental value for GaV_4Se_8 agrees well with the one calculated for GaV_4S_8 .

Interestingly, the ferroelectric polarization of GaV_4Se_8 can be controlled not only by electric but also by magnetic fields (H_p). The realization of a monodomain state is possible via cooling the material through T_{JT} in magnetic fields applied along one of the cubic body diagonals, in the present case the P_1 direction (see Figure 8d). The magnetic control of the ferroelectric domain population is facilitated by the uniaxial magnetic anisotropy of the material. As the anisotropy axis coincides with the polar axis, the domain with easy-axis along the field is favored.^[27,29,86] Due to the fact that the magnetic anisotropy energy is an even function of the magnetic field, the same domain state is favored for both positive and negative signs of the field.

The question arises, whether any of the four monodomain states can be established, although the samples usually show a preference on one domain state due to the contact geometry or internal strain. For this, we apply poling magnetic fields along a polar axis, different from the naturally favored one, namely, along $P_2 \parallel [1\bar{1}\bar{1}]$, as shown in Figure 8e. Figure 8f shows the temperature-dependent polarization recorded along P_1 , the polarization direction of the originally favored domain, for various poling magnetic fields applied along P_2 . As clear from Figure 8f, with increasing magnetic field the polarization reduces continuously to values of the order of $\approx 0.1 \mu\text{C cm}^{-2}$ at 4 K with a maximum applied field of $\mu_0 H_p = 14 \text{ T}$. The nearly zero net polarization in 14 T indicates that the volume fraction of the magnetically promoted P_2 domain state is about three times larger than the remaining fraction of the P_1 domain state. Comparing the temperature dependence of the polarization from pyrocurrent measurements after poling with a magnetic field along P_1 (Figure 8d) and along P_2 (Figure 8f, solid lines) reveals

another interesting aspect: for poling magnetic fields $\mu_0 H_p > 7 \text{ T}$ along P_2 , a strong enhancement of the polarization is observed above 25 K, before vanishing at T_{JT} . As the magnetic field is only used for the poling and switched off during the polarization measurement, performed in warming up, this feature indicates a temperature-induced back-switching from the state dominated by P_2 domains to the naturally preferred P_1 domain state. As already shown, via negative poling electric fields applied along the [111] axis, one can also achieve a multidomain state where the fraction of the P_1 domain state is suppressed. However, in that case, a temperature-induced back-switching to P_1 domain state, emerging upon zero-field heating, does not take place, as clear from Figure 8c.

To verify the back-switching mechanism, we recorded the temperature-dependent polarization during cooling in applied magnetic fields of up to 14 T. The results are indicated by dashed lines in Figure 8f. These curves resemble the behavior seen in the electric-field poling measurements (Figure 8c).

In addition to the domain control, external fields can also shift T_{JT} toward higher temperatures, as shown in Figure 8g, which is a magnified view of the box indicated in Figure 8f. At 14 T, the ferroelectric transition temperature is increased by $\approx 1 \text{ K}$. This shift is most likely caused by the higher magnetic susceptibility of the rhombohedral state compared with the cubic state.^[31] This explanation is also supported by the quadratic magnetic-field dependence of the transition temperature, which is obvious from the inset in Figure 8g. Due to technical limitations, recording the ferroelectric polarization upon cooling in the presence of electric fields is not possible in this compound; thus, the electric field-induced shift of T_{JT} could not be investigated.

Finally, Figure 8h summarizes the thorough electric and magnetic field control of the domain states in GaV_4Se_8 . The net saturation polarization is plotted as function of poling electric and magnetic fields. The latter also takes into account the dependence of domain population on the orientation of the applied magnetic field ($H_p \parallel P_1$ and P_2). The polarization measured at the lowest temperatures P_s depends on the poling electric field as depicted by the green circles. A nearly complete control from a mono- to a multidomain state can be achieved. Also, magnetic fields enable the control of the domain states. In this case, however, the saturation polarization has a quadratic magnetic-field dependence, as expected from the field dependence of the magnetic free energy. Resulting from this quadratic dependence, one domain state is favored when applying magnetic fields along any of the polar axes, irrespective of the sign of the field. Moreover, the selection of different monodomain states can be achieved by changing the orientation of the poling magnetic field.

4.2. Spin-Driven Polarization

For GaV_4S_8 it was shown by Ruff et al.^[7] that all magnetic phases emerging at low temperatures, namely, a cycloidal, a Néel-type skyrmion lattice, and a field-polarized ferromagnetic phase, carry different spin-induced ferroelectric polarizations, as shown in Figure 7. The other rhombohedral lacunar spinels, GaV_4Se_8 and GaMo_4S_8 , also undergo magnetic transitions at $T_C = 18 \text{ K}$ ^[29] and $T_C = 20 \text{ K}$ ^[35] respectively. They were also found to exhibit complex magnetic phase diagrams. Bordacs

et al.^[29] detected a Néel-type skyrmion lattice state in GaV_4Se_8 , which was corroborated by Fujima et al.^[9] to exhibit a spin-induced polarization similar to GaV_4S_8 .^[31] In case of GaMo_4S_8 , the existence of a skyrmion lattice^[35,80,84] as well as magnetoelectric coupling^[79] has been proposed, but not experimentally verified yet.

The uniaxial magnetic anisotropy, inherent to the rhombohedral state, leads to the coexistence of distinct magnetic phases on different polar domains for magnetic fields of arbitrary orientation, which makes the determination of magnetic phase diagrams a delicate issue. These difficulties can be overcome by studying the magnetic phase diagrams of these compounds on rhombohedral monodomain crystals, achieved by electric and/or magnetic poling, as demonstrated for GaV_4Se_8 .^[14] Another approach, which has been applied to rhombohedral multidomain samples of GaV_4S_8 and GaV_4Se_8 ,^[14,27,81] is tracing the angular dependence of the critical magnetic fields. As a very important outcome, these studies reveal highly anisotropic magnetic phase diagrams of these materials. While the cycloidal state is always stable in low fields, irrespective of the orientation of the magnetic field, the stability of the skyrmion lattice state is limited to a critical angle of oblique fields, i.e., it is stable for fields applied along the rhombohedral axis but vanishes if the magnetic field is tilted beyond a critical angle.^[14,27,81] The highly anisotropic nature of the magnetic phase diagrams has been reproduced theoretically in these compounds.^[80,82,84]

Here, we briefly describe through the example of GaV_4Se_8 how the progress in domain control helps exploring the magnetic phase diagram via the detection of spin-induced polarization, which exhibits clear anomalies at the magnetic transitions similarly to the magnetic susceptibility. This was first demonstrated in GaV_4S_8 where peaks in the magnetocurrent and corresponding steps in the polarization have been assigned to transitions between the different magnetic phases,^[7] allowing the determination of stability ranges of the cycloidal, Néel-type skyrmion lattice, and ferromagnetic states. **Figure 9a** shows the magnetocurrent (j , time derivative of polarization) and the corresponding polarization on a monodomain GaV_4Se_8 crystal at $T = 12.2$ K. Anomalies observed in the color map of the magnetocurrent over the temperature-field plane clearly reveal the magnetic phase boundaries, as shown in **Figure 9b**. In this compound, we observed four magnetic phases, all of them exhibiting a distinct spin-induced polarization. Small-angle neutron scattering measurements^[14,29] allow to ascribe three phases to cycloidal, Néel-type skyrmion lattice, and ferromagnetic phase, as shown in **Figure 9b**. The precise spin texture of the fourth phase, emerging only below 12 K between the cycloidal and skyrmion lattice phases, is still unknown. Interestingly, the skyrmion lattice phase of GaV_4Se_8 is strongly extended in the temperature range compared with GaV_4S_8 (see **Figure 7d**), which is explained by a weaker magnetic anisotropy of GaV_4Se_8 .^[9,29] This study, carried out on a monodomain crystal, precisely quantifies the magnetoelectric effect in all magnetic phases of GaV_4Se_8 .

Though such a detailed systematic study of the magnetoelectric effect has not been performed in the other rhombohedral lacunar spinels, the spin-induced polarization varies in the same order of magnitude for all compounds.^[7,9,14] From a technical point of view, this spin-induced polarization arising in rhombohedral lacunar

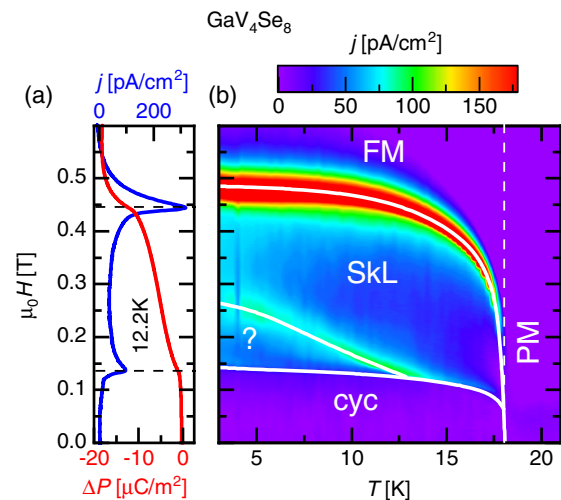


Figure 9. a) Magnetic-field-dependent magnetocurrent and polarization at 12.2 K of a monodomain GaV_4Se_8 crystal along $\langle 111 \rangle$ with magnetic field oriented along the same direction. b) Color map of the full temperature and magnetic-field dependence of the magnetocurrent measured with the same configuration as in (a).

spinel is about two orders of magnitude larger compared with that of Cu_2OSeO_3 , another magnetoelectric insulator hosting Bloch-type skyrmions.^[87,88] In that system, a quadratic magnetoelectric effect is discussed as the origin of the polarization of modulated magnetic phases, including the Bloch-type skyrmion phase.^[87,88] In contrast, the excess polarization in the skyrmion lattice phase of GaV_4S_8 was proposed by Ruff et al. to originate from the exchange-striction mechanism,^[7] which leads to a polar ring around the core of the Néel-type skyrmions. The finding of Néel-type skyrmions carrying an inherent electric polarization could pave the way toward the development of novel energy-efficient electric-field controlled skyrmion-based electronics.

5. Outlook: Toward Multiferroic Domain and Domain Wall Properties

As overviewed in the current work, the optical, dielectric, and polar properties of numerous lacunar spinel compounds have been thoroughly investigated and discussed in the literature. Optical studies classify all the investigated lacunar spinels as narrow-gap semiconductors. As another common aspect, all the investigated compounds exhibit a structural transition, which lowers the symmetry of the lattice from cubic to rhombohedral or orthorhombic. Depending on the compound, this transition can lead to either a ferroelectric or an antiferroelectric low-temperature state. Due to the presence of dielectric relaxations, evidencing coupled dipolar and orbital fluctuations, the polar transition in all compounds can be classified as order-disorder type. This implies the presence of a dynamical Jahn-Teller effect in the cubic phase. Still, many open questions remain to be clarified concerning the noncanonical dielectric behavior of these unconventional ferro- and antiferroelectric materials. A further general aspect of these compounds is the spin-lattice coupling: in case of ferroelectric lacunar spinels this is manifested by a

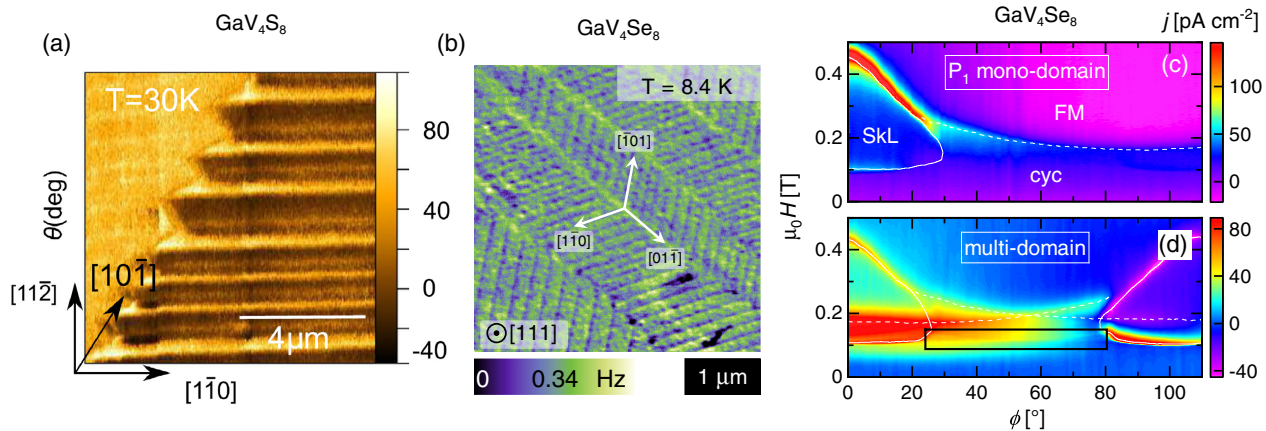


Figure 10. a) Phase of a PFM image recorded on a (111) surface of GaV_4S_8 .^[28] Reproduced under the terms of the CC-BY license.^[28] Copyright 2017, The Authors, published by Springer Nature. b) Frequency shift of a noncontact MFM image recorded on GaV_4Se_8 .^[14] Note that the contrast in this image is not a magnetic one, but stems from the polar domain structure.^[14] Reproduced under the terms of the CC-BY license.^[14] Copyright 2020, The Authors, published by Springer Nature. c,d) Color maps of the magnetoelectric current-density as a function of magnetic-field angle and magnitude measured on GaV_4Se_8 at 12 K in the polar mono- and multidomain state, respectively.^[14] The lines mark anomalies belonging to magnetic transitions in the domains. The corresponding magnetic phases are indicated by labels in (c). The black frame in (d) highlights the area where additional anomalies appear in the multidomain state which are magnetic states confined to polar domain walls. Adapted under the terms of the CC-BY license.^[14] Copyright 2020, The Authors, published by Springer Nature.

change in the exchange interaction from antiferromagnetic (cubic phase) to ferromagnetic (rhombohedral phase), while in the antiferroelectric compounds the symmetry-lowering structural transition is associated with a spin-singlet formation. The ferroelectric compounds exhibit a sizable polarization, which can be controlled by electric as well as magnetic fields. Moreover, the magnetic order, taking place within the polar state, renders these compounds type-I multiferroics, which show a decent magnetoelectric coupling.

Beyond the macroscopic magnetic, electric, and optical properties of the rhombohedral lacunar spinels, also the local microscopic properties of ferroelectric domains and domain walls are fascinating.^[11,14,27,28] Especially, the growing interest in technologically relevant microscopic properties of domains and domain walls of oxide-based multiferroics^[89–91] may also trigger considerable interest in this novel nonoxide family of ferroelectrics. Through the examples of GaV_4S_8 and GaV_4Se_8 ,^[14,28] **Figure 10a,b** shows the typical polar domain patterns in ferroelectric lacunar spinels via scanning probe techniques.

These patterns are dominated by lamellar-like domain structures, formed by the alternation of two types of domains. Adjacent lamellar structures are separated by staircase-like domain walls.^[11,14,28] A recent article,^[14] reporting on the emergence of magnetic states confined to polar domain walls of GaV_4Se_8 , implies that polar domain walls in multiferroics can offer a fertile ground to explore novel magnetic states nonexistent in bulk materials. Through the electric control of the domain state (see Section 4.1), comparative studies of the multi- versus monodomain states in GaV_4Se_8 are feasible.

Though the magnetic states confined to polar domain walls of GaV_4Se_8 are present only in a small volume fraction, their signatures can be observed in macroscopic quantities. This was evidenced by anomalies in the magnetization and polarization exclusively observed in the multidomain samples and assigned

to spin textures emerging only at polar domain walls. **Figure 10c, d**, reproduced from Geirhos et al.,^[14] show color maps of the dependence of the magnetocurrent on the magnitude and the orientation of the magnetic field, obtained on mono- and multidomain samples, respectively. While in the monodomain case only anomalies associated with magnetic transitions of the P_1 domain are present (**Figure 10c**), in the multidomain state the same set of anomalies is observed twice, shifted by $\approx 109^\circ$, the angle spanned by the rhombohedral axes of P_1 - and P_2 -type domains (**Figure 10d**). Most importantly, additional anomalies show up in the multidomain state (in the area marked by the black frame), which cannot be assigned to any of the four polar domains and thus, must originate from magnetic states confined to ferroelectric domain walls.^[14]

These first intriguing results on the domain and domain-wall properties of rhombohedral lacunar spinels are already fuelling the idea of nonoxide-based domain-wall electronics in skyrmion-hosting systems. The electric and magnetic field-control of macroscopic properties, directly linked to polar domain architectures, makes systems such as GaV_4S_8 , GaV_4Se_8 , and GaMo_4S_8 prime candidates for exploratory research. Thorough local-probe studies are required and absolutely essential to explore dielectric, magnetoelectric, and piezoelectric properties of these compounds from the macro- to the nanoscale.

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Conflict of Interest

The authors declare no conflict of interest.

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