

# New multiferroics inspired by minerals

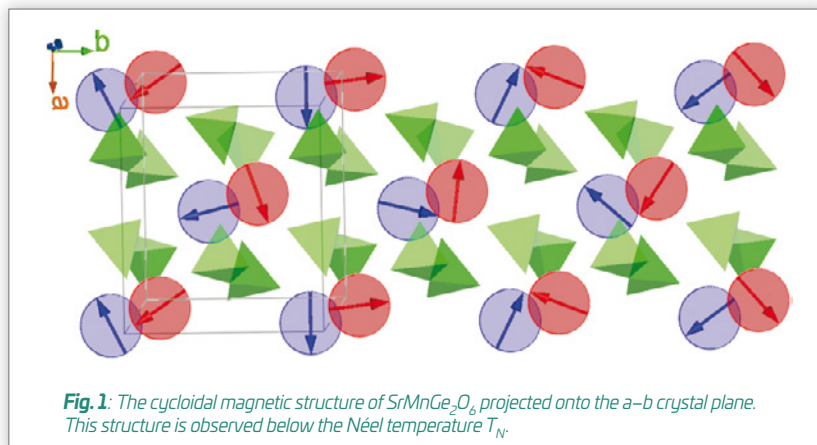
Multiferroics are materials that show both magnetism and ferroelectricity (spontaneous electric polarization) at the same time. A coupling of electric fields and magnetic fields in materials was speculated as early as 1894 by Pierre Curie. However, magnetism and ferroelectricity are generally antagonistic properties and multiferroics have long remained rather rare “creatures”. Recently, it has been understood that some specific types of magnetic order can induce ferroelectricity, and this has boosted the search for corresponding compounds. Minerals have always been a source of inspiration for the design of new materials. Among them, the pyroxenes, a major class of minerals that constitutes more than 20 volume% of the Earth’s crust, have a flexible, quasi-one dimensional architecture with all the necessary ingredients to achieve the complex magnetic structures required for multiferroicity.

In recent years, the coupling between magnetic and electric properties in transition metal oxides has given rise to a significant research effort. This effort is driven by the emergence of new fundamental physics and potential technological applications, for instance in memories and logic devices. In 2009, Khomskii proposed a classification of multiferroics into two categories. For Type-I multiferroics, the ferroelectric order does not depend on the magnetism. Contrarily, in Type-II multiferroics, the ferroelectricity is actually induced by the appearance of magnetic order. As an obvious consequence, a large magneto-electric coupling can be achieved in the Type II case.

However, the microscopic mechanism governing the induction of ferroelectricity by the spin ordering is not yet fully understood and various mechanisms have been proposed, depending on the compound. In all cases, the appearance of ferroelectric polarization can be considered as a side effect of the symmetry-breaking caused by the magnetic ordering. So, one way to design new type II multiferroics is to induce complex magnetic orders that lead to a low symmetry, and especially polar symmetry. In recent years, two ingredients have proved to be favourable for stabilization of such magnetic structures: magnetic “frustration” and low-dimensionality.

Pyroxenes are so-called chain-silicates of general composition  $AMSi_2O_6$ , where A stands for mono- or divalent metals while M represents divalent or trivalent metals. Their crystal structures having orthorhombic or monoclinic symmetries can accommodate a wide variety of M and A elements, especially the magnetic 3d-transition metals. In most cases, by appropriate synthetic routes, silicon may also be replaced by germanium. The pyroxene crystal structure presents isolated zig-zag chains of edge-sharing  $MO_6$  octahedra giving rise to low-dimensional magnetic behaviour. These quasi-1D chains are bridged together by corner-linked  $SiO_4$  tetrahedra chains and the general magnetic chain arrangement forms a triangular lattice which may result in magnetic frustration (three magnetic moments on a triangle cannot be simultaneously anti-parallel to each other). Thus, the pyroxenes are promising materials in the search for new multiferroics.

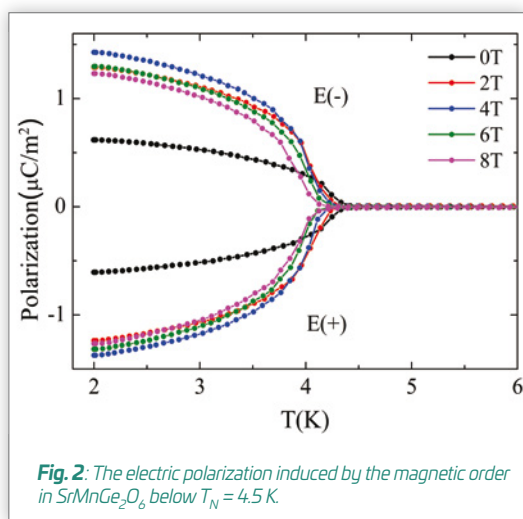
Since pyroxenes are known for the sensitivity of their properties to steric effects (that is, the size of the constituent atoms), we investigated synthetic pyroxene compounds with the heavy atom Strontium replacing the usual Calcium atom on the A site. We have synthesized powders and single crystals of  $SrMGe_2O_6$  (with M = Cobalt or Manganese) and investigated in detail, for the first time, their crystal and magnetic structures, using both X-ray diffraction



**Fig. 1:** The cycloidal magnetic structure of  $SrMnGe_2O_6$  projected onto the  $a$ - $b$  crystal plane. This structure is observed below the Néel temperature  $T_N$ .

and neutron diffraction. We found that the compound  $SrMnGe_2O_6$  indeed orders antiferromagnetically below a Néel temperature  $T_N = 4.5$  K. Its magnetic structure is characterized by a cycloidal spin configuration (see Fig. 1). Such a structure can lead to ferroelectric order through the so-called Inverse Dzyaloshinskii-Moriya effect.

Measurements of the electrical properties (Fig. 2) show a spontaneous electric polarization developing precisely in coincidence with the magnetic ordering, proving that  $SrMnGe_2O_6$  is indeed a new type II multiferroic, where the ferroelectricity is induced by a cycloidal spin structure. A large single crystal grown at the Institut NÉEL by Pascal Lejay is now being used for investigating the structural details of the magnetoelectric coupling, by diffraction and magnetic measurements.



**Fig. 2:** The electric polarization induced by the magnetic order in  $SrMnGe_2O_6$  below  $T_N = 4.5$  K.

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## FURTHER READING...

“ $SrMGe_2O_6$  (M = Mn, Co): a family of pyroxene compounds displaying multiferroicity”

L. Ding, C. V. Colin, C. Darie and P. Bordet

*J. Mater. Chem. C* **4**, 4236 (2016).

“One-dimensional short-range magnetic correlations in the magnetoelectric pyroxene  $CaMnGe_2O_6$ ”

L. Ding, C. V. Colin, C. Darie, J. Robert, F. Gay and P. Bordet

*Phys. Rev. B* **93**, 064423 (2016).