

Pyroelectric effect and possible ferroelectric transition of helimagnetic GdMn_2O_5 , TbMn_2O_5 and YMn_2O_5

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 2673

(<http://iopscience.iop.org/0953-8984/8/15/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:31

Please note that [terms and conditions apply](#).

Pyroelectric effect and possible ferroelectric transition of helimagnetic GdMn_2O_5 , TbMn_2O_5 and YMn_2O_5

Akihiro Inomata and Kay Kohn

Department of Physics, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Received 24 July 1995, in final form 2 January 1996

Abstract. In a series of papers, we have reported the results of dielectric, magnetic and magnetoelectric studies of RMn_2O_5 ($R =$ rare earth between Nd and Lu, Y or Bi), proposing the possibility of ferroelectricity in these oxides, but the direct demonstration of ferroelectricity was lacking.

In this paper we present the results of pyroelectric current measurements of GdMn_2O_5 , TbMn_2O_5 and YMn_2O_5 single crystals between 4.2 and 273 K. These results indicated the existence of spontaneous polarization at low temperatures. The spontaneous polarization was switched by an applied electric field. Its possible direction is along the b axis of an orthorhombic crystal.

The supposed temperature dependence of spontaneous polarization was complicated except for the case of GdMn_2O_5 , suggesting a ferroelectric origin of the polarization.

1. Introduction

In previous papers [1–7], we reported the results of magnetoelectric and dielectric studies of a series of oxides RMn_2O_5 [8–10], where R is a rare earth from Nd to Lu, Y or Bi. From the dependence of the magnetoelectric effect on the poling electric field, we concluded that these oxides were polar below a certain transition temperature, suggesting the possibility of ferroelectricity. We also observed an anomaly in the dielectric constant along the b direction of an orthorhombic crystal [11] at the corresponding temperatures.

On the other hand, neutron diffraction studies [12–16] revealed that these oxides were antiferromagnetic at low temperatures. The helical magnetic ordering of the magnetic moments of Mn^{3+} and Mn^{4+} ions develops below the Néel temperature of about 40 K. This is near to the temperature of the proposed polar–non-polar transition in some oxides of this series. The magnetic ordering of the rare earth ions develops at lower temperatures.

In addition, the magnetic studies of EuMn_2O_5 and YMn_2O_5 suggested the existence of another magnetic transition between 20 and 30 K. In this context, we are interested in these oxides because of the possibility that both ferroelectric and magnetic orderings coexist in these oxides.

In this paper, we present the results of the pyroelectric current measurements of RMn_2O_5 ($R =$ Gd, Tb or Y) single crystals. In all the oxides, we observed a pyroelectric current at low temperatures. The sign of the current was reversed when the sample was cooled in an electric field applied along the opposite b direction. This provides evidence of ferroelectricity in RMn_2O_5 . The ferroelectric transition temperatures of GdMn_2O_5 and TbMn_2O_5 were 24.6 K and 28.6 K, respectively. The supposed ferroelectric transition temperature of YMn_2O_5 was

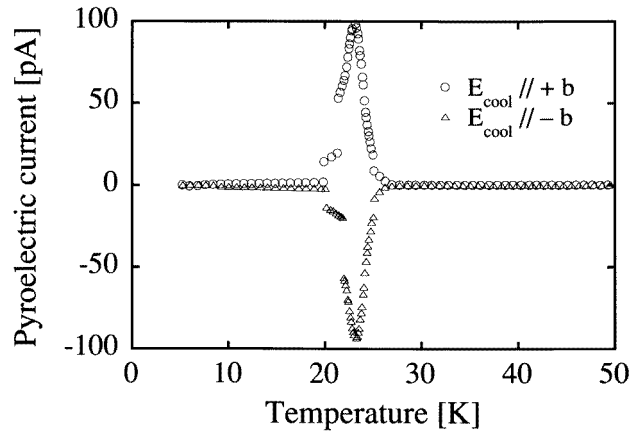


Figure 1. Temperature dependence of the pyroelectric current from a GdMn_2O_5 single crystal with a cross-sectional area of 3 mm^2 and thickness of 1.5 mm . The two curves correspond to opposite directions of the electric field applied during cooling the sample to 4.2 K . As for the direction of the current see the text.

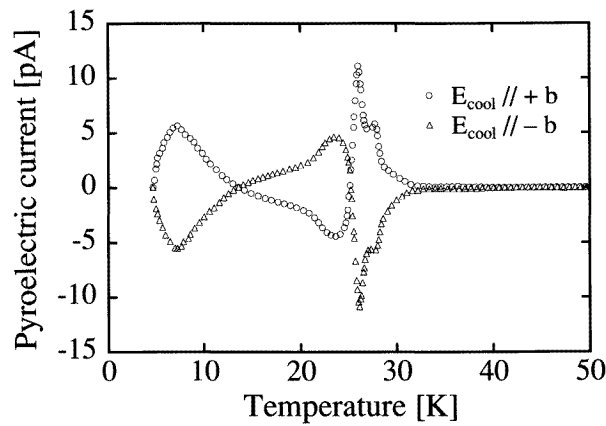


Figure 2. Temperature dependence of the pyroelectric current from a TbMn_2O_5 single crystal with a cross-sectional area of 8.3 mm^2 and thickness of 1.4 mm . The two curves correspond to opposite directions of the electric field applied during cooling the sample to 4.2 K . As for the direction of the current see the text.

39.8 K , although we have not yet confirmed the switching of spontaneous polarization by the applied electric field.

The temperature dependence of spontaneous polarization had a complicated shape except for the case of GdMn_2O_5 . This seems to suggest ferroelectricity as the origin of the observed spontaneous polarization.

2. Experimental methods

The samples were the same single crystals that were used in previous studies of the dielectric constant and magnetoelectric effect. They were prepared from a high-temperature solution in

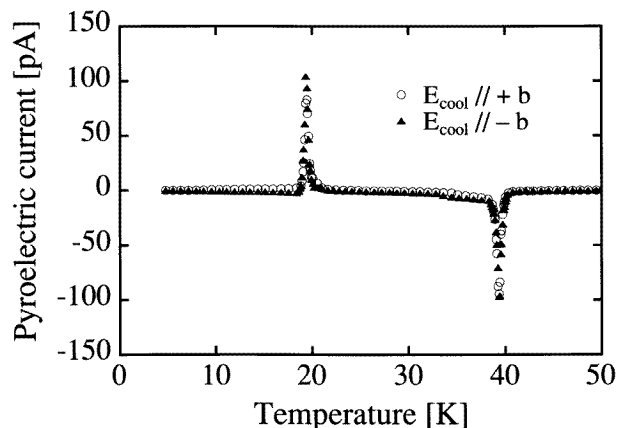


Figure 3. Temperature dependence of the pyroelectric current from a YMn_2O_5 single crystal with a cross-sectional area of 8.9 mm^2 and thickness of 2.5 mm . The two curves correspond to opposite directions of the electric field applied during cooling the sample to 4.2 K . As for the direction of the current see the text.

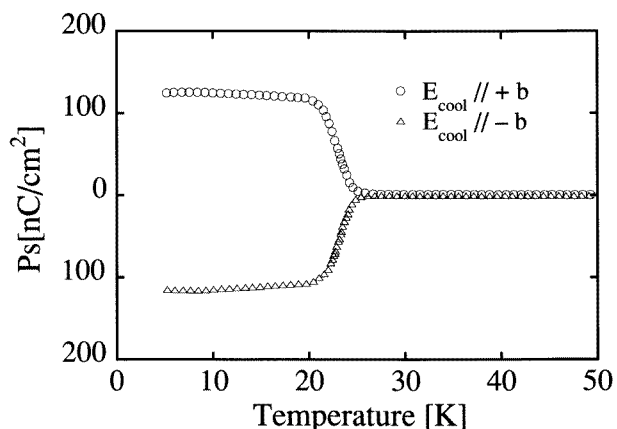


Figure 4. Temperature dependence of the estimated spontaneous polarization along the b axis of a GdMn_2O_5 single crystal.

PbO-PbF_2 flux [17] and shaped into parallelepipeds with the edges along the three principal axes.

In pyroelectric measurements, we used capacitor-type samples with a pair of electrodes of silver conducting paint on the parallel b faces. The separation between the electrodes was between 1 and 2 mm and the area of the cross section was between 3 and 9 mm^2 . The pyroelectric current was recorded as a function of temperature between 4.2 and 273 K with a quasi-static method. We used an electrometer (Keithley 6512) in the current mode to measure the current through a circuit between the electrodes. The level of background noise current was less than 50 fA .

Before each measurement run, the sample was cooled from room temperature to 4.2 K within an electric field E_{cool} of between 3 and 8 kV cm^{-1} . After that we short-circuited the electrodes of the sample capacitor for approximately 90 min to maintain the zero-charge

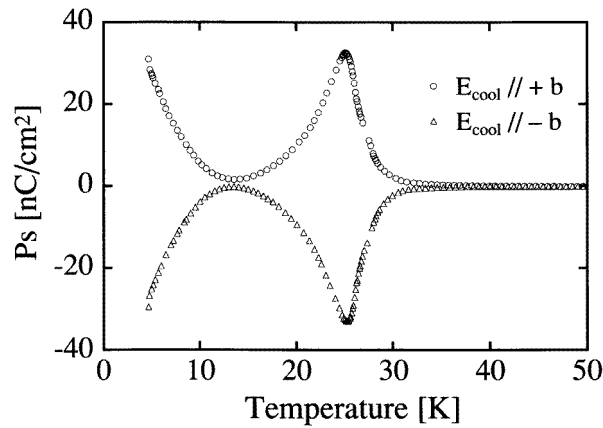


Figure 5. Temperature dependence of the estimated spontaneous polarization along the b axis of a TbMn_2O_5 single crystal.

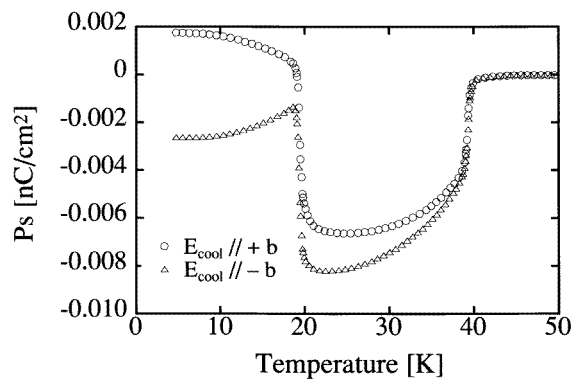


Figure 6. Temperature dependence of the estimated spontaneous polarization along the b axis of a YMn_2O_5 single crystal.

state. Then we recorded the pyroelectric current, during heating at a rate of $0.5\text{--}5\text{ K min}^{-1}$. The direction of the current was from the electrode facing the negative side of the sample polarization to the electrode of the positive side. We defined the positive direction of the current as that after the poling in E_{cool} along the positive b direction. We derived spontaneous polarization by integrating the pyroelectric current. In the calculation, we assumed that the spontaneous polarization was zero above 200 K.

The temperature was detected with an (Au–Fe)–chromel thermocouple in all the measurements.

3. Results and discussion

In figures 1–3, we depict the temperature dependences of the pyroelectric current along the b axis for GdMn_2O_5 , TbMn_2O_5 and YMn_2O_5 , respectively. In every case we noticed a few anomalies in the temperature dependences. The sign of the current was reversed, according to the direction of the electric field E_{cool} applied during cooling the sample to

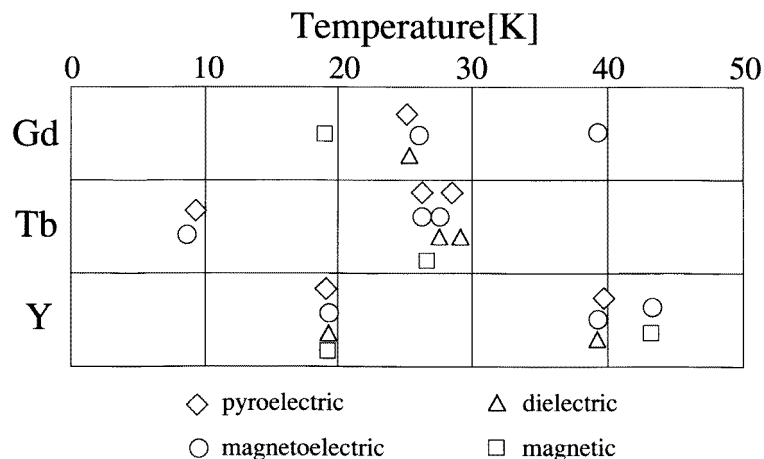


Figure 7. Temperatures of the anomalies of the pyroelectricity, dielectric constant and magnetoelectric effect for GdMn_2O_5 , TbMn_2O_5 and YMn_2O_5 .

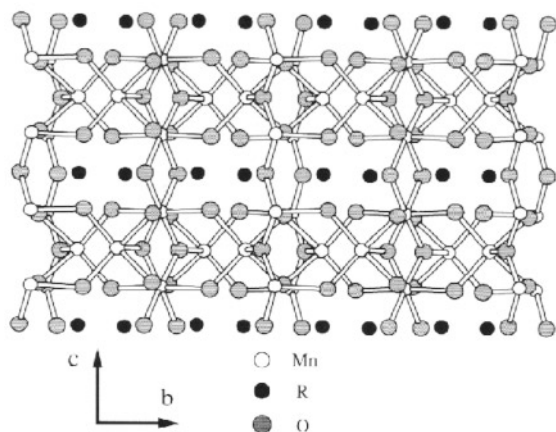


Figure 8. Structure of RMn_2O_5 .

4.2 K. An exception was YMn_2O_5 , where the current was reversed only below 20 K. A similar dependence on E_{cool} has also been observed in the magnetoelectric effect of this oxide [7].

We show the temperature dependences of spontaneous polarization derived from the pyroelectric current in figures 4–6. In all the oxides studied, we detected a transition temperature T_c . The spontaneous polarization was zero above this temperature. In addition, we recorded some other anomalies, suggesting other transitions. In figure 7, we summarized them as well as the anomalies of dielectric constant and magnetoelectric susceptibility.

For GdMn_2O_5 , the spontaneous polarization decreased monotonically with increasing temperature from 4.2 K and vanished at $T_c = 25$ K, which is the temperature of the peak dielectric constant. The spontaneous polarization P_S of TbMn_2O_5 varied with temperature in a more complicated way. However, we can recognize a correspondence between the temperature dependence of P_S and those of the dielectric constant and magnetoelectric effect. The maximum value of the recorded polarization was of the order of magnitude of 100 nC cm^{-2} in these oxides. It is comparable with or a little smaller than the maximum

spontaneous polarization of typical ferroelectric crystals.

There are a few problems in the results on YMn_2O_5 . The polarization could not be completely switched by the electric field applied during cooling. In addition, its magnitude was much smaller than those of GdMn_2O_5 and TbMn_2O_5 . We suppose that these phenomena are not intrinsic properties but are due to the poor quality of the crystal. We had a similar problem in an as-grown crystal of HoMn_2O_5 . In this case, the spontaneous polarization of a well annealed crystal could be switched by electric field cooling [18].

From the above results, we conclude that GdMn_2O_5 , TbMn_2O_5 and possibly YMn_2O_5 have a spontaneous polarization, whose sense can be switched by an external electric field, at low temperatures. In short, they are ferroelectric. A possible direction of spontaneous polarization is along the b axis in TbMn_2O_5 and YMn_2O_5 , because the anomaly in the dielectric constant was observed only in this direction.

A possible model explaining the complicated temperature dependence of spontaneous polarization of these oxides is that they are ferrielectric and the net polarization is composed of a few different contributions. It seems natural to assume such a model, because the displacements of three different kinds of ion, Mn^{4+} , Mn^{3+} and R^{3+} , with different coordinations of oxygen ions could be the origin of such contributions to the polarization.

In this context, it seems interesting to note that the b direction is unique in RMn_2O_5 structure (figure 8), because both MnO_6 octahedra and MnO_5 bipyramids, respectively, form a folded chain along this axis. However, a previous x-ray structure analysis of DyMn_2O_5 concluded that the averages of the square of the displacement of Mn^{3+} and Mn^{4+} ions were smaller along the b direction than along the a and c axes [11].

Acknowledgments

The authors would like to express their sincere thanks to Professor H Schmid and Dr J-P Rivera of the University of Geneva for their valuable advice about pyroelectric measurements. This work was partly supported by a Grant-in-Aid for Scientific Researches from the Ministry of Education, Science and Culture.

References

- [1] Doi T and Kohn K 1992 *Phase Trans.* **38** 273
- [2] Tsujino H and Kohn K 1992 *Solid State Commun.* **83** 639
- [3] Tsujino H, Tanaka Y and Kohn K 1992 *Ferrites: Proc. 6th Int. Conf. on Ferrites (Tokyo and Kyoto, 1992)* ed M Abe and T Yamaguchi (Tokyo: Japan Society of Powder and Powder Metallurgy) p 714
- [4] Tanaka Y, Saito K, Tsujino H and Kohn K 1994 *Ferroelectrics* **161** 125
- [5] Kohn K 1994 *Ferroelectrics* **162** 1
- [6] Saito K and Kohn K 1995 *J. Phys.: Condens. Matter* **7** 2855
- [7] Ikeda A and Kohn K 1995 *Ferroelectrics* **169** 75
- [8] Quèzel-Ambrunaz S, Bertaut E F and Buisson G 1964 *C. R. Acad. Sci., Paris* **58** 3025
- [9] Sanina V A, Sapozhnikova L M, Golovenchits E I and Morozov N V 1988 *Sov. Phys.-Solid State* **30** 1736
- [10] Golovenchits E I, Morozov N V, Sanina V A and Sapozhnikova L M 1992 *Sov. Phys.-Solid State* **34** 56
- [11] Abrahams S C and Bernstein J L 1967 *J. Chem. Phys.* **46** 3776
- [12] Bertaut E F, Buisson G, Quèzel-Ambrunaz S and Qu zel G 1967 *Solid State Commun.* **5** 25
- [13] Buisson G 1973 *Phys. Status Solidi a* **16** 533
- [14] Buisson G 1973 *Phys. Status Solidi a* **17** 191
- [15] Wilkinson C, Sinclair F, Gardner P, Forsyth J B and Wanklyn B M R 1981 *J. Phys. C: Solid State Phys.* **14** 1671
- [16] Gardner P, Wilkinson C, Forsyth J B and Wanklyn B M R 1988 *J. Phys. C: Solid State Phys.* **21** 5653
- [17] Wanklyn B M R 1972 *J. Mater. Sci.* **7** 813
- [18] Kato S and Kohn K 1995 unpublished