Some Properties of Ferroelectric and Ferromagnetic Compounds $RMnO_3$

by

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Current interest in materials research has lead to the discovery of many new materials with novel properties. In this respect, we noted a system of compounds recently discovered in Grenoble[1] with unusual properties. We will discuss some of these properties in this letter.

These compounds are $RMnO_3$, where R represents Y, Ho, Er, Tm, Yb, and Lu,[1] also Sc[2]. In recent years, some ferroelectric materials were reported with ferromagnetic properties,[3,4] but to our knowledge, $RMnO_3$ are the only ferroelectric compounds whose ferromagnetic properties have been definitely established by neutron diffraction analysis.[5,2] Ferromagnetic hysteresis loops have been observed in $YMnO_3$ below the magnetic Curie temperature of 48° K. The coercive field is about 500 Oe.[6] Due to the weak ferromagnetic moment, an observation of the magnetic hysteresis loop in the rare earth compounds with large magnetic susceptibilities becomes difficult.

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Probably the most interesting experiment on these compounds will be a search for a ferroelectric-ferromagnetic interaction. A magnetic coercive field of 500 Oe is easily accessible. On the other hand, the ferroelectric coercive field of $YMnO_3$ has been reported [1,7,8] as excessively high, in the order of 20 to 100 Kv/cm for 50 cps field at room temperature, with a large variation from specimen to specimen. In Ref. 1, the mated electrodes to the crystal were air-drying Ag-paste and presumably this is also the case in the work of Ref. 7 and 8. Recently we found that with Au evaporated electrodes, the coercive field is only $4.0 \pm .5$ Kv/cm. This reduced requirement will alleviate greatly experimental difficulties in the contemplated studies of ferroelectric-ferromagnetic interactions.

The ferroelectric switching speed of $YMnO_3$ is reported to be 5 to 10×10^{-8} sec.[7] This represents highest speed of the ferroelectric switch reported. Due to the above observation of a large reduction of coercive field values by different electrode preparation, it would be interesting to repeat the experiment with Au evaporated electrodes.

The optical properties of the $RMnO_3$ make them unusual among ferroelectric crystals: aside from the compounds described in Ref. 4, to our knowledge, the $RMnO_3$ are the only crystals with almost complete total absorption in the region of visible light. However, we observed that appreciable transmission occurs after 0.8μ and extends to the infrared region of 15μ, which is about 3μ farther than that of $BaTiO_3$ or $Bi_4Ti_3O_{12}$. Recent interest in optical non-linear dielectric interactions would make the $RMnO_3$ an interesting set of material to study.

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The variation of dielectric constant of $YMnO_3$ as a function of the temperature is quite slow in the region from 4.6°K to about 100°K, being about 20%. We have not been able to definitely establish whether there is a dielectric anomaly at the magnetic Curie temperature. To ascertain this anomaly, crystals of large area are desirable, but so far not available.

Single crystals were grown with a Bi_2O_3 flux,[1] and usually crystals of cm. dimensions can be obtained, but these crystals bind tightly with the flux materials and a separation by a continuous boiling in HNO_3 for many hours results in crystals with an area of a few mm^2. Another aspect of crystals growth with a Bi_2O_3 flux is that the thickness is usually confined to 1 to 5×10^{-3} cm. This configuration is not ideal for neutron diffraction analysis or electromagnetic interaction studies. It is most desirable to find other types of fluxes or growth methods in this respect.

Finally, the $RMnO_3$ have a very high, or probably have no Curie temperature up to the melting point. By a method described elsewhere,[9] we measured the dielectric constant as a function of the temperature. Up to 850°C, no dielectric anomaly was observed. Therefore, the $RMnO_3$ represent the highest Curie temperature ferroelectric materials.

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REFERENCES

1. E.F. Bertaut, F. Forrat and P.H. Fang, Bull. Am. Phys. Soc. 8, 61 (1963); Comptes Rendus, Acad. d. Sci. Paris 256, 1958 (1963).

2. W. C. Koehler, H. L. Yakel, E. O. Wollan and J.W. Cable, Phys. Letters 9, 93 (1964).

3. G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya and N.N. Krainik, Fiz. Tverd. Tela 2, 2982 (1960), [English transl. Soviet Phys. – Solid State 2, 2651 (1961)].

4. P.H. Fang and R.S. Roth, J. Appl. Phys. Suppl. 31, 2785 (1960). The identification of ferromagnetic properties in these materials is in error. Dr. E. W. Gorter of Philips Research Laboratory at Eindhoven has observed optically a minute amount of small crystals of barium hexaferrite imbedded in these materials. An attempt to prepare specimens entirely free from the barium hexaferrite was not successful.

5. E.F. Bertaut and M. Mercier, Phys. Letters 5, 27 (1963).

6. R. Pauthenet (Private communications during 1963 Magnetic Conference, Atlantic City).

7. P. Guinet, Comptes Rendus, Acad. d. Sci. Paris, 257, 90 (1963).

8. V.A. Bokov, G.A. Smolenskii, S.A. Kizhaev and I.E. Myl'nikova, Fiz. Tverd. Tela 5 3607 (1963).

9. P.H. Fang and C.R. Robbins, Phys. Rev. 126, 892 (1962).