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Ferroelectricity in the Compound $Ba_2Bi_4Ti_5O_{18}$

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Some ferroelectric and crystallographical properties of the compound $Ba_2Bi_4Ti_5O_{18}$ are presented. The compound represents a new structure with the unit cell consisting of one $Bi_2O_2^{2+}$ layer and five perovskite layers. From $-196°$ to $+580°C$, a maximum in the real part of the dielectric constant was observed at 329°C. No thermal hysteresis was observed within the precision of $\pm 2°C$. A remanent polarization of 2×10^{-6} coul/cm^2 and a coercive field of 10 kv/cm were observed at room temperature.

I. INTRODUCTION

SEVERAL mixed bismuth oxides with layer lattice structure were discovered by one of us (B.A.) in 1950.[1] In recent years, a considerable number of papers were published describing ferroelectric properties found in some of these compounds.[2–8] In reference 1, a hypothetical formula was proposed to represent these layer structure compounds: $Me_2O_2(Me'_{m-1}R_mO_{3m+1})$, where Me so far is found to be valid only for Bi, while Me' can represent many elements with different valences, such as, monovalent K, Na, divalent Ba, Sr, Pb, Ca, and R can represent 4-valent Ti and 5-valent Ta, and Nb. All these compounds have a number $m-1$ of perovskite layers between two nearest $Bi_2O_2^{2+}$ layers. In the work of reference 1, compounds with values of $m=1$, 2, 3, and 4 were found and all recent publications on electrical properties are confined to these cases, except in a preliminary note by one of us (P.H.F.) with Robbins and Forrat,[5] in which a compound with the formula of $Bi_4Ti_3O_{12}\cdot 2BaTiO_3$ was described briefly. This composition corresponds to the general formula with $m=5$. In the present paper, we confirmed that this compound indeed fits the scheme of layer structures. Therefore, this compound has the largest number of mixed layers hitherto reported. In addition, we described some ferroelectric properties.

II. PREPARATION

The compound was synthesized in the following way. Weighed amounts of the appropriate proportions of $BaCO_3$, TiO_2, and Bi_2O_3 were mixed and heated in a platinum crucible to 650°C, held for one hour, then heated slowly to 800°C, and held for four hours; after that, the temperature was increased to the melting point of 1150°C and held for two hours. As the compound melts congruently, by cooling slowly overnight from the melt, small crystals were obtained, the largest with the dimensions of $0.5\times 0.5\times 0.25$ mm.[3] The slow heating from 650 to 800°C is to prevent a volatilization of Bi_2O_3 which might occur before the formation of the compound.

III. CRYSTAL STRUCTURE

Weissenberg photographs and rotation photographs were taken of a single crystal of $Ba_2Bi_4Ti_5O_{18}$ with Cu K radiation. The Weissenberg photograph registered the reflections $h0l$ and the rotation photograph showed the layer lines $k=0$, $k=\pm 1$, $k=\pm 2$. From these single crystal measurements and from a powder photograph taken with a Guinier focusing camera, the following

TABLE I. Powder diagram of $Ba_2Bi_4Ti_5O_{18}$.

h	k	l	$10^4 \sin^2\theta_{\mathrm{obs}}$	$10^4 \sin^2\theta_{\mathrm{calc}}$	I_{obs}	I_{calc}
0	0	10	235	235	9	10
0	0	12	338	338	10	11
0	1	1	396	395	25	21
0	1	9	585	585	5	12
0	1	11	679	679	100	100
1	1	0	787	790	50	54
0	1	13		792		4
0	0	20	940	940	3	2
1	1	10	1024	1025	3	6
1	1	12	1127	1128	27	14
0	0	22	1135	1137	6	8
0	0	24	1356	1353	8	3
0	2	0	1576	1580	27	23
0	1	23	1640	1638	9	11
0	2	8	1733	1730	2	3
1	1	20		1730		6
1	1	22	1926	1927	13	15
2	1	1	1975	1977	6	4
2	1	11	2257	2259	28	32
0	0	34	2721	2716	8	1
0	2	22		2717		9
0	2	24	2937[a]	2933	4	3
0	1	33		2953		5

[a] This line is very broad.

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[1] B. Aurivillius, Arkiv Kemi **1**, 463, 499 (1949); **2**, 519 (1950); **5**, 39 (1952).

[2] G. I. Skanavi, Ya. M. Ksendzev, V. A. Trigubenko, and V. V. Prokhvatilov, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 320 (1957) [translation: Soviet Phys.—JETP **6**, 250, 1958], and references therein for their earlier work.

[3] P. Popper, S. N. Ruddlesden, and T. A. Ingles, Trans. Brit. Ceram. Soc. **56**, 356 (1957).

[4] G. A. Smolenskii, V. A. Isupov, and A. I. Agranoskaya, Soviet Phys.—Solid State **3**, 895 (1961), and references to their earlier work.

[5] P. H. Fang, C. Robbins, and F. Forrat, Comp. rend. **252**, 683 (1961).

[6] E. C. Subbarao, J. Chem. Phys. **34**, 695 (1961); Phys. Rev. **122**, 804 (1961).

[7] L. G. Van Uitert and L. Egerton, J. Appl. Phys. **32**, 959 (1961).

[8] P. H. Fang, C. R. Robbins, and B. Aurivillius, preceding paper [Phys. Rev. **126**, 892 (1962)].

cell dimensions were obtained: tetragonal, $a=3.88$ Å and $c=50.3$ Å. Observed and calculated values of $\sin^2\theta$ for the powder diagram were given in Table I. These cell dimensions are in good agreement with those which might be expected for a compound with $m=5$, as can be seen from the following calculations:

c axis of Bi_3NbTiO_9	25.1 Å
c axis of $Bi_4Ti_3O_{12}$	32.8 Å
Difference	7.7 Å;
c axis of $Bi_4Ti_3O_{12}$	32.8 Å
c axis of $BaBi_4Ti_4O_{15}$	41.8 Å
Difference	9.0 Å.

Therefore, an extrapolation yields the expected value for the c axis of $Ba_2Bi_4Ti_5O_{18}$ of $41.8+\frac{1}{2}(7.7+9.0)=50.2$ Å. This is in agreement with the actual observed value of 50.3 Å. Table I shows that the observed and calculated intensities also agree with the assumption that m is equal to 5 as all observed strong reflexions have l values in the vicinity of $11n$ (m, n are integers). I_{obs} was estimated visually.

$$I_{\text{calc}}=2\times10^{-4}F^2\times\exp(-1.52\sin^2\theta)p\varphi(\theta),$$

with

$$\varphi(\theta)=\frac{1+\cos2\alpha\cos^2 2\theta}{\sin\theta(1+\cos2\alpha)\cos^2(2\theta-\beta)\sin2\theta},$$

where α is the glancing angle of the monochromator crystal quartz and β is the angle between the primary beam and the normal to the plane of the sample. The values of I_{calc} correspond to a tentative structure of the phase derived geometrically. The agreement between I_{calc} and I_{obs} is as good as could be expected for a structure derived from space considerations only. This structure is given in Fig. 1, and the values of the parameters for the atoms are given in Table II.

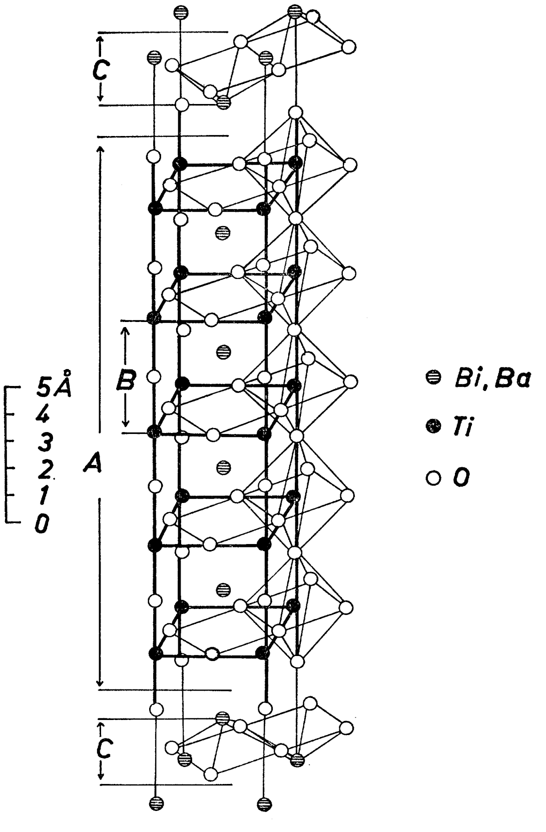

FIG. 1. Schematic drawing showing the structure of $Ba_2Bi_4Ti_5O_{18}$. One half of the tetragonal unit cell from $z=0.25$ to $z=0.75$ is given. A denotes the "perovskitic layer" of $Ba_2Bi_2Ti_5O_{16}{}^{2-}$, B denotes a unit cell of the hypothetical perovskite structure (Ba,Bi)TiO_3, and C the layers of $Bi_2O_2{}^{2+}$.

TABLE II. Parameter values of the atoms of $Ba_2Bi_4Ti_5O_{18}$.

$I\,4/mmm$ (No. 139);		(0,0,0; 1/2,1/2,1/2)+	
4 Bi	in 4(e):	±0, 0, z:	$z=0.2255$
4 (Bi,Ba)	in 4(e):		$z=0.0420$
4 (Bi,Ba)	in 4(e):		$z=0.1300$
2 Ti	in 2(b):	±0, 0, 1/2	
4 Ti	in 4(e):		$z=0.3370$
4 Ti	in 4(e):		$z=0.4185$
4 O	in 4(c):	0, 1/2, 0; 1/2, 0, 0	
4 O	in 4(d):	0, 1/2, 1/4; 1/2, 0, 1/4	
4 O	in 4(e):		$z=0.2962$
4 O	in 4(e):		$z=0.3378$
4 O	in 4(e):		$z=0.4593$
8 O	in 8(g):	±(0,1/2, z; 1/2,0,z)	$z=0.0815$
8 O	in 8(g):		$z=0.1630$

All compounds of this layer structure type can be described by subcells with the same a axes as the real cells but with c axes equal to $c'/(2m+1)$, where c' is the length of the c axes of the real cell. These subcells are indicated by strong reflections in the x-ray photographs. The value of $c'/(2m+1)$ is found to diminish when m is made larger, as illustrated in Table III.

IV. FERROELECTRIC PROPERTIES

We observed distinctive hysteresis loops on single crystals of $Ba_2Bi_4Ti_5O_{18}$ at room temperature (Fig. 2). Air-drying silver paste electrodes are applied on the two surfaces perpendicular to the c axis of the crystal and the usual Sawyer-Tower circuit is used for the measurement. At room temperature, the remanent polarization is found to be about 2 μcoul/cm² and the coercive field about 10 kv/cm. These values are not accurate because the minute size and irregular shape of the crystal do not allow a precise measurement to be made of the geometrical configuration of the crystals.

TABLE III. The decrement of c' due to the increment of perovskite layers.

m'	c'	$c'/(2m+1)$	a b	Substance
1	16.6	5.54	3.87	Bi_2NbO_5F
2	25.1	5.02	3.84	Bi_3NbTiO_9
3	32.8	4.69	3.84	$Bi_4Ti_3O_{12}$
4	41.8	4.65	3.86	$BaBi_4Ti_4O_{15}$
5	50.3	4.57	3.87	$Ba_2Bi_4Ti_5O_{18}$

The appearance of the unambiguous shape in the hysteresis loop, and the structural similarity of this compound with a series of other compounds, support the premise that $Ba_2Bi_4Ti_5O_{18}$ is ferroelectric. Another evidence of the ferroelectricity in this compound is the observation of the switching time in the ferroelectric polarization. Measurements on the field dependence of the switching time of the compound were made by one of us (P.H.F) and Fatuzzo and will be published elsewhere.[9]

At high temperature (above 150°C), the hysteresis loop measurement becomes difficult because the specimen becomes appreciably conductive. However, we have measured the dielectric constant (ϵ') and the dielectric loss (ϵ'') of the compound as a function of the temperature up to 500°C. A small piece of polycrystalline $Ba_2Bi_4Ti_5O_{18}$ broken off from the solidified melt was used. Two cavities of approximately 0.5 mm in diameter and 2 mm between centers were sandblasted in the specimen. One Nichrome wire, which served as one electrode, and one fine Chromel-Alumel thermocouple, which served as the other electrode, were inserted in the cavities and packed with Ga-Cu alloy.[10] The specimens were then suspended in a temperature bath by the electrode wires which were connected directly to a Q meter for the permittivity measurement. The configuration of this system is not suitable for an accurate determination of the absolute values of ϵ' and ϵ''. Nevertheless, the system permitted relative dielectric measurements from liquid nitrogen up to about 800°C and proved satisfactory for our purpose of determining the temperatures of the dielectric anomaly. The result is shown in Fig. 3. The numerical values of ϵ' and ϵ'' are adjusted, based on a measurement of a minute single crystal at room temperature. As we have indicated in the ferroelectric measurement, these values are not accurate due to the inaccuracy of the determination of the dimensions of the crystal. However, the temperature measurement is quite accurate through the whole range of temperature; the temperature readings from the electrode thermocouple were less than 1°C different from those of an auxillary thermocouple which was placed in the heating zone near the specimen.

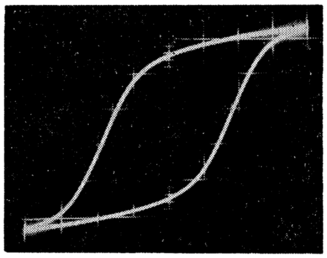

FIG. 2. Ferroelectric hysteresis loop of $Ba_2Bi_4Ti_5O_{18}$ at room temperature. Applied field: 20 kv/cm.

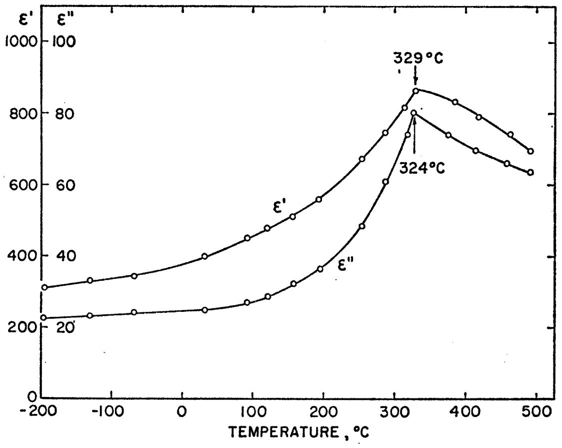

FIG. 3. Real (ϵ') and imaginary (ϵ'') dielectric constant of $Ba_2Bi_4Ti_5O_{18}$ as a function of the temperature, measured at 100 kc/sec.

On increasing temperature from −196°C to room temperature, there is a gradual change of ϵ' from 360 to 400, and ϵ'' from 22 to 25. From room temperature upward, both ϵ' and ϵ'' increase and there is a maximum of ϵ'' at 324±2°C and ϵ' at 329±2°C; the uncertainty of ±2°C is due to the small change of the values of ϵ' and ϵ'' in those small temperature intervals such that definite values of the maxima cannot be ascertained. On decreasing temperature, there is, sometimes, a slight change of the values of ϵ' and ϵ'', presumably involving a reorientation of some domains. But within the experimental precision of ±2°C, we cannot detect any temperature hysteresis. The temperatures of the maxima are independent of the measuring frequency. Although we have not investigated the structural change as a function of the temperature, in view of the similarity of all these layer structure type materials,

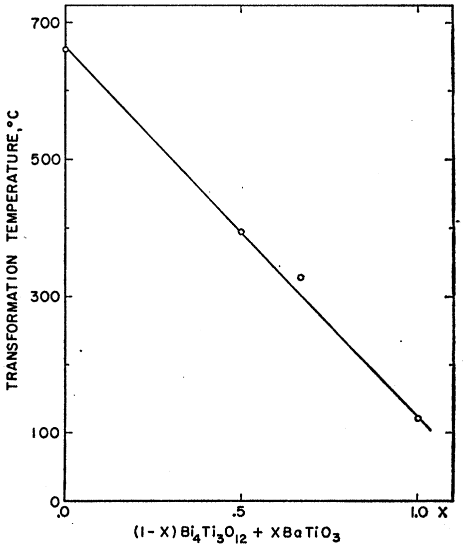

FIG. 4. Transformation temperature vs composition of the system $(1-x)Bi_4Ti_3O_{12}+xBaTiO_3$.

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[9] P. H. Fang and E. Fatuzzo, J. Phys. Soc. Japan **17**, 238 (1962).
[10] G. G. Harman, Rev. Sci. Instr. **31**, 717 (1960).

presumably a pseudotetragonal to true tetragonal transformation occurs near 329°C. It is interesting to observe the change of the transformation temperature in these layer compounds: If we represent these compounds by $(1-x)\mathrm{Bi_4Ti_3O_{12}}+x\mathrm{BaTiO_3}$, the transformation temperature is almost a linear function of the composition concentration x (Fig. 4). The tetragonal cubic transformation temperature of 120°C is used for $x=1$ ($\mathrm{BaTiO_3}$).

In conclusion, we have reported a new ferroelectric compound with a layer structure. This compound represents a layer structure with a largest number of layers reported to date. In fact, one of us (P.H.F.) in collaboration with R. S. Roth, has prepared materials with a composition such that if they form single phase, these compounds would have still larger number of layers, such as the cases $m=6$, 7, and 9. Preliminary results show that all these materials have two phases: one is the phase of $\mathrm{Ba_2Bi_4Ti_5O_{18}}$, and the other one is a cubic perovskite phase. Therefore, we conclude for the present that, at least in the system which consists of BaO, $\mathrm{Bi_2O_3}$, and $\mathrm{TiO_2}$, prepared in the ordinary atmosphere, the largest possible number of layers is 5.

ACKNOWLEDGMENTS

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Moriya Interaction and the Problem of the Spin Arrangements in βMnS†

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A study is made of the nature of the anisotropic superexchange interaction of the form $\mathbf{D}_{ij}\cdot\mathbf{S}_i\times\mathbf{S}_j$ recently proposed by Moriya. This interaction is permitted in βMnS, with symmetry requiring that $\mathbf{D}_{ij}$ be normal to the plane defined by i, j, and the single intervening anion. It is conjectured that this interaction leads to a screw spin arrangement, with a 90° screw angle; in crystals considered heretofore the Moriya energy produces only a slight canting. The observed powder neutron diffraction pattern has been interpreted as indicating ordering of the third kind with spins normal to the ordering axis; this arrangement, however, does not have minimum dipolar energy. The present proposed arrangement leads to the same diffraction pattern, and the Moriya energy probably overbalances the dipolar.

I. THE NATURE OF THE MORIYA INTERACTION

It has been demonstrated by Moriya[1] that, under certain restricted symmetry conditions, the combination of spin-orbit and superexchange interactions can produce an effective coupling between neighbor spins $\mathbf{S}_i$ and $\mathbf{S}_j$ of the form

$$(E_M)_{ij}=\mathbf{D}_{ij}\cdot\mathbf{S}_i\times\mathbf{S}_j. \tag{1}$$

Here $\mathbf{D}_{ij}=-\mathbf{D}_{ji}$ is an axial vector, the precise form of which is derived in Moriya's paper and also below in Eq. (11).

It is illuminating to obtain the Moriya coupling from elementary configuration interaction. Let the ground-state configuration G involving neighbor spins $\mathbf{S}_i$ and $\mathbf{S}_j$ already contain whatever configuration mixing is required to produce an energy of the form

$$E_G=C_0-2J_0\mathbf{S}_i\cdot\mathbf{S}_j, \tag{2}$$

where J_0 arises from direct exchange and/or superexchange, and C_0 is independent of spin directions. Thus it is assumed that the various configurations entering into the usual theory of superexchange[2] already have been incorporated into G. The theory is now extended to include a group of intermediate configurations I_n, I_m in which either atom i is raised to its nth excited state or atom j is raised to its mth excited state. The matrix element connecting G and a given configuration I_n will be of the form

$$\langle I_n|H|G\rangle=\lambda_n\mathbf{l}_{nG}\cdot\mathbf{S}_i-2J_n\mathbf{S}_i\cdot\mathbf{S}_j+C_n, \tag{3}$$

and similarly for $\langle I_m|H|G\rangle$. Here J_n arises from direct and/or superexchange between configurations G and I_n, as will presently be discussed; C_n is independent of spin or orbit operators; and $\mathbf{l}_{nG}$ is the appropriate orbital matrix element connecting the basis functions of G and I_n.

The basis functions of G and I_n, in this method, are to be taken as single products of one-electron orbitals,

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[1] T. Moriya, Phys. Rev. **120**, 91 (1960).

[2] See, for example, F. Keffer and T. Oguchi, Phys. Rev. **115**, 1428 (1959).