

Rare Earth Titanates with a Perovskite Structure*

BY J. BROUST†, I. FANKUCHEN AND E. BANKS

Polytechnic Institute of Brooklyn, Brooklyn 2, N.Y., U.S.A.

(Received 13 August 1952)

A mixed oxide of europium and titanium, in which the europium is apparently divalent, has been prepared by heating Eu_2O_3 with TiO_2 in a reducing atmosphere. The product is isostructural with SrTiO_3 and has almost exactly the same lattice constant. No phase changes occurred down to 108°K . It was found that the reaction does not occur in an oxidizing or neutral atmosphere, which increases the likelihood that it is a compound of Eu(II) , which should have about the same ionic radius as Sr(II) . This is the first known case of the existence of Eu(II) in an oxide lattice.

A series of compounds which are isostructural with SrTiO_3 have been prepared with the Sr^{+2} replaced by La^{+3} and one of the alkali cations Li^+ , Na^+ , K^+ and Rb^+ . No such compound was formed with Cs^+ . By leaching with hot water, it was determined that the fraction of alkali cation entering the lattice decreased with increasing ionic size. The X-ray diagrams indicate a progressive increase in lattice constant up to the potassium compound. The rubidium compound has almost the same lattice constant as the potassium compound, because the increase in ionic size is compensated by a decrease in the extent of solid solution.

Introduction

In recent years, the study of the alkaline earth titanates and many other compounds with a similar perovskite structure has aroused much interest. Many of these materials have been found to exhibit ferroelectric properties which make these compounds of great practical and theoretical value. The titanates of barium (Wainer & Salomon, 1942-3; Wainer, 1946; Wul & Goldman, 1945; Wul & Vereschagen, 1945) and lead (Shirane, Hoshino & Suzuki, 1950), the tantalates of sodium, potassium (Hulm, Matthias & Long, 1950) and rubidium (Smolenskii & Kozhevnikova, 1951), and the niobates of sodium and potassium (Matthias, 1949; Wood, 1951) are a few of many compounds which have been found to exhibit such properties as high dielectric constants, ferroelectric transitions and dielectric hysteresis.

For barium titanate, these properties have been attributed to the spontaneous polarization of the titanium ions within the octahedral positions of the oxygen lattice (Slater, 1950). This spontaneous polarization becomes a cooperative phenomenon throughout the entire lattice of the crystal as the temperature of the material is lowered through the Curie temperature. With barium titanate, this temperature is found near 395°K . Dielectric measurements of pure strontium titanate, however, indicate that no ferroelectric transition is to be found at temperatures down to 1.3°K . (Hulm, 1950). This is apparently due to the diminished size of the octahedral holes available to the titanium ions in strontium titanate as

compared with barium titanate. Solid solutions of barium and strontium titanate have their Curie temperatures lower than 395°K ., continuously decreasing in temperature as a function of the strontium titanate content (Jackson & Reddish, 1945). By such solid solution formation, the average ionic radius of the divalent cation can be varied and the octahedral holes available to the titanium ions varied in size.

This paper reports on attempts to substitute other ions and mixtures of ions into the lattice in place of the divalent strontium or barium ions. The ions which were introduced were either divalent rare earth ions or a solid solution of a trivalent rare earth ion with a monovalent ion.

A. Preparation and identification of EuTiO_3

Of the rare earth elements, europium was the only one which was found to be sufficiently stable in the divalent state to be substituted for the divalent alkaline earth ion in the perovskite lattice. A small sample of spectroscopically pure Eu_2O_3 was mixed with a stoichiometric amount of anatase (purity 99.9%). The oxide mixture was ground together very thoroughly, transferred to a small platinum boat and heated for two hours at 1200°C . in an hydrogen atmosphere. The product was black and stable in air at room temperatures. X-ray diffraction powder diagrams showed that the material had a primitive cubic lattice. The diagram was completely devoid of any extraneous lines which might have indicated unreacted materials or another phase present in some concentration greater than about 5%. Because of the scarcity of europium compounds of the purity used, only a very small sample was prepared. The method

* This work was supported by the U.S. Army Signal Corps.

† This work is in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the Polytechnic Institute of Brooklyn.

which was used to show that the product is actually EuTiO_3 was therefore one employing X-ray techniques instead of chemical analysis which would have destroyed most or all of the very small existing sample. In this method, an ideal EuTiO_3 composition was assumed, arranged in a perovskite structure. The expected intensities of the various lines were then calculated. The intensities observed on the X-ray diffraction powder diagram was compared with these calculated values in Table I and diagrammatically in Fig. 1. The intensities of the lines are sensitive functions of both the composition of the material and the positions of the ions in the lattice. The positions of the ions were

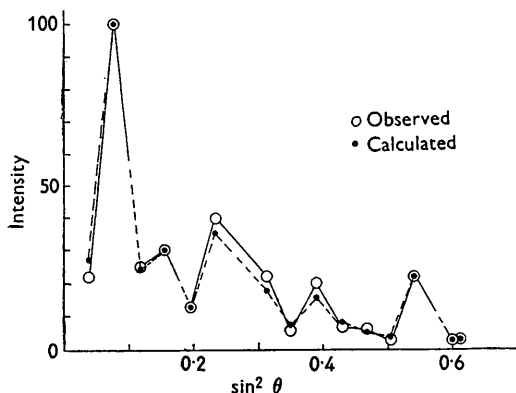


Fig. 1. Comparison of calculated and observed intensities of EuTiO_3 ; X-ray powder photograph.

Table I. Calculated and observed intensities for lines of EuTiO_3

| $\sin^2 \theta$ | $h^2 + k^2 + l^2$ | I_o | I_c |
|-----------------|-------------------|-------|-------|
| 0.0386 | 1 | 22 | 27.2 |
| 0.0782 | 2 | 100 | 100 |
| 0.1175 | 3 | 25 | 24.2 |
| 0.1560 | 4 | 30 | 30.3 |
| 0.1955 | 5 | 12 | 12.6 |
| 0.2340 | 6 | 40 | 35.3 |
| 0.3110 | 8 | 22 | 17.8 |
| 0.350 | 9 | 5.5 | 7.0 |
| 0.391 | 10 | 20 | 15.5 |
| 0.430 | 11 | 7 | 8.0 |
| 0.468 | 12 | 6 | 5.1 |
| 0.505 | 13 | 3 | 3.6 |
| 0.542 | 14 | 22 | 21.8 |
| 0.600 | 16 | 3 | 2.87 |
| 0.625 | 17 | 3 | 2.82 |

assumed in calculating the intensities of the lines for the cubic perovskite structure. The composition was assumed by calculating the scattering for each line assuming all of the appropriate lattice positions filled with Eu^{+2} , O^{-2} and Ti^{+4} . It is seen in Table I and Fig. 1 that the agreement between the observed intensities and those calculated is quite good. It is therefore inferred that the above assumptions are correct, i.e. that the black material has a perovskite structure, and the ratio $\text{Eu}:\text{Ti}:\text{O}$ is close to 1:1:3.

The lattice constant of EuTiO_3 (3.897 kX.) is close

to that of strontium titanate (3.899 kX.). This would be expected since the ionic radii of Eu^{+2} and Sr^{+2} are almost the same.

The X-ray intensity measurements indicated little, if any, oxygen deficiency in the lattice. The sum of the charges of the europium and the titanium ions must be close to six. This can be distributed either as $(\text{Eu}^{+2}\text{Ti}^{+4})$ or $(\text{Eu}^{+3}\text{Ti}^{+3})$ or possibly some intermediate state.

Calculations were made to determine in what manner the lattice constant would vary if one of the intermediate states prevailed. The unit cell edge is given here by one of two equations:

$$a = 2(r_{\text{Ti}} + r_{\text{O}}),$$

$$a = \sqrt{2} \cdot (r_{\text{Eu}} + r_{\text{O}}).$$

The choice of which of these two equations should be used is determined by whether there is ion contact between the titanium and the oxygen or the europium and the oxygen. A wide range of reasonable radii was assumed for each of these ions. These values were also adjusted for their coordination numbers. Thus the radius of O^{-2} was assumed to have some value between 1.33 Å and 1.46 Å, that of Ti^{+4} between 0.49 Å and 0.65 Å, and the adjusted value of Eu^{+2} was assumed to lie between 1.16 Å and 1.21 Å.

If one assumes the upper limit of the range of possibilities for the radius of O^{-2} (1.46 Å), then, according to the first equation above, the Ti^{+4} cannot be any larger than 0.49 Å since the lattice constant is found experimentally to be 3.897 kX. Using the same value for r_{O} , one can recalculate the lattice constant assuming $\text{Eu}-\text{O}$ ion contact to exist and using the largest possible value for Eu . The lattice constant is thus calculated from the second equation above to be 3.77 kX., which is considerably under the observed value of ~ 3.90 kX. Thus, in order to obtain a lattice constant of ~ 3.90 kX., we cannot assume $\text{Eu}-\text{O}$ ion contact but only $\text{Ti}-\text{O}$ contact. We have used here the largest possible values for the ionic radii of Eu^{+2} and O^{-2} and the smallest possible radius of Ti^{+4} . If it were possible to conclude that $\text{Eu}-\text{O}$ contact exists it would be favored for these extreme values. These calculations indicate that the Eu^{+2} and O^{-2} will not make contact even when the most favorable values for the radii are assumed.

Since this seems to be a case of $\text{Ti}-\text{O}$ contact, the observed lattice constant should indicate which of the states prevail for the europium and the titanium ions. Any substitution of a larger trivalent titanium ion for a tetravalent titanium ion in a position where ion contact already exists with the smaller ion will result in an increase of the lattice constant beyond that observed. Since strontium titanate has all of its titanium ions in the tetravalent state, it can be concluded that the europium compound also contains tetravalent titanium in the octahedral positions because of the close agreement of the lattice constants.

Further evidence of the stability of tetravalent titanium in similar mixed oxides was found when

attempts were made to prepare perovskites with other divalent rare earth ions such as samarium and ytterbium. When the oxides of samarium or ytterbium were heated with TiO_2 under conditions identical with those in which the EuTiO_3 was prepared, white products with complex X-ray powder patterns were obtained. A reaction had evidently taken place and a new phase was formed. TiO_2 when heated alone under similar reducing conditions was reduced to lower valent titanium oxides, as was indicated by the deep blue-black color of the product. Thus it is found that the reduction of Ti^{+4} proceeds with greater difficulty when the TiO_2 enters into mixed oxide formation.

X-ray powder diagrams of the EuTiO_3 sample were obtained at temperatures down to $108^\circ \pm 5^\circ$ K. by blowing a stream of cold nitrogen gas over the sample in the X-ray beam. At this temperature the sample was found to remain cubic.

B. Preparation of solid solutions containing lanthanum and monovalent cations

In selecting ions to substitute into the alkaline earth lattice positions, lanthanum was chosen as the trivalent ion, it being the largest trivalent ion of the rare earths. Various samples were prepared using lanthanum and each of the alkali metals, and in addition monovalent thallium and silver. The lanthanum and titanium were weighed as the oxides and the monovalent cations as the carbonates and nitrates. The weighed samples were placed in a platinum crucible and treated with a moderately strong solution of nitric acid. The crucible and its contents were then heated slowly to dryness. The products were then heated slowly and cautiously until the nitrates were decomposed. This procedure resulted in an intimate mixture of the oxides in a very finely divided state. The heating was continued over a Meker burner at a dull red heat for about a half hour. Finally the crucible was placed in a furnace at 1200° C. for 1 hr.

The products were ground to fine powders and X-ray diffraction powder diagrams were obtained for each sample. All but $(\text{La}, \text{Cs})\text{TiO}_3$ gave a primitive cubic powder pattern. The lattice constants of these samples are listed in Table 2.

A weighed sample of each product was treated with boiling dilute nitric acid and filtered on an asbestos mat in a weighed Gooch crucible. The sample and crucible were then dried and reweighed. The filtrate in each case was tested for lanthanum and titanium and in each case these ions were found to be absent. The weight loss on washing can then be assumed to be due entirely to the loss of monovalent metal oxide which had not entered the crystal in preparation. The percentages of monovalent oxide which had entered the crystal are shown in column 2 of Table 2.

A cubic $(\text{Ce}, \text{K})\text{TiO}_3$ was also obtained in a similar preparation except in a partial hydrogen atmosphere to insure the reduction of cerium to the trivalent state.

In Table 2 a general increase in lattice constant is observed as univalent ions with larger ionic radii are substituted into the lattice position. The $(\text{La}, \text{Rb})\text{TiO}_3$ is an exception, however, since its lattice constant is slightly smaller than $(\text{La}, \text{K})\text{TiO}_3$. The reason for this deviation can be seen in column 2 of Table 2.

On washing the product with dilute nitric acid solution a considerable amount of the rubidium was dissolved. Thus we find that, despite the large size of the rubidium ion, only enough of the oxide could enter into the solid solution to increase the lattice constant to around that of $(\text{La}, \text{K})\text{TiO}_3$ which has more of the monovalent ion in solid solution with lanthanum. The larger ionic radius difference of caesium from lanthanum (column 6, Table 2) would make solid-solution formation still more difficult. It has thus been observed that a greater weight percentage of this sample is dissolved in the hot dilute acid treatment. In this case, not enough caesium can enter the lattice to form a simple perovskite structure.

Table 2. Summary of data for compounds $(A, B)\text{TiO}_3$

| 1 | 2 | 3 | 4 | 5 | 6 |
|--------------------------------------|---------------------------------|--------------------------------|--|------------------------|--|
| Material | % B_2O which entered crystals | Ionic radius of monovalent ion | Average ionic radius monovalent ion + La^{+3} | Lattice constant found | $R_{\text{cat.}^+} - R_{\text{La}^{+3}}$ |
| $(\text{La}, \text{Li})\text{TiO}_3$ | 100 | 0.70 Å | 0.92 ₅ Å | 3.861 Å | -0.45 Å |
| $(\text{La}, \text{Na})\text{TiO}_3$ | 100 | 1.00 | 1.07 ₅ | 3.865 | -0.15 |
| $(\text{La}, \text{K})\text{TiO}_3$ | 93.8 | 1.33 | 1.24 | 3.899 | 0.18 |
| $(\text{La}, \text{Rb})\text{TiO}_3$ | 65.8 | 1.52 | 1.33 ₅ | 3.895 | 0.37 |
| $(\text{La}, \text{Cs})\text{TiO}_3$ | 42.0 | 1.70 | 1.42 ₅ | — | 0.55 |
| $(\text{La}, \text{Ag})\text{TiO}_3$ | 65.4 | 0.97 | 1.06 | 3.874 | -0.18 |
| $(\text{La}, \text{Tl})\text{TiO}_3$ | 97.2 | 1.50 | 1.32 ₅ | 3.875 | 0.35 |
| SrTiO_3 | — | — | 1.18* | 3.899 | — |
| $(\text{Ce}, \text{K})\text{TiO}_3$ | 100 | 1.33 | 1.21 ₅ † | 3.889 | 0.23 † |
| EuTiO_3 | — | — | 1.18 ‡ | 3.897 | — |

* Average radius in this case is taken as that of Sr^{++} .

† Radius of Ce^{+3} (1.10 Å) is used instead of La^{+3} .

‡ Average radius in this case is taken as that of Eu^{++} . The ionic radii are those given by Wyckoff (1948). The radius of Eu^{++} is assumed to be the same as that of Sr^{++} .

The deficiency of monovalent ion in the perovskite structure may be accounted for in the following manner: Had all of the Rb_2O entered the crystals, a mixed oxide would be formed with the composition $\text{Rb}_2\text{O} \cdot \text{La}_2\text{O}_3 \cdot 4\text{TiO}_2$. Since a considerable amount of Rb_2O was washed out of the product, the material may be represented as $X\text{Rb}_2\text{O} \cdot \text{La}_2\text{O}_3 \cdot 4\text{TiO}_2$, where X is the fraction of the Rb_2O which had gone into the crystal. This will result in lattice vacancies in both the lanthanum and the oxide ion positions of the perovskite lattice.

Another alternative is to assume that for each unit of Rb_2O which did not go into the solid solution, a corresponding amount of TiO_2 likewise failed to go into the crystal. This would result in a deficiency of ions in the lanthanum positions only. The resulting products will have the empirical formulae: $X\text{Rb}_2\text{O} \cdot \text{La}_2\text{O}_3 \cdot (3+X)\text{TiO}_2$. The limiting case for $X=0$ will be $\text{La}_2\text{O}_3 \cdot \text{TiO}_2$ or $\text{La}_{2/3}\text{TiO}_3$, where one-third of the 12-coordinated positions will be empty. For any value of X , the fraction of unfilled 12-coordinated lattice sites will then be given by $\frac{1}{3}(1-X)$.

The possibility was considered that the deficit of monovalent ions in the twelve coordinated positions was compensated by the presence of trivalent titanium. It was noted, however, that these solid solutions were all white, which indicates the absence of trivalent titanium.

The lattice constant of $(\text{La}, \text{K})\text{TiO}_3$ is found to be very close to that of SrTiO_3 . This would be expected since the average ionic radius of the La^{+3} and K^+ ions is close to that of Sr^{++} .

The $(\text{La}, \text{Li})\text{TiO}_3$ lattice constant is close to that of $(\text{La}, \text{Na})\text{TiO}_3$ despite the observation that all of the univalent metal ions had entered the solid solution lattice in both cases. This may be caused by anion repulsion, preventing close contact between the small lithium ions and the oxide ions. In the case of the lithium ion, the available 'hole' would be somewhat larger than the monovalent ion. The effective average ionic radius would then be the average between the lanthanum radius and that of the hole, and would be

found to be larger than that radius expected from averaging the radii of La^{+3} and Li^+ .

The thallium compound has a smaller lattice constant than would be expected from the ionic radius of thallium. This may be due to the partial covalent character of the $\text{Tl}-\text{O}$ bond in these materials.

The cubic $(\text{Ce}, \text{K})\text{TiO}_3$ was found to have a lattice constant which is slightly smaller than that of $(\text{La}, \text{K})\text{TiO}_3$. This is the expected result of the lanthanide contraction of the rare earth ions.

Low-temperature X-ray powder diagrams were obtained with $(\text{La}, \text{K})\text{TiO}_3$ and $(\text{La}, \text{Rb})\text{TiO}_3$. The materials remained cubic down to $108^\circ \pm 5^\circ \text{K}$., the lowest temperature obtained with our equipment. Like strontium titanate, these compounds exhibit no low temperature phase changes.

The authors wish to express their gratitude to Dr Benjamin Post for his invaluable assistance with the X-ray work reported in this paper.

References

- HULM, J. K. (1950). *Proc. Phys. Soc. A*, **63**, 1184.
 HULM, J. K., MATTHIAS, B. T. & LONG, E. A. (1950). *Phys. Rev.* **19**, 885.
 JACKSON, W. & REDDISH, W. (1945). *Nature, Lond.* **156**, 717.
 MATTHIAS, B. T. (1949). *Phys. Rev.* **75**, 1771.
 SHIRANE, G., HOSHINO, S. & SUZUKI, K. (1950). *Phys. Rev.* **80**, 1105.
 SLATER, J. C. (1950). *Phys. Rev.* **78**, 748.
 SMOLENSKII, G. A. & KOZHEVNIKOVA (1951). *Dokl. Akad. Nauk, S.S.S.R.* **76**, 519.
 WAINER, E. & SALOMON, A. N. (1942-3). Titanium Alloy Manufacturing Co., Electrical Reports Nos. 8-10.
 WAINER, E. (1946). *Trans. Electrochem. Soc.* **89**, 331.
 WOOD, E. A. (1951). *Acta Cryst.* **4**, 353.
 WUL, B. M. & GOLDMAN, I. M. (1945). *C. R. Acad. Sci. (U.R.S.S.)*, **46**, 139.
 WUL, B. M. & VERESCHAGEN, L. F. (1945). *C. R. Acad. Sci. (U.R.S.S.)* **48**, 634.
 WYCKOFF, R. W. G. (1948). *Crystal Structures*, Volume I. New York: Interscience Publishers.