M. S. KOSMAN and É. V. BURSIAN

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Abstract

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M. S. KOSMAN and É. V. BURSIAN

COLORATION OF $BaTiO_3$ SINGLE CRYSTALS

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It is known that, as a result of growing barium metatitanate single crystals, crystals are obtained with shades ranging from light yellow to dark brown, almost black. We have found that the nature of the coloration of these crystals is close to the nature of coloration in alkali-halide crystals and silver halide salts. A change in the color of polycrystalline specimens—blackening—as a result of a number of treatments has already been noted ([1]). This blackening is associated with partial reduction and separation of the metal, which naturally increases the conductivity and entails a change in other electrical parameters. The coloration observed by us proceeds differently and is a purely physical process connected with the displacement of charge carriers.

The specimens were prepared by the Mattias method, but the ratio of the components of the charge was varied ([2]). The crystals grew in the form of flat triangles, rectangular parallelepipeds, or cubes. The appearance, color, and shape of the crystals depended strongly on the composition of the charge and on the growth conditions. In their ferroelectric properties the crystals did not differ from those described in the literature. For optical measurements, plates with plane-parallel faces were selected, as far as possible containing no internal defects that might cause scattering. Absorption was measured with an SF-4 spectrophotometer.

In Fig. 1, curve A gives the absorption spectrum of a single crystal of a brown shade, acquired by it already during the growth process. The crystal was then annealed in hydrogen at 1000° or simply in the reducing part of the flame of an alcohol burner; as a result it became almost transparent with a slight yellow tint; the absorption spectrum is given by curve B. In this case our data almost coincide with those obtained earlier ([3]). After annealing in air or in oxygen, the crystals again acquire a brownish-red color (curve C). By analogy with alkali-halide crystals, this coloration may be called additive.

Coloration by a field, known in alkali-halide crystals, is also observed in $BaTiO_3$. If a single crystal about 1.5 mm thick is decolorized, placed in a furnace mounted on the stage of a microscope, and a voltage is applied (the electrode material is immaterial: fired-on silver, copper and platinum plates, and aquadag were tested), then at a temperature of 300° and a voltage of 500 V one can observe the slow (about 1 mm per minute) advance from the anode of a dense reddish-brown coloration with a very sharply defined front (Fig. 2, I). Sometimes this is preceded by a comparatively rapid spreading from the cathode of

Fig. 1. Changes in the absorption curve as a result of coloration. D—optical density of the crystal; D_0—optical density of the bleached crystal

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Fig. 2. Photograph of a crystal partially colored by the field (a), and an explanatory diagram for it (b)

Figure 2: Fig. 2. Photograph of a crystal partially colored by the field (a), and an explanatory diagram for it (b)

a blue coloration of irregular shape (Fig. 2, *II*), which soon ceases. The brown coloration moves not only from the electrode, but also from all cracks and other macrodefects. At the point where the brown and blue colorations meet, the progress of the brown front is delayed (something like annihilation of the colorations occurs). Then the blue coloration is destroyed by the brown, and the entire crystal becomes uniformly colored reddish-brown.

color, which corresponds to curve D (Fig. 1). Curve E gives an idea of the position of the absorption band arising as a result of coloration by oxygen, and F—by the field.

If, at the moment shown in Fig. 2, the sign of the field is reversed, the brown coloration disappears, but not completely, and the coloration entering from the other side can catch up with the previous one. Thus it becomes possible to produce coloration by an alternating field. Such coloration simultaneously from both electrodes at a frequency of 50 Hz is easily detected experimentally. The rate of propagation of the brown coloration depends strongly on temperature. At room temperature this rate is about 1 mm per day at an electric-field strength $E = 10$ kV/cm.

Probably, coloration by the field and coloration by oxygen may be regarded as being caused by the same coloring centers. It should be noted that the curves in Fig. 1 were taken only for two specimens, since crystals acceptable in optical respects are rarely encountered and, consequently, the exact form of the curves cannot yet be considered established; but the very fact of reddish-brown coloration has been established on a large number of specimens, and has also been verified on specimens kindly provided to us by I. E. Mylnikova. Blue coloration is unstable and is encountered more rarely. Weak reddish coloration can also be noticed in ceramic specimens, but in ceramics the observations are greatly hindered by the impossibility of observation in transmitted light.

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The very fact of coloration of $BaTiO_3$ is of interest in that coloration is always associated with ionic conductivity (4), whereas there are a number of works according to which $BaTiO_3$ has purely electronic conductivity (5).

It follows from preliminary measurements that the coloration of single crystals changes their electrical characteristics; however, research in this direction is still under way. Since coloration also occurs at room temperature, it is possible that a comparison of the properties of colored and uncolored specimens will clarify the problem of aging of barium titanate capacitors (6,7).

Leningrad State
Pedagogical Institute
named after A. I. Herzen

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Note: Figure translations are in progress. See original paper for figures.