X-ray and dielectric studies of irradiated Perovskite type compounds
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Résumé. — On obtient par irradiation gamma de Co60 ou électrons rapides le même changement réversible de la perméabilité diélectrique dans des échantillons polycristallins BaTiO3, SrTiO3, PbTiO3, NaNbO3 et PbZrO3. Après irradiation de PbTiO3 dans la pile jusqu’au flux intégré de neutrons rapides $\Phi > 10^{20}$ cm$^{-2}$, on a mis en évidence une transformation structurale vers un état amorphe qui est suivie par la formation d’une phase $\beta$-PbO2. En même temps le changement des paramètres réticulaires dans PbTiO3 montre la tendance à la transformation d’état induite par irradiation qui est analogue à celle dans BaTiO3 et PbZrO3.

Abstract. — As a result of irradiating polycrystalline samples of BaTiO3, SrTiO3, PbTiO3, NaNbO3 and PbZrO3 by fast electrons, and by gamma-radiation of Co60, qualitatively identical reversible changes in the dielectric constant have been revealed. X-ray evidence of the crystal structure transformation into an amorphous state, followed by the formation of a $\beta$-PbO2 phase, have been found in PbTiO3 as a result of in-pile irradiation by fast neutron integrated fluxes $\Phi > 10^{20}$ cm$^{-2}$. Lattice parameter measurements in PbTiO3 indicate a tendency toward the radiation induced phase transformation, analogous to that of BaTiO3 and PbZrO3.

Experimental data obtained in the last years have made it possible to outline the general features of processes which take place in perovskite type materials under the effect of various irradiation conditions [1]. Nevertheless additional information is necessary to solve a number of problems concerning the nature of reversible and irreversible radiation effects in various materials of this type.

This work deals with a study of the experiments pertaining to two aspects of the problem mentioned above.

1. The effect of electron and gamma irradiation on the dielectric constant of some ferro-, antiferro-, and paraelectric perovskites. — Changes of low field dielectric constant ($\varepsilon$) for polycrystal SrTiO3, BaTiO3, PbZrO3, NaNbO3, PbTiO3 which occur because of gamma and fast electron irradiation are shown in figures 1a and 1b respectively (also see [2]). Radiation stability of SrTiO3 appears to be maximum but that of PbTiO3 — minimum though qualitative changes of $\varepsilon$ are similar for all the compounds under study. Herewith electron energy (1.14 and 9.0 MeV) and also dose rate (100 and 400 rd/s) changes do not affect the nature of the changes of $\varepsilon$. Crystal lattice parameters of all the irradiated materials remain unchanged within $\pm$ 0.001 Å.

Radiation induced changes of $\varepsilon$ vanish as a result of subsequent annealing at 150 °C for about an hour. Therefore one may consider these changes to be reversible [1], [3], [4] and they may be treated as radiation induced ageing found earlier on the $\varepsilon$ values measured both in high [5] and low electric fields [6].

In the course of irradiation the accumulation of reversible defects are accompanied by the annealing both of...
the radiation and the natural defects in the virgin material [5]. This annealing explains the increase of $e$ in some irradiated samples of SrTiO$_3$ (Fig. 1b). It follows from the given data that the common physical nature of the interaction of electron and gamma radiation (through the Compton electrons) with BaTiO$_3$, holds well for all the materials which we have studied.

It is noteworthy that the observed radiation changes of $e$ appear to be independent of the dielectric properties of the compounds (ferro-, antiferro-, paraelectrics) and must be due only to the character of the packing and disordering of the structural elements AO and BO$_2$ when one uses a molecular model of ABO$_3$-crystals [3], [4] in interpreting reversible radiation effects.

2. Crystal structure transformations in PbTiO$_3$ highly irradiated by fast neutrons. — It has been shown [2], [3], [7] that the irradiation of PbTiO$_3$ by fast neutrons with integrated fluxes up to $\Phi \approx 8 \times 10^{19}$ cm$^{-2}$, gives rise to the Curie point ($T_c$) shift to higher temperatures and to the increase of the tetragonality of the crystal lattice ($c/a$), in contrast with BaTiO$_3$ and PbZrO$_3$, whose values of $c/a$ decrease with increasing $\Phi$ until the radiation induced phase transition from tetragonal to cubic takes place at $\Phi < 10^{19}$ cm$^{-2}$.

In the case of PbTiO$_3$ a continuous increase of $c/a$ is accompanied by the deterioration of the X-ray diffraction pattern typical of perovskite type lattices, and by the reduction of metallic Pb upon irradiation of Cd-shielded samples ($T \sim 300$ °C) with fluxes up to $\Phi \approx 8 \times 10^{19}$ cm$^{-2}$ [3], [4]. To explain the unusual behaviour of PbTiO$_3$ we have carried out X-ray powder measurements at $\Phi$ up to $2 \times 10^{20}$ cm$^{-2}$ using the method described in [2], [3]. In contrast with our earlier experiments the irradiation of the samples has been accomplished without Cd-shielding at 40-70 °C.

A brief account of the results obtained is as follows. With increasing $\Phi$ the diffraction pattern of PbTiO$_3$ deteriorates and at $\Phi > 10^{20}$ cm$^{-2}$ vanishes completely. At the same time a diffraction pattern of the $\beta$-PbO$_2$ phase appears. The formation of the $\beta$-PbO$_2$ phase also was found in highly irradiated PbO. The appearance of $\beta$-PbO$_2$ instead of Pb probably is due to different temperature conditions of irradiation of Cd-shielded and unshielded samples.

It is noteworthy that the annealing of irradiated samples of PbTiO$_3$ for 2-3 hours at 300 °C causes a vanishing of the diffraction pattern of $\beta$-PbO$_2$ and a reappearance of the fairly distinct diffraction pattern of PbTiO$_3$ tetragonal phase with slightly changed lattice parameters (Fig. 2). A prolonged annealing at 600 °C does not give rise to additional changes in the X-ray diffraction patterns of PbTiO$_3$.

The data shown in figure 2 seem to state for sure that the behaviour of fast neutron irradiated PbTiO$_3$ is qualitatively similar to that of BaTiO$_3$ [3], [4], [7] and PbZrO$_3$ [7]. From the $c/a$ tendency to the decrease at $\Phi > 10^{20}$ cm$^{-2}$ one can expect the radiation induced phase transition in PbTiO$_3$ at $\Phi < 2 \times 10^{20}$ cm$^{-2}$. Corresponding values of $\Phi$ for BaTiO$_3$ ($\approx 5 \times 10^{18}$ cm$^{-2}$ [3], [4], [7]), PbZrO$_3$ ($\sim 2 \times 10^{19}$ cm$^{-2}$ [7]) and PbTiO$_3$ ($\sim 2 \times 10^{20}$ cm$^{-2}$) are in agreement with the differences of their Curie points (120 °C, 230 °C and 490 °C respectively). This fact is in favour of the validity of our statement concerning the character of radiation induced phase transformations in perovskite type compounds [3], [4].

The disappearance of the PbTiO$_3$ X-ray diffraction pattern at $\Phi > 10^{20}$ cm$^{-2}$ indicates an amorphisation phenomenon known for materials of different types (e.g. see [8]). However this amorphisation in PbTiO$_3$ is quite different because of the much lower temperatures ($\sim 300$ °C) of annealing of the radiation defects. It means that these radiation defects must be due to the above mentioned disordering of AO and BO$_2$ structural elements and can not be statistical Frenkel point defects.

It is reasonable to assume that in contrast with the case of gamma and electron irradiation the disordering of AO and BO$_2$ «molecules» in the course of neutron irradiation goes on up to the total destroying of the atomic periodicity arrangement and hence up to the disappearance of coherent X-ray scattering. Taking into account this assumption one can treat all the changes of PbTiO$_3$ X-ray diffraction patterns as a result of irradiation and subsequent annealing. It is also possible to give a tentative explanation (see [9]) to the formation of $\beta$-PbO$_2$ in highly irradiated PbTiO$_3$ and PbO. However further information is necessary to give a detailed account of this interesting effect.
References


ERRATUM
A la place de la relation (7) lire :
UK = - c + A exp \[- BX113\]
tous les calculs sont corrects.