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**FIELD-EXCITED ELECTRON EMISSION
FROM LANTHANUM-DOPED,
BARIUM-STRONTIUM-TITANATE CERAMICS**

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ABSTRACT

The field-excited electron emission from lanthanum-doped barium-strontium-titanate ceramics was studied. Emitted charge densities up to 100 nC/cm^2 were measured. The results from field-excited emission and from dielectric measurements, obtained with the same samples, support the hypotheses of the existence and of the reversibility of fast-switching ferroelectric microdomains. These ceramics have properties, such as electrical conductivity, dielectric constant, thermostimulated currents, which are typically related to ferroelectric relaxors. It is shown that these properties can be modified by adequate thermal and electrical treatments.

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FIELD-EXCITED ELECTRON EMISSION FROM LANTHANUM-DOPED, BARIUM-STRONTIUM-TITANATE CERAMICS

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1. INTRODUCTION

A new method of strong electron emission based on the fast polarization change of ferroelectric materials was discovered recently. Its application to electron sources seems promising and straightforward [1]. The electron emission from ferroelectrics was first demonstrated with PLZT ceramics [2-5]. In this paper the results of studies with La-doped $(\text{Ba,Sr})\text{TiO}_3$ are reported. This solid solution has such a Sr content that the ferroelectric (FE)-paraelectric (PE) diffuse phase-transition boundary is shifted near room temperature. The behaviour of this material, as also that of PLZT, seems to be based on ferroelectric relaxors [6]. The polar microregions and especially the ferroelectric microdomains dispersed in the PE or the antiferroelectric (AFE) matrix, are responsible for the specific features of the relaxors [7-9]. Also the fast-switching and the electron generation and emission produced with PLZT ceramics seem to be caused by the fast response of these microdomains to electric field pulses. Some data [10-15] indicate the presence of relaxor properties in $(\text{Ba,Sr})\text{TiO}_3$ solid solutions, similarly to what happens in other BaTiO_3 -based ceramics, such as for instance $\text{Ba}(\text{Ti,Zr})\text{O}_3$ [16].

The tests described below, especially the dielectric and the thermally stimulated current measurements, seem to confirm the relaxor behaviour. For these investigations, we have chosen La-doped (1% La_2O_3)- $(\text{Ba}_{0.7},\text{Sr}_{0.9})\text{TiO}_3$ and $(\text{Ba}_{0.75},\text{Sr}_{0.25})\text{TiO}_3$, where the PE-FE phase transition is shifted below room temperature because of the high strontium content. The electron emission studies were performed at higher temperatures, where the PE state dominates.

2. INVESTIGATIONS OF ELECTRON EMISSION

The ceramics $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ ($x = 0.25$ and 0.3) doped with 1% La_2O_3 were sintered using conventional mixed-oxide methods. The disk-shaped samples of 0.5-0.8 thick-

ness were polished and covered with evaporated-gold electrodes. The preparation of the sample, of the experimental set-up, of the electrical circuits, and the method of the field-excited electron emission were described in detail earlier [2-5]. The samples were coated with a striped electrode on the emitting surface and a solid one on the rear. The length of the exciting electric pulse was fixed at 150 ns. Typical excitation current amplitudes were 20-40 A. In Fig. 1a the emitted charge density Q_e is shown as a function of the exciting electric field strength amplitude. The emission starts at a threshold field of about 15 kV/cm and 22 kV/cm for the samples containing 25% and 30% Sr, respectively. Breakdown through the sample occurs when a field of $E_p > 25$ kV/cm is applied to $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{TiO}_3$, whereas $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ can sustain stronger field amplitudes. The density of the emitted charge decreases with increasing temperature, but the $Q_e(T)$ -dependence could only be determined approximately because of the rather large scattering of the experimental data (Fig. 1b).

Fig. 1 : a) The emitted charge density Q_e as a function of the amplitude of the exciting electric field pulse measured at room temperature. In (b), Q_e is shown as a function of the temperature at constant strengths [23 kV/cm ($x = 0.25$) and 30 kV/cm ($x = 0.3$)] of the exciting field.

3. DIELECTRIC MEASUREMENTS

The dielectric characteristics were measured during heating of the sample at a field of 1 kHz frequency. The temperature dependences of the dielectric constant ϵ , the dielectric loss factor D and the sample resistance R_p are shown in Fig. 2. The curves 1 and 1' in Figs. 2a and 2b belong to a $(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3 + 1\% \text{La}_2\text{O}_3$ sample which was aged during 3 months, starting from the moment it was electroded. These characteristics correspond to those of normal ferroelectrics, with the exception of a relatively narrow temperature range above the temperature where ϵ is at a maximum (T_{max}).

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Fig. 2 : Temperature-dependence of the dielectric constant ϵ , of the dielectric loss factor D and of the resistance R_p at various ageing and prepoling states of the La-doped (Ba,Sr)TiO₃ samples.

The curves 2 and 2' in Figs. 2a and 2b were measured with an annealed sample by heating it to 500°C and then quenching it to the FE state. The curves 3 and 3' were obtained from a previously prepoled sample: a d.c. field of 2 kV/cm strength was applied at 200°C and the sample quenched to the FE state. The dependence of ϵ and D on the temperature T is shown in Fig. 2c for the sample (Ba_{0.75}Sr_{0.25})TiO₃, annealed as above (curve 1,1') and prepoled successively at 100°C, 150°C, and 200°C (curves 2-4 and 2'-4').

The annealed and prepoled samples show typical effects of ferroelectric relaxors [7]: the loss factor D reaches a maximum near $T_{\max}$, then decreases or remains constant in a wide temperature range above $T_{\max}$, the resistivity has a positive temperature coefficient in this range (Fig. 2b). All these measured relations can be reproduced very easily. Two local maxima can be distinguished in the $\epsilon(T)$ curve (Fig. 2d) for the sample previously quenched rapidly under d.c. field. A sample was first immersed in silicon oil, which was rapidly cooled in liquid nitrogen, and finally heated back to the PE state. Consequently, a considerable number of the FE domains are preserved in the PE matrix.

4. DEPOLARIZATION AND THERMALLY-STIMULATED CURRENTS

Detailed investigations of the depolarization current I_d and of the thermally stimulated current (TSC) were undertaken in the temperature range where the unusual behaviour of ϵ , D , and R_p was observed. The polarizing d.c. field across the sample was switched off at selected constant temperatures. The sample was then connected to a sensitive x - t recorder in order to measure the emerging current. To ensure a good stabilization and homogeneity of the temperature distribution, the sample was immersed in a silicon-oil bath, which could be heated and cooled. Figure 3a shows the currents I_d and TSC as a function of time: I_d gradually disappears after several tens of minutes, and only a weak and almost time-independent TSC remains. This allows the temperature dependence of the TSC (Fig. 3b) to be determined. The TSC depends exponentially on the inverse temperature (Fig. 3c).

Fig. 3 : Depolarization I_d and thermally stimulated (TSC) current versus time at room temperature and temperature-dependence of the TSC (b and c) for the $(Ba_{0.75}, Sr_{0.25})TiO_3 + 1\% La$. Sample prepoled under 2 kV/cm at 200 $^{\circ}C$.

5. DISCUSSION

The relaxor behaviour of the ferroelectric materials is believed to depend on both the ferroelectric microdomain dispersed in the PE and AFE matrices and on other types of polar microregions based on heterogeneities in the A and B crystal sublattice. The experiments reported here and elsewhere (see, for instance, Ref. [8]) seem to confirm that the relaxor properties can be modified in a controlled way by adequate thermal and electrical treatments and, especially, by quenching under the influence of a d.c. field. Fast quenching causes freezing of a large number of defects in the crystal structure created at high annealing temperature. Mobile ion defects can migrate to the domain walls and even into the surface layers when a high concentration of vacancies is present in the crystal lattice. In perovskites, oxygen vacancies enhance the p- and the n-conduction in the anodic and the cathodic regions, respectively [8, 15].

The unusual stability of the microdomains dispersed in a PE matrix results from a mutual compensation of the spontaneous and of the space-charge polarization. Parts of the ion and electron components are also mutually compensated, forming the oxygen vacancies that can trap one or two electrons (F_1' , F_2' colour centres). The generation of electrons from the colour centres, caused by fluctuations of thermal energy, their diffusion towards the bulk of the sample, and the refilling of the electron traps by electrons injected from the sample electrodes can explain the origin and the characteristic behaviour of the TSC. The activation energy of 0.60 to 0.65 eV deduced from Fig. 3c is of the order of the binding energy level of one of the two electrons occupying an F_2 centre in a perovskite structure.

The compensation between the spontaneous and the space-charge polarization, and the resulting dynamic equilibrium, is rapidly changed when the spontaneous polarization P_s of the FE microdomains is reversed under an applied HV pulse. At this moment high electron charges are generated by the internal electric fields in the surroundings of such domains [17] and a part of the liberated electrons can be emitted from the bare stripes of the sample surface. (This hypothesis is also supported by earlier experiments on the electron emission from PLZT ceramics [2-5].) Many more details on the switching dynamics of FE domains under fast rising electric pulses can be found in Refs. [18-20]. Polarization-switching experiments can be considered not only as a new tool for investigating the dynamics of the ferroelectric microdomains in relaxors, as suggested in Ref. [5]; they also form a necessary basis for the selection of ferroelectric materials to be used in applications such as the electron emission for particle sources and for high-field gradient accelerating gaps.

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