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FROM PLZT-X/65/35 CERAMICS**

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ELECTRIC FIELD-EXCITED ELECTRON EMISSION
FROM PLZT-X/65/35 CERAMICS

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Abstract This paper reports the experimental results on electron emission from PLZT ceramics, of composition X/65/35 (X = 7, 8, 9, or 10%), excited by short, rectangular, high-voltage pulses. The charge emission in the surroundings of the diffuse ferroelectric phase transition is investigated. Strong correlation has been found between the sum of pyroelectric and thermostimulated current on the one hand, and the emitted charge density on the other hand. Some details concerning this correlation are discussed.

INTRODUCTION

Electron emission phenomena from ferroelectric materials excited by an external electric field have been under investigation since 1965¹⁻³, but only relatively weak effects were observed. Recently, we obtained emitted charge and current densities from PLZT-2/95/5 ceramics that are orders of magnitude greater^{4,5}. In the case of prepoled PLZT samples, fast and strong polarization changes are induced by high-voltage pulses. A ferroelectric phase transition takes place and leads to copious electron liberation by thermal and field generation. The origin of the electrons lies in the defects of the sample-forming donor states.

In our earlier paper⁵ we showed that the electric conductivity and the pyroelectric current (I_p) together with the thermostimulated current (I_{ts}) increase in the neighbourhood of the antiferroelectric

(AFE)-ferroelectric (FE) diffuse phase transition (DPT). In prepoled PLZT-2/95/5 ceramics, local maxima appear in this temperature range. Here the current density of the emitted electrons is also considerably greater. This encouraged us to investigate PLZT-X/65/35 ceramics with a lanthanum content of 7, 8, 9, or 10%. A characteristic of these materials is the diffuse ferroelectric (FE)-paraelectric (PE) phase transition.

The phase diagram of the samples used in our experiments is shown in Fig. 1. The ceramics containing 7% and 8% of La are close to the phase boundary separating the tetragonal and the rhombohedral ferroelectric phases and the region of the so-called pseudoferroelectricity (dashed area). The two other materials (9% and 10% of La) belong to this latter region. It has been pointed out by many authors that DPTs occur in all these materials⁶⁻⁹. Some characteristics of DPT are: the broadened maxima in the electrical permittivity curves, the gradual changes of the spontaneous polarization P_s with with temperature (Fig. 2), and the differences in the phase transition temperatures as obtained by different techniques.

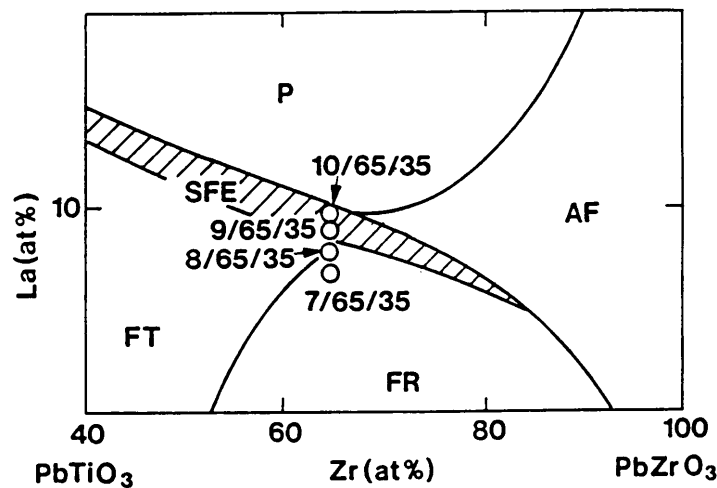
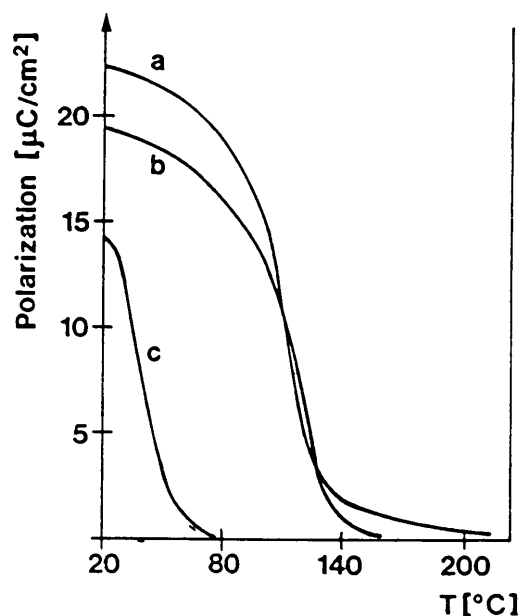


Fig. 1 - Samples investigated in the phase diagram from Ref. 6.

Fig. 2

The polarization as a function of temperature of
 a) PLZT-7/65/35,
 b) PLZT-8/65/35, and
 c) PLZT-9/65/35 from Ref. 8.
 The samples were prepoled at 22°C.



The present paper reports the dependence of the emitted electron density on the temperature in the surroundings of the FE-PE DPT.

SAMPLE PREPARATION

The ceramics that were investigated were prepared by conventional oxide sintering. The high-purity oxides PbO, TiO, ZrO, and LaO were used to obtain ceramics with an established Zr/Ti ratio equal to 65/35 and a La content equal to 7, 8, 9, and 10%, respectively.

The disk-shaped samples, 1 mm thick and 17 mm in diameter, were polished and coated with gold electrodes of 10 mm diameter, solid on one side and in the form of a striped grid on the opposite side. The interconnected gold stripes of 200 μm width were separated by bare stripes of the same width. The outer bare sample surface and the sample edge were covered with an insulating layer. The samples were prepoled by applying a dc electric field of 2 kV/cm at 150°C during 0.5 h and by cooling down under the same field strength through the PE-FE phase transition.

ELECTRICAL PROPERTIES, AND PYROELECTRIC AND THERMOSTIMULATED CURRENT MEASUREMENTS

Much data on the temperature dependences of the electrical permittivity of the PLZT-X/65/35 materials⁶⁻⁹ are available in the literature. Because of the specific types of electrodes, the electrical properties of the PLZT ceramics were investigated. The capacity and the resistance were measured with a frequency of 1 kHz with samples having the geometry described above, and using the prepoling procedure.

Figure 3 shows the capacity of the PLZT-X/65/35 samples versus temperature during heating. Apart from the broadened maxima on the C-T curves, one can see hump-like anomalies in a temperature region below these maxima. This kind of anomaly, observed for prepoled PLZT-X/65/35 samples, was also reported earlier⁷. The temperature dependence of the resultant current ($I_p + I_{tS}$) recorded during heating of the prepoled samples is also shown in Fig. 3, in arbitrary units. The temperature rate was about 2 K/min. In the case of the sample 10/65/35, the current maximum does not occur at temperatures above 20°C. The current maxima described occur at temperatures that are considerably lower than those of the broadened maxima in the C-T curves. They coincide approximately with the broadened minima of the sample resistance (not shown in Fig. 3), obtained both for ac and dc electrical field measurements. A typical example of resistance is shown later in Fig. 6. At these temperatures the maxima of the pyroelectric coefficient have also been found⁸. It is known that the proper pyroelectric current results from the change of spontaneous polarization ΔP_s with temperature (Fig. 2). In contradiction to this, the thermostimulated current does not change

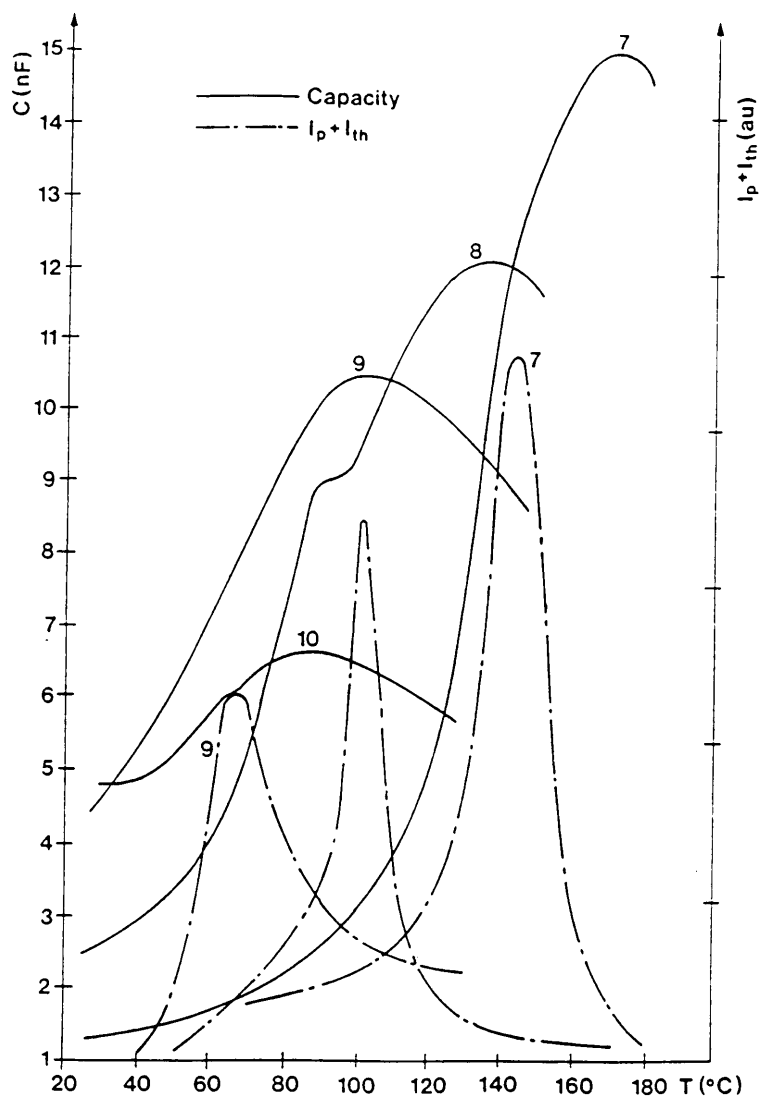


Fig. 3 The temperature dependence of the capacity (solid lines) and the resulting current $I_p + I_{ts}$ (dashed lines) for the PLZT ceramics indicated.

sign during the heating and cooling procedure and occurs also at constant temperatures. It is caused mainly by time and temperature changes of the space-charge polarization, and especially by thermally liberated electrons from the donor states. Its relaxation time depends on the temperature. Both current components are mutually dependent, as are both polarization components, namely the spontaneous and the space-charge polarization^{10,11}.

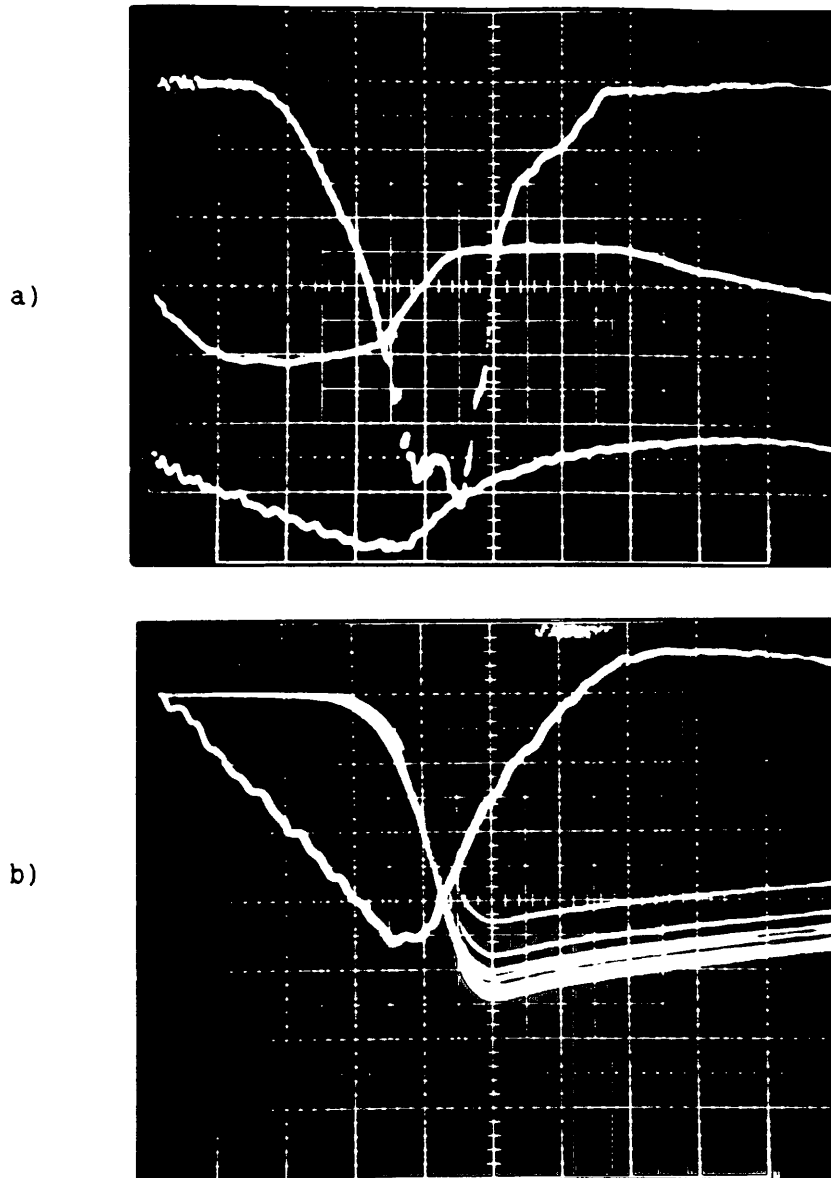


Fig. 4 - a) Electron emission from a PLZT-7/65/35 ceramic at a temperature of 130°C . Collected current on the Faraday cup: 20 mA per small div. (top); charging current wave form 20 A per small div. (middle); applied HV pulse 500 V per small div. (bottom). The time is 50 ns per small div.
 b) Scattering of the integrated current for a PLZT-7/65/35 ceramic at a temperature of 90°C . Ten emission pulses can be seen on the background of the applied HV pulse.

ELECTRON EMISSION INVESTIGATIONS

The mechanical set-up and the electric circuits that were used during the electron emission experiments have been described in

detail in Ref. 4. The emitting side of the ferroelectric sample, which is coated with the striped electrode, was exposed to a vacuum of $p \approx 10^{-6}$ mbar. The electron emission is initiated by a negative HV pulse of ~ 300 ns duration applied to the rear electrode, whilst the striped electrode is grounded.

Figures 4a and 4b show the sample response to the applied rectangular HV pulse (lower trace), the charging and discharging current wave form (middle trace), and the emitted electron beam current measured on a 50Ω Faraday cup (upper trace). An integrator with a capacity of 90 nF ($RC = 4.5 \mu\text{s}$) was generally used to measure the total collected charge. The measured charge has to be multiplied by a factor of 32 to allow for the transparency of the auxiliary grids and for the bare areas of the sample surface.

There was a considerable pulse-to-pulse scatter in the current and charge measurements (Fig. 4b), which decreased gradually when the applied voltage and temperature were increased. The experimental points for the emitted charge density Q_e in Figs. 5 to 7 represent the average value over 10 randomly chosen shots.

First, the field that is necessary to cause electron emission was investigated. The emitted charge density Q_e as a function of the electric field E_p at room temperature is shown in Fig. 5 for PLZT-8/65/35. The emission starts at a threshold of about 6 kV/cm and increases, at first slowly and then rapidly. The Q_e - E_p curves depend on the La content, on the state of the sample prepolarization, and on the distance from the average phase-transition temperature.

When investigating the temperature dependence of the emitted charge density, we limited the applied field to 15 kV/cm in order to

avoid breakdown and damage to the striped electrodes and the emitting bare parts of the sample surface. In some cases, after pulsing, several stripes of the electrode were interrupted and damaged near their edges. Small holes were visible on the bare areas.

The temperature dependence of the emitted charge at a constant electric field strength ($E_p = 15$ kV/cm)

is shown in Fig. 6 for PLZT-8/65/35. In addition, the electric characteristics and the resultant current curve, formed by the pyroelectric and the thermostimulated current, are given. The Q_e measurements were performed during slow heating of the sample (temperature rate $\sim 0.5^\circ\text{K}$ to $1^\circ\text{K}/\text{min}$) through the FE-PE DPT region.

In order to keep the voltage on the sample constant, the charging voltage had to be regulated in the temperature range where the capacity strongly increases and the electron emission takes place.

The Q_e -T curves for three different PLZT-X/65/35 samples are shown in Fig. 7. Comparing these curves with the data in Fig. 3, one can see the correlation between the sum of the pyroelectric and thermostimulated current and the emitted charge density. Apart from the rapid increase of Q_e , there are at least local maxima coinciding

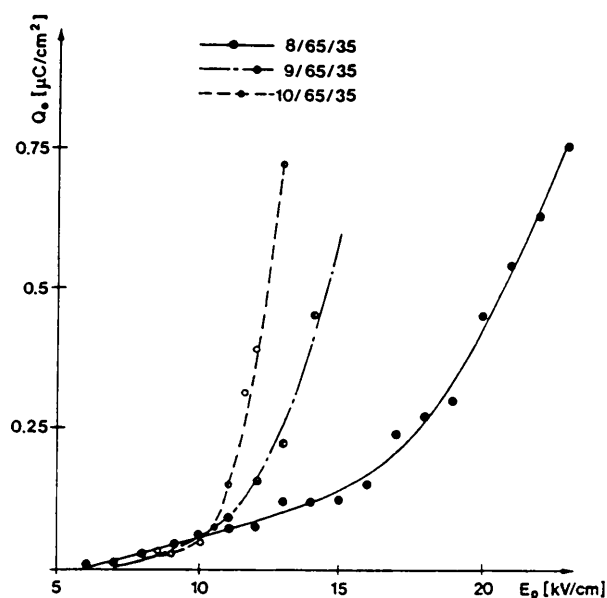


Fig. 5

The emitted charge density Q_e as a function of the applied electric field strength E_p . The data are obtained at room temperature for PLZT-8/65/35.

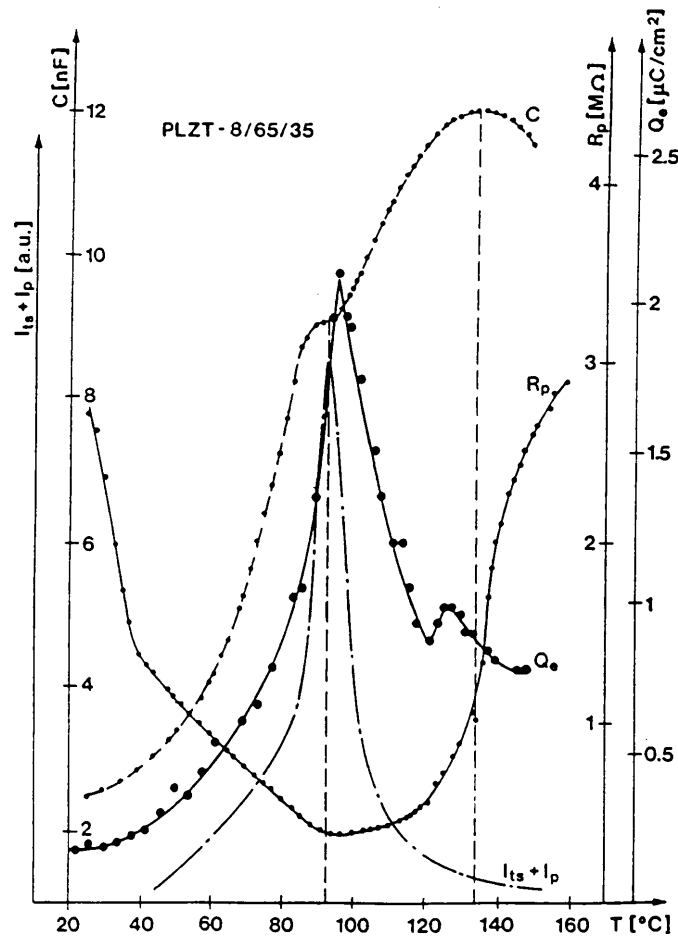


Fig. 6 - Emitted charge density Q_e , capacity C , resistance R_p , and pyroelectric and thermostimulated current ($I_p + I_{ts}$) as a function of temperature in the vicinity of the FE-PE phase transition.

with the resultant current maxima. In the case of the sample 9/65/35, this maximum is strongly diffuse. Similar behaviour of Q_e - T has been observed for the ceramics 10/65/35. In this case, however, the emitted charge density reached values up to $5 \mu\text{C}/\text{cm}^2$ in the temperature range between 20 and 60°C , which are beyond the Q_e scale of Fig. 7.

The curve Q_e - T for the cooling process of the PLZT-8/65/35 sample, which was previously partially depolarized by a heat treatment at 150°C during several hours, is shown in addition in Fig. 7.

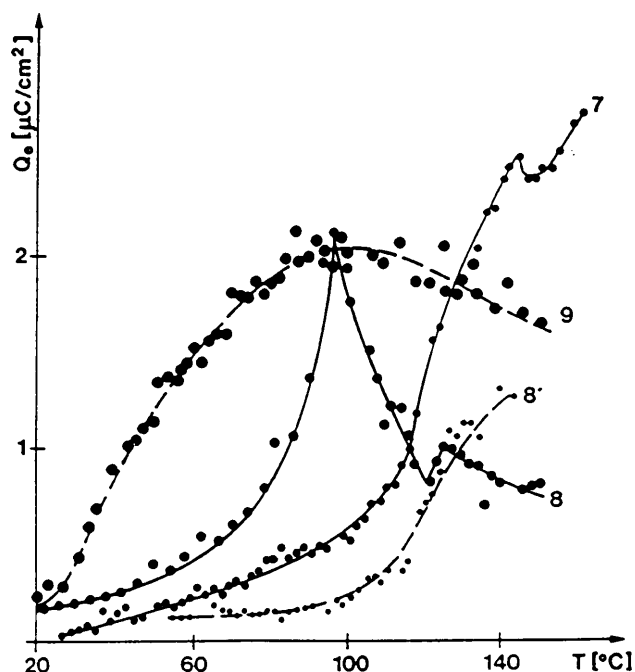


Fig. 7 - Emitted charge density Q_e versus temperature for the PLZT-X/65/35 ceramics with the La content indicated on the curves. The results were obtained during heating. For PLZT-8/65/35, the emission during cooling (8 min) of the depolarized sample is shown as well.

DISCUSSION

There is an evident correlation between the pyroelectric and thermally stimulated currents and the changing electrical conductivity in the DPT region on the one hand and, on the other hand, the intense electron emission excited by the HV pulses. This is proved by the data in Fig. 7 concerning the FE-PE DPT and probably that of the FE(T)-FE(R) DPT (see Fig. 1) as well. Earlier data on electron emission in the surroundings of AFE-FE DPT also confirm this⁵. In Fig. 7 one can see that the regions where the FE and the PE (or FE and AFE) phases coexist, favour the electron liberation and emission. In the case of PLZT-9/65/35 and 10/65/35 ceramics, where all these phases coexist (Fig. 1) and where the phase transition to the PE state is much more diffuse, the electron emission is considerably stronger over a wide

temperature range. Probably the existence of insulated FE domains in the PE or the AFE matrix increases electron liberation considerably, owing to the excitation by a strong internal field appearing in the process of gradual spontaneous polarization change (ΔP_S) during DPT. This field penetrates not only the surface layers but also the bulk of the crystal. The process is strongly accelerated under the influence of external HV pulses. The domains near the surface are responsible for the electron emission from the bare stripes. The average AFE-FE and FE-PE phase-transition temperatures decrease and increase, respectively, under the external electric field¹². The same is valid for individual microregions with different Curie points. Apart from the orientation processes of P_S in existing FE domains, new domains appear in the AFE or the PE matrix. The suddenly rising concentration of free electrons liberated mainly from local donor levels (for example, the emptying of F2-centres as discussed in Ref. 4), and the strong internal field in the surface layer due to the rapid change of P_S , are the cause of the anomalous emission activity observed in the DPT region.

As discussed above, there exists complex phase composition with local differences of the polarization behaviour on both the electrode and the bare parts of the sample surface. This is caused by the inhomogeneous field distribution and by different ways of P_S compensation. On the electrode, this compensation is reached by induced charge injection, and on the bare surface by screening processes. All these facts should be taken into consideration when interpreting the emission phenomena.

Some important details concerning the switching kinetics in PZT

ceramics under rapidly changing electric field¹³⁻¹⁵ will be very useful for a more detailed analysis of the data on electron emission, from both PZT and PLZT ceramics.

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