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Correlation between temperature-dependent permittivity dispersion and depolarization behaviours in Zr^{4+}-modified $BiFeO_3$–$BaTiO_3$ piezoelectric ceramics

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Abstract. **The correlation between permittivity frequency dispersion and depoling process upon heating was investigated in Zr^{4+}-modified $0.75BiFeO_3$–$0.25BaTiO_3$ (BF–BZT) ceramics. The temperature-dependent permittivity $\varepsilon_r(T)$ and the piezoelectric coefficient d_{33} for poled samples were measured under heating conditions to clarify the depolarization mechanism. The results indicate that the poling temperature plays a crucial role in the domains' alignment process, as expected. The temperature-dependent permittivity frequency dispersion and depolarization behaviours may have same origin. The aligned domains' break up into random state/nanodomains at depoling temperature (T_d), which causes strong frequency dependence of the permittivity, simultaneously, induces the loss of piezoelectricity. It suggests that the temperature-dependent permittivity measurements method is a simple way to determine the depolarization temperature.**

Keywords. **High-temperature piezoelectric ceramics; conventional solid-state reaction; depolarization; permittivity frequency dispersion.**

1. Introduction

Piezoelectrics have been widely used for piezoelectric transducers, sensors and actuators with a wide range of operating temperatures.[1,2] In recent years, in many new application areas such as space exploration, oil exploration and automotive industries have expressed strong needs for actuating and sensing at higher temperatures more than 300°C.[3–6] However, the Curie temperatures (T_C) of the most widely used commercial Pb(Zr, Ti)O_3 (PZT) piezoelectric ceramics are in the range of 180–386°C varying with different compositions, and generally the operating temperatures have been limited to one half of the T_C due to depolarization and increased conductivity.[1,7,8] On the other hand, the commercial manufacture and application of lead have in recent times become a concern from the viewpoint of the health and environmental protection.[9,10] Legislation governing the use of lead containing compounds has been enforced in many countries. Therefore, it is desirable to search for high Curie temperature lead-free materials with excellent piezoelectric properties.

In recent times, the Bi-based perovskite structures lead-free $BiFeO_3$–$BaTiO_3$ solid solutions are popularly studied due to the high Curie temperature (T_C). It was reported that the $BiFeO_3$–$BaTiO_3$ system possessed high piezoelectric constant $d_{33} = 116$–170 pC N^{-1} and high Curie temperature $T_C = 480$–619°C.[11–16] Thus, the $BiFeO_3$–$BaTiO_3$ solid solutions with high piezoelectric coefficients and thermal stability can provide a viable replacement for lead-based materials for high-temperature piezoelectric devices.

As it is known, in most cases, the as-prepared polycrystalline piezoelectric ceramics have domains with random orientations resulting in zero net macroscopic polarization and thus the macroscopic polarization must be induced by an external electric field larger than their coercive field (E_C).[17] It is generally believed that the poling temperature and the electric field strength play important roles in the poling process.[18] For some materials, however, poling is quite difficult. This is especially true for most newly developed high-temperature lead-free piezoceramics $BiFeO_3$–$BaTiO_3$ due to high electrical conductivity, high coercive field or low breakdown strength.[11,15,19,20]

Similarly, the poled piezoelectric ceramics often begin to lose their piezoelectric properties at a temperature somewhat below the Curie temperature (T_C) due to aligned domains returning to a random state in the poled piezoelectric ceramic. Therefore, thermal depoling behaviour is a key feature to determine the upper temperature limit of the piezoelectric ceramics in application.[21] However, a systematic investigation of the influence of the poling electric field and poling temperature on the piezoelectric properties and thermally induced loss of piezoelectricity in the $BiFeO_3$–$BaTiO_3$ ceramics is missing so far.

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Here, how increasing poling electric field at elevated temperature leads to higher piezoelectric coefficients in Zr^{4+}-modified $BiFeO_3$–$BaTiO_3$ piezoelectric ceramics has been reported. Compared with poling electric field, the poling temperature has significant effect on the piezoelectric properties. However, the poling temperature has insignificant effect on the thermal depoling behaviours. In addition, the depoling process is highly correlated to dielectric behaviour with increasing temperature. These results afford a better understanding of the poling and depoling process of high-temperature ferroelectric ceramics.

2. Experimental

Briefly, $0.75BiFeO_3$–$0.25Ba(Zr_{0.05}Ti_{0.95})O_3$ (BF–BZT) + 0.6 wt% MnO_2 (used as a donor to reduce oxygen vacancies formed during calcination and sintering) ceramics were prepared by the conventional solid-state reaction method. Dried oxides of high-purity Bi_2O_3, TiO_2, Fe_2O_3, MnO_2, ZrO_2 and $BaCO_3$ were mixed in a planetary ball mill for 24 h, with acetone as the mixing medium using yttrium-stabilized ZrO_2 balls. After drying, the mixed powders were calcined at 800°C for 2 h in an alumina crucible. The calcined powders were then mixed with polyvinyl alcohol (PVA) solution (5%) before pressing pellets of 12 mm diameter and 1.2 mm thickness at 100 MPa uniaxial pressures. Following removal of binder at 600°C for 2 h, pellets were then sintered in air at 990°C for 4 h.

Sintered ceramics were coarsely polished and silver paste electrodes were formed on both surfaces of the disk-shaped specimens after firing at 600°C for 10 min. The temperature dependences of the dielectric properties were measured using an automated dielectric measurement system with a precision impedance analyzer (Agilent 4294A). Poling was carried out at room temperature and 60 and 120°C in silicone oil by applying a dc electrical field of 0–90 kV cm^{-1} for 10 min on the sintered pellets. The direct piezoelectric coefficient (d_{33}) was measured approximately 24 h after poling using a Berlincourt d_{33} meter (ZJ–3A, China). Their electromechanical coupling factor (k_p) was determined by a precision impedance analyzer (Agilent 4294A) using the resonance/antiresonance technique. The thermal depoling experiments were conducted in the temperature region from 25 to 400°C. The poled samples were annealed for 30 min at various temperatures. After cooling to room temperature (RT), piezoelectric properties of each sample were measured at RT.

3. Results and discussions

Piezoelectricity appears on ferroelectric ceramics when the random ferroelectric domains are aligned through the poling process. The poling electric field dependence of the piezoelectric coefficient d_{33} and the planar electromechanical coupling factor k_p for the BF–BZT ceramics poled at 20, 60 and 120°C are plotted in figure 1. With increasing poling electric fields up to 4 kV cm^{-1}, the d_{33} and k_p levels poled at 20°C have little change. A gradual increase in d_{33} and k_p values is observed until poling electric field above 6 kV cm^{-1} as shown in figure 1, and the maximum $d_{33} = 36$ pC N^{-1} and $k_p = 0.15$ can only be obtained at 9.0 kV cm^{-1} poling field. In contrast, the samples at high poling fields show distinctly different poling behaviour compared with low poling temperature. It can be seen that the saturation piezoelectric properties for poling at high temperature are larger than that for poling at relatively low temperature. On the other hand, the threshold of poling field for saturation piezoelectric properties is decreased with the increase in poling temperature. The maximum $d_{33} = 110$ pC N^{-1} is observed with sample poled at 120°C and 4.0 kV cm^{-1}. For polycrystalline piezoelectric ceramics, it is generally accepted that elevated poling temperature induces decreased coercive field and reduced lattice distortion, thus helps facilitating a higher fraction of domain reorientations leading to improved piezoelectric properties.

The poling state for domain alignment degree during the poling process could be judged by the maximum phase angle, θ_{max} of impedance in the inductance region between

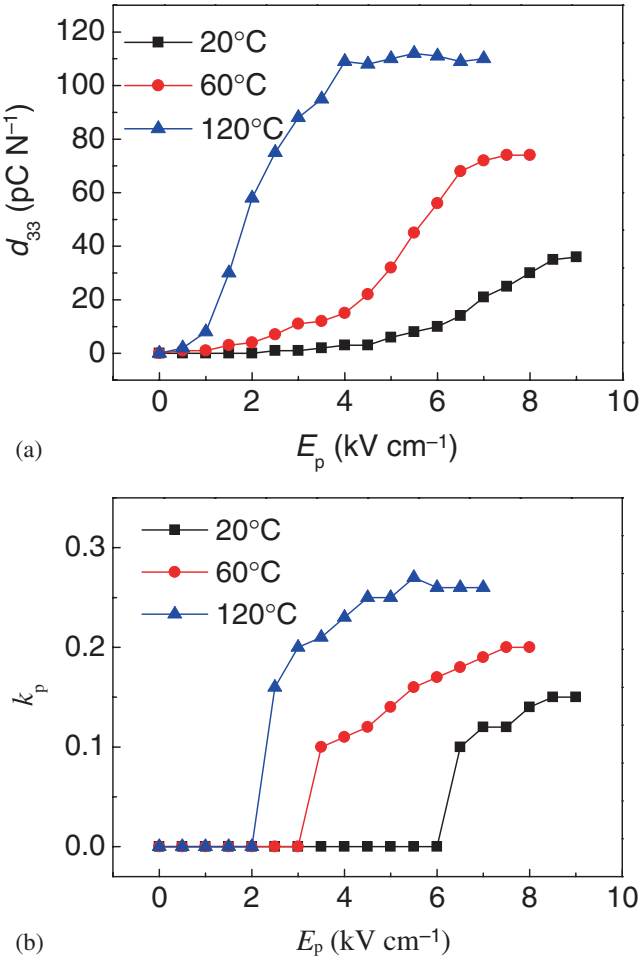

Figure 1. Poling electric fields' dependence of piezoelectric properties for the BF–BZT ceramics poled at 20, 60 and 120°C: (**a**) piezoelectric constant d_{33} and (**b**) planar electromechanical coupling factor k_p.

resonance and anti-resonance frequency.[22,23] The reference reported the frequency characteristics of the impedance $|Z|$ and phase angle θ for the 33-, 31-, p-, t- and 15-modes, and their piezoelectric constants d_{33}, d_{31} and d_{15} of the $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) ceramics.[24] It is interesting to find an obvious feature that a linear relationship between maximum phase angle θ_{max} and piezoelectric constants for different modes exists. In other word, the large θ_{max} is corresponding to high piezoelectric constants.

The frequency dependence of the impedance in the inductance region between resonance and antiresonance frequencies on the radial mode of the BF–BZT ceramics has been measured at room temperature for poled samples, as shown in figure 2a. The values of maximum phase angle (θ_{max}) as a function of poling fields are shown in figure 2b. As can be seen, the maximum phase angle for samples poled at 120°C with 3 kV cm^{-1} poling field ($\theta_{max} = 40°$) is far from full poling state with the maximum theoretical value (90°). The θ_{max} variation with the poling temperature shows similar evolution of the piezoelectric constants with poling electric fields as a consequence of the reorientation of the ferroelectric domains. The results indicate that the maximum phase angle (θ_{max}) is a simple method to characterize poling degree and domain reorientation of ferroelectric ceramics.

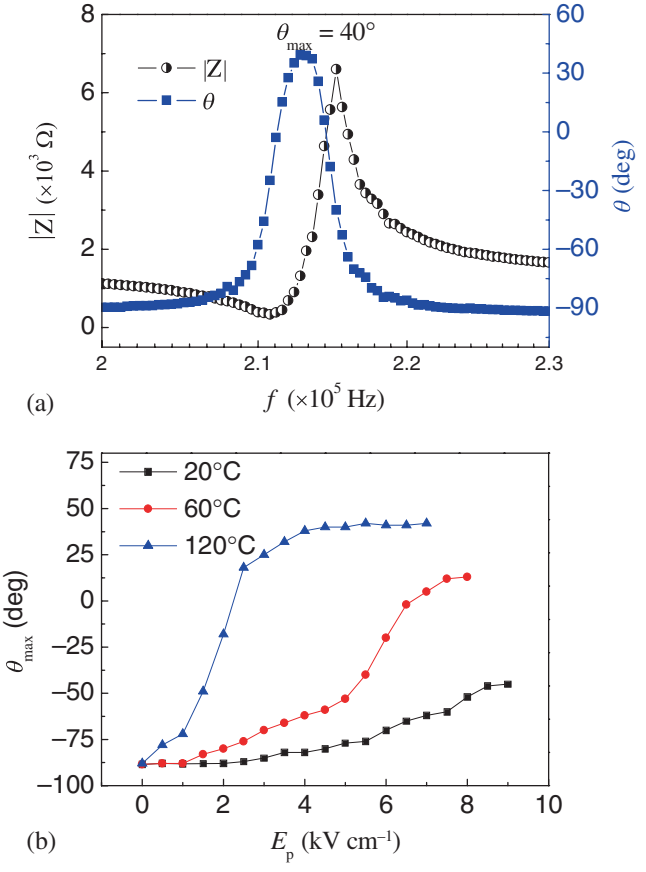

Figure 2. (**a**) Frequency characteristics of the impedance |Z| and phase angle θ for the BF–BZT ceramics poled at 120°C with 3 kV cm^{-1} poling field and (**b**) poling electric fields dependence of maximum phase angle θ_{max} for the BF–BZT ceramics poled at 20, 60 and 120°C.

Commonly, the depoling temperature T_d of piezoelectric materials is an important figure of merit for their application at elevated temperature. However, until now, the T_d is not unambiguously and universally defined.[25] Several methods have been proposed in the literature to determine the T_d, which are based on different physical origins.[21,24,25] The temperature dependences of the piezoelectric constants d_{33} poled at different temperatures are shown in figure 3. The d_{33} for three samples poled at different conditions are gradually decreased in the temperature range from RT to 180°C and decreased rapidly in the vicinity of 180°C. As previously described, the field-induced reoriented domain of the ferroelectric ceramics would return to a random state in the thermal depolarization process. The change can be reflected in the dielectric permittivity $\varepsilon_r(T)$ of the BF–BZT ceramics as well. However, the physical correlation between increasing permittivity $\varepsilon_r(T)$ and the actual depolarization of ferroelectrics is still not clarified.

The dielectric permittivity $\varepsilon_r(T)$ characterized by a weak frequency dispersion in the low-temperature regime indicates a long-range order with field-induced domain reorientation for poled BNT–BT ceramics.[23,26] In those well-described relaxor materials $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})_{0.23}O_3$ (PLZT), the frequency dependence of $\varepsilon_r(T)$ is attributed to the existence of polar nanoregions (PNRs).[27,28] Furthermore, the existence of nanometre-sized domain has been observed by TEM in $Bi(Mg_{1/2}Ti_{1/2})O_3$–doped $BiFeO_3$–$BaTiO_3$ high-temperature piezoelectric ceramics.[29] Upon heating, the long-range order reoriented domain can often be induced into short-range order nanodomains/PNRs that are correlated with relaxation of the observed strong frequency dispersion in the high-temperature regime.

Figure 4 provides the temperature-dependent permittivity $\varepsilon_r(T)$ of poled BF–BZT ceramics measured upon heating.

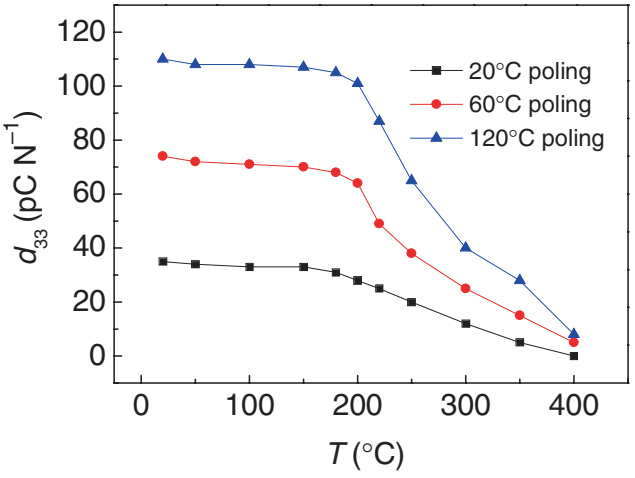

Figure 3. Temperature dependence of piezoelectric constant d_{33} for the BF–BZT ceramics poled at 20, 60 and 120°C.

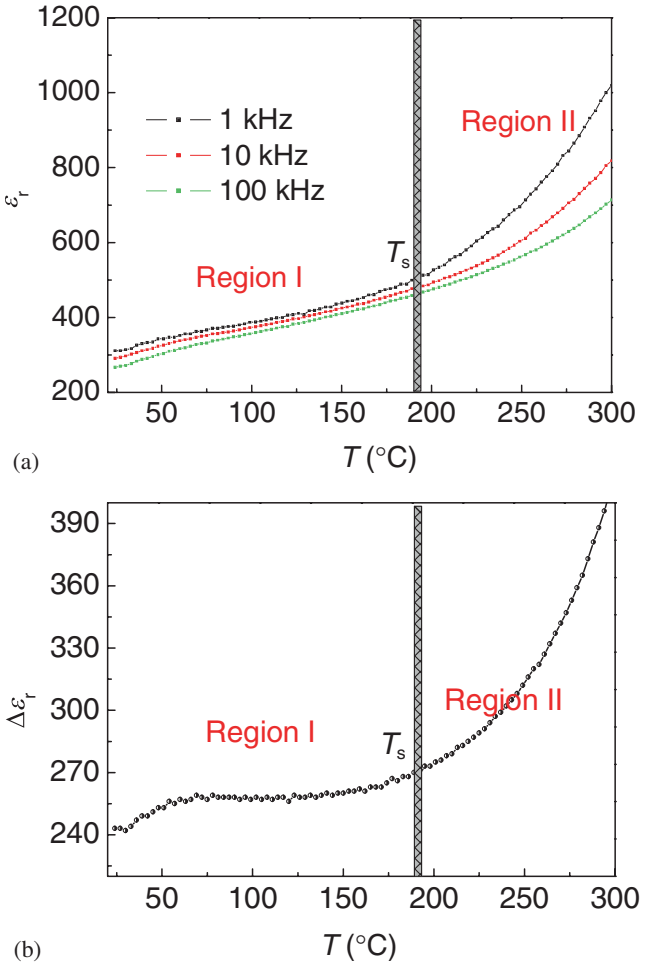

Figure 4. Temperature dependence of permittivity ε_r and $\Delta\varepsilon_r$ with 1, 10 and 100 kHz frequencies for poled BF–BZT ceramics: (**a**) ε_r and (**b**) $\Delta\varepsilon_r$.

Obviously, the transition divides the $\varepsilon_r(T)$ curves into two parts. In region I, below the critical temperature (T_s), weak frequency-dependent $\varepsilon_r(T)$ curves are found to occur. In region II, above T_s, a significant change in $\varepsilon_r(T)$ curves with increasing measurement frequency is observed. The permittivity frequency dispersion can be determined by $\Delta\varepsilon_r = \varepsilon_{r1\ kHz} - \varepsilon_{r100\ kHz}$. The temperature dependence of $\Delta\varepsilon_r$ is presented in figure 4b. Like the shape of the $\varepsilon_r(T)$ curves, $\Delta\varepsilon_r$ is almost constant in region I, and begins to increase evidently in region II.

It has been noted that the critical temperature (T_s) at $\varepsilon_r(T)$ curves is corresponding to the obvious loss of piezoelectricity (depoling). It is assumed that the poling electric field-induced reoriented domain is stable upon heating until T_s, where the order state breaks up and the material converts to its original short-range ordered state with nanodomains/PNRs. The nanodomains/PNRs give rise to the frequency dispersion above T_s. The results indicate that the temperature-dependent permittivity measurements method is able to detect depolarization directly by the measured resulting permittivity frequency dispersion. Therefore, it has been suggested that loss of piezoelectricity and increase of permittivity frequency dispersion in the BF–BZT ceramics are attributed to same origins. Heating above T_d destroys the aligned domains, or the aligned domains break up into nanodomains/PNRs, which causes the observed strong frequency dependence of permittivity.

4. Conclusion

Polycrystalline ceramics of lead-free $0.75BiFeO_3$–$0.25Ba(Zr_{0.05}Ti_{0.95})O_3$ have been synthesized via the conventional solid-state reaction method. Compared with increasing poling electric fields, increasing poling temperature can induce more ordering aligned domains, thus improving piezoelectric properties more evidently. The poling fields and temperatures have insignificant effect on the thermal depoling behaviours. The critical temperature (T_s) with obvious permittivity frequency dispersion at $\varepsilon_r(T)$ curves is almost close to depoling temperature (T_d). Heating above T_d destroys the aligned domains, and causes strong frequency dependence of both permittivity and depolarization process.

Acknowledgements

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References

1. Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric ceramics* (New York: Academic)
2. Jo W, Dittmer R, Acosta M, Zang J, Groh C, Snapper E, Wang K and Rödel J 2012 *J. Electroceram.* **29** 71
3. Sehirlioglu A, Sayir A and Dynys F 2009 *J. Appl. Phys.* **106** 014102
4. Zhang S, Eitel R E, Randall C A, Shrout T R and Alberta E F 2005 *Appl. Phys. Lett.* **86** 262904
5. Zou T, Wang X, Wang H, Zhong C, Li L and Chen I W 2008 *Appl. Phys. Lett.* **93** 192913
6. Sterianou I, Sinclair D C, Reaney I M, Comyn T P and Bell A J 2009 *J. Appl. Phys.* **106** 084107
7. Turner R C, Fuierer P A, Newnham R E and Shorout T R 1994 *Appl. Acoust.* **41** 299
8. Ahart M, Somayazulu M, Cohen R E, Ganesh P, Dera P, Mao H, Hemley R J, Ren Y, Liermann P and Wu Z 2008 *Nature* **451** 545
9. Rödel J, Jo W, Seifert K T P, Anton E M and Granzow T 2009 *J. Am. Ceram. Soc.* **92** 1153
10. Chen J and Cheng J 2014 *J. Alloys Compd.* **589** 115
11. Leontsev S O and Eitel R E 2009 *J. Am. Ceram. Soc.* **92** 2957
12. Luo L, Jiang N, Lei F, Guo Y, Zheng Q and Lin D 2014 *J. Mater. Sci.: Mater. Electron.* **25** 1736
13. Yang H, Zhou C, Liu X, Zhou Q, Chen G, Li W and Wang H 2013 *J. Eur. Ceram. Soc.* **33** 1177

14. Kumar M M, Srinivas A and Suryanarayana S V 2000 *J. Appl. Phys.* **87** 855
15. Zhou C, Feteira A, Shan X, Yang H, Zhou Q, Chen J, Li W and Wang H 2012 *Appl. Phys. Lett.* **101** 032901
16. Zhou Q, Zhou C, Yang H, Chen G, Li W and Wang H 2012 *J. Am. Ceram. Soc.* **95** 3889
17. Kounga A B, Granzow T, Aulbach E, Hinterstein M and Rödel J 2008 *J. Appl. Phys.* **104** 024116
18. Foronda H, Deluca M, Aksel E, Forrester J S and Jones J L 2014 *Mater. Lett.* **115** 132
19. Cen Z, Zhou C, Yang H, Zhou Q, Li W and Yuan C 2013 *J. Mater. Sci.*: *Mater. Electron.* **24** 3952
20. Zhou C, Yang H, Zhou Q, Cen Z, Li W, Yuan C and Wang H 2013 *Ceram. Int.* **39** 4307
21. Ge H, Hou Y, Rao X, Zhu M, Wang H and Yan H 2011 *Appl. Phys. Lett.* **99** 032905
22. Zhou C and Liu X 2008 *Mater. Chem. Phys.* **108** 413
23. Hiruma Y, Yoshi K, Nagata H and Takenaka T 2007 *Ferroelectrics* **246** 114
24. Hiruma Y, Nagata H and Takenaka T 2009 *J. Appl. Phys.* **105** 084112
25. Anton E M, Jo W, Damjanovic D and Rödel J 2011 *J. Appl. Phys.* **110** 094108
26. Sapper E, Schaab S, Jo W, Granzow T and Rödel J 2012 *J. Appl. Phys.* **111** 014105
27. Bobnar V, Kutnjak Z, Pirc R and Levstik A 1999 *Phys. Rev. B* **60** 6420
28. Ye Z G and Schmid H 1993 *Ferroelectrics* **145** 83
29. Yabuta H, Shimada M, Watanabe T, Hayashi J, Kubota M, Miura K, Fukui T, Fujii I and Wada S 2012 *Jpn. J. Appl. Phys.* **51** 09LD04