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PLZT 铁电陶瓷的相变及直流电场下畴变的
原位 Raman 光谱观测

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***In-situ* Raman Observations on Domain Switches under a DC Electric
Field and Phase Transitions of PLZT Ferroelectric Ceramics**



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摘要

Raman 光谱与铁电体中的晶格振动模相关，能从晶格动力学的角度反映铁电体中畴变与相变的物理本质。本项工作运用 Raman 散射光谱技术，建立了对 PLZT 铁电陶瓷的相变及直流电场下的电致畴变进行原位观测的方法和装置，对未极化和经过极化的两种 PLZT 试样在温度变化过程中的相变现象和外电场作用下的畴变行为进行了系统的观测；探索了铁电陶瓷材料的 Raman 光谱的分峰拟合方法，并利用该方法获得了各晶格振动模的强度与温度及外加直流电场之间的变化规律。

不同温度下的电滞回线测试表明，在温度约 320℃ 处试样的电滞回线消失，即在该温度点发生铁电至顺电相变。而高温原位 Raman 观测结果表明，随着温度的升高，Raman 各特征峰的峰位发生移动，强度下降。实验结果显示准同型相界附近的 PLZT 铁电陶瓷在 240℃ 和 360℃ 分别发生两次相变，表明样品中可能存在混合相。

外加直流电场条件下的 Raman 原位观测结果表明，各峰的峰位不随加载时间和电场强度的变化而变化，这表明外加电场不改变试样的晶格结构。在电场强度为 1375 V/mm 的直流电场下加载 60 分钟后，各 Raman 峰的强度增加；在不同电场强度的变化过程中，当外加电场的强度超过矫顽场时，各 Raman 峰强随外加电场的增加而增加，随外加电场的减弱而减弱；电场作用下未极化试样峰强变化较极化试样更明显。

推出了单晶材料 Raman 光学振动模散射强度与极化取向角度的关系，结果表明，Raman 散射强度与电畴取向密切相关，受 90° 畴变的影响。在此基础上提出了利用分布函数建立多晶材料 Raman 散射强度的计算方法，指出 90° 畴变使得多晶材料电畴取向分布发生改变，从而导致 Raman 光谱强度的变化。直流电场下原位 Raman 观测结果证实铁电多晶材料在外加直流电作用下产生的 90° 畴变使得 Raman 光谱强度发生变化。

关键词：原位 Raman 观测；铁电陶瓷；相变；畴变

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ABSTRACT²

Since Raman spectrum is closely related to the lattice vibrations of ferroelectrics, it may be used to investigate the essence of domain switches and phase transitions of ferroelectrics from the perspective of lattice dynamics. In this work, an *in-situ*, nondestructive method and experimental setup for Raman observations of phase transitions and electric-field-induced domain switches of PLZT at micro scale were established. A series of measurements on electric-field-induced domain switches in unpoled and poled PLZT ceramics under a DC electric field was carried out and the phase transitions at various high temperatures were observed. A fitting procedure was employed to deconvolute the measured Raman spectra to identify the Raman modes. The variations in spectrum intensities at each of the modes caused by changing the temperature and the applied electric field were obtained.

It was shown that the phase transition temperature from ferroelectric to paraelectric phase is about 320°C since at this temperature the hysteresis loops of samples vanished. *In-situ* Raman spectra revealed that Raman shifts of the modes varied with temperatures, and the Raman intensity at each of the modes decreased with increases of temperature. However, the *in-situ* Raman spectra demonstrated that two types of different phase transitions occurred at 240°C and 360°C. This may imply the existence of mixed phases in the specimens.

In-situ Raman spectra under the applied DC electric fields revealed that the Raman shifts of the modes remained unchanged with variation in the loading time and strength of the applied electric fields. This may imply that the applied electric field may not change the structure of the lattice. When a DC electric field of 1375 V/mm was applied to the samples for over 60 min, the intensities of the modes increased significantly. It was found that the Raman intensities increased appreciably when the applied electric field exceeded the coercing electric field of the material, in particular, the unpoled specimen displayed more apparently than the poled one.

A formula relating the scattering strength of the Raman modes for a singly crystal of 4mm symmetry to the direction of polarization was developed. It indicates that the scattering strength of the Raman modes is closely related to orientation of domains and varies when a 90° domain switching occurs. Based upon this formula with the help of the concept of distribution functions, a method for calculating the Raman scattering strength of polycrystalline materials was established. It suggests that a 90° domain switching changes the distribution of domains, and therefore changes the strength of the scattered light. The experimental results obtained from the *in-situ* Raman observations under a DC electric field verified this conclusion.

Key words: *in-situ* Raman observation; ferroelectric ceramics; phase transition; domain switching

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