京都大学	博 士 （ 理 学 ）	氏名	PEZZOTTI GIUSEPPE
論文題目	An expansion of theoretical principles of Raman spectroscopy towards fully quantitative algorithms for the analysis of electronic materials and related devices		

（論文内容の要旨）

Raman spectroscopy represents an insightful characterization tool in electronics, which comprehensively suites the technological needs for locally and quantitatively assessing crystal structures, domain textures, crystallographic misalignments, and residual stresses in electronic materials and related devices. Recent improvements in data processing and instrumental screening of large sampling areas have provided Raman spectroscopic evaluations with rejuvenated effectiveness and presently give spin to increasingly wider and more sophisticated experimental explorations. However, the quantum-mechanics aspects of the physics underlying the Raman effect represents an issue of deep complexity and its applicative development to non-cubic crystallographic structures can yet be considered in its infancy. This thesis revisits some applicative aspects of the physics governing Raman emission from crystalline matter, in particular exploring the possibility of disentangling the convoluted dependences of the Raman spectrum on crystal orientation and mechanical stress with preserving their multidimensional nature in space. Emphasis is placed on the technologically important class of electronic materials, as explained in the introductory Chapter I, while Chapter II is tutorial to the overall Raman effect (in particular its description in terms of group theory). The main target of both theoretical and experimental assessments in this thesis is the analysis of piezoelectrics and semiconductors with non-cubic crystallographic structures, for which working algorithms are newly and explicitly worked out in order to quantitatively extract both structural and mechanical information from polarized Raman spectra. An introductive part (Chapter III) is dedicated to the quantitative analysis of the sample/probe interaction in the case of a confocal Raman probe for the materials of interest. In this context, deconvolutive procedures in the Euclidean space are explicitly worked our. The Raman responses of complex crystal structures to crystallographic orientation and stress are comprehensively rationalized and de

scribed in Chapters IV and V of this thesis, according to a unified formalism and including quantitative calibrations and verifications of both selection rules and secular equations, respectively. An additional newly developed tool, which was needed for translating the worked out algorithms from single-crystalline to polycrystalline (partly textured) materials, is represented by a statistical description of domain textures based on orientation distribution functions. These latter developments are extensively described in Chapter VI. The entire body of spectroscopic achievements is then interpreted as a means for assessing both crystallographic textures and stress-related issues in the three-dimensional space (thus preserving their vectorial and tensorial nature, respectively), and extensively applied in Chapter VII through a number of working examples based on real electronic devices. Such systematic characterizations of electronic materials and devices not only vividly represent a direct application of the newly developed equations, but also solve some long-standing technological issues, like as the effect of residual stresses on both structural reliability and functionality of multilayer ceramic capacitors and the mm-scale (i.e., *in toto*) evaluation of crystallographic homogeneity of piezoelectric wafers. In the final Chapter VIII, the overall achievements are summarized and a perspectival bird-eye view offered, which stigmatizes both present state and expected future developments of quantitative Raman spectroscopy, including current aspects related to the development and evolution of the Raman device. Three tutorial appendices are attached to the end of the thesis, which deal with group theory, phonon dispersion, and anisotropy of elastic constants. In substance, this thesis aims at providing rigorous spectroscopic foundations to Raman approaches dealing with the analyses of non-cubic crystals and, providing long missing pieces in the complex field of quantitative Raman spectroscopy, could represent a substantial step ahead in designing new electronic devices with improved functional behavior and structural reliability.

（続紙　2　）

（論文審査の結果の要旨）

本論文では、強誘電体および半導体材料とそのデバイスの最も主要な構成部材である$BaTiO_3$、$LiNbO_3$、PMN-PT、GaN、AlNなどの単結晶および多結晶体材料におけるラマン分光について検討を行っている。ラマン分光の理論的な選択測を３オイラー角の依存性において導出を行い、明確にし、３次元的に結晶方向を定量化するアルゴリズムを開発している。一方、ひずみが加わった単結晶の振動の運動方程式から応力(ひずみ)テンソル各成分と各フォノン振動モードの波数シフト量(フォノン振動数変化)の関係について導出を行っている。ひずみによる結晶のバネ定数の変化しやすさを示すフォノン変形ポテンシャル係数を、バルクを作製できない微小材料においても導出できる手法を開発し、さらに、顕微ラマン分光装置を用いて偏光測定を実施することにより各フォノン振動モードの波数シフト量を選択測の確認し、この測定結果に三次元応力状態における応力成分分離評価を先駆者として非常に精度高く実施することを確立している。更に、実際に電子部品として利用されている材料を用いて、ドメイン構造、残留応力解析を行っている。多結晶体のデバイスの場合において、単結晶の場合と同様の方法で構造解析を行う為に、方位分布関数（ODF）と呼ばれる数学的手法を用いたアルゴリズムを開発している。例えば、電子部品として利用されているMLCC（マルチレイヤーセラミックキャパシター）を用いて、ドメイン構造、残留応力解析と内分電極付近の結晶配向分布について測定を行っている。この結果、角部、中心部に共通して、内部電極に近い程、格子配向が均一である事、また電極から離れるほどその配向が乱れる事が分かった。これは、電極に近い部分では何らかの外的要因が発生しているためであると確認されている。つまり、本論文で作られているアルゴリズムにより量子力学に値する基礎知識から産業界に役立つ測定まで幅広く、架け橋となっている事は高く評価出来る点である。

　以上より、本論文は学術的基礎理論および基礎技術的にも興味深く、極めて有用であると高く評価できる。平成25年11月19日に論文内容とこれに関連する口頭試問を行った。申請者の発表、質疑応答、専門分野における知識は優秀であり、この結果博士（理学）に値する論文と認めた。

要旨公表可能日：　　　　　　年　　　　月　　　　日以降