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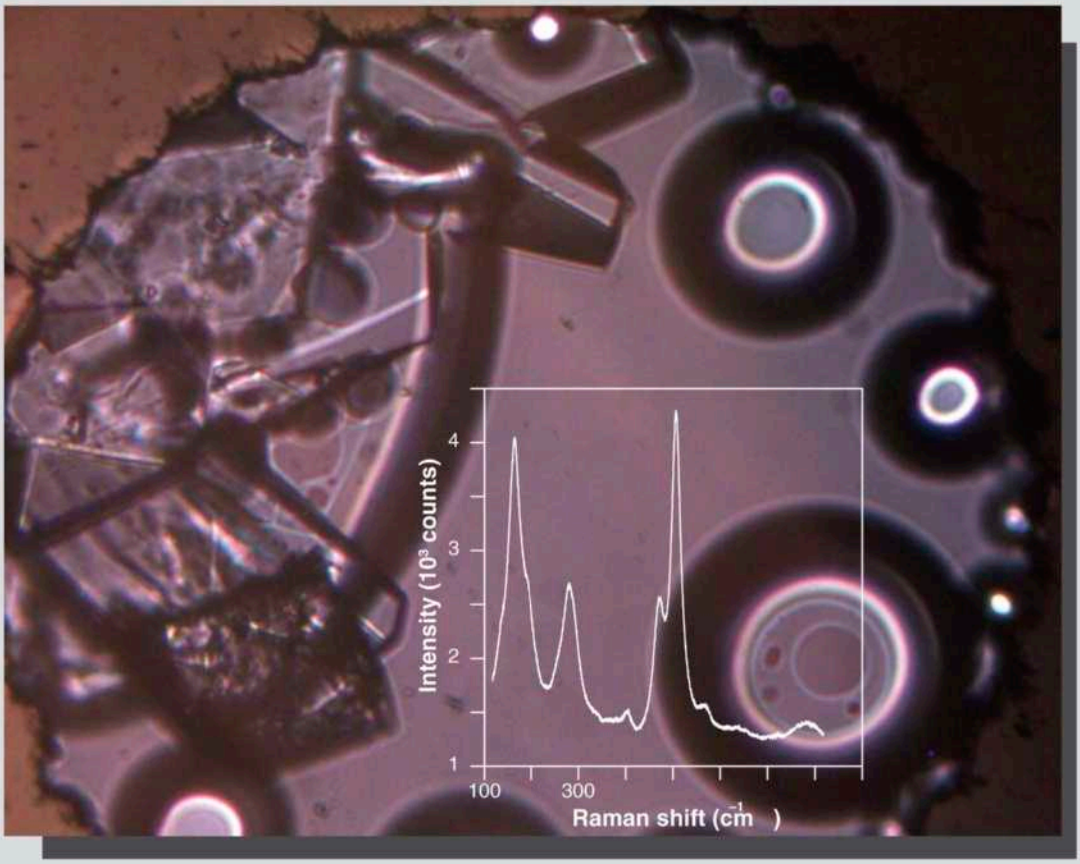
12

Raman Spectroscopy

applied to Earth Sciences and Cultural Heritage

Editors

J. DUBESSY, M.-C. CAUMON and F. RULL



THE MINERALOGICAL SOCIETY OF GREAT BRITAIN & IRELAND

EUROPEAN MINERALOGICAL UNION
NOTES IN MINERALOGY

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Volume 12

APPLICATIONS OF RAMAN SPECTROSCOPY TO EARTH SCIENCES AND CULTURAL HERITAGE

UNIVERSITY TEXTBOOK

Edited by
J. Dubessy, M.-C. Caumon and F. Rull

Mineralogical Society

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On the front cover: Metastable assemblage of albite crystals, silicate melt globules and aqueous fluid at 600°C, 1.06 GPa in the sample chamber of a hydrothermal diamond-anvil cell: bulk composition $H_2O + 54$ wt.% $NaAlSi_3O_8$, zircon chip added as Raman spectrocopic pressure sensor; the sample chamber diameter is ~ 400 μm The editors thank C. Schmidt, GFZ for providing the photograph and Raman spectrum.

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Contents

Preface

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In Earth Sciences and Cultural Heritage Science we can only understand the formation of the 'objects' if they are well characterized. Optical observation, including optical microscopy, is still the primary tool and is essential in obtaining a preliminary, qualitative determination of an object, to determine the relations between it and other objects, and to place it in a general context. Most of the time, however, optical observations are insufficient. Spectroscopic methods are the second "set of eyes" used to gain greater insight into these objects and to use physical chemistry, if applicable, to derive the mechanisms of formation. Spectroscopic methods are numerous and have been described in a previous volume (6) in the EMU *Notes in Mineralogy* series, edited by A. Beran & E. Libowitzky (2004). In chapter 7 of that volume, Raman spectroscopy was addressed by Nasdala *et al.* (2004). Though that volume provides a very useful means to gain a general understanding of the contribution of each spectroscopy to mineralogy, no details of the theory, instrumentation and applications to the different types of objects could be provided. In the past eight years, there have been many improvements in the instrumentation which makes Raman spectroscopy a versatile technique used in many Earth Science and Cultural Heritage laboratories and so it appeared appropriate to have a school and a book dedicated to Raman Spectroscopy alone.

Four main topics are addressed here:

(1) **Theory**: in Chapter 1, dedicated to the Raman effect, in Chapter 4, dealing with the modelling of Raman spectra, in Chapter 2 to the links between fluorescence and Raman spectroscopy, in Chapter 10 for the exploitation of Raman spectra of minerals at high pressure and temperature, and in Chapter 12 for the rationale behind Raman spectra of graphitic carbon compounds; the basic theory of the instrumentation is developed in Chapter 3.

(2) **Methodology including the instrumentation**: in Chapter 3 and the Raman data analysis in Chapter 5.

(3) **Experimental aspects**: for the investigation of Raman spectra at high pressure and temperature using diamond anvil cells for minerals (Chapter 10) and geological fluids (Chapter 7) and with fused silica capillary for fluids (Chapter 6).

(4) **Application**: to different types of objects: geological fluids (Chapter 8), silicate glasses and melts (Chapter 9), biogeology and astrobiology (Chapter 11), graphitic carbons (Chapter 12), gemmology with a link with fluorescence spectroscopy (Chapter 13), and Cultural Heritage (Chapter 14).

A given chapter may address several topics, as it is impossible to obtain relevant information from the Raman study of a given object without considering the theory for the interpretation of the spectra, or instrumental set-up including special cells, or handling raw spectra.

It is also clear that the whole theory could not be developed thoroughly with all the details as it deals with quantum mechanics and group theory. This would require at least two further volumes! Thus, chapters focused on the theoretical aspects are written with the aim of giving the main steps and the results obtained from the theory and how theory can be used for the interpretation of Raman spectra. Readers who want to know the details of the theory and their associated calculations should consult specialized textbooks or publications which are referred to in the chapters hereafter.

References

Nasdala, L., Smith, D.C., Kaindl, R., Gaft, M. & Ziemann, M.A. (2004) Raman spectroscopy: Analytical perspectives in mineralogical research. In: *Spectroscopic Methods in Mineralogy* (A. Beran & E. Libowitzky, editors). EMU Notes in Mineralogy, **6**, Eötvös University Press, Budapest, pp. 281–343.

Beran, A. & Libowitzky, E. (2004) *Spectroscopic Methods in Mineralogy*. EMU Notes in Mineralogy, **6**, Eötvös University Press, Budapest, 661 pp.

Foreword

The present volume of the EMU *Notes in Mineralogy* series describes the 'Applications of Raman Spectroscopy to Earth Sciences and Cultural Heritage'. It is associated with the 12th EMU 'school' co-sponsored by the French Centre National de la Recherche Scientifique (CNRS) as a 'thematic school' and by the Société Française de Minéralogie et Cristallographie (SFMC).

The present volume contains chapters arising out of lectures given at this 'school' which was held at the Université de Lorraine (Nancy, France) from 14–16 June 2012, immediately after the GeoRaman X meeting.

Spectroscopic methods such as Raman are used to investigate the structure and dynamics of matter. They are essential for the study of the different types of mineral or organic materials produced at the Earth's surface or interior. As a result of technological improvements in gratings, detectors, filters and personal computers in the last decade, many micro-Raman spectrometers have become plug-and-play instruments, very easy to use and available at a lower cost than the early Raman microprobes. Thus, many laboratories in Earth Sciences and Cultural Heritage are equipped with these new spectrometers. Commercial portable Raman spectrometers working in the field have also contributed to the spread of Raman spectroscopy. However, poor levels of education in terms of Raman spectroscopy in undergraduate courses in Earth Sciences make it difficult for individuals to obtain information of the highest quality relevant to Earth sciences and Cultural Heritage.

The bid by G^{2}R (Géologie et Gestion des Ressources Minérales et Energétiques UMR 7566) to organize the GeoRaman X meeting and the associated school was accepted by the International GeoRaman meetings Scientific committee. Members of the SFMC council and especially its President, Anne-Marie-Karpoff who supported this proposition, are thanked for their support. Christian Chopin, vice-President of EMU and SFMC Council member suggested contact with the EMU with a view to attracting an international audience to the school. Roberta Oberti and Herta Effenberger, President and Secretary, respectively, of EMU, together with the EMU committee welcomed this proposition and subsequent publication of the lectures in the EMU *Notes in Mineralogy* series. The organizers are grateful to the 'Institut National de l'Univers' (CNRS) and the 'Formation Permanente of CNRS' for badging this event as a thematic CNRS school and to the Université de Lorraine for hosting the event. Many thanks to the contributing authors for publishing their chapters here, and to Kevin Murphy of the Mineralogical Society for his efficiency in the production of the volume. Finally, the editors are very grateful to Marie-Christine Boiron, Patrick Lagrange and Christine Leonard of the G2R laboratory for their help in organizing the school.

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