

# PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://spiedigitallibrary.org/conference-proceedings-of-spie)

## Front Matter: Volume 10304

, "Front Matter: Volume 10304," Proc. SPIE 10304, Large-Area Chromogenics: Materials and Devices for Transmittance Control, 1030401 (28 March 1990); doi: 10.1117/12.2283604

**SPIE.**

Event: Institutes for Advanced Optical Technologies, 1989, Hamburg, Germany

## Preface

The concept of the Institutes for Advanced Optical Technologies developed out of SPIE's desire to foster increased interaction and collaboration among researchers working in emerging optical technologies. The Institutes provide a forum for experts in these areas to analyze and document the state of the art and to point toward future trends and applications. Institute topics are selected for their timeliness as well as for their significance to future progress in the application of optics. Institute organizers invite selected experts to participate as paper contributors and discussion participants. It is intended that the interaction generated by the small-group structure in a retreatlike setting will foster productive discussions that are beyond the scope and possibility of a regular conference format.

Each Institute has two primary objectives: first, that the interactions and dialogue stimulate technical advancement, and second, that the publication of the Institute volume results in an authoritative collection of significant papers covering key topics in the field. While each editor and committee has unique criteria for determining the acceptability of contributions, it is intended that the Institute process itself will establish the worth and appropriateness of the individual contributions. Each contributor is asked to prepare a draft manuscript and circulate it to the other participants in advance of the Institute. The editor/chair organizes an agenda for discussing critical technical issues. The interactions and collegial discussions by the Institute members are the basis for the ensuing Institute volume. The final action of the Institute is to decide the scope of the volume and what material is to be included and what other material is to be added and by whom.

The Institute on Large-Area Chromogenics: Materials and Devices for Transmittance Control, held in Hamburg, Federal Republic of Germany, September 22-24, 1988, addressed technical issues for this emerging technology and the future impacts it might have on society. The interactions and discussions were lively, at times warm, and gave the participants a more comprehensive grasp of the subject. The resultant volume is this authoritative Institute publication emphasizing topics such as photochromic materials, organic and inorganic electrochromic materials, electrochromic devices, and liquid-crystal materials and devices.

**Roy F. Potter**

General Editor, SPIE Institute for Advanced Optical Technologies

**Other publications in the SPIE Institutes for Advanced Optical Technologies series:**

*Transformations in Optical Signal Processing*, William T. Rhodes, James R. Fienup, Bahaa E. A. Saleh, Editors, 1984, SPIE Volume 373 (Out of print)

*Optical and Hybrid Computing*, Harold H. Szu, Editor, 1987, SPIE Volume 634

*Photonics: High Bandwidth Analog Applications*, James Chang, Editor, 1987, SPIE Volume 648

*Dosimetry of Laser Radiation in Medicine and Biology*, Gerhard J. Müller, David H. Sliney, Editors, 1989, Volume IS 5

*Photodynamic Therapy*, Charles J. Gomer, Editor, Volume IS 6  
(To be published Fall 1990)

*Automatic Object Recognition*, Hatem Nasr, Editor, Volume IS 7  
(To be published Fall 1990)

# Large-Area Chromogenics: Materials and Devices for Transmittance Control

## Contents

	iii	Preface
	viii	Institute Participants and Authors
	xii	Introduction
<b>Part One</b>	2	<b>Introduction to chromogenics</b>
<b>Introduction</b>		C. M. Lampert, Lawrence Berkeley Lab. (USA); C. G. Granqvist, Chalmers Univ. of Technology (Sweden)
<b>Part Two</b>	22	<b>Application of large-area chromogenics to architectural glazings</b>
<b>Applications</b>		S. E. Selkowitz, C. M. Lampert, Lawrence Berkeley Lab. (USA)
	46	<b>Automotive applications of chromogenic materials</b>
		N. R. Lynam, A. Agrawal, Donnelly Corp. (USA)
<b>Part Three</b>	86	<b>Photochromic glass</b>
<b>Photochromic</b>		H. J. Hoffmann, Schott Glaswerke (FRG).
<b>Materials</b>	102	<b>Photochromic plastics</b>
		N. Y. Chu, American Optical Corp. (USA)
<b>Part Four</b>	122	<b>Science and technology of thermochromic materials</b>
<b>Thermochromic</b>		J. H. Day, Ohio Univ. (USA); R. D. Willett, Washington State Univ. (USA)
<b>Materials</b>	142	<b>Thermochromic materials and devices: inorganic systems</b>
		G. V. Jorgenson, J. C. Lee, Honeywell Systems and Research Ctr. (USA)
	160	<b>Thermochromism of sputter-deposited vanadium oxyfluoride coatings</b>
		K. A. Khan, C. G. Granqvist, Chalmers Univ. of Technology (Sweden).
<b>Part Five</b>	170	<b>Fundamentals of electrochromism in metal oxide bronzes</b>
<b>Inorganic</b>		T. E. Haas, R. B. Goldner, Tufts Univ. (USA)
<b>Electrochromic</b>	181	<b>Electrochromism in sputtered WO<sub>3</sub> thin films</b>
<b>Materials: Tungsten</b>		K. W. Marszalek, Academy of Mining and Metallurgy (Poland);
<b>Oxide and</b>		M. J. Marszalek, Institute of Nuclear Physics (Poland); T. Stapinski, E. Leja,
<b>Molybdenum Oxide</b>		Academy of Mining and Metallurgy (Poland).
	191	<b>Studies of polycrystalline WO<sub>3</sub> and MoO<sub>3</sub> coatings prepared by chemical vapor deposition</b>
		A. Donnadiou, Univ. des Sciences et Techniques du Languedoc (France).
	215	<b>Plasma-enhanced CVD of W and Mo oxides</b>
		D. K. Benson, Solar Energy Research Institute (USA); J. S. Svensson, Chalmers Univ. of Technology (Sweden).

(continued)

	230	<b>Electrochemistry of tungsten-compound film prepared by liquid-phase-deposition method</b> H. Tada, Nippon Sheet Glass Co., Ltd. (Japan).
	246	<b>Modulation of absorption spectra by the use of mixed films of <math>\text{Mo}_c\text{W}_{1-c}\text{O}_3</math></b> S. Yamada, M. Kitao, Shizuoka Univ. (Japan).
	260	<b>Large-area/high-rate sputtering of materials for electrochromic devices</b> R. P. Howson, Loughborough Univ. of Technology (UK).
<b>Part Six</b>	272	<b>Hydrated nickel oxide films: electrochemical and related physical properties</b> A. Gorenstein, F. Decker, M. Fantini, IFGW/UNICAMP (Brazil); W. Estrada, Univ. Nacional de Ingeniería (Peru).
<b>Inorganic</b>	285	<b>Sputter-deposited nickel-oxide-based electrochromic coatings</b> J. S. Svensson, C. G. Granqvist, Chalmers Univ. of Technology (Sweden).
<b>Electrochromic</b>	298	<b>Electrochromic nickel hydroxide films and the effects of foreign metal ions</b> D. A. Corrigan, M. K. Carpenter, General Motors Research Labs. (USA)
<b>Materials: Nickel</b>	313	<b>Electrochromic vanadium pentoxide</b> S. F. Cogan, EIC Labs., Inc. (USA)
<b>Oxide and Others</b>	328	<b>Electroactive polymers in large-area chromogenics</b> O. Inganäs, Univ. of Linköping (Sweden).
	335	<b>Conducting polymer as an electrochromic material: polyaniline</b> S. C. Yang, Univ. of Rhode Island. (USA)
<b>Part Seven</b>	368	<b>Liquid electrolytes</b> J. Nagai, M. Mizuhashi, T. Kamimori, Asahi Glass Co., Ltd. (Japan).
<b>Organic</b>	378	<b>Polymeric ion conductors</b> J. Nagai, M. Mizuhashi, T. Kamimori, Asahi Glass Co., Ltd. (Japan).
<b>Electrochromic</b>	386	<b>Inorganic ion conductors</b> V. Truong, F. E. Girouard, P. V. Ashrit, Univ. de Moncton (Canada).
<b>Materials</b>	402	<b>Transparent electronic conductors in electrochromic devices</b> M. Misonou, H. Kawahara, Nippon Sheet Glass Co., Ltd. (Japan).
<b>Part Eight</b>	414	<b>Chemical and optical studies of electrochromic hydrated nickel oxide films and devices</b> C. M. Lampert, Lawrence Berkeley Lab. (USA)
<b>Conductors for Ions and Electrons in Electrochromic Devices</b>		
<b>Part Nine</b>		
<b>Electrochromic Devices</b>		

- 447 **Optical techniques for the study of electrochromic phenomena: application of Raman spectroscopy and optical multichannel analysis to the coloration of oxides and polymer films**  
P. Falaras, A. Hugot Le Goff, S. Joiret, Univ. Pierre et Marie Curie (France).
- 471 **Electrochromic  $\text{Li}_x\text{WO}_3$ /polymer laminate/ $\text{Li}_y\text{V}_2\text{O}_5$  device**  
A. M. Andersson, C. G. Granqvist, Chalmers Univ. of Technology (Sweden); J. R. Stevens, Univ. of Guelph (Canada).
- 482 **The  $\alpha\text{-WO}_3/\alpha\text{-IrO}_2$  electrochromic system**  
S. F. Cogan, R. D. Rauh, EIC Labs., Inc. (USA)
- 494 **Electrochromic device design toward large-scale applications**  
M. Mizuhashi, J. Nagai, T. Kamimori, Asahi Glass Co., Ltd. (Japan).
- 504 **Performance of tungsten oxide/Prussian blue device**  
T. Kase, T. Miyamoto, T. Yoshimoto, Y. Ohsawa, Nissan Motor Co., Ltd. (Japan);  
H. Inaba, K. Nakase, Central Glass Co., Ltd. (Japan).
- 518 **Reflectance control of automotive mirrors**  
F. G. Baucke, Schott Glaswerke (FRG).
- 539 **Response time of large-scale electrochromic devices**  
J. Randin, Asulab SA (Switzerland).
- Part Ten**
- Liquid-Crystal**
- Materials and**
- Devices**
- 550 **Introduction to liquid crystals**  
C. M. Lampert, Lawrence Berkeley Lab. (USA)
- 557 **Liquid-crystal guest host devices and their use as light shutters**  
N. Basturk, J. Grupp, Asulab SA (Switzerland).
- 577 **Polymer-dispersed and encapsulated liquid-crystal films**  
G. P. Montgomery, Jr., General Motors Corp. (USA)

## Institute Participants and Authors

Mr. Anoop Agrawal  
Donnelly Corporation  
414 East 40th Street  
Holland, MI 49423-5313  
USA

Miss Anne M. Andersson  
Chalmers University of Technology  
Department of Physics  
S-412 96 Gothenburg  
Sweden

Dr. Pandurang V. Ashrit  
Université de Moncton  
Physics Department  
Moncton New Brunswick E1A 3E9  
Canada

Mr. Naci Basturk  
Asulab SA  
Research Laboratories of the SMH Group  
Passage Max-Meuron 6  
CH-2001 Neuchatel  
Switzerland

Dr. Friedrich G. Baucke  
Schott Glaswerke Zentralbereich Forschung und  
Entwicklung Abteilung Elektrochemie  
Hattenbergstrasse 10  
D-6500 Mainz 1  
FRG

Mr. Dave K. Benson  
Solar Energy Research Institute  
Materials Branch  
1617 Cole Boulevard  
Golden, CO 80401-3305  
USA

Mr. Michael K. Carpenter  
General Motors Research Laboratories  
Physical Chemistry Department  
Warren, MI 48090-9055  
USA

Dr. Nori Y. Chu  
American Optical Corporation  
Precision Products Division  
14 Mechanic Street  
Southbridge, MA 01550-2555  
USA

Dr. Stuart F. Cogan  
EIC Laboratories, Inc.  
111 Downey Street  
Norwood, MA 02062-2612  
USA

Mr. Dennis A. Corrigan  
General Motors Research Laboratories  
Physical Chemistry Department  
Warren, MI 48090-9055  
USA

Prof. Jesse H. Day  
Ohio University  
Department of Chemistry  
Athens, OH 45701  
USA

Mr. F. Decker  
IFGW/UNICAMP  
P.O. Box 6165  
Campinas, SP  
Brazil

Dr. Albert Donnadieu  
Université des Sciences et  
Techniques du Languedoc  
Laboratoire de Spectroscopie II  
Laboratoire de Spectroscopie UV des Solides/  
UA CNRS n 790  
Place Eugene Bataillon  
F-34060 Montpellier Cedex 1  
France

Mr. W. Estrada  
Universidad Nacional de Ingeniería  
Facultad de Ciencias  
P.O. Box 1301  
Lima  
Peru

Mr. Polycarpos Falaras  
Université Pierre et Marie Curie  
Physique des Liquides et Electrochimie  
LP15 du CNRS  
tour 22. 4 place jussieu  
F-75230 Paris Cedex 05  
France

Dr. M. Fantini  
Universidade Estadual de Campinas  
Rua Coelho Neto  
13023 Campinas Sao Paulo  
Brazil

Mr. Fernand E. Girouard  
Université de Moncton  
Physics Department  
Moncton New Brunswick E1A 3E9  
Canada

Prof. Ronald B. Goldner  
Tufts University  
Electro-Optics Technology Center  
Medford, MA 02155  
USA

Ms. Annette Gorenstein  
IFGW/UNICAMP  
Caixa Postal 6165, 13.100  
Campinas, Sao Paulo  
Brazil

Dr. Claes G. Granqvist  
Chalmers University of Technology  
Department of Physics  
S-412 96 Gothenburg  
Sweden

Dr. Joachim Grupp  
Port-Roulant 12  
CH-2003 Neuchatel  
Switzerland

Prof. Terry E. Haas  
Tufts University  
Electro-Optics Technology Center  
Department of Chemistry  
Medford, MA 02155  
USA

Dr. Hans J. Hoffmann  
Schott Glaswerke  
Central Research & Development Division  
ZFG-1  
Hattenbergstrasse 10  
D-6500 Mainz  
FRG

Prof. Ronald P. Howson  
Loughborough University of Technology  
Department of Physics  
Ashby Road  
Loughborough Leicestershire LE11 3TU  
UK

Dr. Anne Hugot Le Goff  
Université Pierre et Marie Curie  
Physique des Liquides et Electrochimie  
LP15 du CNRS  
tour 22. 4 place jussieu  
F-75230 Paris Cedex 05  
France

Mr. Hiroshi Inaba  
Central Glass Company, Ltd.  
Central Glass Technical Center  
1510, Ohguchi-cho, Matsuzaka  
Mie-ken 515  
Japan

Mr. Olle Inganas  
University of Linköping  
Laboratory of Applied Physics  
Department of Physics and Measurement Technology  
S-581 83 Linköping  
Sweden

Ms. Suzanne Joiret  
Université Pierre et Marie Curie  
Physique des Liquides et Electrochimie  
LP15 du CNRS  
tour 22. 4 place jussieu  
F-75230 Paris Cedex 05  
France

Mr. Gordon V. Jorgenson  
Honeywell, Inc.  
Systems Research Center  
MS 65-2600  
3660 Technology Drive  
Minneapolis, MN 55418-1006  
USA

Mr. Tadatoshi Kamimori  
Asahi Glass Company, Ltd.  
1150 Hazawa-cho, Kanagawa-ku  
Yokohama 221  
Japan

Mr. Takao Kase  
Nissan Motor Company, Ltd.  
Central Glass Technical Center  
1 Natsushima-cho  
Yokosuka 237  
Japan

(continued)



Mr. Hideo Kawahara  
8-2-312 Makiochi 5 Chome  
Mino City, Osaka 562  
Japan

Mr. K. A. Khan  
University of Rajshahi  
Department of Applied Physics and Electronics  
Rajshahi  
Bangladesh

Mr. Michihiko Kitao  
Shizuoka University  
Research Institute of Electronics  
Johoku 3-5-1  
Hamamatsu 432  
Japan

Dr. Carl M. Lampert  
Lawrence Berkeley Laboratory  
Applied Science Division  
MS/ 62-203  
1 Cyclotron Road  
Berkeley, CA 94720  
USA

Mr. James C. Lee  
Honeywell, Inc.  
Systems and Research Center  
MS MN 17-2345  
P.O. Box 1361  
Minneapolis, MN 55440-1361  
USA

Mr. E. Leja  
Academy of Mining & Metallurgy  
Physics and Electron Technology Department  
al. Mickiewicza 30  
30-059 Cracow  
Poland

Dr. Niall R. Lynam  
248 Foxdown Road  
Holland, MI 49424-2789  
USA

Dr. Konstanty W. Marszalek  
University of Wuppertal  
Department of Electrical Engineering  
Fuhlrottstr. 10  
5600 Wuppertal 1  
FRG

Mr. M. J. Marszalek  
Institute of Nuclear Physics  
Radzikowskiego 152  
PL-31 342 Cracow  
Poland

Dr. Masao Misonou  
Nippon Sheet Glass Company, Ltd.  
Central Research Laboratories  
Konoike, Itami  
Hyogo 664  
Japan

Mr. Takeshi Miyamoto  
Nissan Motor Company, Ltd.  
Central Glass Technical Center  
1 Natsushima-cho  
Yokosuka 237  
Japan

Dr. Mamoru Mizuhashi  
Asahi Glass Company, Ltd.  
R & D Center  
1150 Hazawa-ChoKangawa-Ku  
Yokohama 221  
Japan

Dr. G. P. Montgomery, Jr.  
General Motors Corporation  
Research Laboratories  
Physics Department  
30500 Mound Road  
Warren, MI 48090-9055  
USA

Mr. Junichi Nagai  
Asahi Glass Company, Ltd.  
Advanced Glass R&D Center  
1150 Hazawa-cho  
Kanagawa-ku, Yokohama 221  
Japan

Mr. Kiyoshi Nakase  
Central Glass Company, Ltd.  
Central Glass Technical Center  
1510, Ohguchi-cho, Matsuzaka  
Mie-ken 515  
Japan

Mr. Yasuhiko Ohsawa  
Nissan Motor Company, Ltd.  
Central Glass Technical Center  
1 Natsushima-cho  
Yokosuka 237  
Japan

Dr. Roy F. Potter  
SPIE  
P.O. Box 10  
Bellingham, WA 98227-0010  
USA

Dr. Jean-Paul Randin  
Asulab SA  
Research Laboratories of the SMH Group  
Passage Max-Meuron 6  
CH-2001 Neuchatel  
Switzerland

Dr. R. D. Rauh  
EIC Laboratories., Inc.  
111 Downey Street  
Norwood, MA 02062-2612  
USA

Mr. Steven E. Selkowitz  
Lawrence Berkeley Laboratory  
Building 62 Room 235  
1 Cyclotron Road  
Berkeley, CA 94720  
USA

Dr. Tomasz Stapinski  
Academy of Mining & Metallurgy  
Physics and Electron Technology Department  
al. Mickiewicza 30  
PL-30 059 Cracow  
Poland

Mr. James R. Stevens  
University of Guelph  
Physics Department  
Guelph Ontario N1G 2W1  
Canada

Mr. J. S. Svensson  
Chalmers University of Technology  
FYSIK  
S-41296 Gothenburg  
Sweden

Mr. Hiroaki Tada  
Nippon Sheet Glass Company, Ltd.  
Central Research Laboratory  
1, Kaidoshita Kounoike  
Itami 664  
Japan

Prof. Vo-Van Truong  
Université de Moncton  
Department of Physics  
New Brunswick E1A 3E9  
Canada

Prof. Roger D. Willett  
Washington State University  
Department of Chemistry  
Pullman, WA 99164-4630  
USA

Dr. Shoji Yamada  
Shizuoka University  
Research Institute of Electronics  
Johoku 3-5-1  
Hamamatsu 432  
Japan

Prof. Sze C. Yang  
University of Rhode Island  
Pastore Chemical Laboratory  
Department of Chemistry  
Kingston, RI 02881-0801  
USA

Mr. Teruko Yoshimoto  
Nissan Motor Company, Ltd.  
Central Glass Technical Center  
1 Natsushima-cho  
Yokosuka 237  
Japan

## Introduction

Chromogenic materials can alter their optical properties in a persistent yet reversible manner when subjected to a change in external conditions such as irradiation intensity, temperature, or electric-field strength. The most well-known chromogenic devices are probably photochromic sunglasses, which color in the sun and bleach in the dark. In the future, chromogenic materials may be used on a large scale to regulate the throughput of radiant energy for windows in buildings and cars, so that comfortable lighting and temperature are maintained without excessive air conditioning. Chromogenic materials can also be used in variable reflectance mirrors, in displays (such as road signs), and so forth. Traditionally, chromogenics has not been viewed as a self-contained subject for study. However, for some years it has been the opinion of the editors of this book that the time has come for a change, and that both the interrelations between the different materials enabling variable optical properties and the similarities between their potential applications warrant a unified approach to chromogenics. This is the first book on the subject. Many people have contributed, which in itself is a manifestation of the fact that the importance of chromogenic studies is becoming widely recognized.

The first idea that a book should be written on large-area chromogenics—even though the term had not yet been coined—materialized in June 1985. Concrete plans for such a book were made in 1988, when we approached the newly begun Optical Engineering Press. We asked a number of hand-picked researchers to contribute chapters on various aspects on chromogenics for the book, which was met with enthusiasm. The decisive days for this book were 22–24 September 1988—immediately following a topical conference in Hamburg, Germany, on Optical Materials Technology for Energy Efficiency and Solar Energy Utilization—when many of the contributors met in a quiet German hotel. Those were days filled with scientific discussions and culinary extravagances in an atmosphere that was inspiring indeed. Without exception, we seemed to be filled with zeal and a feeling that we were about to embark on a project of lasting importance.

The ambitious goal of this book is to give a broad coverage of all aspects of chromogenics. This is of course impossible to accomplish, and whether we have come close or not is up to the reader to judge. We are aware of some unfortunate omissions in the text, the most apparent perhaps being the lack of a detailed discussion of polaron absorption in amorphous electrochromic materials. Further, we are concerned that some relevant research conducted in Eastern Europe and certain Third World countries has not been given due consideration.

During the completion of this book we were informed of the death (22 February 1989) of one of the contributors, Professor Jesse H. Day of Ohio University, Athens, Ohio. His contribution to this book, we regret to say, is his last scientific paper. We are grateful to Professor Roger Willett of Washington State University, Pullman, Washington, who rewrote and expanded Professor Day's original draft chapter.

We wish to thank all of you who contributed for your kind cooperation and unfailing support, and for lessening the editors' burden by submitting your papers promptly. Without all of your efforts, this book would not exist. Special thanks go to Roy Potter of SPIE, who inspired and supported us from the beginning of this project. To all others who have helped us to bring this book to completion, we owe our deepest appreciation.

**Carl M. Lampert**

Lawrence Berkeley Laboratory (USA)

**Claes G. Granqvist**

Chalmers University of Technology and University of Gothenburg (Sweden)