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Generation of Emission Centers for Broadband NIR Luminescence in Bismuthate Glass by Femtosecond Laser Irradiation

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Bismuth-doped glasses have recently received significant interest as potential material for ultrabroadband optical amplification in the telecommunication spectral bands, as well as as gain material for fiber lasers. However, the nature of the active centers that are responsible for the observed near-infrared (NIR) luminescence is still highly debated. In order to probe the mechanism that leads to NIR emission in bismuth-containing glasses, femtosecond (fs) laser irradiation was used. It is shown that local absorption properties in the visible spectral range can be altered in initially transparent bismuthate glasses after fs laser irradiation. Induced absorption centers exhibit the well-known broadband optical emission peaking at ~ 1250 nm when excited with a 785 nm diode laser. Absorption and emission intensities increase with increasing average pulse energy. These observations are interpreted as a photo-induced reduction reaction of Bi^{3+} to Bi^+ species, while the previously discussed formation of Bi-clusters by ion diffusion is excluded due to the very short interaction time that results from the use of fs laser. Bi^+ species are, therefore, proposed as the major origin of NIR emission from Bi-doped glasses.

I. Introduction

RAPID growth in data capacity of telecommunication networks continues to stimulate exploration of luminescent materials (glasses) with improved emission bandwidth in the near-infrared (NIR) spectral range. In the future, such materials are expected to provide a new generation of broadband optical fiber amplifiers: the larger the bandwidth of the optical amplifier, the more transmission channels can be accessed, and the more data can be transferred simultaneously in a single optical fiber.[1–5] In this context, Bi-doped glasses have experienced extensive research efforts.[2–8] Under a variety of excitation conditions, such glasses exhibit NIR emission in the range of 1000–1700 nm with bandwidths varying between ~ 200 and 500 nm. Fluorescence occurs with lifetimes of up to several hundred microseconds.[3–8] After the first report by Murata *et al.*,[2] NIR emission has now been observed in silicate,[4,5,7–9] germanate,[3,6,10] borate,[11] phosphate,[12,13] and chalcogenide[14] glasses. All these glasses have been proposed as gain medium for ultrabroadband fiber amplifiers.[2–14] In subsequent experiments, optical amplification, laser output, tunable laser operation, and all-fiber lasers were demonstrated based on Bi-doped glasses.[15–18] More re-

cently, Bi-doped glasses were further considered for use as spectral converters and planar luminescent concentrators for photovoltaic energy conversion using low-bandgap semiconductors.[19] On the other hand, the origin of NIR emission still remains highly debated. It is now widely accepted that Bi^{3+} and Bi^{2+} ions do not contribute to NIR emission.[3–5,7–15] Several proposals have been made tentatively, assigning the role of emission center to Bi^{5+},[7,20] Bi^+,[11–15,21] and even Bi-ion clusters.[10,22] Fujimoto and colleagues[7,23] suggested Bi^{5+} ions as NIR emission centers and confirmed the presence of Bi^{5+} species in NIR-luminescent Bi-doped alumino-silicate glasses by X-ray absorption fine structure analysis. However, other authors[9,11] showed that increasing basicity of the host glass (what generally favors the higher valence states of Bi) resulted in disappearing NIR emission. Furthermore, introducing reducing agents such as carbon into the batch, Arai *et al.*[24] clearly demonstrated improved emission intensity. Truong *et al.*[21] found similar results when heat-treating Bi-doped silicate glass in H_2 atmosphere. These experimental results point to Bi^+ as the responsible emission center. Other opinions are based on the fact that at high temperatures, Bi_2O_3 can dissociate and convert into BiO or even into Bi metal. Then, Bi clusters may form by aggregation of Bi atoms.[10,22]

Femtosecond (fs) ultrashort pulse lasers are powerful tools for fabricating different functional optical devices, such as optical waveguides, couplers, photonic crystals, 3D optical storage devices, and rewritable optical memory, because they can in a controlled way induce various microstructural changes in transparent materials.[25,26] For example,[25] fs laser irradiation has been applied to Sm^{3+}-doped alumino-borate glass to selectively and permanently reduce Sm^{3+} to Sm^{2+}. If such a glass was used as an optical storage device, data could be read-out in form of luminescence with a very high signal-to-noise ratio. As another example, Qiu *et al.*[26] developed a method to space-selectively precipitate gold nanoparticles in Au^{3+}-doped silicate glass by combining fs laser irradiation and successive annealing, and they proposed to produce 3D Au nanocircuits in Au^{3+}-doped glass by utilizing this scheme.

In the following, the interaction between fs laser pulses and Bi^{3+} containing glass will be addressed for two reasons: (a) bismuthate glasses could provide a competitive alternative as base material for 3D laser writing of colored structures and, (b) such experiments may, indirectly, help to deduce the mechanism that leads to NIR luminescence in similar glasses.

II. Experimental Procedure

Glass samples were synthesized by conventional melting and quenching. Analytic-grade reagents H_3BO_3, SiO_2, $SrCO_3$, Sb_2O_3, PbO, $Al(OH)_3$, and Bi_2O_3 were selected as raw materi-

als. Approximately 60 g of a bismuthate glass with composition (in wt%) $52Bi_2O_3 \cdot 23B_2O_3 \cdot 4SiO_2 \cdot 17PbO \cdot 4Sb_2O_3$ (BBSPS) were melted in an alumina crucible at 1200°C for 30 min, cast onto a stainless-steel plate immediately after melting, and finally annealed at 300°C for 1 h. Obtained samples were cut and polished into suitable shapes for optical analyses. Optical absorption spectra were recorded using a JASCO V-570 spectrophotometer (JASCO International Co. Ltd., Japan), and infrared fluorescence spectra were determined using the set-up as follows: for excitation, a 100 mW/785 nm laser diode was used; emitted light was introduced into a monochromator equipped with three gratings (1200 G/mm for 200–600 nm; 600 G/mm for 500–1500 nm; 300 G/mm for 800–2500 nm) and collected by an InGaAs detector. The current signal from the detector was transformed to a voltage signal by an I–V converter and transferred to a lock-in amplifier that was triggered by an optical chopper operating in the beamline at 80 Hz. Fluorescence decay curves were obtained using a digital oscilloscope (500 MHz Tektronix TDS3054, Tektronix GmbH, Germany). All measurements were carried out at room temperature.

In order to study the interaction between fs laser pulses and the BBSPS glass, a commercial mode-locked multipass amplified Ti:sapphire laser system (Femtopower Compact PRO, Femtolaser Produktions GmbH, Germany) with emission at 800 nm, pulse duration of 33 fs, and a repetition rate of 1 kHz was used. A variable neutral density filter was used to control pulse energy. The laser beam with an average pulse energy of 2.5 µJ (or 1 µJ) was focused into the glass sample with a ×10 lens (NA = 0.3) with the help of a computer controlled XYZ translation stage. In order to measure absorption and emission spectra of the glass after laser irradiation, a plane of 2.5 mm × 2.5 mm was written into the sample, consisting of damaged lines at an interval of 10 µm, by scanning the laser beam at a rate of 1 mm/s. The distance of the plane from the surface of the glass sample was 1 mm.

III. Results

Figure 1 shows the absorption spectra of BBSPS glass samples before and after fs pulse laser irradiation. In the as-received glass, very high transparency is observed in the visible range from 400 to 800 nm. The glass appears weakly yellow due to the presence of Bi^{3+}. Irradiation caused apparition of a strong absorption peak at around 500 nm, and peak intensity increased as the average pulse energy was increased from 1.0 to 2.5 µJ (Figs.
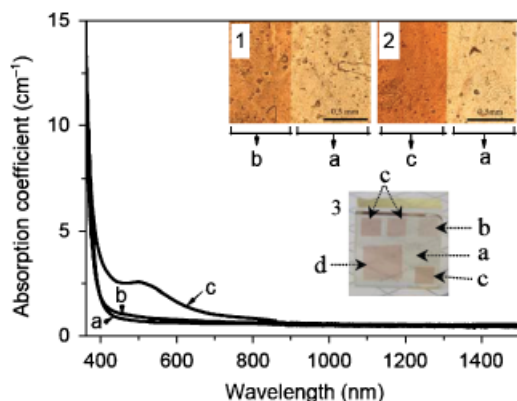

Fig. 1. Absorption spectra of BBSPS glasses before femtosecond (fs) laser illumination (a), after fs laser illumination with average pulse energy of 1 µJ (b), and 2.5 µJ (c), respectively. Insets 1 and 2 show samples after fs laser irradiations with average pulse energy of 1 and 2.5 µJ, respectively. Scale bars are 0.5 mm. Inset 3 is the photograph of the glass with fs laser-irradiated areas a–d. The 5 mm × 5 mm area d in inset 3 was written with fs laser with average pulse energy of 2.5 µJ in March 2005. The experiment of irradiating with fs laser with average pulse energy of 2.5 µJ was repeated two more times to demonstrate reproducibility. BBSPS, $52Bi_2O_3 \cdot 23B_2O_3 \cdot 4SiO_2 \cdot 17PbO \cdot 4Sb_2O_3$.
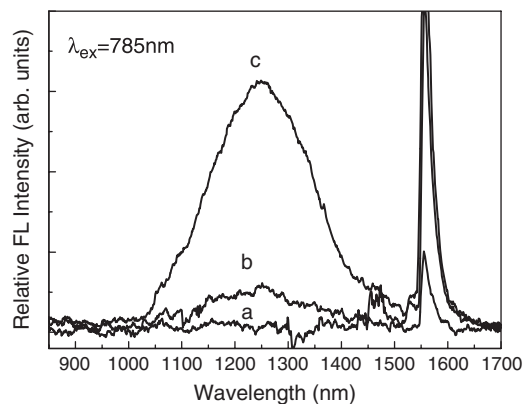

Fig. 2. Emission spectra of BBSPS glasses when pumped by 785 nm laser diode: (a) before femtosecond (fs) laser illumination, (b) after 1 µJ fs laser irradiation, and (c) after 2.5 µJ fs laser irradiation. BBSPS, $52Bi_2O_3 \cdot 23B_2O_3 \cdot 4SiO_2 \cdot 17PbO \cdot 4Sb_2O_3$.

1(b) and (c)). Correspondingly, in areas where the glass was irradiated, it turned pink (inset of Fig. 1). The experiment of irradiating by 2.5 µJ fs pulse laser was repeated two more times to prove reproducibility (inset of Fig. 1).

NIR emission spectra of BBSPS glass samples are shown in Fig. 2. While in as-received glass, no NIR emission can be detected after excitation (785 nm laser diode, Fig. 2(a)), in the fs laser-irradiated area of the sample (1.0 µJ, area of inset of Fig. 1(b)), a weak emission peak protrudes in the range of 1000–1500 nm (Fig. 2(b)). When increasing the average energy to 2.5 µJ, the peak position remains unchanged, but its intensity is enhanced by a factor of ∼6 (Fig. 2(c), and area of inset of Fig. 1(c)).

Figure 3 is a representation of the decay curve of the emission at 1250 nm. For comparison, data were fitted to a first order exponential decay equation, $y = 1.00475e^{-x/179}+0.02395$, which produced a fluorescence lifetime of 179 µs.

IV. Discussion

Bismuthate (Bi-rich) glasses are long known for several applications, e.g. sealing glasses, glazes, etc. If melted in air, in such glasses bismuth is usually present in the form of Bi^{3+}, and glasses appear yellowish. When illuminated with UV-light (∼230–250 nm), low concentrations of Bi^{3+} may result in emission of blue light (∼450 nm), with very short fluorescence decay times of <10 µs.[27] The observed emission properties of fs laser-irradiated BBSPS glass are similar to those of other Bi-doped glasses,[2–14,22,24] which leads to the conclusion that in the considered glass, fs laser-induced NIR emission originates from the same emission centers as it does in other Bi-doped glasses.
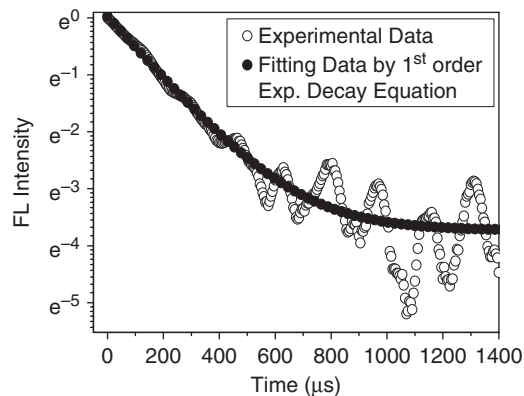

Fig. 3. Fluorescent decay curve of BBSPS glass irradiated by femtosecond 800 nm pulse laser with average pulse energy of 2.5 µJ when pumped by 785 nm laser diode. The monitored emission wavelength is 1250 nm. BBSPS, $52Bi_2O_3 \cdot 23B_2O_3 \cdot 4SiO_2 \cdot 17PbO \cdot 4Sb_2O_3$.

Given the pulse width of ~ 33 fs and the average pulse energy of 1 μJ of the used laser, a power density of up to 3.8×10^{13} W/cm^2 results in the focal point of irradiation. In most glasses, this is sufficient to induce various nonlinear physicochemical reactions. For instance, the already mentioned fs laser-induced photoreduction of Au^{3+} to Au in Au^{3+}-doped silicate glass[26] and Sm$^{3+} \rightarrow$ Sm^{2+} in Sm^{3+}-doped alumino-borate glass[25] were attributed to multiphoton absorption processes. In the case of Au-containing silicate glasses, additional thermal treatment is necessary to obtain the desired 3D coloration effects by diffusion-driven formation of metallic clusters. Typically, the desired gold particles form while heat-treating 0.5–1 h at 550°C.[26] Therefore, the present observation that NIR emission (as well as changes in the absorption spectrum) occur directly after fs laser irradiation (i.e., no additional thermal treatment is required) enables an important conclusion on the underlying emission mechanism.

The focal spot of the laser beam has a diameter of ~ 10 μm. In view of the scanning speed of 1 mm/s and the repetition rate of 1 kHz, the number of laser pulses applied to each focal point can be calculated as ~ 10. This means that the interaction time is about 330 fs between fs laser and BBSPS glass. Although quantitative data on diffusion is not available in sufficient detail, some conclusions can be drawn from comparison with Ag diffusion. Atomic radii of silver and bismuth are comparable. Effective ionic radii of six-fold coordinated Bi^{3+} (here, we refer to Bi^{3+} because data for Bi$^+$ are not available; note that the effective radius of Bi$^+$ would be even higher than that of Bi^{3+}) and Ag$^+$ are 103 and 125 pm,[28] respectively. An order-of-magnitude of the diffusion coefficient of Ag, $D_0 = 4.7 \times 10^{-2}$ cm^2/s and the corresponding activation energy of diffusion, $E_A = 161$ kJ/mol, can be taken from Euken.[29] This results in an estimated diffusion coefficient 6.2×10^{-13} cm^2/s (6.2×10^{-28} cm^2/fs) at 500°C. This means that during the estimated interaction time of ~ 330 fs, virtually no diffusion occurs at a length scale > 1 nm. Instead, it is assumed that the observed effects are based on fast photo-induced reduction of Bi^{3+} to Bi$^+$. At sufficiently high laser intensity, electrons simultaneously absorb multiple photons that allow them to pass from valence to conduction band. Once an electron is promoted to the conduction band, it will nucleate a process of avalanche ionization: by impact ionization, excess energy may be transferred to another electron, resulting in two electrons in the conduction band. Increasing the pulse energy leads to an increase of the number of these electrons and thereby improves the probability of permanent reduction, resulting in increasing concentration of Bi$^+$ and, consequently, increasing NIR emission intensity (Figs. 1 and 2).

It is further noteworthy that the fs laser-induced coloration does not, at ambient temperature, fade with time; some irradiated samples have been stored for more than 3 years (since March 2005) without any visible alteration of laser-written features (such as area in inset 3 of Fig. 1(d)). Compared with expensive Au^{3+}- or Ag$^+$-doped glasses, where fs pulse lasers in combination with subsequent heat treatment have been used to space-selectively precipitate gold or silver nanoparticles to produce colored images in transparent glass blocks, Bi^{3+}-doped glasses where the bismuth ions can be reduced to Bi$^+$ may offer a convenient alternative. Similarly colorful structures can be written into such glasses, but without any additional thermal treatment.

V. Conclusions

For the first time, it was demonstrated that fs laser irradiation can be used to write colored features into bismuthate glasses. Upon optical excitation, irradiated areas exhibit NIR emission, peaking at ~ 1250 nm. Induction of coloration and NIR emission do not require thermal annealing subsequent to laser irradiation. Emission properties are similar to these of other Bi-doped glasses. It is concluded that, thus, emission occurs from the same emission centers. Because of the short interaction time between fs laser and glass, diffusion-driven formation of

Bi-containing clusters is excluded. Rather, it is concluded that Bi$^+$ species are responsible for NIR emission in this class of materials. Laser irradiation results in photo-induced reduction of Bi^{3+} to Bi$^+$ by multiphoton absorption. It is suggested that for the fabrication of colored, 3D structures in transparent glasses via fs laser writing, Bi^{3+}-containing glasses offer a convenient alternative for Au^{3+} or Ag$^+$-doped glasses.

References

[1]T. Suzuki and Y. Ohishi, "Broadband 1400 nm Emission from Ni^{2+} in Zinc–Alumino-Silicate Glass," *Appl. Phys. Lett.*, **84** [19] 3804–6 (2004).

[2]K. Murata, Y. Fujimoto, T. Kanabe, H. Fujita, and M. Nakatsuka, "Bi-Doped SiO$_2$ as a New Laser Material for an Intense Laser," *Fusion Eng. Des.*, **44**, 437–9 (1999).

[3]M. Peng, X. Meng, J. Qiu, and Q. Zhao, "GeO$_2$:Bi, M (M = Ga, B) Glasses with Super-Wide Infrared Luminescence," *Chem. Phys. Lett.*, **403**, 410–4 (2005).

[4]M. Peng, X. Meng, D. Chen, and J. Qiu, "Comment on 'Enhanced Room-Temperature Emission in Cr^{4+} Ions Containing Alumino-Silicate Glasses' [Appl. Phys. Lett. 82, 4035 (2003)]," *Appl. Phys. Lett.*, **87** [6] 066103-1–2 (2005).

[5]M. Peng, J. Qiu, D. Chen, X. Meng, and C. Zhu, "Broadband Infrared Luminescence from Li$_2$O–Al$_2$O$_3$–ZnO–SiO$_2$ Glasses Doped with Bi$_2$O$_3$," *Opt. Express*, **13**, 6892–8 (2005).

[6]M. Peng, J. Qiu, D. Chen, X. Meng, L. Yang, X. Jiang, and C. Zhu, "Bismuth- and Aluminum-Codoped Germanium Oxide Glasses for Super-Broadband Optical Amplification," *Opt. Lett.*, **29**, 1998–2000 (2004).

[7]Y. Fujimoto and M. Nakatsuka, "Infrared Luminescence from Bismuth-Doped Silica Glass," *Jpn. J. Appl. Phy.*, **40**, L279–81 (2001).

[8]T. Suzuki and Y. Ohishi, "Ultrabroadband Near-Infrared Emission from Bi-Doped Li$_2$O–Al$_2$O$_3$–SiO$_2$ Glass," *Appl. Phys. Lett.*, **88**, 191912-1–3 (2006).

[9]M. Peng, C. Wang, N. Da, D. Chen, X. Jiang, and J. Qiu, "Bismuth-Activated Luminescent Materials for Broadband Optical Amplifier in WDM System," *J. Non-Cryst. Solids*, **354**, 1221–5 (2008).

[10]M. Peng, J. Qiu, D. Chen, X. Meng, and C. Zhu, "Superbroadband 1310 nm Emission from Bismuth and Tantalum Codoped Germanium Oxide Glasses," *Opt. Lett.*, **30**, 2433–5 (2005).

[11]X. Meng, J. Qiu, M. Peng, D. Chen, Q. Zhao, X. Jiang, and C. Zhu, "Infrared Broadband Emission of Bismuth-Doped Barium–Aluminum–Borate Glasses," *Opt. Express*, **13** [5] 1635–42 (2005).

[12]X. Meng, J. Qiu, M. Peng, D. Chen, Q. Zhao, X. Jiang, and C. Zhu, "Near Infrared Broadband Emission of Bismuth-Doped Aluminophosphate Glass," *Opt. Express*, **13** [5] 1628–34 (2005).

[13]B. Denker, B. Galagan, V. Osiko, S. Sverchkov, and E. Dianov, "Luminescent Properties of Bi-Doped Boro-Alumino-Phosphate Glasses," *Appl. Phys. B*, **87**, 135–7 (2007).

[14]J. Ren, D. Chen, G. Yang, Y. Xu, H. Zeng, and G. Chen, "Near Infrared Broadband Emission from Bismuth–Dysprosium Codoped Chalcohalide Glasses," *Chin. Phys. Lett.*, **24**, 1958–60 (2007).

[15]E. Dianov, V. Dvoyrin, V. Mashinsky, A. Umnikov, M. Yashkov, and A. Gur'yanov, "CW Bismuth Fibre Laser," *Quant. Electron.*, **35**, 1083–4 (2005).

[16]V. Dvoyrin, V. Mashinsky, I. Bulatov, A. Shubin, M. Melkumov, E. Kustov, E. Dianov, A. Umnikov, V. Khopin, M. Yashkov, and A. Guryanov, "Bismuth-Doped-Glass Optical Fibers—A New Active Medium for Lasers and Amplifiers," *Opt. Lett.*, **31**, 2966–8 (2006).

[17]I. Razdobreev, L. Bigot, V. Pureur, A. Favre, G. Bouwmans, and M. Douay, "Efficient All-Fiber Bismuth-Doped Laser," *Appl. Phys. Lett.*, **90**, 031103-1–3 (2007).

[18]E. Dianov, A. Shubin, M. Melkumov, O. Medvedkov, and I. Bufetov, "High-Power CW Bismuth-Fiber Lasers," *J. Opt. Soc. Am. B*, **24**, 1749–55 (2007).

[19]M. Peng and L. Wondraczek, "Bismuth-Doped Oxide Glasses as Potential Solar Spectral Converters and Concentrators," *J. Mater. Chem.*, (2009), DOI: 10.1039/b812316k.

[20]T. Ohkura, Y. Fujimoto, M. Nakatsuka, and S. Young-Seok, "Local Structures of Bismuth Ion in Bismuth-Doped Silica Glasses Analyzed Using Bi LIII X-Ray Absorption Fine Structure," *J. Am. Ceram. Soc.*, **90**, 3596–600 (2007).

[21]V. Truong, L. Bigot, A. Lerouge, M. Douay, and I. Razdobreev, "Study of Thermal Stability and Luminescence Quenching Properties of Bismuth-Doped Silicate Glasses for Fiber Laser Applications," *Appl. Phys. Lett.*, **92**, 041908-1–3 (2008).

[22]S. Khonthon, S. Morimoto, Y. Arai, and Y. Ohishi, "Luminescence Characteristics of Te- and Bi-Doped Glasses and Glass-Ceramics," *J. Ceram. Soc. Jpn.*, **115**, 259–63 (2007).

[23]T. Ohkura, Y. Fujimoto, M. Nakatsuka, and S. Young-Seok, "Local Structures of Bismuth Ion in Bismuth-Doped Silica Glasses Analyzed Using Bi LIII X-Ray Absorption Fine Structure," *J. Am. Ceram. Soc.*, **90**, 3596–600 (2007).

[24]Y. Arai, T. Suzuki, and Y. Ohishi, "Ultrabroadband Near-Infrared Emission from a Colorless Bismuth-Doped Glass," *Appl. Phys. Lett.*, **90**, 261110-1–3 (2007).

[25]J. Qiu, K. Miura, T. Suzuki, T. Mitsuyu, and K. Hirao, "Permanent Photo-reduction of Sm^{3+} to Sm^{2+} Inside a Sodium Aluminoborate Glass by an Infrared Femtosecond Pulsed Laser," *Appl. Phys. Lett.*, **74**, 10–2 (1999).

[26]J. Qiu, X. Jiang, C. Zhu, M. Shirai, J. Si, N. Jiang, and K. Hirao, "Manipulation of Gold Nanoparticles Inside Transparent Materials," *Angew. Chem. Int. Ed.*, **43**, 2230–4 (2004).

[27]S. Parke and R. S. Webb, "The Optical Properties of Thallium, Lead and Bismuth in Oxide Glasses," *J. Phys. Chem. Solids*, **34**, 85–95 (1973).

[28]R. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chaleogenides," *Acta Cryst.*, **A32**, 751–67 (1976).

[29]A. Euken, *Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 6*, **Vol. I/4**. Springer, Berlin, 1955. □