

Advantage of anti-Stokes Raman scattering for high-temperature measurements

Hirotaka Fujimori^{a)}

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, 755-8611, Japan

Masato Kakihana

Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, 226-8503, Japan

Koji Ioku and Seishi Goto

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, 755-8611, Japan

Masahiro Yoshimura

Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, 226-8503, Japan

(Received 17 May 2001; accepted for publication 15 June 2001)

We present the results of experiments that assess the viability of anti-Stokes scattering to investigate *in situ* materials at high temperatures. Both anti-Stokes and Stokes Raman measurements have been performed at various high temperatures using hafnia as a test material. As compared with Stokes Raman spectra, anti-Stokes spectra were observed with lower thermal emission backgrounds in accordance with Planck's equation. The intensity ratio of anti-Stokes to Stokes scattering approaches 1 as the temperature increases at high temperatures satisfying the Boltzmann distribution law. These results clearly demonstrate the advantage and feasibility of anti-Stokes Raman scattering for the elimination of the thermal emission in comparison with Stokes scattering. © 2001 American Institute of Physics. [DOI: 10.1063/1.1394174]

The extension of Raman scattering from materials at temperatures above 1000 °C is an important challenge because structural changes and chemical reactions of various industrial materials and minerals occur in this temperature range. However, the measurable region of temperatures is limited in the conventional Raman spectroscopy using visible region excitation. This can be explained in terms of the fact that it is difficult to detect weak Raman scattering from substances at high temperatures in comparison with an intense continuous background due to thermal emission. Such high-temperature measurements have been performed by means of the pulsed-excitation method^{1,2} and micro-Raman technique.^{3,4} However, these techniques require quite high-energy density (typically 80–5000 kW for 5–10 ns for the pulsed-excitation method) which can cause serious damage to the sample. cw UV Raman spectroscopy is suitable for the measurements at high temperatures as an alternative to the pulsed-excitation method, because the UV excitation shifts the Raman scattering to shorter wavelengths away from the intense thermal emission peak. We have recently demonstrated that the Raman scattering with UV excitation is eminently well suited to *in situ* investigation of materials at high temperatures up to 1500 °C.⁵ Later, Zouboulis *et al.*⁶ have also shown the advantages of UV Raman scattering for high-temperature investigations up to 1420 °C. Recently, by means of UV Raman spectroscopy, we have observed the phase transition and soft phonon modes in SrZrO₃,⁷ OH vacancies arising in hydroxyapatite at high temperatures,⁸

phase transition of hafnia up to 2085 K,⁹ and anharmonic lattice mode in Ca₂SiO₄.¹⁰ Here we demonstrate that anti-Stokes Raman scattering is even more suitable for high-temperature measurements following the Boltzmann distribution law and Planck's equation. Such an idea would open up the possibility of new vistas for high-temperature science and technology.

A spherical HfO₂ specimen obtained by the quenching of melts in air using an arc-imaging furnace was used in this study, because Raman spectra of this specimen show continuous change with increasing temperature.⁹ Raman spectra were excited by a cw ultraviolet (363.8 nm) laser line. The Raman instrument used here is detailed in the literature.⁵ The sample was mounted in a furnace with a Pt–Rh heater where the sample was placed and then fixed on a Pt/13%Rh thermocouple with alumina cement. The specimen was heated at rate of 10 °C/min, and then the temperature was kept constant during the measurements (within ±1 °C). Each measurement was done in air after a given constant temperature was maintained for 10 min. The central position of spectrograph was set at bands denoted by symbols (●) in Fig. 1 in order to measure intensity ratio of anti-Stokes to Stokes Raman scattering precisely. The laser power at the tube level was set at 70 mW. In consideration of the spectral resolution and high spectral intensity at high temperatures, the entrance slit width was set at 100 μm, which corresponds to the full width at half maximum of 4.7 cm⁻¹. The apparent thermal emission background from the sample and furnace was measured without laser excitation. No artificial smoothing was used on the acquired Raman spectra.

Figure 2 shows the continuous thermal radiation spectra

^{a)} Author to whom correspondence should be addressed; electronic mail: fuji@amse.yamaguchi-u.ac.jp

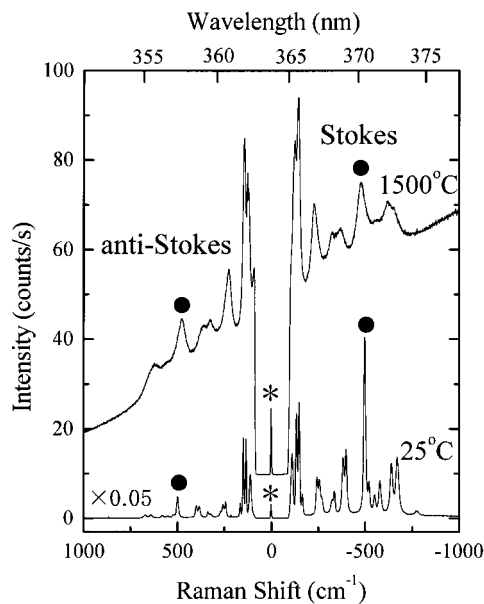


FIG. 1. Raman spectra of hafnia recorded at 25 and 1500 °C. The spectrum at 1500 °C is shown with offset. Note scale factor to spectrum at 25 °C. The lines denoted by symbols (*) are due to Rayleigh scattering.

in the range of both anti-Stokes and Stokes Raman scattering. With increasing temperature, the intensity of the apparent thermal emission, I_B , became rapidly pronounced, which is more notable in the Stokes spectral region because of the stronger background in the longer wavelength region in ac-

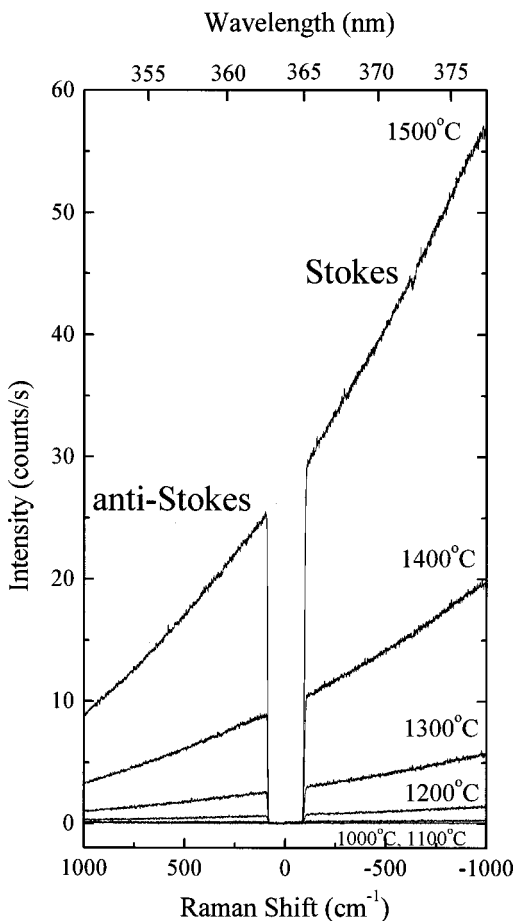


FIG. 2. The apparent thermal emission background from the sample and furnace measured without laser excitation.

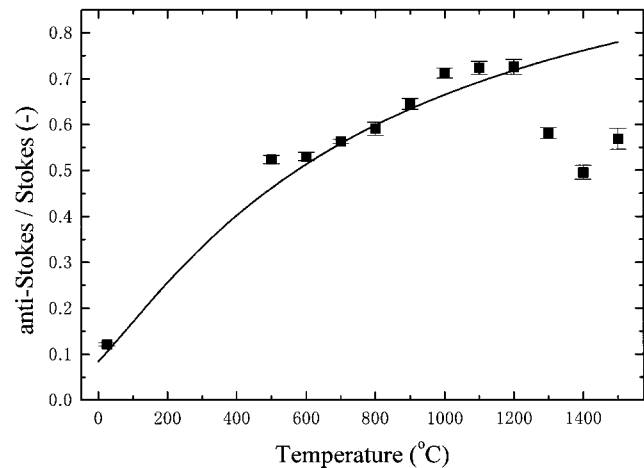


FIG. 3. Temperature dependence of the intensity ratio of anti-Stokes to Stokes Raman bands represented by symbols (●) in Fig. 1. Solid line shows the theoretical curve indicated by Eq. (1) without the coefficient, A , which depends to the instrument.

cordance with Planck's equation, $I_B = A \nu^3 / [\exp(h\nu/kT) - 1]$, where A is the instrument dependent coefficient, ν is the frequency of light (s^{-1}), k is Boltzmann's constant ($1.3807 \times 10^{-23} \text{ J/K}$), h is Planck's constant ($6.6261 \times 10^{-34} \text{ J s}$), and T is the absolute temperature (K). At 1500 °C, for example, the background level was 9 and 57 (counts/s) at the spectral position of 1000 cm^{-1} in the anti-Stokes and Stokes regime, respectively. This result clearly shows the anti-Stokes Raman scattering is well suited to the *in situ* investigation of samples at high temperatures. Usually only the Stokes lines are measured, since the intensity of the anti-Stokes lines is eminently much lower than that of the Stokes lines at ambient temperature. Here we present the results of experiments that assess the validity of anti-Stokes scattering to investigate *in situ* materials at high temperatures. At elevated temperatures, Raman lines were redshifted and their width was increasing with increasing temperature (Fig. 1). In the present study, we pay attention to the band represented by symbols (●) in Fig. 1. The pattern decomposition of the Raman spectra was performed using a commercial profile-fitting program GRAMS assuming Lorentz functions. In Fig. 3, the obtained values of the intensity ratio of anti-Stokes to Stokes Raman scattering are plotted as a function of temperature. The ratio shows remarkable increase with increasing temperature satisfying the Boltzmann distribution law. The intensity ratio is given by¹¹

$$\begin{aligned} \frac{\text{anti-Stokes}}{\text{Stokes}} &= \left[\frac{\nu_0 + \Delta\nu_i(T)}{\nu_0 - \Delta\nu_i(T)} \right]^4 \exp \left[-\frac{hc\Delta\nu_i(T)}{kT} \right] \\ &= \left[\frac{\nu_0 + \Delta\nu_i(T)}{\nu_0 - \Delta\nu_i(T)} \right]^4 \exp \left[-1.4387 \frac{\Delta\nu_i(T)}{T} \right], \end{aligned} \quad (1)$$

where c is the speed of light ($2.9979 \times 10^8 \text{ m/s}$), ν_0 is the wave number of the exciting laser light (27489 cm^{-1}), and $\Delta\nu_i(T)$ is the temperature-dependent wave number of i th Raman mode (cm^{-1}). The intensity ratio approaches 1 with increasing temperature. The intensity of the anti-Stokes component is practically comparable to that of the Stokes component at temperatures above 1000 °C (Figs. 1 and 3). There-

fore, the anti-Stokes Raman scattering allows one to improve the high-temperature limit of *in situ* Raman measurements. The utility of this scheme will not only have a great effect on UV Raman spectroscopy but also on conventional visible Raman measurements, in which experimental temperatures are limited to relatively low values (Fig. 5 in Ref. 5).

We conclude that the anti-Stokes Raman scattering has potential to become a powerful technique for *in situ* high-temperature investigations. Raman spectra at various high temperatures up to 1500 °C were measured. These results reveal that the anti-Stokes Raman scattering can improve an upper limit of the experimental temperature achievable by the Stokes Raman scattering. To diminish the strong thermal emission, which hampers experiments at high temperatures, this concept would open a door for high-temperature science and technology.

The authors are thankful to Professor Masatomo Yashima for help with the UV Raman system for high-temperature materials. The authors are greatly indebted to Ryosuke Shimidzu (Photon Design, Inc.) for his valuable

comments. The present work has been supported partly with cooperative programs in Materials and Structures Laboratory of Tokyo Institute of Technology.

- ¹A. B. Kudryavtsev and A. A. Sobol', *Kratk. Soobshch. Fiz.* **1**, 17 (1984).
- ²G. J. Exarhos and J. W. Schaaf, *J. Appl. Phys.* **69**, 2543 (1991).
- ³B. O. Mysen and J. D. Frantz, *Chem. Geol.* **96**, 321 (1992).
- ⁴I. Daniel, P. Gillet, B. T. Poe, and P. F. McMillan, *Phys. Chem. Miner.* **22**, 74 (1995).
- ⁵M. Yashima, M. Kakihana, R. Shimidzu, H. Fujimori, and M. Yoshimura, *Appl. Spectrosc.* **51**, 1224 (1997).
- ⁶E. Zouboulis, D. Renusch, and M. Grimsditch, *Appl. Phys. Lett.* **72**, 1 (1998).
- ⁷H. Fujimori, M. Yashima, M. Kakihana, and M. Yoshimura, *Phys. Rev. B* **61**, 3971 (2000).
- ⁸H. Fujimori, H. Toya, K. Ioku, S. Goto, and M. Yoshimura, *Chem. Phys. Lett.* **325**, 383 (2000).
- ⁹H. Fujimori, M. Yashima, M. Kakihana, and M. Yoshimura, *J. Am. Ceram. Soc.* **84**, 663 (2001).
- ¹⁰H. Fujimori, H. Komatsu, K. Ioku, S. Goto, and M. Yoshimura (unpublished).
- ¹¹D. A. Long, *Raman Spectroscopy* (McGraw-Hill, New York, 1977), Chap. 4.3.7.