Invited Paper

Terahertz absorption spectroscopy of ammonia vapor detection based on $Bi_2Sr_2CaCu_2O_{8+\delta}$ intrinsic Josephson junction stacks

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(Received December 23, 2017)

Abstract: We report on the application of terahertz (THz) waves radiated from $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) intrinsic Josephson junction (IJJ) stacks on the gas detection. The THz emission is provided by controlling the voltage across the stack, and the ammonia gas absorption peak at a frequency of about 0.572 *THz* was observed by adjusting the bias current for a direct and mixing detection technique. The minimum absorption linewidth turned out to be as narrow as about 5 *MHz*. The obtained ammonia-absorption spectra suggest that the BSCCO emitter can be an important terahertz source for potential THz applications in trace-gas detection.

Keywords: BSCCO, Terahertz emitter, Terahertz spectroscopy

doi: 10.11906/TST.065-072.2018.09.07

1. Introduction

The terahertz (THz) science and technology has attracted much attention for decades due to its potential applications in radio astronomy, broad band communications, medical diagnostics, public security and so on [1-2]. For sources of terahertz radiation, femtosecond laser pulses, quantum cascade lasers, and backward wave oscillators etc, have been reported to generate THz electromagnetic waves. However, their high cost, complexity and radiation frequency limit their applications. Therefore, compact and stable solid-state THz sources are needed to fill the "THz-gap" [1-3].

THz emitters of intrinsic Josephson junction (IJJ) stacks made of the high critical temperature (T_c) superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) have fascinating potentials as THz generators especially at sub-THz frequencies [4-17]. According to the theory of the ac Josephson effect, a Josephson junction biased at a voltage V_0 can have an oscillation frequency $f_e = 2eV_0/h$, where e is the elementary charge and h is the Planck constant. The emission power (P_0) from a single Josephson is typically in the order of pW to nW. To achieve a powerful terahertz emission, a large number (N) of junctions in an array should oscillate coherently. The high-T_c superconductor

BSCCO IJJs are naturally formed by the layered crystal structure, for instance, a 1.5 μm thick stack consists of N =1000 junctions. In 2007, the THz emission from the IJJs was firstly detected in a 1 μm thick mesa with an extrapolated output power up to 0.5 μW and frequencies between 0.5 and 0.85 *THz* [4]. So far, the THz radiation has been proved to be continuous and coherent [5-10, 12-16], and a highest emission frequency up to 2.4 *THz* [9]. A detected maximum emission power $P \sim 610\ \mu W$ from a synchronized three-mesa array was reported [10]. One the other hand, the emission linewidth is not less than 0.5 *GHz* at low bias regime, while at high bias regime the linewidth can be as narrow as 23 *MHz* [12]. Such properties, which are essential for THz spectroscopy applications, allow us to sweep the bias voltage across the stack.

Many polar molecules such as H_2S, NH_3, and SO_2 are the sources of environmental pollution, and each of them exhibits unique spectral signatures of strong absorption in sub-THz range arising from transitions between rotational quantum levels [1-3, 5, 15, 17, 20-21]. To detect and recognize gas molecules, the THz spectroscopy is a fast and effective way, especially for the high-resolution THz spectroscopy. In the past decades, the gas tracing detection has been taken by the THz time-domain spectroscopy (TDS) [20] with a frequency resolution of about 2 *GHz*, which is not capable for delicate trace gas detection. Recently, the BSCCO THz emitters exhibit as a promising way to be applied as the THz spectroscopy for dilute gases, as already introduced in Ref 15.

In the present work, BSCCO sources with an in-line structure was also used to study the gas THz spectroscopy. By sweeping frequencies with varying the bias voltage of these sources, the THz absorption spectra are observed for the existence of ammonia. As a comparison, we also showed THz absorption characteristics of ammonia vapor obtained earlier by a heterodyne mixing detection method. A 5 *MHz* linewidth of absorption peak was observed at vapor pressure of P = 0.1 *mbar*.

2. Experiments

The IJJ THz oscillation devices were fabricated from high-quality single crystals of BSCCO by traditional microfabrication techniques. The fabrication process of mesa structure IJJ stacks used in mixer detection experiment are described in previous work [12]. For the in-line IJJ stacks, its fabrication process is similarly to that of the double-sided structure [7, 18], and will be described in a future work. To form the stack, a piece of BSCCO single crystal was annealed at 650°*C*, 18 Pa Ar + 2 Pa O_2, for 48 *h*. After annealing, the critical temperature T_c is ~ 89 *K*. The fabricated rectangular IJJ stack has an in-plane size of $(330 \times 80)\ \mu m^2$ and a thickness of about 2.7 μm, corresponding to $\sim$ 1800 junctions in series, as shown in Fig. 1(b).

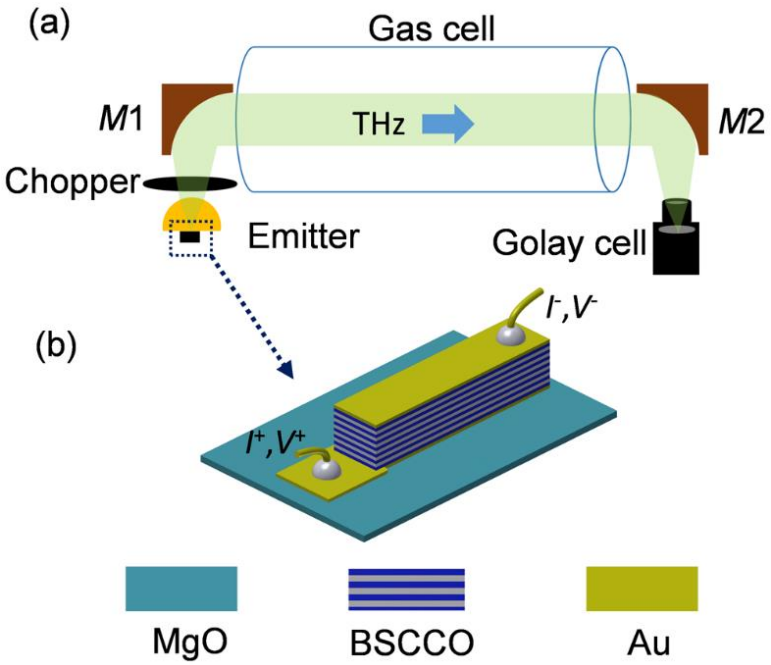

Fig. 1(a) Schematic diagram of the THz gas-detection system using high-T_c intrinsic Josephson junctions as a frequency-tunable THz source. (b) In-line structure BSCCO THz emitter.

For the direct detection experiment, we use an effective and economical transmission THz gas-detection system as shown in Fig. 1. The stack was placed in a Stirling Cryocooler which can provide a controlled low temperature environment from 30 *K* to room temperature. The emission was directed to a 52-*cm*-long gas cell via an off-axis parabolic mirror, where both windows of the chamber are a 2 *mm* thick THz-transparent Teflon. To detect the phase-locked signal, a mechanical chopper with a modulated frequency of 14 *Hz* was placed on the light-path, as shown in Fig. 1(a). The chamber was firstly pumped into a vacuum of about 3×10^{-5} *mbar*, and then the target gas was introduced into the chamber via a gas valve. On the other side of the chamber, a room temperature THz detector, so-called Golay cell, was employed to detect the absorption spectrum. Here, we should note that the ammonia vapor used for the experiment volatilized from the ammonia water, which contained tiny amount of water vapor with a proportion of less than 10%, and the environmental humidity is about 40%. In the second experiment, the setup is similar to the one shown in Ref 17.

3. Results

Figure 2(a) shows current-voltage curve (IVC) of the emitter, as measured at T = 42.6 *K*. The nonlinear contact resistance of the IJJs has been subtracted with a systematic error on V of 5% level. The stack switches to its resistance states when the bias current is above 29 *mA*. By further increasing I to 40 *mA* and then back to zero, the outmost *I-V* branch was obtained, with the typical heating-induced S shape. The emission characteristics, as detected by the Golay cell, are

shown in Fig. 2(b), for a case of an evacuated gas cell ($p \approx 3\times10^{-5}$ *mbar*). The IJJ emitter has a wide current range of stable emission power at high-bias regime from 8 *mA* to 43 *mA* according to the "hot spot" theory. The highest emission power at this bias regime is about 1.7 μW at the bias point (10.22 *mA*, 2.155 *V*), with an emission frequency of about 577 *GHz*, corresponding to $N \approx 1806$ emitting junctions.

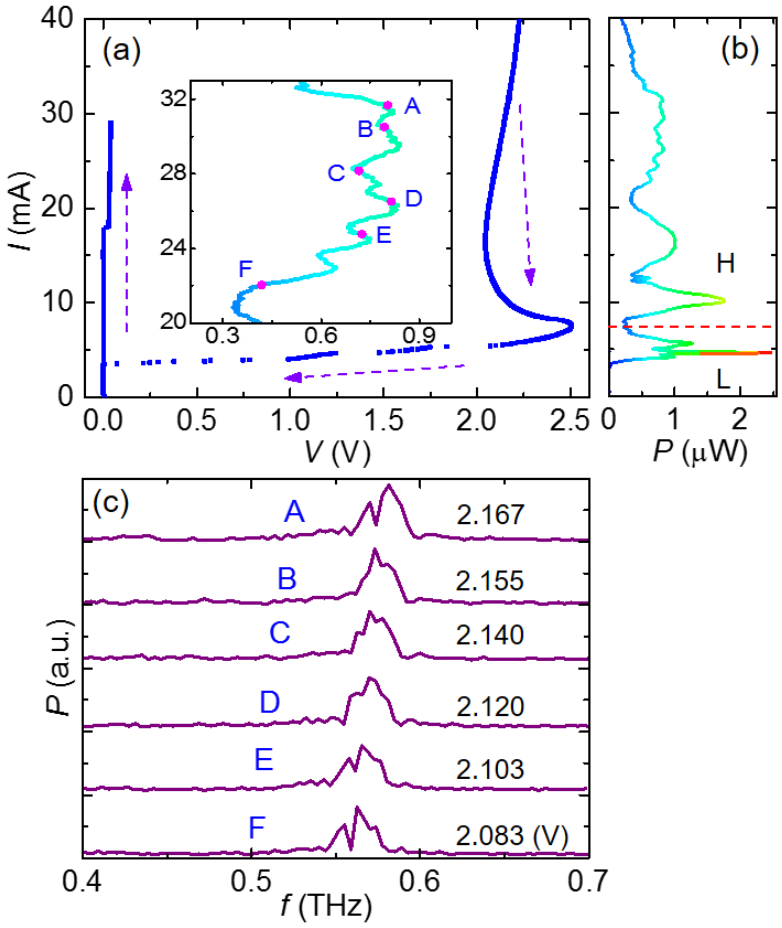

Fig. 2 (a) IVC of the stack, as measured at T_b = 42.6 *K*. Contact resistance has been subtracted. Dashed lines indicate the current sweep sequence (b) Emission intensity curves vs. current across the stack detected Golay cell. The curve is plotted by using color code according to the output voltage of the Golay cell detector. Inset in (a) shows part of the emission intensity vs. current curves, points A-F are marked, their emission spectra are shown in (c). Dashed line in (b) is the boundary between high-bias (**H**) and low-bias (**L**) regime.

To investigate the frequency characteristics of the radiation, frequencies of the bias points (A-F) marked in Fig. 2(b) were measured, varying from 562 to 580 *GHz*, which just covers the rotational frequency of ammonia molecules. The measured Fourier spectra of points (A-F) are shown in Fig. 2(c).

Figure 3 shows the terahertz absorption spectra of ammonia vapor for different pressures ranging from 0.27 to 910 *mbar*. The THz absorption becomes larger with increase of gas

pressures, meanwhile the absorption linewidth broadens. The latter phenomenon is the frequency expanding due to the collision among the molecules. For P = 910 *mbar*, plotted by a purple line in Fig. 3(a), the THz emission is greatly absorbed by the ammonia vapor not only near the absorption center but also far from this point even at I = 24.78 *mA*, where the measured frequency is 565 *GHz*. The absorption center of the curves, as shown in Fig. 3 (a), is at I = 26.56 *mA*, where the frequency, measured with our interferometer, is about 569 *GHz*. It is close to the well-known rotational-transition frequency (f =572.5 *GHz*) of ammonia molecules. Note the above frequency difference is caused by the resolution limit of our interferometer, and can in principle be reduced by increasing the displaced distance of two mirrors used in the interferometer. The minimum pressure of the ammonia vapor, where we can also observe the small absorption peak, is p =0.27 *mbar*.

Figure 3(b) plots the amplitude of absorption vs. V curve, with a maximum absorption of about 36%，as measured at p =7.6 *mbar*. For this pressure, the absorption center of this curve is at V = 2.1302 *V*. Here, we use the rotational -transition frequency of ammonia molecules and the Josephson relation to recalculate the number of emitting IJJs and obtain a more precise value, N = 1799. The linewidth of the absorption curve，as marked by the dark arrow，is about 3.7 *mV*，corresponding to about 0.994 *GHz* according to the ac Josephson effect $\Delta f = 2\Delta Ve/Nh$.

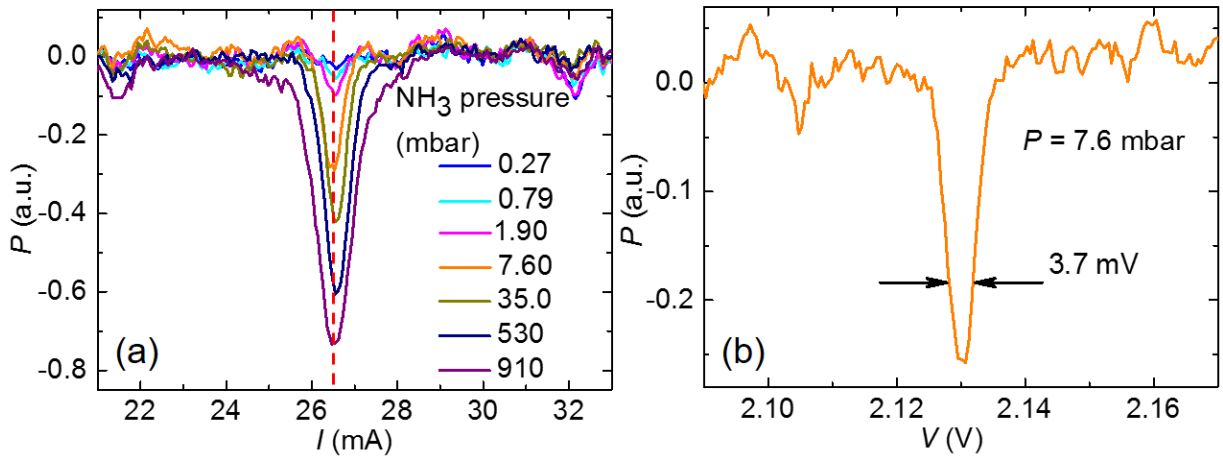

Fig. 3 Amplitude of absorption vs. (a) bias current and (b) bias voltage. Panel (a) shows absorption curves of different ammonia vapor pressure. In panel (b) the bias pressure is 7.6 *mbar* and the linewidth of the absorption curve is 3.7 *mV*.

For accurately measuring the THz absorption spectra of ammonia vapor, a Nb/AlN/NbN superconducting integrated receiver (SIR) [12, 17, 19], with an effective working frequency from 450 to 700 *GHz* and a confirmed frequency resolution of well below 100 *kHz*, was used for detecting terahertz emission from an IJJ mesa stacks. The experiment was taken in Moscow with an optical path similar to Fig. 1. In the experiment, the bias voltage on the BSCCO emitter was changed continuously, meanwhile the frequencies and amplitude of THz emission were detected by the SIR for gas detection.

Thanks to the noise control on the BSCCO emitter and SIR, high resolution THz absorption spectra of ammonia were achieved in a narrow frequency range, as shown in Fig. 4. It also performs absorption improving and frequency expanding phenomenon with increase of the concentration of ammonia vapor. At P = 0.1 *mbar* of ammonia vapor, which is the order of trace gases, clear absorption peak with an absorption linewidth of about 5 *MHz* was observed as shown in the inset of Fig. 4. Here, we note that the measured rotation frequency of ammonia molecule is 572.498 *GHz* in this sub-THz range.

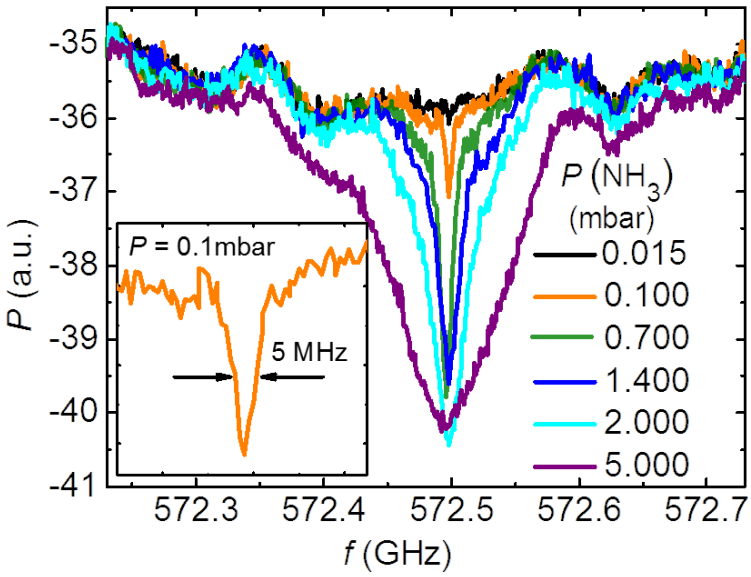

Fig. 4 THz absorption spectra of ammonia vapor at different pressure measured by a BSCCO emitter and a SIR terahertz detector. Inset shows an absorption spectrum of ammonia at p=0.1 mbar, with an absorption linewidth of 5 *MHz*.

4. Conclusions

In summary, using THz waves generated from BSCCO IJJ stacks, we have achieved THz absorption spectra of ammonia vapor through an effective and economical transmission THz gas-detection system. Clear absorption peaks of different gas pressures were observed in the THz spectra by sweeping the voltage across the stacks. We also measured THz absorption characteristics of the ammonia vapor with a SIR detector for comparison, and achieved a minimum absorption linewidth of about 5 *MHz* by changing the voltage between the electrodes. The results have made the BSCCO THz sources amazing THz emitters for terahertz spectroscopy and provided experimental evidence for the application of BSCCO THz emitters in environmental monitoring.

Acknowledgments

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Grants No. 11234006, No. 61611130069), RFBR Grant No. 17-52-12051, and the Deutsche Forschungsgemeinschaft via Project No. KL930-13/2.

References

[1] M. Tonouchi. "Cutting-edge terahertz technology". *Nat. Photonics*, 1, 97-105 (2007).

[2] B. Ferguson and X. C. Zhang. "Materials for terahertz science and technology". *Nat. Materials*, 1, 26-33 (2002).

[3] B. S. Williams. "Terahertz quantum-cascade lasers". *Nat. Photonics*, 1, 517-525 (2007).

[4] L. Ozyuzer, A. E. Koshelev, C. Kurter, et al.. "Emission of Coherent THz Radiation from Superconductors". *Science*, 318, 1291-1293 (2007).

[5] U. Welp, K. Kadowaki and R. Kleiner. "Superconducting emitters of THz radiation". *Nat. Photonics*, 7, 702-710 (2007).

[6] H. B. Wang, S. Guénon, J. Yuan, et al.. "Hot spots and waves in $Bi_2Sr_2CaCu_2O_8$ intrinsic Josephson junction stacks: A study by low temperature scanning laser microscopy". *Phys. Rev. Lett.*, 102, 1-4 (2009).

[7] M. Ji, J. Yuan, B. Gross, et al.. "$Bi_2Sr_2CaCu_2O_8$ intrinsic Josephson junction stacks with improved cooling: Coherent emission above 1 *THz*". *Appl. Phys. Lett.*, 105, 122602 (2014).

[8] D. Y. An, J. Yuan, N. Kinev, et al.. "Terahertz emission and detection both based on high-T_c superconductors: Towards an integrated receiver". *Appl. Phys. Lett.*, 102, 092601 (2013).

[9] T. Kashiwagi, K. Sakamoto, H. Kubo, et al.. "A high- T_c intrinsic Josephson junction emitter tunable from 0.5 to 2.4 terahertz". *Appl. Phys. Lett.*, 107, 082601 (2015).

[10] T. M. Benseman, K. E. Gray, A. E. Koshelev, et al.. "Powerful terahertz emission from $Bi_2Sr_2CaCu_2O_{8+\delta}$ mesa arrays". *Appl. Phys. Lett.* 103, 022602 (2013).

[11] T. Kashiwagi, K. Nakade, Y. Saiwai, et al.. "Computed tomography image using sub-terahertz waves generated from a high-T_c superconducting intrinsic Josephson junction oscillator". *Appl. Phys. Lett*., 104, 082603 (2014).

[12] M. Y. Li, J. Yuan, N. Kinev, et al.. "Linewidth dependence of coherent terahertz emission from $Bi_2Sr_2CaCu_2O_8$ intrinsic Josephson junction stacks in the hot-spot regime". *Phys. Rev. B*, 86, 060505R (2012).

[13] X. J. Zhou, J. Yuan, H. Wu, et al.. "Tuning the terahertz emission power of an intrinsic Josephson-junction stack with a focused laser beam". *Phys. Rev. Applie*d. 3, 044012 (2015).

[14] L. Y. Hao, M. Ji, J. Yuan, et al.. "Compact Superconducting Terahertz Source Operating in Liquid Nitrogen". *Phys. Rev. Applied*, 3, 024006 (2015).

[15] H. C. Sun, Z. B. Yang, N. V. Kinev, et al.. "Terahertz spectroscopy of diluted gases using $Bi_2Sr_2CaCu_2O_{8+\delta}$ intrinsic Josephson junction stacks". *Phys. Rev. Applied*, 8, 054005 (2017).

[16] Y. Huang, H. C. Sun, D. Y. An, et al.. "Self-mixing spectra of terahertz emitters based on $Bi_2Sr_2CaCu_2O_{8+\delta}$ intrinsic Josephson junction stacks". *Phys. Rev. Applied*, 8, 054023 (2017).

[17] E. Sobakinskaya, V. L. Vaks, N. Kinev, et al.. "High-resolution terahertz spectroscopy with a noise radiation source based on high-T_c superconductors". *J. Phys. D*, 50, 035305 (2017).

[18] H. B. Wang, P. H. Wu, and T. Yamashita. "Stacks of intrinsic Josephson junctions singled out from inside $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals". *Appl. Phys. Lett.*, 78, 4010 (2001).

[19] V. P. Koshelets and S. V. Shitov. "Integrated superconducting receivers". *Supercond. Sci. Technol.*, 13, 53-69 (2000).

[20] D. M. Mittleman, R. H. Jacobsen, R. Neelamani, et al.. "Gas sensing using terahertz time-domain spectroscopy". *Appl. Phy. B*, 67, 379-390 (1998).

[21] E. Gerecht, K. O. Douglass, and D. F. Plusquellic. "Chirpedpulse terahertz spectroscopy for broadband trace gas sensing". *Opt. Express* 19, 8973 (2011).